WATER QUALITY CRITERIA

SECOND EDITION
By
McKEE & WOLF
(1963)

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CALIFORNIA STATE WATER RESOURCES CONTROL BOARD



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WATER QUALITY CRITERIA

SECOND EDITION

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U. S. PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

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THE RESOURCES AGENCY OF CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

Publication No. 3-A

PREFACE TO THE FIRST EDITION

Strictly speaking, the first edition of WATER QUALITY CRITERIA did not have a preface as such. Instead, the information normally presented in a preface was contained in the letter of transmittal. The following

material has been excerpted from that letter.

In compliance with the terms of the contract by and between the State of California and the California Institute of Technology, dated 4 January 1951, an investigation has been made of the technical and legal literature pertaining to water-quality criteria for the various beneficial uses of water. The report submitted herewith embodies a condensation and critical evaluation of such literature, along with a bibliography and appendices.

A prominent feature of the new legislation for waterpollution control in California is the provision for a "case-by-case" study of each problem of pollution, with abatement requirements to be based upon the economics of waste treatment as well as upon the injury to potential beneficial uses of polluted waters. Of necessity, this "case-by-case" stipulation precludes a broad-brush treatment on a state-wide or even regional basis, and it rules out rigid stream standards and the arbitrary zoning of streams or underground basins. In effect, then, it depends on astute judgment by members of the waterpollution-control boards and such judgment must be founded on the most recent, complete, and reliable compendium of data pertaining to the limiting and threshold concentration of each potential polluting substance, for each possible beneficial use of the water.

It was the primary aim of this project to assemble, condense, and evaluate the readily available literature pertaining to water quality and its effects upon the beneficial uses of water. Such literature includes the fundamental work of original investigators, as well as standards and requirements of other state and interstate agencies. The scope of the survey included, furthermore, a review of judicial expressions to determine court rulings and decisions that have dealt with the reasonableness or unreasonableness of water-quality standards as established by public agencies. The second aim of the project was to present the material in a manner that would be most useful to the water-pollution-control boards and their staffs, i.e., to design the report to serve as a manual or handy reference for water-

quality criteria.

The State Water Pollution Control Board has been designated as the state agency with which the U.S. Public Health Service deals for the purposes of the Federal Water Pollution Control Act. Because the state board has ultimate over-all power and responsibility for enforcing the state laws relating to water pollution, the scope of this report has been broadened to include all potential pollutants and contaminants, whether chemical, physical, biological, or radioactive, regardless of their origin in municipal sewage or industrial wastes. Each substance that may enter the waters of the State is deemed to be a "potential" pollutant—potential in

the sense that, if concentrated sufficiently, it can adversely and unreasonably affect such waters for one or more beneficial uses; and yet, if diluted adequately, it will be harmless to all beneficial uses.

Inasmuch as the concentration of a potential pollutant in water is a function not only of the amount of polluting substance added but also of the factors of dilution and self-purification in surface waters and ground waters, a chapter entitled "General Considerations" has been included in the report to describe and explain such factors. Other chapters include an enumeration of the standards promulgated by other state and interstate agencies, a review of judicial expression pertaining to water-quality criteria, and a summary of the quality requirements for the major beneficial uses of the water.

The bulk of the report, however, consists of a survey of the potential pollutants, whether chemical, physical, biological, radiological, or mixed, arranged in alphabetical order according to the most logical designation, with appropriate cross-referencing. For each pollutant is given a brief statement of general information, such as its characteristics and typical sources, followed by cross-references and bibliography, and finally a summary of limiting and/or threshold concentrations for various beneficial uses, as demonstrated by original investigators or as promulgated by enforcement agencies. It is this chapter that should prove of most value for the

California concept of water-pollution control.

The factors that influence pollution and enter into case-by-case studies include, in addition to the strength and volume of the polluting waste, the effects of pH, temperature, synergism or antagonism, dilution, mixing, chemical and biochemical changes, velocity of flow, requirements of beneficial uses, and many other variables. The combination and interplay of these many factors are so complex and they exert such an influence on each pollution problem that any attempt to establish a classification system or a tabulation of standards appears to be inadvisable. In fact, the use of the word "standard" has been avoided in the title of this report, for it signifies "any definite rule, principle, or measure established by authority". Instead "criterion" has been chosen for it designates "a means by which anything is tried in forming a correct judgment respecting it". This report, therefore, presents water-quality criteria, and any attempt to generalize or condense them into rigid standards or requirements has been avoided as contrary to the California concept of water-pollution control.

The conduct and the management of this project and a large proportion of the detailed work of abstracting, evaluating, and organizing the material was the responsibility of Mr. Richard H. Gilman, III, project engineer. In this work he was ably assisted by Mrs. Thelma Linderman, who also served as secretary and typed most of the manuscript. For the review of the law literature and the preparation of much of Chapter IV, "Judicial Expression", we are indebted to Mr. Earl C. Borgeson of

the Los Angeles County Law Library. Mrs. Pearl Horowitz served as biological consultant and abstracter during the early phases of the project and later prepared much of the manuscript for Chapters V and VI. We are also grateful for the assistance of several part-time abstractors and stenographers. To the many people throughout California, the entire U.S., and many foreign lands who responded so generously to our requests for information and data, and to the staff of the California Institute of Technology library which secured innumerable obscure references, we offer our deepest thanks and appreciation.

As Euripides wisely observed, "One man does not see everything". With this thought in mind and cog-

nizant of the limitations of the project staff, an Advisory Committee was selected to provide assistance and guidance. The names and affiliations of the members of the Advisory Board are tabulated on the following page. Members of the Committee twice met formally with the project staff, and several individual members called at the project office, or communicated with the staff, to provide valuable suggestions and sources of information. We are deeply indebted to the members of the Advisory Committee for their helpful assistance and advice, and we trust that this report fulfills their expectations.

J. E. McKee

Pasadena, California June, 1952

PREFACE TO THE SECOND EDITION

The overwhelming response to the published version of the original report on WATER QUALITY CRI-TERIA came as a surprise to the authors and to the California State Water Pollution Control Board. Written to fill a need in the case-by-case analysis of water pollution in California, this compendium was sought, accepted, and used extensively throughout the United States and indeed in many other countries. By permission of the state board, the book was translated into Japanese and published in Japan. Despite a second printing by the State of California in 1957, the steady local, national, and international demand exhausted the supply within a few years. A third printing, however, would have been ill-advised in view of the tremendous amount of literature that has accumulated in the past decade and the progress that has been made in waterquality control. Instead, the State WPC Board elected to have a thorough revision and expansion of the original report.

The second edition bears many resemblances to the first report. The objectives, scope, and limitations are generally the same as before. Format and style remain unchanged, perhaps to the chagrin of some readers. But there are many improvements in the second edition. The bulk of it has been rewritten to incorporate a wealth of new information. Indeed, data on certain aspects of water quality have accumulated to the extent that separate chapters were needed to do justice to their presentation. For this reason, biological pollutants, radioactivity, pesticides, and surface-active agents became the subjects of chapters separate from the parent chapter on potential pollutants.

A significant change in the second edition has been the attempt to summarize. It is not easy to do so. As pointed out in the first edition, the independent variables tending to cause a diversity of data (e.g., synergism, antagonism, temperature, species, prior exposure) often outweigh the factors of central tendency. As a consequence, definitive threshold concentrations and limiting values are difficult to establish. It was the policy in the first edition to present a condensation of the literature and let the reader draw his own conclusions.

It has been reasoned, however, that the abstracters and project staff are in a better position than the reader to summarize the data. For that reason, summaries are presented for many potential pollutants in Chapters V to X inclusive. They are given, however, only when the data are so definitive that they can be summarized logically. Where there is much of a question about threshold concentrations, no attempt has been made to summarize.

The chapter entitled "Judicial Expression" has been completely rewritten, this time by Mr. Paul Freeman, an

attorney who specialized in water law. Having personally abstracted much of the literature in relation to pesticides, Dr. Ralph Pressman was asked to prepare the original draft of the chapter on this subject. For a similar reason, Mr. Jack Patton was the logical person to write the chapter on surface-active agents. We are grateful indeed for the assistance of these three researchers and writers.

The project was managed by Mr. Harold W. Wolf, Senior Sanitary Engineer of the U.S. Public Health Service, who proved to be a real "bird dog" in tracking down obscure references. To him goes the credit for the fact that this second edition covered the original version of many references in German, French, and Russian, and not merely their English summaries or abstracts. Mr. Wolf also wrote two of the chapters and helped to edit the others. He was ably assisted during most of the project by Mrs. Sharon McMichael, who served as secretary and also typed some of the manuscript. She was retired to motherhood in the later stages of the project and replaced by Miss Joann Kiekover to whom we are indebted for much of the final manuscript.

To cover thousands of references, it was necessary to rely on abstracters with technical training in chemistry, biology, engineering, and pharmacology. In this work we received excellent service from Dr. Ralph Pressman, Mr. Jack Patton, and Mr. Adolph Gottfurcht who among them handled German, French, and Russian literature as well as that in English. The project also utilized the services of seven other abstracters, including Mrs. John F. Kennedy. Finally, we are indebted to the staff of the library at the California Institute of Technology who secured innumerable obscure references and provided valuable advice in the literature survey. To the many authorities throughout the world who responded so generously to our requests for information and technical data we shall be eternally grateful.

During the preparation of the first edition an Advisory Committee was formed to provide assistance and guidance. The services rendered by this group made imperative the appointment of a similar committee for the second edition. The names and affiliations of the members of this second Advisory Committee are tabulated on the following page. Although the group did not meet formally, individual members provided valuable suggestions and sources of information. To the entire Committee we wish to extend our sincere thanks.

J. E. McKee

Pasadena, California February, 1963

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- Mr. Herbert C. Davis, Industrial Waste Committee, California Manufacturers Association.
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- Mr. Max K. Socha, Chairman, California Section, American Water Works Association.
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- Mr. Fred G. Nelson, Past President, California Sewage and Industrial Wastes Association.
- Mr. W. J. O'Connell, Consulting Engineer, W. J. O'Connell Associates.
- Mr. Robert M. Paul, Sanitary Engineer, Department of Fish and Game, State of California.
- Mr. Oswald Speir, Corps of Engineers, South Pacific Division.
- Mr. Frank M. Stead, Chief, Division of Environmental Sanitation, Department of Public Health, State of California.
- Mr. P. H. Sunnes, Past Chairman, Industrial Waste Committee, California Manufacturers Association.

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FOREWORD

This is the second edition of WATER QUALITY CRITERIA (Publication No. 3A). The general format remains the same, but the second edition has been thoroughly revised to incorporate the great amount of new information available. One of the authors in the "Preface to the Second Edition" describes the revisions in more detail. His "Preface to the First Edition" gives background information, particularly the need for the publication in relation to water pollution control.

WATER QUALITY CRITERIA was first published in 1952 and proved to be a necessary and exceedingly valuable reference book in the California water pollution control program. An addendum was published in 1954 to bring WATER QUALITY CRITERIA up to date. In 1957 a second printing was made of the combined original edition and the addendum. This printing was exhausted in a few years.

In light of the demand for WATER QUALITY CRITERIA and realizing the importance of keeping this publication up to date, the former State Water Pollution (later Quality) Control Board on July 1, 1960, contracted with the California Institute of Technology for a revised and updated review and evaluation of technical and scientific literature pertaining to criteria of water quality. The project was under the direction of Dr. Jack Edward McKee, Professor of Environmental Health Engineering, and was managed by Mr. Harold W. Wolf, Senior Sanitary Engineer of the U. S. Public Health Service. The succeeding pages present the report prepared (with others) and edited by Dr. McKee and Mr. Wolf. It was submitted on February 28, 1963. Printing and distribution of the report was authorized by the State Board on May 7, 1963.

Although the investigation reported herein was conducted under the sponsorship of the State Water Pollution Control Board, and with the assistance of the U. S. Public Health Service, it should be pointed out that the conclusions and recommendations given in the report WATER QUALITY CRITERIA, Second Edition, are those of the editors and authors. Attention is also invited to the fact that this report is primarily a survey and evaluation of the literature and a compendium of data on water quality criteria. It does not represent, establish, or recommend specific values for standards, requirements or objectives of water quality for either the State of California or the Public Health Service; nor is it intended to reflect official opinions or policies.

The Legislature of the State of California by enacting Chapter 284, Statutes of 1967, consolidated the functions of the former State Water Rights Board and the State Water Quality Control Board (successor agency to the former State

Water Pollution Control Board) under the State Water Resources Control Board. This change is reflected on the cover of this publication but not in the text.

April, 1971

W. M. KECK LABORATORY OF ENVIRONMENTAL HEALTH ENGINEERING California Institute of Technology Pasadena

28 February 1963

State Water Pollution Control Board Mr. Paul Beermann, Chairman State of California, Résources Agency 1227 "O" Street Sacramento 14, California

Gentlemen:

In compliance with the terms of Standard Agreement No. 12-14 between the State of California and the California Institute of Technology, dated 1 July 1960, an investigation has been made of the technical and scientific literature pertaining to the criteria of water quality for various beneficial uses of water. The report submitted herewith embodies a condensation and critical evaluation of such literature, along with an extensive list of references.

Supplementary to the requirements of the contract relative to scientific and technical information, a thorough search was made of the legal literature by a practicing attorney hired by the California Institute of Technology for that purpose. This literature is summarized in Chapter IV entitled "Judicial Expression".

It is difficult to summarize this investigation, for the entire project represented a condensation of voluminous literature on the subject of water quality. In effect, then, the entire report is a summary. Although to X inclusive.

As indicated in the agreement, the U.S. Public Health Service participated in this investigation by assigning an engineer to the project and by providing valuable advice and encouragement. We are grateful for this collaboration. We are especially appreciative of the assistance and cooperation rendered by your executive officer, Mr. Paul R. Bonderson

Respectfully submitted, J. E. McKee Professor of Environmental Health Engineering

CHAPTER I

INTRODUCTION

BACKGROUND OF WATER POLLUTION CONTROL IN CALIFORNIA

The control of water pollution in the State of California turned a monumental corner in 1949 with the passage of Assembly Bill No. 2034, Chapter 1549, which added Division 7 to the Water Code. This act provided means for coordinating the programs of the various state agencies and political subdivisions of the State in the control of water pollution, through a State Water Pollution Control Board and nine regional boards. That such coordination was necessary is evident from the Report of the Assembly Interim Fact-Finding Committee on Water Pollution (1) popularly known as the Dickey Report, after its Chairman, the Honorable Randal F. Dickey. For further background information dealing with problems of water-pollution abatement in California and the legislative hearings that led to the present law, the reader is referred to the Dickey Report and its appendices.

A decade of experience and progress in water-pollution control in California revealed that certain changes in the original act were advisable in order to implement, clarify, and strengthen the statutes. At its 1959 Regular Session, therefore, the Legislature made substantive changes in the Water Pollution Control Act as set forth in Division 7 of the California Water Code (2). Provisions in the act were added, repealed, or amended by the enactment of three bills: Assembly Bill No. 1974 (Chapter 1299), Assembly Bill No. 1063 (Chapter 2053), and Assembly Bill No. 1947 (Chapter 854). A full review of the 1949 Act and the changes of 1959 is beyond the purview of this report. All further references to the California Water Pollution Control Act relate to the statutes in effect after 1959.

In Division 7 of the State Water Code (2), the Legislature wisely recognized that problems of water pollution in California are primarily regional and dependent upon factors of precipitation, topography, and population, as well as upon recreational, agricultural, and industrial development, all of which may vary greatly from region to region. Insofar as problems of water pollution are involved, the snow-capped mountains of northern California differ from the Mojave Desert as significantly as Vermont differs from Arizona; and the industrialized San Francisco Bay area is as different from the San Joaquin Valley as New York Harbor is from central Texas. Consequently, Division 7 established nine regional water-pollution-control boards that have the primary responsibility for administration, investigation, and enforcement of the program.

It is State policy in California "that the water resources of the State be put to beneficial use to the fullest extent of which they are capable and that the waste or unreasonable use or unreasonable method of use of water be prevented." Moreover, "because of the widespread demand and need for the full utilization of the

water resources of the State for beneficial uses, it is the policy of the State that the disposal of wastes into the waters of the State shall be so regulated as to achieve highest water quality consistent with maximum benefit to the people of the state and shall be controlled so as to promote the peace, health, safety, and welfare of the

people of the State" (2).

Although the primary responsibility for the program rests at the regional board level, there are certain powers and duties reserved unto the State Water Pollution Control Board. It is significant to note Section 13022, which reads: "The state board shall formulate and adopt a state-wide policy for control of water pollution with due regard for the authority of the regional boards. Such policy shall be in conformity with the policies set forth in Chapter 1" (largely described in the foregoing paragraph), and also Section 13025, which states: "Whenever a regional board fails to take or obtain appropriate action to correct any particular existing or threatened condition of pollution or nuisance, the state board shall direct that action to correct the condition be taken by any state agency having jurisdiction or may, itself, take such action."

In the light of these two important duties, the state board considered early in 1950 that it had the responsibility to make known its ideas on the subject of waterquality requirements, the factors that enter into their determination, and the means by which water-pollution problems may be analyzed so as to reach an equitable decision as to water-quality requirements. At that time, the board recognized that it should analyze and summarize the thoughts of its members on this subject before any issue demanding decision came before them, and it also recognized that the regional boards were entitled to be advised in advance of the procedure that the state board would follow in reviewing the actions of the regional boards.

To facilitate matters, the state board appointed from among its members a Committee on Water Quality Criteria and charged it with studying the problem, reviewing what had been done in other states, and preparing a preliminary draft of a document that would set forth the principles involved in the establishment of equitable

water-quality requirements.

The first progress report of the committee (3) appeared on 2 March 1950 and was given wide circulation among technical and trade journals, trade associations, and individuals throughout California and the rest of the United States in order to stimulate criticism, suggestions, and discussion. It was also published in the Journal of the American Water Works Association (4) concurrently with the new set of standards adopted by the New York State Water Pollution Control Board. The report was divided into three parts: (a) a statement of the new concept of water-pollution control in California, (b) an outline of a proposed method of analysis of wastedisposal problems with an example, and (c) a table of water-quality requirements, known as "Exhibit A."

As they would to any such document that was distributed so widely, criticism, suggestions, and other comments poured into the State WPC Board. Most of the replies were complimentary to the statement of philosophy and the approach to problems of pollution abatement, but some were critical of the tabulation of waterquality requirements or to certain parts thereof. Among the constructive criticisms were several suggestions that "Exhibit A" be deleted until after a thorough survey of the technical literature had been made and research had established numerical water-quality criteria that, with judgment and discretion, could be applied safely and equitably in California.

The Committee on Water Quality Criteria took cognizance of many of the favorable comments and constructive criticisms by amending its original progress report. The second report, entitled "Water Quality Evaluation", differed from the initial report primarily in that "Exhibit A" and the example of analysis of wastedisposal problems were deleted. This revised report was approved at the 3 May 1951 meeting of the state board.

CURRENT STATEWIDE POLICY

As a result of 1959 legislative amendments to the California Water Pollution Control Act, and in light of ten years of operating experience, the two documents described above were superseded by rules and regulations of the State WPC Board pertaining to statewide policy for the control of water pollution, filed in the California Administrative Code under Subchapter 4, Chapter 3, Title 23.

Article 1 of Subchapter 4, titled "Declaration of Policy", was adopted on 8 June 1960. In general terms, it sets forth the general and fundamental principles that are inherent in the pollution control legislation, by which state and regional boards will be guided in exercising their assigned duties. For the most part, these principles are described above under the heading of background information.

Article 2, adopted 11 January 1961, is the first of a series of detailed policy statements. Titled "Principles and Factors to be Considered in Formulating Waste Discharge Requirements for the Control of Water Pollution", it makes known the ground rules upon which the state board will base its decisions in the event that discharge requirements established by a regional board need to be reviewed. Although it was developed primarily for the use of the state board in fulfilling its own duties, this regulation also serves as a suggested procedure for the guidance of the regional boards. Much of the following information is quoted directly from Article 2.

"In the formulation of waste-discharge requirements, it is recognized that:

- (a) Beneficial uses made of a water are the controlling factors in determining water-quality levels that are to be maintained.
- (b) For every beneficial use, there are certain water-quality requirements which must be met to as-

sure that the water will be suitable for that beneficial use.

- (c) Receiving waters have varying degrees of waste assimilative capacity, and the addition of waste materials may change the chemical, physical, and biological characteristics of the water without necessarily creating significant adverse effects on the beneficial water uses.
- (d) The formulation of waste-discharge requirements should be so designed as to (1) secure that degree of care in the planning and operation of works for the treatment and disposal of sewage and industrial wastes as will adequately protect the public health and the beneficial uses of waters of the State and (2) at the same time permit the legitimate planned usage of those waters for receiving suitably prepared wastes so that an orderly growth and expansion of cities and industries may be possible."

Before a regional board can prescribe requirements for specific waste discharges, it must determine the beneficial water uses that it intends to preserve and protect. The board must next define water-quality objectives which will assure the suitability of the water for the recognized beneficial uses, giving due regard to the environmental characteristics of the hydrographic unit under consideration. The enunciation of beneficial uses and the definition of water-quality objectives can be accomplished by either of the following methods:

"(a) Under the statutory authority of Water Code Section 13052(e), adopting water-quality plans and policies for the major hydrographic units within the jurisdiction of the regional board or, until such plans and policies are adopted,

"(b) Considering, on a case-by-case basis, the beneficial uses and water-quality objectives in the immediate area of the waste discharge.

"Where practical and feasible, the state board encourages use of the first method on the grounds that it provides the most sound and rational long range approach to an effective water-pollution-control program by making it possible to simplify and integrate the prescribing of waste discharge requirements on major hydrographic units. The second method, however, may be used pending the formulation and adoption of basinwide or regionwide plans and policies."

It is important for the out-of-state reader to note at this point that California does not have statewide or even regionwide water-quality standards or the planned zoning of streams or underground basins. Instead, each problem of actual or potential pollution is studied on the basis of local conditions and current knowledge. Hearings are held to establish the beneficial uses of the water to be protected and to enable all interested parties to submit relevant information. The regional board then promulgates "requirements" which govern the quality of the effluent, and/or the conditions to be maintained in the receiving waters (surface or underground). Examples of these requirements are presented in Chapter III.

It is the present policy of the state board to maintain the highest possible water quality, in contrast to following a direction of making maximum use of receiving waters for waste assimilation. Waste-discharge requirements are designed to achieve this objective so as to give full protection to recognized beneficial water uses. If requirements developed under this philosophy appear unreasonable to the discharger, the burden of proof rests with the discharger to show why it is reasonable and proper that the requirements be made less restrictive. In evaluating reasonableness, the board will recognize the principle of cost-benefit relationship.

Of necessity, the "case-by-case" study of each problem of pollution precludes a "broad-brush" treatment on a statewide or even regional basis and it rules out rigid stream standards and the planned zoning of streams or underground basins. In effect, then, it depends on astute judgment by the members of the waterpollution-control boards and such judgment must be based on the most recent, complete, and reliable compendium of data on the limiting and threshold concentration of each potential polluting substance for each possible beneficial use of the water.

THE ORIGIN OF WATER QUALITY CRITERIA

Receognizing the need for such a compendium upon which water-quality objectives or requirements could be based, the State WPC Board entered into an agreement with the California Institute of Technology on 4 January 1951 to make a literature survey dealing with waterquality criteria for various beneficial uses of water, and to submit a final report of its survey. This contract led to the printing in 1952 of Publication No. 3 of the State WPC Board, entitled WATER QUALITY CRITERIA. By permission of the state board, the book was translated into Japanese and published in Japan. As a handy source of information on the limiting and threshold concentration of hundreds of potential water pollutants, the first edition proved to be a necessary and exceedingly valuable reference book in water-pollution control, not only in California but throughout the United States and in many foreign countries.

Realizing the importance of keeping this publication up to date, in view of the rapid accumulation of literature in this field, the state board on 1 July 1953 contracted with J. E. McKee to prepare an Addendum to WATER QUALITY CRITERIA, which was published in 1954. A steady local, national, and international demand for the original volume, which was quickly out of print, led the U. S. Public Health Service to assist the State in financing a limited second printing in 1957; but it too was soon exhausted.

The Addendum of 1954, although patterned after the original volume and thoroughly integrated with it, proved to be cumbersome and inconvenient to use. A second addendum would have compounded the difficulty. For this reason and in light of the 1959 amendments to the California Water Pollution Control Act and the new statewide policy as described hereinbefore, it was deemed advisable not to make a second reprinting of the original volume of WATER QUALITY CRITERIA and not to prepare further addenda. Instead, a thorough resumption of the investigation and critical evaluation of water-quality criteria was authorized by the State WPC Board,

to be undertaken by the California Institute of Technology through an agreement dated 1 July 1960. It was expected that this project would result in a complete, up-to-date, integrated second edition of WATER QUALITY CRITERIA. The scope of this work and the aims of the project staff in preparing the following report are described later in this chapter.

OTHER ASPECTS OF THE NEED FOR WATER QUALITY CRITERIA

The foregoing paragraphs describe the origin of this report on criteria of water quality insofar as the State of California is concerned; but who else needs such criteria and why? What is the need in other states and other countries? How can the need be defined? How urgent is it? Why hasn't it been filled over the decades? Why is the term criteria used? Why not speak of the need for data, or standards, or objectives? It is germane for this report to examine these questions and especially to determine the magnitude and scope of the need for criteria of water quality. It is also important to describe some of the problems facing authorities who are responsible for the management of this nation's water resources (1742).

Criteria of water quality are needed (1) by waterpollution-control authorities on federal, state, and local levels who must restrict or regulate the discharge of sewage and industrial wastes to the nation's water courses and ground-water basins, (2) by waterworks engineers and chemists who are responsible to the consumer for the quality of treated and delivered water, despite any pollution of the source, (3) by aquatic and marine biologists who strive to protect fisheries resources and other water life, (4) by irrigation engineers who are responsible to the farmer for the quality of water delivered to crops, (5) by veterinarians and animal husbandrymen who are concerned about the tolerance of livestock to polluted water, (6) by public-health authorities and by engineers in environmental health who are concerned with all of man's contact with his environment, including bathing and boating, (7) by hydraulic engineers who design and operate impounding dams, navigational facilities, water power plants, and harbor works, and finally (8) by municipal, industrial, and consulting engineers who must design and operate systems for handling municipal and industrial wastes.

What criteria are needed? What analyses are important for the protection of our water contact? Can some tests be dispensed with or perhaps minimized? How are decisions made relative to the significance of criteria? At present, chemists and microbiologists in water-supply organizations and regulatory agencies for the most part are performing the tests that they know how to perform. More specifically, they are running the tests that are conventional. It is possible, indeed probable, that several important trace constituents are being overlooked. Conversely, some of the conventional tests are relatively meaningless for the protection of water quality in certain instances.

To establish a current picture of water quality, it is essential to collect, collate, and evaluate all available information relative to the effects of each potential pollutant on each possible beneficial use of water. Such a compendium is bound to reveal that there are many gaps in current knowledge and it will indicate areas where further research and investigation are needed.

Urgency of the Need for Criteria

That the need exists for better criteria of water quality is beyond contention, but how urgent is this need? Why hasn't it been filled before? Until recently, many people believed that the nation's water resources, except in the arid West, were abundant and virtually inexhaustible. The flow of these waters has been measured for many decades by the U. S. Geological Survey, and the probability of each magnitude of flow in future years can be predicted with increasing reliability.

One thing is certain. Barring a major change in climate or geological configuration, the average volume of available water resources will not increase. Indeed, it may even decrease slightly as more reservoirs permit higher evaporative losses and as more water is used consumptively. Attempts are being made to increase the supply of fresh water by desalinization of sea water, by artificial nucleation of clouds, and by suppression of evaporation. It is unlikely, however, that these measures will provide a sizable increase in the total fresh-water resources. This nation must learn to live within its natural water budget and to manage its present water resources wisely.

In contrast with a fixed supply of water, the demand for fresh water is being increased by a growing population, expanding industry, and complex changes in technology. Concomitant with the expanding demands for fresh water of good quality are the increased discharges of waste products to the nation's water courses. Worse still are the magnitude and variety of new substances being discharged—substances about which little is known in relation to their effects on the beneficial uses of water.

In his message to Congress on 23 February 1961, President Kennedy said, "Pollution of our country's rivers and streams has—as a result of our rapid population and industrial growth and change—reached alarming proportions. To meet all needs—domestic, agricultural, industrial, recreational—we shall have to use and reuse the same water, maintaining quality as well as quantity. In many areas we need new sources of supply—but in all areas we must protect the supplies we have" (1743).

To epitomize, the supply of natural water remains constant, the demand for it increases, and its quality deteriorates. Can there be any question that the need is urgent for additional information relative to the effects of water quality on beneficial uses?

Why hasn't this need been filled more adequately in past decades? One reason has been the lack of an acute urgency. More plausible, however, is the fact that until recently analytical techniques and instruments for measuring many of the pollutants were not available. Where once the water chemist relied on simple physical and chemical tests, he now has at his disposal equipment such as the flame photometer and the infra-red spectrophotometer to measure trace elements, molecular-filter-membrane techniques for bacteriological and biological analyses, adsorptive devices such as the carbon filter for microanalysis of odoriferous compounds, and chromato-

graphic apparatus for partition separation of organic liquids and gases.

While many of these techniques are still confined to research laboratories, their impact will be felt increasingly in waterworks and irrigation practice and in water-pollution control. In addition to improved laboratory techniques, there is a trend toward electronic instrumentation to provide continuous analyses and graphic records of water quality of a flowing stream.

Criteria, Objectives, Requirements, and Standards

The title of this report and the foregoing discussion deal with *criteria*. Why not use the more common designation of *standards* or *objectives* or *requirements?* Wherein do these words differ?

The term "standard" applies to any definite rule, principle, or measure established by authority. The key words in this definition are definite and established by authority. The fact that a standard has been established by authority makes it quite rigid, official, or quasi-legal. An authoritative origin does not necessarily mean that the standard is fair, equitable, or based on sound scientific knowledge, for it may have been established somewhat arbitrarily on the basis of inadequate technical data tempered by a cautious factory of safety. Where health is involved and where scientific data are sparse, such arbitrary standards may be justified. There is a tendency, however, for regulatory authorities to promulgate standards of questionable scientific justification to serve as a crutch that facilitates administrative action and enforcement. A further discussion of various types of standards and their use is contained in Chapter III.

A far better word to describe an administrative decision by a regulatory body is "requirement." It represents a requisite condition to fulfill a given mission. It does not necessarily have the connotation of scientific justification nor does it give an impression of immutability. Requirements are less likely to be as rigid or fixed as standards. In California, the regional water-pollution-control boards are directed to prescribe requirements for every existing or proposed discharge of sewage or industrial waste, but such requirements may be revised from time to time (Section 13054 and 13054.1 of Division 7, California Water Code). Indeed, "No regional board, by prescribing requirements, shall be precluded thereafter from revising requirements relative to the same disposal area or receiving waters. A discharge pursuant to the prescribed requirements shall not create a vested right to continue such discharge under the same requirements" (Section 13002, Division 7, California Water Code). Examples of requirements by California WPC Boards are given in Chapter III.

The word "objective" represents an aim or a goal toward which to strive, and it may represent an ideal condition that is difficult, if not impossible, of economic attainment. Most certainly, however, it does not imply strict adherence nor rigid enforcement by a regulatory agency. It is gaining favor among engineers on boards and commissions that strive to achieve water-pollution control by persuasive methods and cooperative action. It avoids the rigidity and authoritativeness of standards and it does not have the enforcement element of requirements.

A "criterion" designates a means by which anything is tried in forming a correct judgment respecting it. Unlike a standard it carries no connotation of authority other than that of fairness and equity; nor does it imply an ideal condition. When scientific data are being accumulated to serve as yardsticks of water quality, without regard for legal authority, the term "criterion" is most applicable. For this reason, this report has been entitled WATER QUALITY CRITERIA. As a compendium of criteria, it should be useful in prescribing requirements in California, and it can be used as a guide by any agency that desires to establish standards or objectives.

To be useful, a criterion should be capable of quantitative evaluation by acceptable analytical procedures. Without numerical criteria, vague descriptive qualitative terms are subject to legal interpretation or administrative decisions. A criterion should also be capable of definitive resolution, i.e., unaffected insofar as possible by synergism, antagonism, or other complicating factors.

There is a tendency, which should be avoided assiduously, to let criteria become rigid and perhaps ripen into standards. For this reason, every criterion should be regarded as flexible information to be kept constantly under surveillance.

AIMS OF THIS INVESTIGATION

Compliance with the contract between the State WPC Board and the California Institute of Technology required resumption of the previous investigations and reports involving a review and critical evaluation of the technical and scientific literature or other sources of information that have appeared since the preparation of WATER QUALITY CRITERIA and its Addendum dealing with water-quality information related to various beneficial uses of fresh and/or salt water, such as domestic water supplies, industrial water supplies, irrigation, stock and wildlife watering, the propagation of fish and other aquatic or marine life, recreational use, and navigation.

The agreement specifies that the investigation and report shall include, but not necessarily be limited to, the following items:

- 1. A collation and evaluation of up-to-date waterquality standards or requirements embodied in and applied through ordinances, legislation, and the rules and regulations of state and interstate agencies dealing with water pollution.
- 2. A review and critical evaluation of literature reporting original research to establish deleterious concentrations of potential pollutants for specific beneficial uses of water.
- 3. A survey of recent technical papers dealing with dilution, mixing, tidal actions, purification mechanisms in surface and ground waters, synergism, antagonism, and other factors that may influence the application of water-quality criteria to individual problems of water pollution.
- 4. Findings, conclusions, and recommendations from which the State WPC Board can promulgate guidelines of water quality for specific beneficial uses.

- 5. Recommendations for further investigations and/or research into water-quality problems.
- 6. A final report, including a bibliography of reference material, consisting of a manuscript ready for printing.

The original project and the first edition of WATER QUALITY CRITERIA included an investigation of court rulings and judicial expressions that have involved water-quality standards as established by public agencies. Although this phase of the project was not renewed for the Addendum and not specified in the current contract, the Executive Officer of the State WPC Board asked that it be included in this report and made current.

Shortly after the inception of the original project, it became apparent to the staff that the California philosophy of water-pollution control, involving a case-by-case study of each potential problem of pollution, called for more than a conventional literature survey. Each regional board and its staff, as well as the state board, needed a handy reference book in which could be found a synopsis of the literature relating to the effect of each potential pollutant upon each possible beneficial use of water, with proper bibliographical notations so that further reading could be pursued, when necessary.

The enthusiastic reception and international use of the first edition of WATER QUALITY CRITERIA indicated to the State WPC Board that publication of this information filled a need far beyond that of the regional boards within California. Revision and modernization of the text, therefore, represented a contribution to the science and practice of water-pollution control throughout the U.S.A. and elsewhere. For this reason, the cooperation and assistance of the U.S. Public Health Service was solicited and obtained, as described in the Preface and Acknowledgements.

It is the primary aim of this report, therefore, to serve as a compendium of current literature on the subject of water-quality criteria. Correlated with the primary aim is an attempt to present the material in a manner that will be most useful to the water-pollution-control boards and their staffs. For this purpose, the report has been cross-referenced extensively and may seem to be repetitious in places, but the repetition helps to make the volume easier to use, as explained under "Organization of the Report," which follows.

SCOPE AND LIMITATIONS

The scope of this investigation is delineated for the most part by the agreement and the aims described above. In addition, however, cognizance should be taken of certain definitions in Division 7 of the California Water Code as they relate to the scope of this report.

Section 13005 is explicit in its definitions of three terms that otherwise are frequently confused or used synonymously. "Contamination" is defined as "an impairment of the quality of the water of the State by sewage or industrial waste to a degree which creates an actual hazard to public health through poisoning or through spread of disease. Contamination should include any equivalent effect resulting from disposal of sewage or industrial waste whether or not waters of the State

are affected." "Pollution" is defined as "an impairment of the quality of the waters of the State by sewage or industrial waste to a degree which does not create an actual hazard to public health but which does adversely and unreasonably affect such waters for domestic, industrial, agricultural, navigational, recreational, or other beneficial use, or which does adversely and unreasonably affect the ocean waters and bays of the State devoted to public recreation." "Nuisance" is defined as "damage to any community by odors or unsightliness resulting from unreasonable practices in the disposal of sewage or industrial waste."

The term "degradation" is frequently used to express a deterioration in water quality as a result of natural causes. Whether a deterioration of water quality results from contamination, pollution, nuisance, or degradation has no bearing on the scope of this survey, however, inasmuch as the investigation pertains only to the concentration of potential pollutants without regard to their origin. Attention is invited particularly to what is referred to in this report as "corollary pollutants," i.e., substances that are of natural origin but grow excessively and cause an impairment of the waters of the State as a result of the discharge of sewage or industrial wastes. Such a corollary pollutant would be the heavy algal growth that may result from the discharge of a highly oxidized and nitrified sewage or industrial waste. Although they are of natural origin and seldom added directly by sewage or industrial wastes, corollary pollutants are considered to be within the scope of this report.

In defining the aims of the report it is also well to delineate the limitations of the project. No attempt has been made to do any original research work in connection with this project; in fact an effort has been made to exclude any opinions or special unpublished knowledge of members of the staff. Literature dealing with methods of treating municipal and industrial wastes or domestic and industrial water supplies (including boiler-water treatment) were deemed to be beyond the scope of this survey. Other limitations are referred to throughout the body of the report. No claim is made, moreover, that the survey is exhaustive or that very important references have not been overlooked, for the members of the staff are subject to human oversight. Every source of information that was recommended by the Advisory Committee and other interested parties, however, was investigated. It must be recognized, furthermore, that any literature survey is outdated shortly after its publication, and may become less useful as new information appears in current publications.

This second edition differs in one significant respect from the original volume. In the first edition, no attempt was made to draw conclusions or to make recommendations relative to any potential pollutant. Instead, a certain amount of background information was given for each substance, the available literature was abstracted and cited in relation to each beneficial use, and the reader was expected to draw his own conclusions. This policy was in line with the philosophy of case-by-case analysis, for it was reasoned that the proper concentration for one situation might not apply in a separate instance. Indeed, it was feared that any attempts to summarize or suggest a limiting criterion would lead to

rigid interpretations that might gel by continuous use into fixed standards.

Nevertheless, many users of the first edition have commented that the volume would have been more useful if conclusions, summaries, or recapitulations had been added where feasible. These users contended that the authors of the report were generally better qualified than the readers to draw such conclusions.

Accordingly, many of the reviews of potential pollutants in this second edition include brief statements or conclusions to summarize the current status of knowledge. Summaries could not be attempted for most of the substances because the available data are too sparse. In other instances, it was unwise to specify limiting concentrations because the effects of synergism, antagonism, temperature, pH, and many other factors far outweigh the exact concentration of the specific substance in determining its effect on a beneficial use. Where summaries and recommendations are feasible, however, they have been included in this edition.

CONDUCT OF THE SURVEY

At the outset of the original project in 1951, it became evident that the scope of the survey was so broad and the variety of potential pollutants affecting the numerous beneficial uses was so great that all possible direct assistance from known authorities should be sought, not only from within the State of California, but also from the entire country and even foreign nations. For this reason, an Advisory Committee was established in 1951, as acknowledged and listed in the front of this report. Comprising representatives of diverse background and varied interests, the 1951 Advisory Committee was of tremendous assistance in recommending numerous sources of material and specific references to the project staff. Furthermore, several of the members of the Committee reviewed the manuscript prior to publication and suggested important modifications.

The service of the original Advisory Committee was so valuable to the project staff that a decision was reached early in the resumption of the investigation to form a new Advisory Committee, as shown hereinbefore. Several members of the new committee followed the progress of the survey carefully and made numerous suggestions that helped to guide the project.

A literature survey of this type involves a thorough search of all possible sources of information. Of inestimable value are the various abstracting agencies and journals such as Water Pollution Abstracts (British), Public Health Engineering Abstracts, Journal of the American Water Works Association, Journal of the Water Pollution Control Federation, Chemical Abstracts, Biological Abstracts, and the book reviews of many journals. These abstracting services provided a good starting point for the survey, but the original article for each abstract was consulted if it could possibly be obtained. To make sure that no significant references were missed, many journals that normally or even occasionally carry articles on water quality were combed for relevant material, through December 1961. Finally, extensive correspondence with numerous authorities in the U.S.A. and foreign countries produced references to obscure articles, reprints of manuscripts or unpublished

reports, and other sources of information relative to water quality. Needless to say, each technical article referred to several others, each of which in turn also contained a bibliography, so the list of potential sources of

information soon pyramided.

Each reference became the subject of an 8" x 5" card, the margins of which were punched in accordance with a code that designated the journal, the beneficial use involved, the nature of the potential pollutants, legal or statutory considerations, and other factors. During the course of the original survey which resulted in the first edition of WATER QUALITY CRITERIA over 2340 references were investigated, of which 1369 were cited in the text and listed in the bibliography. The Addendum of 1954 utilized and cited 371 additional references. The current survey scrutinized a total of over 3560 additional references of which 2087 have been added to the bibliography.

Relatively few of this great number of references actually proved to be significant to the project, that is to say, significant to the extent of containing the results of original investigations with actual threshold or limiting concentrations. The remainder of the references were either couched in general terms, without specific values of use to this project, or else they were rewrites or abstracts of previously published material. Consequently, the bibliography at the end of this report is much smaller

than the list of references investigated.

In connection with the review of standards utilized by other states and interstate agencies, a questionnaire was sent to the primary water-pollution-control organization in each state and to each interstate agency. The fact that replies were received from all states and interstate agencies is a tribute to the quality of personnel engaged in water-pollution-control work throughout the nation. These replies form the framework for Chapter III of the report. Other questionnaires dealing with court decisions that passed on the reasonableness or unreasonableness of water-quality standards were sent to the Attorneys General of each state in 1951, the replies of which assisted in the preparation of Chapter IV. Without the formality of a specific questionnaire, numerous inquiries were directed to industrial associations, schools of animal husbandry, foreign laboratories and research centers, state departments of fish and game or natural resources, and similar groups. Each recipient of a letter of inquiry was most cooperative and each agency was most willing to contribute to the future usefulness of this publication, for almost all had heard of the original volume and had used it extensively.

Finding sources of information is the least work involved in a survey of this type. Much more effort and thought must be directed toward scanning the available literature, abstracting the significant articles to obtain water-quality information, and finally collating and evaluating the profuse data. In this respect the project was fortunate in having the services of the abstractors listed

under "Acknowledgements."

ORGANIZATION OF THE REPORT

Following this chapter of introduction, in which the background, scope and aims, and progress of the survey have been described, a chapter entitled "General Considerations" has been inserted. This chapter was deemed necessary to explain and describe factors and areas of surface-water and ground-water pollution that affect many, if not all, specific pollutants and beneficial uses. It deals with such matters as available dilution in streams, estuaries, oceans, and ground-water basins; natural purification; frequency and reliability of sampling; lateral and longitudinal mixing in streams and ground water; and the significance of synergism and antagonism. An understanding of all of these factors is essential to an appreciation of the entire field of water-

quality criteria.

The third chapter contains an enumeration of the standards that are utilized, in some manner or other, by other state and interstate agencies, along with a brief history of the development of such standards. Although it is conceded that Chapter III will not be nearly as useful as Chapters V-X to the state and regional WPC boards of California, it is included in the report for the sake of completeness and interest, and as a possible source of data. For background information and a general appreciation of the problems involved in formulating and administering water-quality standards, Chapter III should be significant. Furthermore, it is useful for a clearer understanding of Chapter IV, "Judicial Ex-

pression."

Inasmuch as references to instances where the courts have ruled on the reasonableness or unreasonableness of water-quality standards are rare in engineering and technical publications, a thorough search through legal channels was indicated. For this purpose, the original project was fortunate in securing the services of Mr. Earl C. Borgeson of the Los Angeles County Law Library. In this resumption of the investigation, Mr. Borgeson was no longer available, inasmuch as he transferred to the Harvard Law Library in 1953. To bring the chapter on judicial expression up to date, it was deemed advisable to utilize the service of an attorney trained in methods of legal research and interested in problems of water quality. The assistance of the County Counsel of Los Angeles County, Mr. Harold Kennedy, was solicited in this problem and he kindly agreed to have one of his deputy attorneys, Mr. Paul Freeman, handle this phase of the project. The methods by which Mr. Freeman proceeded and the results of his literature search are described in Chapter IV.

The bulk of the report (Chapters V through X) consists of summaries of literature relating to threshold and limiting concentrations for each potential pollutant with respect to each beneficial use of the water. Each substance or waste that may enter the waters of the State is deemed to be a "potential" pollutant—potential in the sense that, if concentrated sufficiently, it can adversely and unreasonably affect such waters for one or more beneficial uses; and yet, if diluted adequately, it will be harmless to all beneficial uses. In order to make the report of maximum utility to the state and regional WPC boards, the same data have been presented in two ways: (1) tabulated by beneficial use in Chapter V and (2) segregated by potential pollutants in Chapters VI through X.

It is anticipated that case-by-case studies will bring up many instances when WPC boards will have to weigh

the effect of many substances upon a specific beneficial use. In such instances, the arrangement of data in Chapter V should prove most useful. Consider, for example, a large river that has been receiving raw or partially treated wastes from several municipalities and industries, without adverse or unreasonable effects upon any existing beneficial use. Suppose also that an irrigation district (or a state or federal agency) proposes to take water near the mouth of this stream and pump it to distant lands for irrigation, which in this example constitutes a new beneficial use. In determining whether or not any of the existing discharges of liquid wastes will cause an adverse or unreasonable effect upon the new beneficial use, the WPC board should consult Chapter V and note the limiting and threshold concentrations tabulated for agricultural use.

More frequently, however, the WPC boards should have reason to refer to Chapters VI through X. Here, for each pollutant, appears a brief statement of general information, such as typical sources of the substance, characteristics, formulae, and principal effects; followed by cross references to other related substances; bibliographical reference numbers that apply; limiting and threshold values for each beneficial use; and finally where feasible conclusions or summaries that might form the basis of usable criteria. Listed among the potential pollutants are mixed wastes or collective terms such as "gas-manufacturing wastes" or "sulfite waste liquors" involving many chemical substances in unknown concentrations. All potential pollutants, whether chemical,

physical, biological, radiological, or mixed, are listed in alphabetical order according to the most-common designation.

The second edition of WATER QUALITY CRITERIA differs from the organization of the original volume in that four additional chapters have been added. Under the category of potential pollutants, the subjects of surface-active substances, radioactivity, pesticides, and biological agents were so important and so profuse that they were removed from Chapter VI and placed in separate chapters.

The technical and scientific literature cited in the text is tabulated in a lengthy bibliography. While most of these references have been used directly in the body of the report, several of them are not referred to directly. They are included in the bibliography for the sake of completeness and because their philosophies guided the writers of this edition.

A word of explanation is in order here to account for the literary style used in this report. Conventional literature surveys are written in an established style that credits each original investigator with his findings; but to have complied with the conventional style would have rendered Chapters V through X of this report ponderous and dull. In the interest of utility and readability, therefore, the work and publications of many investigators are summarized in a few sentences, with the several references being cited at the end of the paragraph. In a few instances, where only one or two references are involved, direct credit is given.

CHAPTER II

GENERAL CONSIDERATIONS

There are certain aspects of water-pollution control that are not strictly part of this literature survey, but they have a direct bearing on the critical evaluations and use of the data contained herein. It is the aim of this chapter to present these aspects for consideration, and to indicate how they affect case-by-case studies of pollution. To many of the readers, the contents of this chapter will bring few new ideas or thoughts, but it is hoped that the references to established principles will help in the evaluation of the detailed data of Chapters V to X inclusive. To other readers, the concepts described herein should serve as a condensed text and handy reference, inasmuch as such considerations are essential to an understanding of the California philosophy of water-pollution control and the application of water-quality criteria.

Not all of the general considerations in this edition are confined to Chapter II. Indeed, the reader will find extensive discussion of the development and use of criteria, standards, requirements, and objectives in the first part of Chapter III. General considerations in the application of criteria to specific beneficial uses, such as agricultural water supply and the propagation of aquatic life, are described in appropriate parts of Chapter V. Finally, the opening pages of each subsequent chapter are devoted to general discussion relative to the use of data presented therein. The factors described in Chapter II, however, do not fall logically into any subsequent chapter and hence they are presented here as general

considerations. The concentration of many pollutants in water depends primarily upon two variables: (a) the amount of polluting substances, and (b) the volume of diluting water. An accurate determination of the former without a similarly precise evaluation of the latter is virtually meaningless. In order that the criteria of Chapters V to X inclusive can be applied properly, it is essential that the concentration of pollutants be determined accurately, and hence that the volume of diluting water be known. For fresh surface waters, fortunately, this problem is relatively simple and straightforward, although complicating factors such as longitudinal mixing and short circuiting are involved in the translation of the pollution to downstream points. For ocean waters, tidal estuaries, and ground waters, however, the problem is much more complex, as described later in this chapter.

There is a need for further investigation and research dealing with factors such as dilution, mixing, self-purification, and synergism. Indeed, such work may be the key to increased economy in waste disposal and improved water quality in streams, tidal estuaries, and ocean shore lines. A striking example of the advantage of such studies is the research that led to the design of the new multiple diffusers for the ocean outfalls of the Los Angeles County Sanitation Districts (1911), the Hyperion plant of the City of Los Angeles, and the metropolitan sewer system at San Diego. Similar basic research is

needed to determine the fundamental reactions and mechanisms that govern the decomposition of pollutants in receiving waters, so that such reactions may be accelerated, or in some instances retarded.

DILUTION IN SURFACE STREAMS

The volume of water for dilution in surface streams is seldom constant, inasmuch as the discharge varies from year to year, day to day, and even hour to hour. While most hydrometric investigations deal with the total availability of water from a stream or the magnitude and frequency of flood flows, the sanitary engineer is more interested in minimum flows and their duration. The probability of occurrence of low flows can be determined from a study of stream discharge data contained in the USGS Water Supply Papers, in records of state departments of water resources, or in reports of local flood control districts. In themselves, these tabulations are sometimes difficult to interpret; but when properly analyzed and presented in graphical form, stream-flow data become very useful.

One of the more convenient methods for the presentation of minimum discharge data is the "duration curve," i.e., a plot of stream flow against the probability of occurrence. This curve may be plotted with arithmetic scales as in Figure 2-1, but such a presentation obscures the low flows during which pollution is most severe. An improved plotting utilizes a logarithmic scale for stream flow with an arithmetic scale for the time axis, as shown in Figure 2-2. Better still, the probability scale can be substituted for the arithmetic time axis, so as to give prominence to infrequent occurrences, as demonstrated in Figure 2-3.

In northern California, water flows in the larger streams throughout the year; but in southern California many streams have no visible or measurable surface flow during several months of each year. For either region, however, the duration curve is applicable and it provides a rapid and convenient means of studying the availability of diluting water. A duration curve for the American River at Fair Oaks, California, which is typical of northern California, is shown in Figure 2-3. The solid line represents the duration curve for the period of record up to 30 September 1955. Folsom Dam was placed in operation on 25 February 1955, just upstream from this gaging station. Thereafter, flows were regulated to reduce peaks and augment periods of low discharge as shown by the dot-dash curve. The broken lines show the duration curves for the driest and wettest years on record prior to construction of Folsom Dam. The duration data corresponding to the solid and dot-dash curves are given in Table 2-1.

The initial preparation of duration tables is a relatively simple but time-consuming procedure. Once a tabulation has been made for the entire period of record, however, the tabulation is relatively easy to keep up-to-

date, and duration curves can be made from the most recent tabulation whenever such curves are needed. Duration curves are utilized extensively by the Ohio River Valley Water Sanitation Commission (1914).

Having a duration curve at his disposal, how can a sanitary engineer use it in determining the availability of dilution water and the concentration of polluting substance at each rate of flow? On what percent of the time should he base his calculations? The answer to these questions involves many factors, primary among which are the beneficial uses to which the water will be put and the damage that will be done if available dilution is too low. No hard and fast rules can be set. In a classic study of the Merrimack River, Camp (6) based his computations of dilution on the 10% flow, i.e., a discharge that would be exceeded 90% of the time but might not occur for 36 days of a year on the average. The flows of this river were highly regulated and discharge virtually stopped on Sundays during periods of low flow. Moreover, the maintenance of fish and wildlife did not constitute the primary beneficial use, and occasional periods of severe droughts could be tolerated. (See Chapter V relative to the tolerances of fish to short-time adverse conditions.) In the Clarion River investigation, however, Camp et al. (7) let the 1% flow govern, inasmuch as fish, wildlife, and the effect of taste and odor upon water supplies were important considerations.

In selecting a minimum stream flow on which to base pollution computations, therefore, a sanitary engineer should consider the following factors:

- 1. Beneficial uses of the water.
- 2. Probability that the selected dilution will not be reached, and the duration of periods during which such dilution will not be attained.

TABLE 2-1 DURATION DATA FOR STREAM FLOW OF AMERICAN RIVER AT FAIR OAKS, CALIFORNIA *

(July 1909 through September 1955, and October 1955 through September 1960)

			id Not Exceed S	tated Value
Discharge		r to Folsom 1909-1955)	(B) Regula Folsom Dam	ted by (1955-1960)
cfs	Days	Percent	Days	Percent
5**	16	0.095	. 0	.0
10	31	0.185	ň	· ň
20	55	0.328	ŏ	ŏ
. 30	72	0.429	ŏ	·ŏ
50	103	0.643	ŏ	ŏ
70	266	1.58	Ŏ	ň
100	405	2,41	ŏ	ň
200	1,392	8.29	Ď	ň
300	2,755	16.4	Ŏ	ň
500	4,848	28.9	ž	0.109
700	6,430	38.3	$18\overline{6}$	10.2
1,000	7,521	44.8	234	12.8
1,500	8,713	51.9	517	28.3
2,000	9,583	57 .1	718	39.3
3,000	10,814	64.4	1,043	57.1
5,000	12,485	74.4	1,494	81.8
7,000	13,832	82.4	1,628	89.1
10,000	15.237	90.77	1,717	93.98
15,000	16,271	96.93	1,776	97.21
20,000	16,556	98.62	1,797	98.36
30,000	16,707	99.523	1,815	99.343
50,000	16,763	99.857	1,823	99.781
70,000	16,773	99,917	1,827	100.0
100,000	16,784	99.982	1,827	100.0
150,000**	16,787	100.0	1,827	100.0

* Flow regulated by Folsom Dam, beginning 25 February 1955. There are many diversions above this station for irrigation, municipal, and domestic water supply.

*Instantaneous peak discharge of record = 180,000 cfs on 21 November 1950. Absolute minimum flow = 3.6 cfs on 16 August 1924.

Mean discharge 1909-1955 = 3748 cfs
Mean discharge 1955-1960 = 3748 cfs (regulated)

- 3. The economic damage that will be done if dilution is insufficient.
- 4. The cost of increased treatment to meet stricter dilution requirements.

In computing the availability and tolerances of dilution, consideration must be given to many other factors. Certain substances such as chlorides, sulfates, sodium, and potassium are relatively stable in water and their concentration beyond the point of initial dilution depends only on subsequent dilution, evaporation, and percolation. Other substances, such as cyanides, phenols, and even nitrates and phosphates, are subject to many factors that tend to change their concentration. Among these factors are biological, chemical, and biochemical action, volatilization, sedimentation, adsorption, and other factors that are discussed in more detail in the sections on natural purification in streams later in this chapter. Although many of these factors are difficult to evaluate, serious consideration should be given to them by the sanitary engineer. In addition, the hydraulic phenomena of turbulence that govern mixing and short-circuiting must not be neglected.

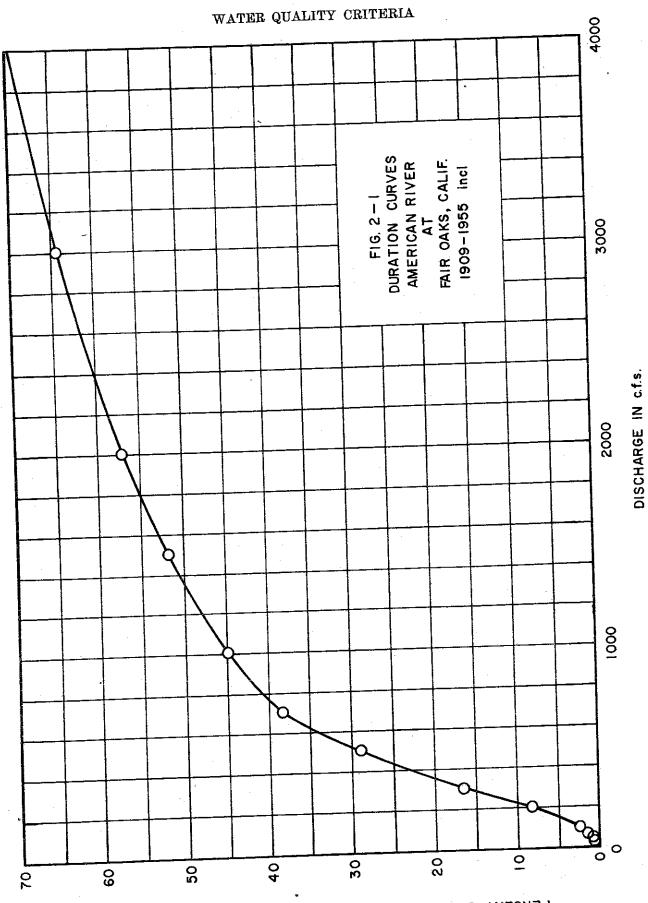
The use of duration curves in case-by-case studies can best be explained by a simple hypothetical example. Let us imagine that an industry planning to locate along the American River near Fair Oaks prior to the construction of Folsom Dam notified the regional WPC board that its wastes, after the proposed treatment, will contain 1000 lbs per day of substance X. By reference to Chapter VI of this report, the engineers of the regional board determine that the "threshold" concentration of substance X for the established beneficial uses is 1.0 mg/l while the "limiting" concentration beyond which economic damage may occur is 2.0 mg/l. The required diluting flow to achieve the threshold concentration is computed to be 186 cfs and the required flow to keep below the limiting concentration is found to be 93 cfs.

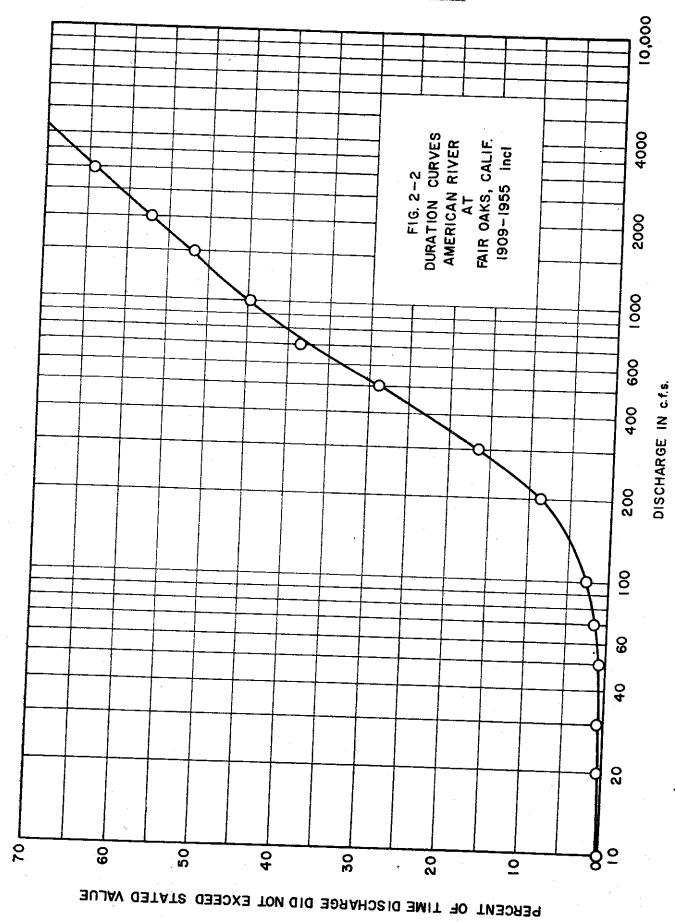
Reference to the solid line on Figure 2-3 shows that the stream flow will fall below 186 cfs about seven percent of the time and below 93 cfs about two percent of the time for all of the years of record. In the driest year, 1924, the threshold concentration would have been exceeded almost 29 percent of the time or for about 106 days, and the limiting concentration would have been exceeded about 25 percent of the time, or 92 days. During the wettest year, 1909, dilution would have been adequate at all times.

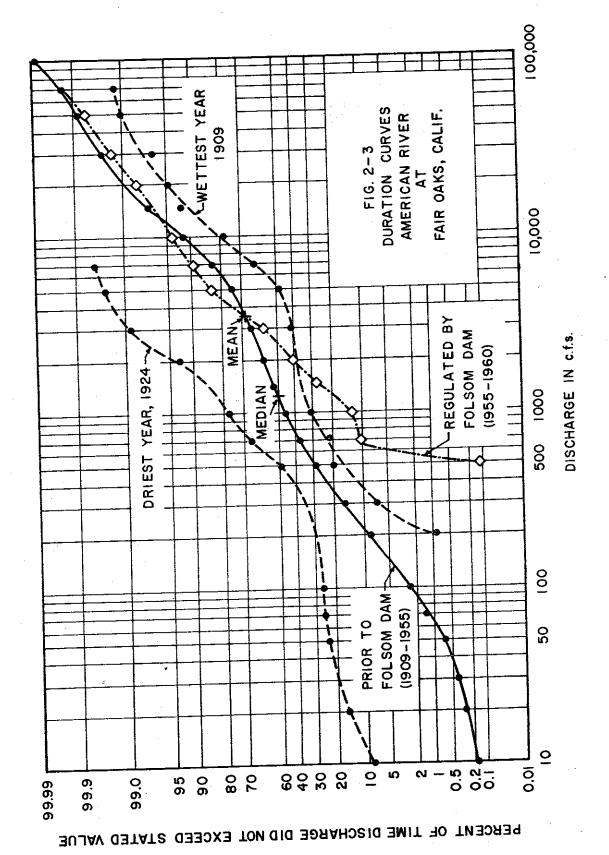
Equipped with these estimates of the probability of occurrence of excessive concentrations of substance X, the engineer can then determine the economic losses involved during periods of excessive concentration as compared with the cost of providing further treatment of the waste prior to discharge.

Duration curves have advantages for specific applications, but they do not reveal the probability of occurrence of drought flows for extended periods, such as a week or longer. For this purpose it is necessary to turn to other methods of analysis.

Phelps and Barry (1374) used an analysis of lowflow frequencies based on the publications of Gumbel (1375, 1376, 1913), who found that maximum and mini-







mum flows in streams are distributed as to magnitude and frequency according to a statistical pattern which is a probability function. An "extreme value" is defined as a maximum or minimum runoff during any one day of a calendar or water year. Gumbel's analysis indicates that a record over N years gives a series of N extreme values which can well be described by a linear trend line in the form, for minimum flows according to Phelps and Barry, of

$$x = \overline{x} + aS - bSy$$

where x is the drought flow of any value, \overline{x} is the mean drought flow of the series, S is the standard deviation of the distribution of the series, y is a dimensionless variate introduced for the purpose of linearizing the relation, and a and b are constants. This line may be plotted and extended for purposes of prediction. Gumbel also developed a skewed probability paper for straightline plotting of the original data.

The frequency of drought flows has also been analyzed by Thomas (1377) who developed a method involving the use of the binomial coefficient to determine from past streamflow records the probability of recurrence of a given drought flow. Like Gumbel, he considered the extreme 24-hour run-off for each year, irrespective of its magnitude in comparison with other extreme values, as a variable subject to statistical analysis. Thomas's general formula is:

$$\phi_k = \frac{m\binom{t}{k}\binom{n}{m}}{(m+k)\binom{t+n}{m+k}}$$

where ϕ_k is the probability that in t future years the mth in magnitude of n past drought flows will be exceeded exactly k times. The notations $t \choose k$, $t \choose m$ denote the binomial coefficient, i.e.,

$$\binom{t}{k} = \frac{t!}{k!(t-k)!}$$

If k = 0, i.e., for the probability that the *mth* drought flow will *not* be exceeded:

$$\phi_0 = \frac{\binom{n}{m}}{\binom{t+n}{m}}$$

As an example, consider a stream with 25 years of record for which the lowest daily flow in any year was 8 cfs and the next lowest daily flow (in a different year) was 10 cfs. What is the probability that during the next five years a flow less than 10 cfs will not occur (i.e., that 10 cfs will be exceeded exactly five times)? Here n = 25, m = 24, t = 5, and k = 5, and hence

$$\phi_{5} = \frac{24 \binom{5}{5} \binom{25}{24}}{(24 + 5) \binom{30}{29}} = 0.69$$

Thus the chances are 69% that a flow equal to or less than 10 efs will not occur during the next five years, or

31% that it will. If a minimum flow of 8 cfs had been considered for the same period (i.e., that m=25) the probability that a worse drought might occur is computed to be about 17%. In their Florida studies, Phelps and Barry (1374) adopted a 25% expectancy value, that is, a mean recurrence period of four years, for the lowest annual 24-hour flood to be used in computing critical concentrations for water quality.

Some engineers prefer to use a period longer than a day to judge low flows, especially for a major stream where the discharge varies slowly. Le Bosquet and Tsivoglou (1378) advocated the use of an average 2-week flow for one large river. They called attention to a "lag period" between the time when the discharge is a minimum and the dissolved oxygen content reaches a minimum. Cleary and Robertson (1914) describe drought-flow analyses based on the frequency of occurrence (or the recurrence interval, e.g., once in 5 years or once in 10 years) of minimum daily, weekly, bi-weekly, and monthly flows. Their figures were based on the statistical theory of extreme values as developed by Gumbel (1375).

Todd (1915) reviewed the basic principles of frequency analysis of streamflow data, while Chow (1916) compared several of the better-known analytical procedures for extending frequency curves. Chow developed a general formula that he maintains is applicable to all of the other methods. Whisler and Smith (1917) found that the frequency of annual peak (or minimum) flood flows can be estimated with sufficient accuracy by an analysis of monthly peak (or minimum) flows. Having determined the probability (P_m) that a given event will occur in any one month, they compute the probability that it will occur in a year (P_y) as follows:

$$P_y = 1 - (1 - P_m)^{12}$$

Thus if the probability of occurrence in any one month is 0.01 or 1.0 percent, the probability of occurrence in a year is 0.114 or 11.4 percent.

A fundamental paper describing the frequency of natural events and utilizing much the same approach as did Gumbel, Thomas, Todd, and others, was published by Riggs (1918).

In California and other western states where stream beds may be dry for many weeks and even months of each year, the methods described above do not appear to be applicable. For western mountain areas where the streams are fed primarily by melting snows, Riggs (1379) proposed a method of forecasting low flows by means of base-flow depletion curves on the premise that stream-flow hydrographs will not fall below the depletion curves. This method is not applicable until the cessation of direct surface run-off from rainfall or snow melt, that is, until stream flow consists solely of groundwater depletion. Thereafter, low flows can be predicted for several months by Rigg's method.

Todd (1380) compared flow-duration curves with frequency-distribution curves to demonstrate that this derivative of the duration curve is more sensitive in illustrating the effects of flood and drought flows. The flow-duration curves are seldom straight lines on logarithmic probability paper, especially near the extremes, owing to varying topography, precipitation, ground cover, and other factors. The frequency distribution curves often

reveal two or more peaks that show more clearly the effects of snow melt, ground-water depletion, storm patterns, and other variables.

IMPOUNDMENTS AND LOW FLOW AUGMENTATION

To provide more efficient utilization of water resources for stream flow, according to Velz (1919), two possibilities exist, viz, regulate the waste discharge and tailor it to the varying pattern of stream flow, or regulate the stream flow to provide greater dilution during periods of naturally low flows. The first approach is sometimes employed for seasonal industrial wastes when large storage lagoons are sufficient to retain the wastes until stream flows increase. A modification of this concept occurs when spent sulfite liquors are discharged intermittently to control the growth of Sphaerotilis natans in receiving streams (1920). The second situation is a by-product of the construction of multi-purpose dams that impound flood flows for subsequent release for power generation or for low-flow augmentation as an aid to navigation. On the other hand, intermittent discharges from dams that are used for peak power generation may be troublesome to downstream waste dischargers (5).

The construction of dams for flood control, power, river regulation, navigation, and diversion of water for irrigation or municipal use will have a marked effect upon duration curves and the availability of water for dilution. Studies such as that by Camp et al. for the Clarion River (7) and by Le Bosquet (8) for the Kanawha River in West Virginia illustrate the benefits to pollution abatement from augmentation of low-water flows. Hazen (1921) describes the effect of storage reservoirs in increasing the minimum flows of typical eastern streams, as measured by duration curves and probability analyses. Costs of improved minimum flows are also

A comprehensive study of low-flow augmentation has been conducted by Hull and his colleagues at The Johns Hopkins University (1922, 1923, 1924, 1925, 1926, 1927, 1928). This investigation included legal aspects, state and national policy, economic factors, and several technical considerations relating to water quality.

In addition to improved dilution from low-flow augmentation, impoundments may produce both beneficial and detrimental effects on water quality (5, 1928, 1929, 1930, 1931, 1932, 1933, 1934, 2007). Among the beneficial effects are decreases in coliform bacteria, turbidity, suspended matter, color, silica, and biochemical oxygen demand. Furthermore, storage tends to smooth out sharp variations in chemical quality. The potential detrimental effects include a decrease in dissolved oxygen, especially when water is withdrawn from below the thermocline, and increases in carbon dioxide, odor, ammonia, iron, manganese, alkalinity, and algae. Diminished temperatures when water is released from below the thermocline are generally beneficial, especially when downstream thermal pollution is a problem. Such changes in temperature are normally considered to be favorable for fish life; although the fauna may be altered in species and numbers as a result of cold summer water in place of the normal warm water.

MIXING IN SURFACE STREAMS

Three types of mixing influence dilution in surface streams and affect the short-circuiting of polluted waters, viz, lateral, vertical, and longitudinal mixing. Lateral mixing governs the rate at which pollution spreads or diffuses from one bank to the other, vertical mixing determines the extent of stratification, and longitudinal mixing controls the rapidity with which a portion of water moves downstream in advance of the average longitudinal velocity. Each type of mixing is a function of the turbulence of the stream, which in turn depends on discharge, slope, depth of flow, channel roughness and configuration, wind action, density currents, and

temperature.

The rate of lateral mixing may be important in many ways. Where it is rapid and thorough, it enables a polluting substance that has been introduced at one bank of the stream to be diffused rapidly into the entire diluting flow, thereby dissipating high local concentrations that may be toxic or deleterious. In broad, deep, slowly moving streams, however, lateral mixing may be so slow that the polluted flow clings to one bank of the stream for many miles, with relatively little effect upon the entire flow. Such a condition may be advantageous in streams used for fish propagation, for the fish may be able to avoid the high concentrations of pollutant by remaining near the clear bank. If the pollutant is of such a nature that the fish cannot detect it and consequently swim unwittingly into toxic concentrations, then the insufficiency of lateral mixing may be deterimental. Water works that draw from the river directly, or from infiltration wells near the river, might also benefit by using water from the less-polluted side. There are many instances of one-sided pollution of streams, according to Mueller (1440). The Elbe River above and in the city of Dresden is heavily polluted especially by waste waters of factories manufacturing cellulose, all of which are on the left bank. This one-sided pollution can be traced for many kilometers downstream before an even distribution of the load across the stream is achieved.

Lateral mixing is a function of turbulence and velocity gradients in a stream. In shallow, steep, rocky channels, turbulence is high and conducive to rapid diffusion of pollution across the width of the stream. In deep, flat, smooth channels, the flow approaches a laminar condition and lateral mixing is inhibited. A precise evaluation of the rate of lateral mixing cannot be made for a general case, for each stream has unique characteristics that

govern such mixing.

An understanding of lateral mixing is important in the establishment of sampling stations. Where mixing is incomplete, samples may be concentrated more or less than would be indicated for thorough mixing, depending upon where the sample is taken. In such cases, it is wise to take samples at several points across the stream and blend them into a composite sample. The State of Mississippi specifies in its standards (9) that "... The sampling place shall be chosen after the waste has been dispersed in the receiving waters and not more than one thousand (1000) feet below or above the waste or sewage outfall.'

Even far downstream from a point of pollution it may be advisable to sample at several points along a traverse across a stream, for lateral mixing also influences the longitudinal displacement of wastes. Haney (1370) illustrates the problem clearly with a chart showing the concentration of phenols from bank to bank in a large stream. In this particular illustration, the phenol concentrations are high near the banks and low at the center. Such a condition might occur, for example, when a discharge of phenolic wastes that had been thoroughly dispersed in the stream is then diluted by a clear stream. The unpolluted water from upstream will dilute and clear up the center of the stream much more quickly than the banks.

According to an abstract from the Russian by Straub (1381), Nesmejanow gives a formula for calculating the point of discharge of wastes in a stream to prevent the possible pollution of water near a bank which may be used for recreational purposes, as follows:

$$L = \frac{q}{hvn}$$

where L is the distance from the bank to the point of discharge, q is the volume of wastes discharged, h is the depth of the stream at the point of discharge, v is the velocity of the stream, and n is a dilution factor. In this simple relationship, quite obviously, the author assumes a complete and presumably rapidly mixing between the point of discharge and the shore, the degree of pollution at the shore depending wholely on the assumed dilution ratio. For domestic wastes, according to Nesmejanow, the required dilution factor ranges from 1:500 to 1:1000 and for industrial wastes it must be determined by laboratory experiments. With small volumes of wastes the value of L will be small and the calculation is straightforward. For lakes, ponds, and open ocean, however, the calculation is more difficult inasmuch as there is no simple velocity relationship. Similar studies have been reported by another Russian (1935).

Vertical mixing in most surface streams generally occurs rapidly in relation to lateral mixing, owing to the low ratio of depth to width. In slow deep rivers, however, thermal differences may cause a density stratification that will interfere with normal turbulent diffusion. This problem may occur when warm wastes are discharged at the surface of cold quiescent receiving waters. In most streams, however, turbulence is so great and depths so shallow that rapid vertical mixing takes place (1936).

Longitudinal mixing influences the translation of pollution downstream and affects the rate of diminution of a pollutant by factors of natural purification in streams. It is related to short circuiting of flow through lakes or deep rivers, as a result of density currents. Mathematical parameters of longitudinal mixing have been derived and evaluated by Thomas and McKee (10) and radioactive tracers have been used to measure longitudinal mixing by Thomas and Archibald (11), and by Parker (1937). An outline of the causes, effects, and parameters descriptive of longitudinal mixing is given by Thomas (1938).

An exact mathematical analysis of longitudinal mixing is exceedingly complex. By assuming that flow in the stream is steady, uniform, and two-dimensional, that no sedimentation, chemical actions, or adsorption occurs,

that the vertical velocity distribution at a cross-section is parabolic, and that the diffusion of substances is not influenced by density currents or solubilities, it is possible to simplify the analysis of longitudinal mixing to the differential equation (11):

$$e \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} - v \frac{\partial c}{\partial x} - kc = 0$$

where e is the kinematic eddy viscosity, c is the concentration of pollutant, x is the distance in the direction of flow, y is the distance perpendicular to the direction of flow, v is the velocity and k is a constant to be evaluated experimentally. In view of the many factors that counteract the assumptions, this formula loses its practical significance in natural stream channels; however, the basic concepts of longitudinal mixing must not be overlooked, for they have a great influence on natural purification in streams. Fortunately, they can be taken into account in the formulations used for analysis of oxygen balance in streams.

Whether lateral, vertical, or longitudinal in dimension, the mixing or dispersion of wastes in streams (and in lakes and oceans too) is largely a function of the turbulence, as measured by eddy diffusion. Strictly speaking, diffusion is a combination of molecular and eddy action; but in open bodies of water, eddy diffusion is 10³ to 10⁶ times greater than molecular diffusion. Hence, molecular diffusion is generally ignored in quantitative evaluations of mixing.

Eddy diffusion is attributed to the large-scale eddies and small-scale eddies in which the velocity energy of a stream is dissipated. The intensity of turbulent flow is often related to a parameter of distance, such as the "mixing length," or average distance that a small mass of fluid in an eddy will move before it loses its momentum. In their dissipation, large-scale eddies generate numerous small-scale ones, of shorter mixing lengths. A full discussion of the coefficient of eddy diffusivity, e, and its relation to mixing in surface streams is beyond the purview of this report. The reader is referred, instead, to modern textbooks on fluid mechanics or to the recent articles by Orlob (1939) and Parker (1937).

DILUTION IN TIDAL ESTUARIES

The concepts of dilution of sewage or industrial waste by a river are markedly altered in regions where the river water mixes with and measurably dilutes sea water. In such tidal estuaries normal dilution is complicated by tidal action which carries a portion of the pollutant back and forth through the region for many cycles; by differences in density of fresh water, sewage, and sea water; by factors such as wind action and density currents that militate against vertical mixing and favor longitudinal mixing; by coagulating and flocculating effects of saline waters; and by configurations in the shores and bottoms of estuaries.

Early attempts at evaluation of dilution in estuaries utilized the tidal-prism concept. Taken as the difference between the volumes of water in the estuary at high and low tides, the tidal prism is contributed in part by fresh river water and in part by ocean water that enters through the seaward boundary of the estuary on the flooding tide. The proportion of fresh water and sea

water depends on the size and configuration of the estuary as well as the discharge of river water into the estuary on each tidal cycle. In the classical application of the tidal-prism concept, the volume of water entering the estuary from the ocean is presumed to be the volume available for dilution and for the removal of pollution added during each tidal period. This concept assumes, therefore, that mixing of the polluted fresh water and the diluting sea water is complete and uniform during each cycle and that the mixture escapes to the open ocean on each ebb tide and does not return to the estuary on the next flood tide.

That the tidal-prism concept was grossly in error became apparent after the wartime perfection of the salinity-temperature-depth indicator, as described by Ketchum (18). Extensive measures of several estuaries in the Pacific Northwest and along the East Coast revealed stratification and stability that militated against mixing within the tidal-prism. These measurements led to redevelopment of the theory of dilution in tidal estuaries, by Tyler (17) and by Ketchum (18, 19, 20).

In his modification of the tidal-prism concept, Ketchum (20) divides the estuary into segments defined by the average excursion of a particle of water on the flooding tide. He assumes, furthermore, that the water within each segment is completely mixed at high tide, with the proportion of water removed on the ebb tide being given by the ratio between the intertidal volume

and the high-tide volume of the segment.

Ketchum's theory is a distinct improvement on the former tidal-prism concept, but still it does not eliminate entirely the effects of incomplete vertical mixing within a segment and the transverse or longitudinal mixing in a horizontal plane. As pointed out by Rawn in his discussion of Ketchum's paper (19), there is a tendency for fresh water, because of its lower density, to stratify and flow over the top of the salt water and for colder, heavier sea water on the incoming tide to move shoreward underneath the overlying warmer and less dense fresh waters.

Salinity studies at the mouth of the Columbia River described by O'Brien (1393) showed a marked tendency for the reversal of current from flood to ebb to occur first at the surface, while the change from ebb to flood started near the bottom. Furthermore, at maximum current strength, the ebb velocities increased almost linearly from bottom to surface, while the flood velocities showed the level of maximum velocity to be depressed markedly

below the surface.

Ketchum's success in applying his theory to actual observations in the Raritan River estuary led Arons and Stommel (1390) to attempt a translation of Ketchum's fundamental idea (that the element of mixing volume is bounded by the length of the tidal excursion) into the language of physics of continua. Arons and Stommel computed salinity distribution using an eddy diffusivity based on the distribution of tidal currents and excursions. By a relatively simple mathematical analysis they arrived at the relationship:

$$\frac{S}{\sigma} = e^{F(1-1/\lambda)} = e^{F(1-L/x)}$$

where S is the actual salinity and σ is the ocean salinity; F is a "flushing number" depending on the geometry of

the estuary, the fresh-water discharge, the coefficient of diffusivity, and the angular frequency of the tide; and λ is the ratio of the distance downstream (x) to the length (L) of the estuary, both measured from an origin where $\grave{S}=0$. Empirical data for several estuaries appear to fit this theoretical formulation quite well. It should be recognized, however, that the methods of analysis based on segmentation and complete mixing within each segment apply only to estuaries that are so intensively turbulent that they exhibit no vertical stratification. In such cases, the salt is carried upstream against the main river flow by turbulent eddies.

In a later paper, Stommel (1940) used the distribution of river water in an estuary as a means of discovering the magnitude of the turbulent diffusion coefficients at various locations. Using these coefficients, he devised a method to yield the dilution of pollution at any point in the estuary. Again, however, this analysis applies only to vertically unstratified estuaries in which the mixing is

due to tides.

In a review of the theories of tidal dilution, Diachishin, Hess, and Ingram (1391) point out that there are a host of variables that are difficult to evaluate accurately, especially in view of long-range tidal changes. These authors favor the use of models to study the range of tides, the effect of density currents, changes in river flow, fluctuations in ocean level, and other variables.

Simmons (1941) discusses the application and limitations of models in the analysis of pollution in estuaries. By proper distortion of horizontal and vertical scales and by adjustment of channel roughness and other friction effects, it is possible to construct models to operate in accordance with Froudian scale relationships for time, velocity, discharge, etc. With a salinity scale of 1:1 it is possible to establish density gradients and to maintain

stability during the test. Tracers can be used to study the movement and dispersion of wastes in a model estuary, either by instantaneous release of a slug of tracer or by continuous release at a predetermined rate over a relatively long period of time. Based on the instantaneous release of a tracer, it is possible to study the movement of the peak concentration, the movement of the center of mass of the contaminant, and the physical dilution of the peak concentration, all as a function of time and tidal cycles. Continuous release of a tracer will reveal the extent and ultimate level of contamination of a given area for a given source of waste. It must be recognized, however, that models can only reproduce the physical phenomena of dispersion, dilution, and transport. They cannot simulate to scale the chemical and biochemical reactions that affect the decay of non-conservative wastes, nor other physical factors such as atmospheric reaeration. These phenomena in an estuary are not amenable to model analysis, but determination of physical dilutions and residence time by means of models will greatly assist in the theoretical evaluation of other factors. Selleck and Pearson (1942, 1943) and Pritchard and Carpenter (1955) have recently utilized conservative tracers in large estuaries for the direct observation of movement and dispersion.

Considerable research and several investigations of pollution in tidal estuaries have been undertaken in recent years (1944, 1945, 1946, 1947, 1948, 1949, 1950) but a thorough review of this work is beyond the scope of this chapter. It is significant, however, to call attention especially to the publications of Pritchard and his colleagues at the Chesapeake Bay Institute (1392, 1951, 1952, 1953, 1954, 1956).

In his earlier work (1392, 1951), Pritchard classified estuaries as positive, inverse, or neutral. A positive estuary is one in which there is a measureable dilution of sea water by a fresh-water stream or other land drainage, e.g., where a large river discharges to the ocean. Inverse estuaries are those that receive little or no fresh water so that evaporative losses exceed the fresh-water input, i.e., the estuarine water becomes more saline than the flushing sea water. A neutral estuary is one in which neither fresh-water inflow nor evaporation dominates.

An example of a neutral tidal estuary is that of San Diego Bay, as reported by Nusbaum and Miller (1394). The bay was divided into three regions and a modification of Ketchum's analysis was applied. It was assumed that no stratification occurred, which is essentially true inasmuch as very little fresh water enters the bay, and that the tidal prism of each region was thoroughly mixed and distributed both on flood and ebb tides with the adjacent regions. Thus, it required three complete tidal cycles for water entering the mouth to pass into the furthermost region. Based on this analysis, the total dissolved-oxygen content of the bay, as provided by tidal exchange, was computed.

Positive estuaries are discussed by Pritchard in a subsequent paper (1952) and further delineated as type A (highly stratified), type B (moderately stratified), type C (vertically homogeneous, with large tidal velocities and great width), and type D (vertically homogeneous but with no upstream net advection). The type of estuary depends on river flow tidal velocities depth and width

depends on river flow, tidal velocities, depth, and width. In his later papers (1952, 1953, 1954), Pritchard groups coastal-plain tidal estuaries into four classes according to the physical structure of the water and to the net motion. Class I is a salt-wedge estuary in which the river inflow is large compared to the tidal effect. Here the fresh water flows seaward on top of a sea-water wedge. The extent to which the wedge intrudes the estuary depends on the frictional drag between the lighter river water and the denser sea water. For low flows, the sea-water wedge is only slightly diluted by fresh water and extends many miles upstream, e.g., over 100 miles up the Mississippi River. At high flows, frictional drag restricts the wedge in this river to only a mile or so. A fresh-water pollutant, introduced at the surface of a salt-wedge estuary, will be quickly flushed to sea. On the other hand, if a dense pollutant is introduced into the sea-water wedge, it will disperse very slowly and take a long time to be flushed from the estuary, for the currents in the wedge are relatively weak and exchange with the surface layer is slow.

Class II is a partially mixed estuary in which tidal movements are relatively large compared to river inflow, vertical mixing is sufficiently strong to destroy the sharp boundaries between the salt wedge and the upper waters, and the wedge is no longer identifiable. Most of the estuaries along the eastern coast of the United States fall into this class. A combination of oscillatory tidal currents and fresh-water inflow produces a circulation pat-

tern in which there is a net seaward flow in the surface layers and a net flow towards the head of the estuary in the deeper layers. There is also a small net vertical exchange from the lower layers to the surface layers. These net motions govern the movement and dispersion of contaminants introduced into either the bottom or surface layers. In either case, however, any dissolved or suspended pollutant ultimately reaches the surface layers and is eventually flushed from the estuary.

Class III estuaries are vertically homogeneous owing to the fact that tidal movements are very large compared to the motion induced by the inflowing fresh water. The salinity decreased from the mouth to the head of the estuary. In relatively wide estuaries in the northern hemisphere, the rotation of the earth causes a net seaward flow along the right bank (looking toward the mouth) and a net inward flow along the left bank. A laterally directed flow carries water from the left side to the right, so that there is a large-scale horizontal mixing. These patterns of flow will largely govern the movement of pollutants.

Class IV involves sectionally homogeneous estuaries that are comparatively narrow and vertically homogeneous. Tidal mixing is sufficient to destroy any lateral salinity gradient, although the longitudinal gradient from the mouth to the head of the estuary remains. In such estuaries, a pollutant is rapidly mixed vertically and horizontally. It is also dispersed longitudinally by turbulent diffusion and carried slowly seaward with the net flow. Kent (1956) presents a mathematical analysis of a well-mixed sectionally homogeneous estuary from which quantitative predictions of the mean distribution

of pollutant concentrations may be obtained.

According to Pritchard (1952, 1953) the generalized equation for the local time rate of change of concentration of a pollutant in an estuary is given by the following differential equation:

$$\frac{\partial c}{\partial t} = -v_1 \frac{\partial c}{\partial x_1} - v_2 \frac{\partial c}{\partial x_2} - v_3 \frac{\partial c}{\partial x_3} + \frac{\partial}{\partial x_1} \left[e_1 \frac{\partial c}{\partial x_1} \right] + \frac{\partial}{\partial x_2} \left[e_2 \frac{\partial c}{\partial x_2} \right] + \frac{\partial}{\partial x_3} \left[e_3 \frac{\partial c}{\partial x_3} \right]$$

where c is the concentration of pollutant at the point (x_1, x_2, x_3) at time $t: v_1, v_2$, and v_3 are the x_1, x_2 , and x_3 components of the velocity in the longitudinal, lateral, and vertical directions respectively; and e_1, e_2 , and e_3 are the corresponding coefficients of eddy diffusion. The first three terms on the right side of the equation show the effects of advection while the last three terms represent the non-advective or turbulent diffusive processes. In the three-dimensional form, the equation is too complex for analytical solution. Even when reduced to two- or one-dimensional forms, it is necessary to make simplifying assumptions regarding the velocity fields and diffusivities in order to obtain analytical solutions.

Any sanitary engineer, confronted with the problem of disposal of sewage or other wastes into a tidal estuary, must recognize that the problem of dilution is exceedingly complex and not capable of precise theoretical evaluation. Each tidal estuary presents problems of density currents and configurations that distinguish it markedly from other estuaries, and consequently each must be studied carefully. The older techniques utilizing

floats, both surface and submerged, are still valuable for studies of currents in estuaries. The salinity-temperature-density indicator and the new tracer methodology in prototype estuaries will serve as additional handy tools in such evaluations. Where the estuary is complex and the construction of waste treatment works is costly, the use of models may be indicated. For judicial expression with respect to tidal estuaries, see Chapter IV.

DILUTION IN OCEANS AND LARGE LAKES

The first edition of WATER QUALITY CRITERIA and its Addendum of 1954 described briefly the work of Rawn and Palmer (21, 22), Clifton (23, 1395), Rice and Johnson (1396), and Kersnar and Caldwell (1397) in evaluating the dilution and dispersion of sewage in open ocean waters. Owing to the fact that more than 125 coastal communities in California, including 11 of the 13 largest cities, dispose of their sewage through submarine outfalls, the State Water Pollution Control Board contracted with Dr. Erman A. Pearson of Berkeley for a comprehensive investigation of the efficacy of submarine outfall disposal of sewage and sludge. His report, Publication No. 14 of the California State Water Pollution Control Board (1957), summarized all available information on dilution in marine waters through the year 1955.

Subsequent to that time, the design and construction of several large outfall sewers on the Pacific coast and the problems associated with disposal of radioactive wastes in the ocean have stimulated research and publication related to dilution and dispersion in oceans and large lakes (e.g., 1911, 1958, 1959, 1960, 1961, 1962, 1963). To evaluate and summarize all such literature is far beyond the purview of this chapter. Indeed, Gunnerson (1964) has already published a comprehensive review of literature (256 references) related to marine waste disposal through the year 1960. In addition, Ingram and Wastler (1945) have compiled a bibliography of selected studies on estuarine and marine pollution, including physical as well as biological aspects. Finally, attention is invited to the Proceedings of the First International Conference on Waste Disposal in the Marine Environment (1965) stimulated by, and sponsored in part by, the California State Water Pollution Control Board.

The physical phenomena of dilution, dispersion, and novement of sewage or other liquid wastes in the ocean or large lakes are generally considered in two separate ategories: the initial dilution caused by jet action and/or density differences, and the subsequent disperion and transport of diluted wastes by ocean currents. nitial dilution, described thoroughly by Rawn, Bowernan, and Brooks (1911), is favored by strong density radients, rapid jet velocity, and high ratios of depth elow the surface to the diameter of the jet. Where a hermocline exists, the rising plume of diluted waste aay not break through this stable barrier, but rather pread out below it. The most feasible engineering conrol over these factors is to provide multiple outlet ports f small diameter and to locate the multiport diffuser in eep water.

Subsequent dispersion and transport of diluted wastes by ocean currents are beyond the control of engineering design once the location of the outfall has been chosen and the multiport diffuser designed; but these factors are important in selection of the discharge site and depth.

A thorough analysis of diffusion in ocean waters is presented by Brooks (1960). Relatively little information has been published on the dilution and dispersion of liquid wastes in large lakes, but increasing attention is being given to this subject.

DILUTION AND TRAVEL OF POLLUTANTS IN GROUND WATER

In attempting to estimate the effect of sewage or industrial wastes upon the quality of ground water, a sanitary engineer must consider not only the natural dilution that may be available but also the effects of soil upon the quality of water passing through it. This section deals with dilution only, while the subject of natural purification or other changes in quality is discussed in a later section of this chapter.

Wastes from municipalities or industries may be discharged into underground waters by means of spreading grounds (percolation beds) or recharge wells, provided that such wastes are relatively free of substances that clog the interstices of the soil. From spreading grounds, the wastes may pass through a zone of aeration before reaching the ground-water table, or they may build up a ground-water mound such that the soil beneath the spreading basin is completely saturated with water. In the zone of aeration, which in southwestern states may be scores of feet deep, the only available dilution is that from intersticial water (and after a short time this water comes into equilibrium with the seeping waste) or from percolating rain water during the wet season. Above the ground-water table, then, little or no dilution will be available. If a perched ground-water table is formed by the percolating wastes, concentration of pollutants therein can be diluted only by percolating rain water, or by self-purified waste water where such purification occurs.

When percolating wastes reach a ground-water basin or enter an underground stream, they may be diluted measurably under certain circumstances. The factors of lateral and longitudinal mixing, however, are different from those in surface waters, for ground-water flow is almost always laminar whereas surface-water flow is generally turbulent. Thus, a small ribbon of polluted water injected into ground-water flow will move in a welldefined streamline with a minimum of lateral or vertical diffusion and dilution. In accordance with the same phanomenon, percolating wastes may reach a sloping ground-water table and then follow along its upper surface with a minimum of vertical diffusion. In many instances, vertical diffusion is inhibited by horizontal clay lenses or by extensive aquacludes. Consequently, the total volume of water in an underground stream or basin cannot be considered as effective for diminishing the concentration of pollutants.

The velocity of flow of ground water may be as low as 10 ft. per year, and only in coarse material or fissures

does the velocity exceed one mile per year. Coupled with the aforementioned minimum rates of lateral and vertical diffusion, these low velocities of flow cause two significant conditions to develop in ground-water basins or streams. First, pollution that is being added to the ground at one point may not affect the quality of water-supply wells at nearby points for many years, or at more distant points for decades; consequently no complaints are registered and no one may be aware of the damage being done. Second, when pollution is finally discovered or when the quality of water supplies is degraded, the damage cannot be repaired or otherwise rectified merely by stopping the pollution, for purification by leaching and dilution will require a longer time than the period of original pollution.

Excellent reviews of the geologic and hydrologic factors relating to the movement and dilution of polluted liquids in ground water are contained in the recent Symposium on Ground Water Contamination (1966, 1967), and in the American Society of Civil Engineers Manual on Ground Water Basin Management (1980).

The advent of synthetic detergents and long-lived radioisotopes has brought renewed interest to problems of ground-water flow, for these substances are excellent tracers of pollution by certain waste waters. Moreover, the need for waste-water reclamation and reutilization has focused attention on ground-water reservoirs as a means of natural purification and storage. One Task Group of the American Water Works Association reports periodically on the status of ground-water contamination (1400, 1968, 1969) while another reviews developments in artificial ground-water recharge (1970, 1971).

Recognizing the importance of underground streams and basins as receiving waters for waste disposal as well as a major source of water supply in many areas, the California State Water Pollution Control Board sponsored investigations to determine the effects of travel of pollution and waste-water reclamation in relation to ground-water quality. Those reports (1398, 1972, 1973, 1974) are largely concerned with chemical and biological factors but they also relate to problems associated with lateral, vertical, and longitudinal mixing.

Several investigators (1975, 1976, 1977, 1978, 1979) have reported on the underground travel of radioactive substances and the feasibility of using radioisotopes as ground-water tracers. The hazard of ground-water contamination from underground nuclear explosions and the possibilities of using deep aquifers for the storage of atomic wastes have also been studied. For information relative to these investigations, the reader is referred to the publications of the Atomic Energy Commission.

It should be realized that a thorough treatment of the subject of dilution in ground water, like that of ocean dispersion, is beyond the scope of this report. A few complicating factors are mentioned herein, merely as a warning to the water-pollution-control official. Each problem of ground-water dilution must be studied individually in the light of geophysical and hydrological data, the nature of the pollutants, the type of soil, the location of water-supply wells, and the beneficial uses to which the water may be put.

NATURAL PURIFICATION IN SURFACE WATERS

Pollutants in receiving waters are frequently classified as conservative or non-conservative. A conservative substance is one for which the concentration is directly related to the extent of dilution, i.e., the substance is not decomposed, altered chemically, or removed physically as a result of natural processes. Consequently, it is possible to predict from a measured concentration of a conservative pollutant at a known stream flow what concentration would occur at other stream flows (provided, of course, that physical parameters of mixing do not also change with flow) and also what would be the effect of varying degrees of treatment. The chloride ion is a good example of a conservative substance.

A non-conservative pollutant is one that may be subject to chemical, biological, or physical processes, (other than dilution) that tend to alter it or remove it from solution or suspension. Ammonia, for example, may be oxidized biochemically to nitrates, then assimilated in algal synthesis, and eventually consumed by animal life. Carbonaceous wastes may be converted largely to carbon dioxide, part of which may escape to the atmosphere. Heavy metals may be precipitated as insoluble salts and adsorbed on rocks or removed by sedimentation. The processes by which non-conservative wastes are altered or removed from water (surface or sub-surface) are grouped into the collective term of natural purification.

Water-pollution-control authorities are interested in three major aspects of natural purification; (a) the rate and extent to which pollutants are stabilized or removed, (b) the effect that such stabilization has upon other significant parameters of water quality such as pH and dissolved oxygen, and (c) corollary action such as nutrient enrichment that may lead to algal blooms and other undesirable qualities.

The rate of diminution of many unstable chemical substances in streams can be estimated and evaluated by routine procedures of physical chemistry. In many instances the oxidizing of unstable compounds follows a first-order equation, but in some cases the formulation more closely approximates a second-order reaction. In a solution containing ample dissolved oxygen, for example, sulfites are oxidized to sulfates in a true first-order reaction at a fairly rapid rate, thus

or
$$\frac{dc}{dt} = -Kt = -2.3kt$$

$$C_t = C_o \cdot e^{-Kt} = C_o \cdot 10^{-kt}$$

where $\frac{dc}{dt}$ is the rate of change of concentration with time,

 C_o is the initial concentration of sulfites, C_t is the concentration after time t, and K or k is a reaction-velocity coefficient. For sulfites, k has been evaluated at values ranging from 0.236 per day to 0.412 per day (7). It is possible to evaluate similar reaction-velocity coefficients for other unstable compounds such as nitrites, polythionates, and cyanides. There is a need to accumulate such data for use in predicting the rate of diminution of nonconservative substances; but one must recognize that in a natural stream the reaction-velocity coefficients may be

influenced by temperature, pH, concentrations of other substances, and the extent to which the stream has previously become acclimated to such pollutants (1981, 1982).

German engineers have long recognized that a stream partially polluted by municipal sewage is much better ible to absorb new industrial wastes than a stream previously not exposed to mild pollution and consequently not seeded with the necessary organisms for biochemical lecomposition (1983, 1984).

The second major aspect of natural purification, specifically its effect upon the dissolved oxygen in surface vaters, has received considerable attention from sanitary agineers and chemists for several decades. The comined effects of many putrescible substances have been rouped into the test for biochemical oxygen demand (BOD), the rate of which is commonly considered to be first-order reaction. Thus, for the standard laboratory est for BOD, when samples are tested every day for a veek or so, the equation of the curve so established can e expressed as

$$y_t = L(1 - 10^{-K_1 t})$$

where y_t is the BOD exerted in any time t, L is the ulmate first-stage BOD, and k_1 is the reaction-velocity officient or "bottle k." If BOD were exerted in a stream the same manner as it is in a laboratory bottle, then tany point B, downstream t hours from point A where in initial ultimate BOD had been L_a , the remaining ltimate BOD, L'_b , would be

$$L'_b = L_a - y_t = L_a \cdot 10^{-k_1 t}$$

 $\log L'_b = -k_1 t \log L_a$

lany factors, however, tend to make the changes of BOD a stream different from those in a laboratory bottle, that the actual remaining BOD at the downstream ation, L_b , will be

$$L_b = L_a \cdot 10^{-k_r t}$$

$$k_r = \frac{1}{t} \log \frac{L_a}{L_b}$$

nere k_r is the "river k" as contrasted with k_1 , the pottle k." Inasmuch as k_r differs from k_1 , the difference $k_r - k_1$ is designated as k_3 (k_2 having been assigned eviously to reaeration, as described hereinafter). The lue of k_3 is positive if k_r exceeds k_1 , and negative if k_1 ceeds k_2 . Factors that tend to make k_3 positive include:

- 1. Sedimentation
- 2. Volatilization of organic acids
- 3. Adsorption, as influenced by the area/volume relationship
- 4. Flocculation
- 5. Biological activities of attached growths.

ctors tending to make k_3 negative include:

1. Previously deposited sludge banks that exude BOD to the stream

- 2. Channel scour
- 3. Longitudinal mixing and short-circuiting.

The use of the k_3 concept is convenient because k_3 can be used to group all of the unknown variables and factors that are difficult to evaluate. Longitudinal mixing, which has previously been shown to affect the downstream translation of pollution, is accounted for handily by k_3 . To separate and evaluate the many factors that constitute k_3 are tasks that are difficult, if not impossible, for k_3 depends on the interplay of all of the factors. Thus, k_3 may be positive in the upper reaches of a stream during the summer, especially where preceding spring freshets have washed upstream sludge deposits into the downstream pools. In the spring, however, this same stream may show a negative k_3 in upper reaches, owing to scour, and a positive value in lower reaches where sedimentation occurs. By evaluating k_3 for any reach of a stream, an engineer can learn much about the condition of the channel and the ability of the stream to oxidize or otherwise diminish a pollutional load.

The evaluation of k_3 is relatively simple and straightforward. It depends, however, on the accurate determination of three other variables, viz, k_1 and L at each end of the reach and the time of flow, t, through the reach. Simplifications in the analysis of BOD data, as developed by Moore, Thomas, and Snow (12), lead to a rapid determination of k_1 and L from the BOD curve; consequently these parameters can be evaluated readily for each stream sample.

The remaining variable, time of flow, is just as important as k in the formulation 10^{-kt} , but more difficult to determine precisely. It represents the time required for the centroid of pollution at point A to travel to the corresponding centroid at point B. Unfortunately for the engineer who must determine it, this time does not correspond to the theoretical detention period, for the actual time of passage is influenced by short-circuiting and longitudinal mixing. In small streams, the time of passage, or flowing-through time, can be measured by the use of dye or salt, but in large streams the required quantities of such substances become unreasonable. Radioactive tracers present a possible approach to the problem, but as yet the potential hazards and controls governing the use of radioactive isotopes preclude their serious consideration. Recent innovations in analysis of a stream's capacity to assimilate pollution, as described hereinafter, have an advantage in that they do not require determination of the time of flow.

The foregoing analysis gives a reliable formulation for the change in putrescible organic matter in a flowing stream, but it does not indicate the manner in which the dissolved-oxygen content of the water will be affected. The concepts of oxygen balance in a stream have been formulated and developed by many engineers, foremost among whom have been Streeter and Phelps (13), and Fair (1985). The use of the theory has been improved somewhat by Thomas (14) on whose analysis much of the next few paragraphs has been based.

It has been shown that the rate of deoxygenation in a flowing stream is proportional to L, the ultimate first-stage BOD, or

$$\frac{dD}{dt} = K_d L = 2.3k_d L$$

where
$$\frac{dD}{dt}$$

is the rate of change of the oxygen deficit, D, and K_d or k_d are proportionality coefficients. Note that neither k_1 , the bottle value, or k_r , the river coefficient, was used in this equation. In the case of an incubated sample, $k_d = k_1$; but in a river the rate of deoxygenation is not the same as the rate of reduction of BOD, owing to such phenomena as sedimentation, volatilization, scour, and longitudinal mixing that do not involve deoxygenation. Moreover, k_d is not the same as k_r , for some of the removal of BOD in streams is not related to oxygen utilization. As yet, no way has been developed to measure directly the deoxygenation rate in a river and hence past investigators have assumed it to be equal to k_1 . In certain heavily polluted, shallow, swift-flowing streams, however, the rocks in the channel resemble a trickling filter and give a tremendous k_3 value as a result of biological oxidation. The deoxygenation rate coefficient in such streams is probably closer to k_r than to k_1 . For most streams, however, the value of k_d is approximated by k_1 ,

$$\frac{dD}{dt} = 2.3k_1L$$

At any downstream station, however, $L = L_a \cdot 10^{-k_r t}$, where k_r is used rather than k_1 , hence:

$$\frac{dD}{dt} = 2.3k_1L_a^{-k_r t}$$

To offset deoxygenation, a polluted stream receives oxygen from the atmosphere in accordance with Henry's law. The rate at which oxygen will pass from the atmosphere into solution depends on the rate at which it crosses the air-water interface, the rate at which it diffuses through the depth of the water, and the oxygen deficit. For a given stream with fixed surface characteristics and turbulence, the rate of reaeration is proportional to the deficit, thus with no simultaneous reaeration,

$$\frac{dD}{dt} = K_2D = 2.3k_2D$$

where k_2 , the reaeration-rate proportionality coefficient, is a function of the stream characteristics. The magnitude of k_2 can be determined approximately from the physical characteristics of the waterway, such as slope, depth, and velocity of flow; or it can be computed for an actual situation from field observations of temperature, dissolved oxygen, and BOD by means of the following equation for oxygen balance.

Combining the rate of deoxygenation and the rate of reaeration, the resultant differential equation expressing oxygen balance in a stream is

$$\frac{dD}{dt} = 2.3k_1L - 2.3k_2D$$

which, upon integration gives

$$D = \frac{k_1 L_a}{k_2 - k_\tau} \left(10^{-k_\tau t} - 10^{-k_2 t} \right) + D_a \cdot 10^{-k_2 t}$$

The foregoing analysis of oxygen balance in a stream can be used to predict the effects of certain substances and varying degrees of treatment; provided, of course, that the characteristics of the stream that govern k_2 , k_r , and t are well known. It has been used successfully in several instances, but it requires careful control and adequate experimental data. Some of its limitations are discussed in the following paragraphs.

Literature on the oxygen balance in surface waters is profuse. Hull (1926) has prepared a recent bibliography on biochemical oxygen demand, but it does not cover articles relating to other factors of the oxygen balance in surface waters. Other resumes of current knowledge have been prepared from time to time (1384, 1924, 1986, 1987, 1988, 1989).

Orford and Ingram (1385) criticize the use of the unimolecular or first-order reaction to formulate the BOD curve pointing out that the k_1 and L values do not remain constant over the entire curve. This effect had been noted by several previous investigators who proposed factors in the first-order formulation to compensate for it. Orford and Ingram propose instead that the recognized formulation be abandoned in favor of an entirely new logarithmic BOD equation. They claim that the new equation has more biological significance, that it is better adapted to the interpretation of biological oxidation phenomena, that it is easier to compute, and that the parameters of the formula are constants over a time range of 85 percent of the first-stage BOD. Woodward (1386) refutes these arguments, pointing out that the BOD curve can be formulated by a second-order reaction to give a fit as good or better than the logarithmic BOD equation. He defends the present first-order equation as an established and worthy method, within the limits of reliability of the data, which can be formulated quickly by the new technique with the method of moments. Schroepfer et al. (1990) reappraised deoxygenation rates of various wastes, noting that raw sewage, primary effluent, and chemical-treatment effluent were characterized by a rapidly decreasing reaction rate constant during the first day of incubation.

Photosynthetic action by algae may represent a major source of oxygen for streams, lakes, and estuaries; hence it should be evaluated along with other factors in the analysis of oxygen balance (1394, 1925, 1991, 1992). Similarly, organic bottom deposits cannot be neglected, for they may cause a significant portion of the oxygen demand (1993, 1994).

A great deal of work has been accomplished and published in recent years to evaluate more precisely the reaeration of streams and estuaries. To review all of this work is far beyond the scope of this chapter, but the reader may wish to investigate these cited references (1925, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2097, 2518, 2951, 2952).

Of particular significance in the study of oxygen balance has been the work of Hull at The Johns Hopkins University and Churchill of the Tennessee Valley Authority Using the concept of a self-purification coefficient (f) as developed by Fair (1895), whereby $f = \frac{k_2}{k_1}$, Hull (1927) demonstrated that this coefficient can be determined readily at the critical point of the oxygen-sag curve by the relationship:

$$f_c = \frac{k_{2_c}}{k_{1_c}} = \frac{L_c}{D_c}$$

Where L_c and D_c are the first-stage BOD and the oxygen deficit at the critical point, where the dissolved oxygen reaches its minimum value. By this technique, it is possible to compute f by knowing only the stream temperature, first-stage BOD, and the dissolved-oxygen content at the point of minimum dissolved oxygen. There is no need to determine k_1 , k_2 , or the time of travel. It should be recognized, however, that the self-purification coefficient is not a constant, for it may change along the course of a stream and it will vary with the discharge; hence the f_c value may not apply for computing the oxygen

balance over the length of a watercourse.

Churchill (2008, 2009, 2010) presented a method for finding the decrease in dissolved oxygen in a typical oxygen-sag curve without using the original formula by Streeter and Phelps, or any of its subsequent refinenents. The conventional procedure requires determinaion of the first-stage BOD value (L) and the rate of leoxygenation (k_1) , both of which require long-time 30D incubation. Also, the reaeration coefficient (k_2) and the time of flow (t) must be evaluated for each each of the stream and for each rate of discharge. Intead. Churchill proposed a method of analysis based on nultiple linear correlation of observed dissolved-oxygen lrops (to the lowest point on the oxygen-sag curve) with -day BOD, stream temperature, and stream discharge t a stream sampling point nearby. For the example decribed (in the Tennessee River area) the coefficient of orrelation between observed and computed drops in is solved oxygen was R = 0.869. The formula can be sed to predict the improvement in the stream that can e achieved by reducing the pollutional load.

In addition to oxygen-sag analyses, other less-sophistiated methods have been developed along empirical lines determine the allowable load of pollution that a stream in handle (1387, 1388, 1389, 1437, 2011). They repreint a compromise between thorough case-by-case studies the deoxygenating effect on a stream of each probable possible discharge of waste and the arbitrary zoning streams with concurrent use of effluent standards or

ceiving-water standards.

The third aspect of natural purification of interest to ater-pollution-control authorities is the development of rollary pollutants as a result of nutrient enrichment. ne problem is especially acute in fresh-water lakes, here nutrients hasten the processes of eutrophication of result in heavy blooms of algae. Conventional processes of sewage treatment are of no help in amelioration nutrient enrichment, for the end-products of biochemil stabilization (nitrates, phosphates, carbonates) are e offending substances. Only by advanced waste treatent methods or by complete removal of effluents can the entual eutrophication of lakes be delayed.

In flowing water, nutrient enrichment is not generally a serious problem. Where discharged wastes are high in certain carbohydrates, however, heavy growths of Sphaerotilis natans may develop in streams.

For further discussion of the effects of fertilization on receiving waters, the reader is referred to an excellent review by Lackey (2012), the transactions of a 1960 Seminar on Algae and Metropolitan Wastes (2014), and a description of the eutrophication of Swiss Lakes by Jaag (2013).

NATURAL PURIFICATION IN GROUND WATER

While extensive investigations have been conducted on the physical, chemical, and biological changes that occur in polluted surface waters, relatively little attention has been directed toward similar phenomena in ground water. The need for research in ground-water pollution has been pointed out by Stanley and Eliassen (2015), by McKee (2016), and by recent seminars on this subject (2017, 2018). A Task Group of the American Water Works Association (1969) makes periodic surveys of groundwater pollution and waste-disposal practices.

In estimating the anticipated concentrations of pollutants in ground water, with due allowances for dilution as described hereinbefore, one must recognize that certain substances will pass through soil with little or no physical, chemical, or biochemical changes, whereas other substances will be removed or altered markedly. Stated otherwise, some wastes will be conservative, or unaltered by flow through soil, while others will be nonconservative. Chlorides, for example, will pass through soil with few if any changes in concentration except for the possible effects of dilution or evaporation. Indeed, the chloride ion is probably the best tracer of groundwater flow, for it is least affected by adsorption-desorption lag or by other physical or chemical phenomena.

Non-conservative substances in ground water may be altered by physical, chemical, and/or biochemical phenomena such as oxidation or reduction, adsorption or desorption, ion exchange, precipitation or dissolution, aerobic or anaerobic decomposition, and antibiosis or symbiosis. Sometimes the reaction products from decomposition of non-conservative substances may be more deleterious than the original compounds. Carbonaceous wastes, for example, will be degraded biochemically in the presence of oxygen to produce carbon dioxide, which remains in solution in ground water. The increased CO₂ tension, in turn, might cause dissolution of calcium carbonate from the soil and thereby increase the hardness of the ground water.

It is to be expected that wastes of high organic content will quickly deplete any dissolved oxygen in ground water. Moreover, no opportunity will be available for reaeration. Anaerobic ground water will have a negative redox potential that may lead to the reduction of ferric salts and an increase in soluble ferrous iron in pumped water. In some instances, if the proper bacteria are present, ground water of strongly negative redox potential will lead to dinitrification of nitrates (2019, 2020) and possibly to reduction of sulfates to sulfides. Ground water from organic formations such as peaty soil is notoriously characterized by a high content of hydrogen sulfide and possibly methane.

Some of the most thorough investigations of the behavior of pollutants in ground water have been conducted at the University of California and the University of Southern California under the sponsorship of the California State Water Pollution Control Board (1398, 1972, 1973, 1974, 2021, 2022, 2023, 2024, 2025, 2026, 2027). The reader is referred directly to these publications for details. Attention is invited also to the legal problems associated with possible pollution from cemeteries and other judicial aspects of ground-water flow as described in Chapter IV.

Prior to the widespread use of synthetic detergents, especially the ABS-type compounds, the chloride ion was the only effective tracer of ground-water pollution. Nitrates have also been used as a tracer of ground-water pollution (2028). As a conservative substance in saturated ground water, ABS has proved to be an ideal tracer, for it does not appear to be subject to biochemical decomposition and it is only slightly retarded by the chromatographic effect of adsorption and desorption. Several studies have been made to assess the rate of travel of ABS through various types of soils under known conditions of flow (2029, 2030). For more detail, see Chapter X.

One aspect of natural purification in ground water is the direct application of waste water to soil, either by ridge-and-furrow irrigation or by sprinklers. The past decade has shown an increased interest in land disposal of municipal and industrial wastes. In general, the discharge of polluting substances into water courses is meeting with increased resistance, according to an AWWA Task Group report (1400) and consequently the attractiveness of land disposal of wastes is enhanced. A similar philosophy to show why industry is turning more frequently to land disposal by percolation beds or injection wells is presented by Henkel (1401).

In lieu of lagooning, which frequently results in strong odor problems and unstabilized effluents, the food-processing industries such as canneries and dairies have experimented successfully with spray irrigation, which represents a form of land disposal. According to Sanborn (1402) the objective of spray irrigation of cultivated areas for waste disposal is to apply the maximum amount of waste water that can be absorbed by the soil and vegetation without surface run-off or damage to cover crops. This intent is in direct contrast with the objective of agricultural irrigation, which is to grow the maximum crop with the minimum amount of water. Spray irrigation involves a possible risk of pollution of ground-water strata, especially if persistent toxic substances such as boron are contained in the waste water, inasmuch as a large proportion of the water percolates beyond the root zone of the cover crop and enters the shallow or deep ground-water reservoirs.

Problems of the land disposal of sewage and industrial wastes, too complex and too lengthy to include in this brief synopsis of general considerations, are discussed in detail by several authors (1400, 1402, 1403, 1404, 1438, 1439, 1878, 2021, 2026, 2031, 2032, 2033, 2034).

FREQUENCY OF SAMPLING

In studying and utilizing water-quality data, consideration must be given to the frequency of sampling and

the methods by which such data were obtained. This consideration should take into account many of the factors described hereinbefore, such as dilution, mixing, duration of stream flow, and natural purification. In addition, the evaluation should recognize the nature of polluting substance, the frequency and rate of its discharge, and the harm to beneficial uses caused by infrequent high concentrations.

Municipal sewage is discharged at a fairly uniform rate, with daytime peaks and early-morning minima that can be established relatively well for a given community. Many industries follow a similar pattern of discharge, related to working hours and unit processes for which the character and strength of wastes can be predicted. Some industries, however, utilize batch processes from which discharge is infrequent and irregular, and some may have accidental spillages or surreptitious discharges. One such unpredicted slug of toxic substance might destroy the aquatic life of a stream or ruin the crops in an entire irrigation district.

An ideal stream-sampling program, therefore, should involve continuous sampling and analysis by means of automatic equipment analogous to the continuous stage recorders used for discharge measurements. This is a goal for which the State Water Pollution Control Board should strive, and hence it is recommended that an effort be made to encourage the development of such equipment. In this connection, attention is invited to the 1960 U. S. Public Health Service Seminar on Water Quality Measurement and Instrumentation (2035).

Without continuous water-quality recorders, samples should be taken as frequently as possible, commensurate with the cost of manual sampling and analysis, in regions where slugs of pollution are likely to occur. On other streams not subject to intermittent discharges of wastes, less-frequent sampling is indicated. For ground-water basins and underground streams, changes in water quality occur so gradually that quarterly or semi-yearly sampling may be adequate.

In evaluating water-quality data, an engineer should note whether the results are based on grab samples, daily composites, or monthly or yearly averages. Where averages such as the arithmetic mean or median are employed, the number of samples used to compute the parameters should be considered. In a similar fashion, any standards that are promulgated to govern water quality should specify the number and frequency of samples. The USPHS Drinking Water Standards (2036) recognize this effect insofar as bacteria are involved by designating the minimum number of samples to be analyzed per month. Insofar as the mandatory chemical standards of the USPHS are concerned, analyses need be made only semi-annually, and for the recommended limitations on other physical and chemical tests no mention is made of frequency of sampling. Streeter (26) points out that a noteworthy feature of the stream standards of certain state and interstate agencies is their "use of the month as a time unit in fixing limiting requirements for coliform bacteria, dissolved oxygen, and BOD, and also the separation of these requirements according to monthly averages and daily maxima or minima. The monthly average time unit, first proposed in the Ohio River Basin standards, is in effect a stricter requirement than an annual average, all other things being equal, but tends to narrow very materially the wide range of variations above and below the mean which in the past has introduced difficulties in the application of standards based on the annual period. Moreover, it recognizes the fact that a monthly period affords a fair basis of indicating sanitary conditions in a stream during critical times of the year with respect to various stream uses. The added specification of a daily maximum or minimum limit differing from the monthly average is desirable because critical conditions in a stream with respect to certain water uses, notably the maintenance of aquatic life and certain aspects of water supply sanitation, may occur within periods of a few hours, and must be safeguarded by setting tolerances accordingly. Thus, for desirable stream qualities, each one of the four standards listed has specified a daily minimum dissolved oxygen content of 5 ppm., in order to protect streams from short-time lapses in this respect which might cause serious damage to aquatic life.

"It has been well said that a fish dies only once, and it is a matter of common observation that extensive fish killings often occur as the result of stream conditions prevailing for relatively short periods of time. Although such mortality may be due to the temporary presence of toxic substances rather than asphyxiation due to oxygen leficiency, the principle involved is the same in both cases, and should be applicable to both of them alike, in order to be effective. In general, the tendency appears to be to specify either the total absence of certain toxic substances in streams, or their maximum allowable concentration at any time. This question has an important bearing on the fitness of streams for water supplies as well as for the maintenance of fish life.

'A question may arise as to how the proper relationhip between a monthly average stream characteristic and its daily maximum or minimum may be derived. In leveloping the Ohio River Basin recommendations, and lso those of the Tennessee Valley streams this relationhip was worked out from a study of the daily frequenies with which various observed limits were exceeded, as elated to the corresponding monthly average figure for he same characteristic. For example, it was found from study of a large number of observations in different treams of the Ohio River Basin that the daily minimum issolved oxygen content tends to remain above 5 ppm. then the monthly average is not less than 6.5 ppm. Alhough the findings were slightly different in this respect rom the analysis of stream data covering more limited reas, such as those in the Tennessee Valley, and thus ere reflected by some degree of variation in the actual gures proposed in the different standards, the method f their derivation was substantially similar in each

The effects of diurnal fluctuation in dissolved oxygen, ne importance of brief heavy discharges of strong industial wastes, and the phenomena of mixing are discussed y Haney (1370), Chase (1423), Black and McDermott 1373), and Hoak (1371). These factors were among any that led Hoak to reiterate the necessity for continuous water-quality recorders, as recommended in the riginal volume of WATER QUALITY CRITERIA.

VARIABILITY OF WATER QUALITY DATA

In any analysis of water-quality data, one must recognize that concentrations of specific substances in natural waters change from hour to hour for many reasons. The discharge of polluting material, for example, will seldom be constant throughout the day. The quantity of diluting water, moreover, will change as a result of stream flow, tides and currents, ground-water fluctuations, and other variables of the receiving water. Sometimes water-quality criteria are specified to apply to the low-flow condition in a stream. As a consequence of these two important fluctuations, the concentration of any substance in natural waters may be expected to vary widely from hour to hour.

The question then arises: should the average (arithmetic mean) or maximum concentration be considered for threshold and limiting values? In some instances there is no question that the extreme value must govern. A low concentration of oxygen, for example, may persist in a stream for a few hours only; but it may result in the death of many fish. On the other hand, fluorides slightly in excess of 1.5 mg/l for a short period of time will cause no serious mottling of teeth, although prolonged excesses will be deleterious.

It is possible to define each analysis in terms of the prescribed frequency of sampling, a measure of central tendency (e.g., the arithmetic mean), and a parameter of variability such as the standard deviation. In lieu of these three logical yardsticks, the 80 percent or 20 percent values have frequently been selected as representative measures of central tendency and variability. Where an occasional high (or low) value will cause no serious harm, regulations often specify that the prescribed value should not be violated in more than 20 percent of any 20 consecutive samples. If sampling is infrequent, however, the water may be in violation for a long period of time before this error is evident. To avoid a long wait, with possible irreparable damage, the additional requirement is superimposed that no three consecutive samples can exceed the stipulated concentration. If a water just barely meets the 20 percent rule, the probability that three consecutive samples will be in violation is only 6 percent. Hence, this additional precaution superimposes no further severe restriction and yet it provides a warning signal for violations of the quality requirements.

Reference is made frequently to the 95 percent confidence limits, rather than to the 80 percent rule. Ninety-five percent of all observations should fall between these confidence limits. Thus, a stated value cannot be exceeded more than about 2.5 percent of the time. Expressed otherwise, any value that is outside the 95 percent confidence limits varies from the mean by more than two standard deviations.

BIOLOGICAL INDICES OF POLLUTION

No discussion of self-purification in surface streams would be adequate without reference to the role of biota and their use as indicators of stream conditions. However, the decomposition of complex organic compounds into stable substances by biological and biochemical processes and the synthesis of many end-products of decomposition into algae, crustacea, and fish are fascinating

subjects that defy attempt at condensation and synopsis. Instead of a review of current literature the reader is referred to classical standard works such as "Fresh Water Biology" by Ward and Whipple (15) and "Microscopy of Drinking Water" by Whipple, Fair, and Whipple (16). For more advanced and recent work, the references given for the specific biological pollutant in Chapter VII should be consulted.

Interest and enthusiasm concerning the relationship of macroscopic organisms to self-purification in streams enjoy periodic surges, and currently there appears to be renewed vigor along this line, especially for the use of biota as indicators of pollution and purification. Strictly speaking, the presence, absence, numbers, and diversity of all types of organisms, from viruses and bacteriophages through fishes and even aquatic mammals, could be used as criteria of water quality and consequently should be considered as part of this report. Inasmuch as the chemical, physical, and bacteriological criteria are casier to evaluate and apply, and inasmuch as the biological indices of pollution are relatively undeveloped, most of this report is confined to the conventional criteria. In Chapter VII, however, certain biological pollutants, such as pathogenic bacteria and toxic algae are covered. It should be recognized, furthermore, that biota other than those of fecal origin are seldom primary pollutants, i.e., they are seldom added directly to a stream by a polluting agency; instead, they are generally potential corollary pollutants whose numbers depend upon the concentration of primary polluting substances as well as upon natural conditions of temperature, stream flow, etc.

SYNERGISM AND ANTAGONISM

Throughout the literature relating to water-quality criteria, two terms appear frequently to describe the effects and interaction of two or more substances. Inasmuch as these terms, "synergism" and "antagonism," as used hereinafter may not be familiar to some readers, a few words of explanation are in order.

Webster's New Collegiate Dictionary (Merriam) defines synergism as "cooperative action of discrete agencies such that the total effect is greater than the sum of the two effects taken independently, as in the action of the mixtures of certain drugs." The corresponding adjective is "synergistic—of or relating to synergism." The terms "synergy" and "synergetic" are sometimes used but there appears to be a shade of difference in their meaning as compared with synergism. Thus synergy is "combined action or operation, as of muscles, nerves, etc." and the adjective synergetic is "working together, cooperating, as synergetic muscles." Insofar as waterquality criteria are involved, therefore, the terms synergism and synergistic seem to be more descriptive.

To stress the importance of synergism, let us consider a hypothetical example. Substance A may not be toxic to fish in a concentration of 2.0 mg/l, and substance B may not be toxic at 5.0 mg/l; yet when only 1.0 mg/l of A and 2.0 mg/l of B occur together in water the combined effect may be rapidly toxic. Actual examples of synergism are noted later in this report, especially in Chapter VI. Synergism should not be confused with direct chemical reactions that increase the inimical effects

of separate substances, e.g., as chlorination intensifies the taste of phenols by the formation of chlorophenolic compounds. For an interpretation by the courts of synergistic action, see Jessup and Moore Paper Company v. Zeitler, as described in Chapter IV.

The opposite of synergism is antagonism, in which the total effect of discrete agencies is less than the sum of the separate effects taken independently. Thus, by itself substance C may be toxic in concentrations as low as 1.0 mg/l, but in the presence of substance D, the toxic concentration of substance C may be raised to 5.0 mg/l. Part of this antagonism may result from direct precipitation of the toxic compound, but more often the antagonistic action is not so well defined or understood.

The entire subject of synergism and antagonism is worthy of further investigation, for little is understood about the basic mechanisms or fundamentals governing these processes. Where their effects have been observed in the literature, they are noted in this report, but seldom is an attempt made to explain them.

DELINEATION OF TOXIC CONCENTRATION

The toxicity of many potential pollutants in water toward plant and animal life is a time-concentration phenomenon, i.e., for a given concentration, toxicity increases with continued exposure. For other substances, however, toxicity is relatively independent of time, i.e., if a given concentration is not toxic in one or two hours, it will not be acutely or directly toxic.

Experimental data on toxicity are sometimes reported as "minimum lethal dose" (MLD), or the minimum concentration required to kill one or more of the test species. More frequently in bioassay work the term TL_m (tolerance limit, median) is used to designate the concentration required to kill 50 percent of the tested organisms. For either of these parameters (MLD or TL_m) it is essential that the time of exposure be specified. Thus, one reads about 24-hr. TL_m values or 96-hr. MLD's. For direct feeding experiments or injections, the median toxic dosage is noted as LD_{50} , or the lethal dose for 50 percent of the animals. Many LD_{50} values are based on single feedings or injections, in which case time of exposure is not a criterion; but where ingestion continues over a period of days, the time of exposure should be specified.

Most bioassay work relates to "acute" and "direct" toxicity, i.e., the lethal action within a period of 96 hours or less. The deleterious effects of many substances, however, may not be evident for weeks, months, or longer. Such long-term effects are known as "chronic" toxicity. They may be related to changes in appetite, metabolism, disorders of the nervous system, reproduction, or other vital functions, the alteration of which does not produce early death. For this reason, many investigators prefer to measure toxicity not in terms of death of the test species but rather in relation to respiration, food consumption, reproduction, or other function. It is reasoned that changes in these functions are precursors of chronic toxicity and eventual diminution or elimination of the species. Even more remote in the time sequence is possible mutation of genes that may cause a long-term chronic effect.

Toxicity may be indirect as well as direct, i.e., a substance may have no direct toxic action toward a given species either on an acute or chronic basis; but it may result in eventual elimination of the species by toxic action against one or more of the organisms in the food chain of the species in question. Very little quantitative information is available on indirect chronic toxicity, for such determinations require a complicated study of the

entire ecology.

In this report, toxicities are expressed for the most part in the language of the original investigators. Some data are given as MLD values, others as TLm's, and others in terms of non-lethal effects. In establishing criteria of toxicity, some authorities speak of "threshold" and "limiting" concentrations. A threshold concentration is defined as one at which a given beneficial use of the water is not damaged to any measurable degree by pollution, but slight effects are noticeable. A limiting concentration is one at which the beneficial use is severely in-

Throughout the following report an attempt is made to differentiate between limiting and threshold concentrations, but unfortunately such careful segregation of values is not always possible. Many criteria are reported nerely as "desirable" or "optimum", while others are objectives or goals toward which to strive. This confusion of terms and blending of values is particularly noticeable in Chapter V where criteria for various indusrial water supplies are given. Many industries will pecify water of high purity but will accept inferior ruality if other economic considerations so dictate.

The confusion in parameters of concentration is paricularly evident where biological requirements are involved. Here it is virtually impossible to establish threshold concentrations inasmuch as effects of a specific substance on a particular organism will not portray the over-all changes in the complex interrelationships of ecology. For example, fish, minnows, daphnia and other organisms may be exposed to one mg/l of substance X for 100 hours or longer without apparent injury; yet the continued discharge of substance X so as to give one mg/l in a natural stream might alter materially the natural fauna of the stream and result in the absence of

How can TL_m or MLD values from short-time bioassay tests be converted to safe, threshold, or limiting concentrations? Unfortunately there is no simple application factor or formula to convert 24-, 48-, or 96-hour TLm or MLD data to concentrations that are considered safe for long-time exposure. Simple factors such as one-tenth of the 48-, or 96-hour TLm have been proposed, while other investigators prefer formulas involving ratios of 24-, and 48-hour TL_m values. For a discussion of the merits and limitations of application factors, see the papers by Henderson (2037, 2038) and Pearson (1772).

For man, livestock, and wildlife the concentration of a specific substance in drinking water may represent only a small fraction of the total intake of that substance. As pointed out by Cass (2039) it is essential to consider the total intake from (a) atmospheric exposure through nose, eyes, lungs, and digestive tract, (b) foodstuffs, (c) water and beverages, and (d) skin contact. Man's total intake of sodium, calcium, chloride, and sulfates, for example, is generally far more dependent on his diet than on the concentrations of these substances in his drinking water.

CHAPTER III

WATER QUALITY CRITERIA PROMULGATED BY STATE AND INTERSTATE AGENCIES

The aims of this chapter are restricted to: (1) a brief commentary on the historical development of water-quality standards and water-pollution-control practices; (2) a discussion of the various types of standards or criteria with an evaluation of their significance or utility; and (3) a summary of the standards and/or provisions for standards of the states, interstate agencies, and international groups of which the United States is a member.

No attempt is made to consider the legislation by which water-pollution-control boards or commissions are established, nor the powers and duties delegated to such bodies other than for the establishment of standards and/or systems of stream classification. Furthermore, this investigation does not deal with the action of boards in requiring permits, approving plans, or operation of programs; nor with enforcement, penalties, or appeals from decisions of the boards, except insofar as such actions are relevant to water-quality considerations.

HISTORICAL BACKGROUND

The earliest water-quality criteria were those that employed physical tests such as temperature, taste, odor, color, and turbidity. Although old and familiar to the layman, these criteria scarcely deserve the faith placed in them by a Mississippi jurist in 1904 when he declared, in part "It is not necessary to weigh with tenderness and care the testimony of experts. Any ordinary mortal knows whether water is fit to drink and use" (27).

Many of the physical criteria have been refined and may now be evaluated quantitatively with precision and understanding. Temperature falls in this category. Others, however, are still expressed in contemporary standards by vague terms such as "No discharge shall cause objectionable discoloration or turbidity," thereby leaving to the administrative agency or to the courts the final interpretation.

Chemical criteria of water quality were proposed almost two centuries ago. As early as 1784 waters were said to be "drinkable" if they would "dissolve soap without forming lumps . . . and deposit nothing or very little by tests" (28). Organic matter in water was viewed with suspicion by early observers and attempts were made to determine it quantitatively and relate it to the incidence of disease. That human and animal wastes could contaminate water and render it dangerous for drinking and other domestic uses has been known for centuries (29, 30). Such tragedies as the cholera epidemic resulting from sewage contamination of the Broad Street well in London in 1854 served to increase interest in developing criteria to detect impure and dangerous water.

Such criteria were proposed by De Chaumont (31) who held that a water was "pure and wholesome" if it would yield less than 17 mg/l of residue upon evaporation and the "... solids on incineration should scarcely blacken"; a water was "usable" if it had less than 51 mg/l of residue and the "... solids may blacken a little, but no fumes should be given off"; a "suspicious water" would have 54 to 85 mg/l of residue, with "... much blackening on incineration or nitrous fumes given off"; and an "impure water" would have more than 85 mg/l of residue with "... much blackening and nitrous fumes given off, or smell of burnt horn." These criteria were tempered, however, by the remark that "In peat waters the incinerated solids may blacken considerably" (31). Other early tests were patterned on the rate and quality of color changes of potassium permanganate added to a small sample of the water.

About 1870, criteria based on the amount of ammonia derived from proteinaceous substances in the water came into prominence, and Leeds (27) proposed that, in streams used for water supply, the free ammonia should not exceed 0.12 mg/l and the albuminoid nitrogen 0.28 mg/l.

An early method of measuring the microbiological quality of water depended on its "keeping power." Thus, a relatively pure water could be stored for a much longer time than could an impure water without changes or growths that were visible to the naked eye. With the development of the microscope, criteria were formulated on the number and type of organisms and organic debris observed in the water.

Thresh (32) makes an interesting comparison of two early bacterial criteria relating the total number of bacteria to the quality of the water. His tabulation of the recommendations of Miquel and Mace is shown below:

	Number of bacteria per ml, after		
Designation of Quality	Miquel	Mace	
Very pure water	0-10	0-10	
Very good water		20-100	
Good or pure water		100-200	
Passable water		200-500	
Impure water		500-1,000	
Very impure water	Over 100,000	Over 1,000	

Hence, a water containing 750 bacteria per ml would be "impure" by Mace's standards and "good" by Miquel's.

As might be expected, almost all criteria for determining water quality have been subject to criticism of some sort. Many standards, just by posing as a target for criticism, have served a useful purpose by instigating and inspiring further research, thereby increasing the total knowledge. Bean, in a symposium (1744), discusses the need for high-quality professional standards within the water industry. In a later paper (1745), he presents some finite values for an ideal water. Lubratovich and

Ruble (1746) point out that the U. S. Public Health Service Drinking Water Standards define a safe water, but not necessarily a good quality water, and then proceed to suggest finite high-quality standards. Both sets of standards were published with the same intent, namely, to create interest and discussion. Other standards, however, have been meekly and blindly accepted and somehow did not serve to spark the scientific curiosity that leads to progress.

That some criteria have thus served their exciting or antagonizing purpose, then slid out of sight or been improved upon, is an encouraging fact, for many criteria of today are undoubtedly in error and will be improved upon in time or cast away. Criteria are merely imperfect human-made tools and will be supplanted by other criteria as scientific knowledge advances. Among waterquality criteria there are few if any that can be considered absolute and final, for absolute truth is a rare thing.

DEVELOPMENT OF WATER POLLUTION CONTROL PRACTICES

In the last three decades, there has been an extremely rapid expansion of governmental functions and responsibilities in the field of water-pollution control, closely following the development of the greatly widened governmental activities in other areas of our highly integrated and complex society. Inasmuch as water-pollution control has remained to a large extent a state responsibility, the principles, laws, and methods adopted by each state for such control differ markedly, depending upon the particular needs and experiences of the individual state. In reviewing each state's program of water-pollution control, however, certain patterns, similarities, trends, and styles appear.

The authority to control water pollution began with he common law. Several articles, papers, and reports have been published to describe the water-pollution asbects of the body of law dealing with public nuisances, iparian rights, private damages, equity, and similar

acets of law (33).

The basic doctrine threading through the numerous court decisions affirms the principle that no right can be equired for an unreasonable abuse of a water to the xtent that a downstream user suffers loss or hardship. The earliest and most apparent results of uncontrolled r indiscriminate pollution of water were the threats to ublic health largely from the disposal of untreated sewge, and the mass killing of fish largely from the disposal f strong industrial wastes. It was natural, therefore, hat the first efforts to control water pollution were diected in the fields of public health and wildlife consertion.

The tools for controlling water pollution furnished by he common law were largely punitive, applicable after he pollution was accomplished and the damage was one. However, there appears to be no fundamental reaon why an efficient and adequate system of control could ot develop, over a period of years and with the accumution of custom and precedents, largely in such a hadow of potential litigation. Water-pollution controls ased upon the common law have been used in part, and till are, by various states. In many states it is common p find two different sets of laws applied to the same sub-

stance—water. These states may use the riparian doctrine or the doctrine of prior appropriation to govern the use of surface waters while the common law prevails for the use of ground waters (1747). Although older, the common-law criterion can be quite severe (1748).

As the need for some sort of restraint to the pollution of water grew, health departments of many states were given statutory powers and responsibilities for pollution control. Corollary powers and responsibilities were usually given to other agencies for the protection of fish and game. The legislation of each state differed greatly in scope and powers, but usually the boards of health were given the power to protect the supplies of domestic water from contamination, to abate nuisances, and to pass rules and regulations to insure this protection. The departments of fish and game usually were given analogous powers for the protection of fish and wildlife. Many states adopted a scheme of licensing or issuing permits for the disposal of various wastes in natural waters to facilitate the control of water pollution.

In general, the primary responsibility for water-pollution control fell upon the divisions of sanitary engineering or environmental sanitation in the state health departments. These agencies drew their power from three sources: the common law, specific statutes, and quasilegal rules and regulations of the boards of health. In many states such a foundation in the areas of health and wildlife was deemed to be unsatisfactory for the control of water pollution, inasmuch as there was a lack of delegation of authority and responsibility for pollution abatement to a single administrative agency. Furthermore, there were peculiarities that made such abatement unenforceable in certain conditions, and there was confusion over the very definition of pollution and the deci-

sion of what was to be abated.

To correct some of these inadequacies, the legislatures of several states enacted specific water-pollution-control legislation. Generally, these newer acts supplement the existing statutes by providing for a single administrative agency that is responsible for control and abatement of water pollution in the state. Provisions are often made (a) for representation of the several interests concerned in water pollution, either on an advisory board or on the control board itself, (b) for the definition and determination of pollution, usually by stream standards or classifications, (c) for the enforcement of abatement orders, with penalties for non-compliance, and (d) for hearings and appeals of parties affected by actions of the agency.

More recent developments include the closer alignment of state water-pollution-control agencies with other state water-resource-development activities (see New York, North Carolina, and California), the participation of the Federal Government in interstate pollution-control agencies, and the formation of state-federal basin committees on water-resource activities whereby the various state and federal agencies will have representation.

TYPES OF CRITERIA FOR WATER POLLUTION CONTROL

There are two basic types of criteria or standards that have been used for the control of water pollution. One type dealing with the quality of the receiving water, whether stream, lake, river, estuary, open ocean, or ground water, is commonly designated as "stream standards" or "receiving-water standards." The other type, referring to the quality of the wastes to be discharged from a given plant, is called "effluent standards." Each type has its advantages and disadvantages, each type has its advocates and opponents, and each type is in

common use today (1749, 1750).

Stream standards may be divided into two distinct categories; (a) dilution requirements and (b) standards of receiving-water quality. Largely outmoded now (1751), dilution requirements were favored at the turn of the century as handy yardsticks and rules-of-thumb. They were proposed first in 1887 for the Chicago drainage canal, when Rudolf Hering recommended a dilution rate of 3.3 cfs per 1,000 persons sewered (35). Later Hazen, Goodnough, Stearns and others in New England proposed requirements varying from 2 to 10 cfs per 1,000 persons, depending on the characteristics of the receiving waters (26).

Considerations of dilution entered into the recommendations in the Eighth Report of the Royal Commission on Sewage Disposal, 1913. Although these recommendations were never legalized by Parliament, they are generally quoted in bills before parliamentary committees and in courts of law in Great Britain (36). The Royal Commission recommended that a general standard and several special standards be established, the choice of which in each instance would depend on local circumstances. In order to comply with the general standard, an effluent had to contain not more than 30 mg/l of suspended matter and not more than 20 mg/l of 5-day, 18.3°C BOD, without reference to dilution. In specifying special standards, however, the Royal Commission considered dilution as the chief factor. Where dilution exceeded 150 to 1, the limitation on BOD was omitted and the suspended solids content was allowed to be as high as 60 mg/l. Where dilution exceeded 300 to 1, the standard for suspended solids was relaxed further to 150 mg/l; and with dilution in excess of 500 to 1, all tests could be waived, provided of course that esthetic requirements with regard to screenings and floating solids were considered.

Standards of quality of the receiving water are based on threshold and limiting values for specific substances in the water, and depend on the beneficial uses to which the water may be put. Widely used now and gaining in favor among those who feel that some sort of formalized criteria are necessary, this category of stream standards is frequently correlated with a system of stream classification or zoning whereby separate standards are set for each stream or zone. The principal advantage of standards of stream quality over effluent standards lies in the fact that they take into account dilution and the assimilative capacity of the receiving water and consequently lead generally to an economy of treatment works for pollution abatement. On the other hand, such standards are difficult to formulate and define, and more difficult to administer. Where stream classification is mandatory and complicated, the program may become extremely cumbersome. For an example of stream standards without classification, see the brief description of the Indiana program and for an example of standards coupled with classification see the New York plan. An

example of stream standards that have not been legislated but which have been generally accepted and used as guides (in England) are: a maximum limit of 4 mg/l of BOD; pH in the range of 6.0 to 9.0; suspended solids that will not cause silting of streams; and virtually complete removal of highly toxic substances such as cyanides and certain metal ions (1752).

The second general type, effluent standards, may also be divided into two general categories; those that restrict the strength and/or amount of substance that can be discharged, and those that specify the degree of treatment or percentage removal of a specific pollutant that must be accomplished by treatment or by changes in industrial processes. The first report of the Rivers Pollution Commission in England, 1868, recommended "standards of purity" for effluents, proposing limits for suspended organic and mineral matter, organic carbon, and nitrogen, sulfides, metals (other than the common alkaline earth metals), acidity, alkalinity, arsenic, free chlorine, oil, and color (1753). As an example of restrictions on the strength of wastes, the Interstate Commission on the Delaware River (Incodel) specifies that effluents discharged into Zone 1 shall have a BOD not greater than 50 mg/l, and into Zone 2 not greater than 100 mg/l.

Pennsylvania has pioneered in effluent standards that specify the amount of pollutant that may be discharged by special industries and each process within such industries. This program is based on a percentage removal of pollutants from "normal" for each process, as established by representatives of industry. Consequently the effluent requirements favor good housekeeping and pe-

nalize the inefficient operator.

Standards that specify the degree of treatment are also typified by those of Incodel, which require in addition to the limitations on BOD as specified above that the BOD reduction of wastes discharged into waters of Zones 1 and 2 shall be at least 85 percent and that wastes entering Zone 3 shall have a BOD reduction of at least 35 percent.

Effluent standards have the advantages of simplicity and ease of administration, for they are well defined and equitable among industries. Their primary disadvantage lies in their uneconomical use of the assimilative powers of receiving waters.

SIGNIFICANCE OF CRITERIA

A marked difference of opinion exists among water-pollution-control authorities, in industry, in private practice, and in public agencies, regarding the advantages and disadvantages of various types of standards and systems of classification. Dappert (1421) presents the case for the use of classes and standards, whereas McKee and Bacon (1422) outline the merits of case-by-case studies in lieu of fixed standards. In a panel discussion, Wieters, Knox, Healy, and Chase (1423) present many facets of the arguments for and against classification of surface waters, while Hopkins (1424), Hess (1413, 1754), Gloyna, Wolff, Geyer, and Wolman (1755), and Frederick (1425) discuss the background of several philosophies.

In a comparison with England, Klein notes that in the United States "stream standards rather than effluent standards are preferred for legal purposes and (that) this is understandable in a country where, in general, rivers are large and pollutions occur at wide intervals' (1756). However, Pennsylvania has long favored effluent standards because they are easy to enforce (1757).

The difference of opinion is just as prevalent abroad as it is in the United States. In England, for example, "experience has led to the conclusion that to devise bylaws (standards) which would be satisfactory, effective, and generally applicable would be so difficult as to be almost impossible. Recognizing this, the trade effluents sub-committee of the Central Advisory Water Committee recently (1960) recommended a change in the law in England and Wales whereby the current procedure, suitably modified, would also apply to old discharges. By this, the discharges would be dealt with one by one instead of by reference to a general standard, and this would enable all the circumstances to be taken fully into account" (1758).

The Water Research Association in England discussed the philosophy of establishing limits or standards of water quality. It is their conclusion (1759) that:

- "1. Limitation is clearly advantageous only if those substances that are injurious to human health in concentrations that are lower than those in which the substance may be otherwise deleterious, e.g. lead.
- "2. Limitation may be advisable where the substance is not detrimental to human health, provided the ground for the limitation is generally applicable and clearly stated, e.g. iron on account of coloration imparted.
- "3. Limitation is not desirable where the presence of the substance at concentrations less than that at which it is injurious to health could be objectionable on more than one ground. In such cases a list of the grounds on which the presence is harmful, together with the quantities below which no damage could result, would be advantageous.
- "4. Such tables might be of great complexity as the activity of one substance can depend on the presence of another. Although present knowledge does not permit of their construction a greater understanding should be sought.
- "5. Accurate information and good judgment have no substitute."

King (1760, 1761) also discusses the difficulties in formulating standards and their disadvantages and impracticability. Nevertheless, he states, in order to protect the quality of tidal waters and streams it is necessary for the authorities controlling the waters to adopt conditions of discharge.

For Australia, the impracticability of any universal standard of purification (treatment) is pointed out, but still the need to draw up standards for particular rivers or for sections of rivers is stressed (1762).

In Germany, the fixing of standards of concentration s not recommended (by Bucksteeg), as local conditions and capacity of streams vary (1763). Another writer concluded that general effluent standards are impractical, and that equitable standards for an individual effluent can be established only after careful consideration of

both the effluent and the receiving stream, and as the latter change so would the standards have to change (1764).

The need for effluent standards in South Africa is cited, but separate standards will be necessary for each region of the country as a result of wide climactic and

geographical differences (1765).

On 23 and 24 February 1960, the U.S.S.R. Chief State Sanitary Inspector and the boards of the All-Union and All-Russian Hygiene Societies called a meeting to discuss the problem of establishing maximum permissible concentrations. A discussion of the meeting was published by T. E. Nagibina in a Soviet journal and translated into English by B. S. Levine. According to this account, a Soviet scientist (Ya. M. Grushko) had questioned the basic principle of levying maximum permissible concentrations on harmful substances in water since this practice made it possible for industry to pollute the water "according to law." Such regulation resulted in a hindrance of the work against water pollution. These comments, published in newspapers and magazines, had precipitated a storm of controversy that resulted in the meeting.

Over 60 leading Soviet scientists participated in the meeting. The only person who spoke on behalf of Grushko was Grushko himself. He reaffirmed his position, stating that the policy of relying on standards is wrong. He added, however, that he is not against maximum permissible concentrations per se. He only wanted to see these standards lowered, i.e., a "drastic reduction in the maximum permissible concentrations."

All other participants soundly scolded Grushko's views. V. M. Zhdanov, the U.S.S.R. Chief State Sanitary Inspector, summarized the favorable (almost militant) attitude of these participants for standards with, "We in the State Sanitary Inspection Commission consider the discussion closed . . ."

The results of the meeting were discussed on 3 March 1960 by the staff of the U.S.S.R. Ministry of Public Health who reaffirmed and endorsed the principles and practice of maximum permissible concentrations (1766).

In summary, it appears that sanitary engineers have an almost universal dislike for broadly applied water-quality standards. While all of the partisans of the various views will agree that effective and economic abatement of pollution is the logical goal it remains difficult to assess the merits of each philosophy. Often the engineering and economic aspects are obscured by political and personal factors.

FEDERAL ATTITUDE TOWARD CRITERIA OF POLLUTION CONTROL

Five Federal laws containing major provisions concerned with the control of water pollution have been enacted by the Congress. Two of these, the Rivers and Harbors Act of 1899 (Section 13) and the Oil Pollution Act of 1924, are primarily concerned with preventing damage to shipping, and are administered by the Department of Defense. The 1899 Act prohibits the depositing of waste materials, other than that flowing from streets and sewers in a liquid state, in or on the banks of navigable waters and their tributaries (see Chapter IV, United States v. Republic Steel Corp.). The 1924

Act prohibits the discharge of oil into the coastal navi-

gable waters of the United States.

The third major Federal enactment regarding water pollution was a provision in the Public Health Service Act of 1912, which gave specific authority to the Public Health Service to conduct investigations of the pollution of streams and lakes by sewage and other causes. It was under this legislation that the Service carried out early research and investigations that provided the basis for information and consultative services to other agencies.

The first comprehensive-type legislation in the pollution control field was the Water Pollution Control Act of 1948 (P. L. 845, 80th Congress) which authorized expanded activities by the Public Health Service. This law, passed after a half-century of consideration of national water pollution problems and evaluation of the responsibility of the Federal government, added the principles of State-Federal cooperative program development, limited Federal enforcement authority, and financial aid. Finally, the particular concern of the Federal government in the growing national pollution problem resulted in the new Federal Water Pollution Control Act (P. L. 660, 84th Congress), which was approved by the President on July 9, 1956. Experience had shown that many of the principles and provisions embodied in the Act of 1948 were sound, and many were carried over into the new legislation (1767).

The Federal Water Pollution Control Act Amendments of 1961 considerably elevated the significance of the entire federal water-pollution-control program. Instead of being a Public Health Service program, it is now administered directly by the Secretary of the Department of Health, Education, and Welfare. Also, the amendments greatly increased the area of federal enforcement since the previous restriction to interstate waters has been lifted to include interstate or navigable

waters.

Section 4 of the act states, in part, that the Secretary shall, "in cooperation with other Federal, State, and local agencies having related responsibilities, collect and disseminate basic data on chemical, physical, and biological water quality insofar as such data or other information relate to water pollution and the prevention and control thereof" (1768). The 1961 amendment adds "... the Secretary shall develop and demonstrate under varied conditions . . . practicable means of treating municipal sewage and other waterborne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for repeated reuse . . " (1769).

Following discussions among federal, interstate, state, and local agencies having allied responsibilities, it was agreed by them that the over-all objectives of the pro-

gram should include:

"a. Long-term information on changes in water quality at key points in river systems, as such quality may be affected by change in water use and development.

"b. Continuous information on the nature and extent of pollutants affecting water quality" (1768).

Clearly, the federal position in regards to quality is one of extreme concern. However, no national standards

or regulations have been developed for the control of discharge of wastes into surface waters (1755).

The question of the introduction of national standards was lightly touched upon at the 1960 National Conference on Water Pollution. Recommendation 21 of the Conference states, "Provision should be made within the Public Health Service for developing the water quality criteria which are suited to application on a national basis. However, many water quality criteria are not uniformly applicable because of the effects of area usage differences, stream characteristics and other factors. State and local determinations of some criteria also will have to be made. It is recognized that periodic revision of these criteria not only will be in order, but should be sought as new data are made available" (1772).

Congress recognizes that primary responsibility in the field of water-pollution control rests with the states (1773). The federal role in water pollution is to provide technical services and financial aid to states, interstate agencies, and municipalities. A "Suggested State Water Pollution Control Act" has been issued by the Public Health Service, and as of July 1961 its principles had been used by 40 states (1743). An explanatory statement with respect to classification and standards is as follows:

"Some agencies in the administration of water pollution control programs have classified the waters of the State according to their use and have established standards of quality for such waters in accordance with their respective uses. Proponents of this method have urged that classification and setting of standards is an essential element of any comprehensive program and also that no enforcement action can be undertaken without determination of the use to which a particular body of water should be put and the degree of quality which the water must have in order to be suitable for such use. This approach, however, has been severely criticized by others who maintain that the process is administratively difficult and time consuming, that classifications once made are hard to change and tend to create vested interests. and that the tendency will be to reduce waters to the level of mere carriers of wastes because of the pressure of special interests.

"The Suggested State Water Pollution Control Act authorizes the agency to classify waters and set up standards of quality for water falling within particular classifications but does not make it mandatory to do so. Classifications and standards once promulgated have a definite legal effect and their violation is made unlawful; conversely, discharges which comply with such classifications and standards are not pollution within the meaning of this Act. In view of the number of persons affected by classifications and standards, it is required that their adoption be preceded by a public hearing open to all residents of the areas affected, and that adequate notice thereof be given. The Act provides that in classifying waters and setting standards the agency will be guided by the principle of constantly seeking to improve water quality and upgrading streams for progressively higher uses to the maximum extent practicable" (1774).

The Suggested Act itself deals with the above subject matter in Section 6 as follows (also see 1793):

"Section 6. Classification of Waters; Standards of Water Quality.

(a) In order to effectuate a comprehensive program for the prevention, control and abatement of pollution of the waters of the State, the Board is authorized to group such waters into classes according to their present and future best uses for the purpose of progressively improving the quality of such waters and upgrading them from time to time by reclassifying them, to the maximum extent that is practical and in the public interest. Standards of quality for each such classification consistent with best present and future use of such waters may be adopted by the Board and from time to time modified or changed. (States which adhere to the "prior acquisition doctrine" should take cognizance of the effect that classification will have on water rights established under other laws.)

(b) Prior to classifying waters or setting standards or modifying or repealing such classifications or standards the Board shall conduct public hearings in connection therewith. Notice of public hearing for the consideration, adoption or amendment of the classification of waters and standards of purity and quality thereof shall specify the waters concerning which a classification is sought to be made or for which standards are sought to be adopted and the time, date, and place of such hearing. Such notice shall be published at least twice in a newspaper of general circulation in the area affected and shall be mailed at least twenty days before such public hearing to the chief executive of each political subdivision of the area affected and may be mailed to such other persons as the Board has reason to believe may be affected by such classification and the setting of such standards.

(c) The adoption of standards of quality of the waters of the State and classification of such waters or any modification or change thereof shall be effectuated by an order of the Board which shall be published in a newspaper of general circulation in the area affected. In classifying waters and setting standards of water quality or making any modification or change thereof, the Board shall announce a reasonable time for persons discharging wastes into the waters of the State to comply with such classification or standards, unless such discharges create an actual or potential hazard to public health.

Any discharge in accord with such classification or tandards shall not be deemed to be pollution for the

purposes of this Act" (1774).

Whether or not this new and suggested legislation ndicates an eventual application of federal standards o interstate and to navigable waters remains to be seen. The statutes in effect in each state with respect to

tandards, objectives, requirements, or criteria of water quality are described in the following sections of this

hapter.

LABAMA

The Water Improvement Commission has the primary esponsibility for water-pollution control in Alabama. The Commission was created in 1947 as an investigation nd advisory group (37), and was called the Water Improvement Advisory Commission. In 1949 it was given airly comprehensive powers (38), and in 1953 it was urther strengthened, renamed as indicated, and made more flexible by the creation of an Executive Committee of five designated members of the Water Improvement Commission who act for the full Commission under such powers as are delegated to it by the Commission. Among the duties of the Commission is that of establishing criteria or standards for recognized limits of pollution (1770).

The standards of quality are to be related to the reasonable and necessary use of the waters in the public interest, in the consideration that no single standard of treatment and no single standard of quality are practical, and that future as well as present uses must be

considered (1770, 1771).

The Commission has not yet established any standards of water quality, relying instead upon a review of each situation on the basis of its merits and upon the permissible conditions as governed by downstream water uses. "Permits are required for the discharge of sewage, industrial waste and other wastes subject to the authority and control of the Commission. Each permit shall stipulate the conditions under which such discharge may be permitted. Preservation of water quality for all reasonable downstream uses is a primary factor in the issuance of permits" (39).

ALASKA

In 1949 Alaska enacted a comprehensive water-pollution-control law known as the Alaska Water Pollution Control Act, administered by the Water Pollution Control Board, and created within the Department of Health. The Board was responsible for the setting of standards of pollution and of water purity, and in so doing, recognized that owing to variable factors no single standard of quality and purity is applicable to all of the waters of the state (1776). Then in 1959, the State Organization Act abolished the old Board of Health and the Alaska Water Pollution Control Board. It reconstituted the Water Pollution Control Authority within a new Department of Health and Welfare. The Commissioner of the new Authority is charged with the functions and duties of the former Commissioner of Health and the Board of Health, as well as those of the former Water Pollution Control Board and the Executive Secretary of the Water Pollution Control Board

Industrial wastes from "gravel-washing plants and all phases of Placer Mining Operations shall not be considered pollution within the meaning of this Act" (1776). However, it is the public policy of the State of Alaska to maintain standards of purity of its waters consistent with public health and public enjoyment, the propagation and protection of fish and wildlife, and the industrial development of the state, and to that end require the use of all known available and reasonable methods to prevent and control pollution (1778).

Water-pollution control in Arizona rests largely with the State Department of Health and with the Game and Fish Commission. The State Board of Health establishes the general policies of the Department of Health, and prescribes regulations for minimum standards of the quality of water sold or distributed to the public, for inspection and certification of water supplies, and for correction of those systems which do not comply with minimum standards. Its regulations also provide for sewage treatment, industrial-waste treatment, and the setting of minimum standards therefore. In general, the Commissioner of the Department of Health is given the power to issue and enforce necessary special orders to protect the public health and welfare in cases of pollution of bodies of water (41).

The Arizona Game and Fish Commission is authorized to restrain the discharge of any poisonous, deleterious, or polluting substance or waste into a stream or body of water that may be injurious to fish, fishlife, or wildlife (1779).

The statutes do not provide specifically for establishing stream standards or classifications (40) and none have been established.

ARKANSAS

The Arkansas Water Pollution Control Commission was created and established within the State Board of Health by the 1949 Legislature. Among the powers and duties given to the commission was the responsibility "to make such classification of the waters of the State as it may deem advisable..." (42).

Amendments to the act were passed in 1953 and 1959 which were primarily concerned with administrative details. But the amendments of Act 120 of 1961 considerably broadened the definitions of the earlier act and, further, charged the commission with the power of "setting standards of water quality, classifying waters or evidencing any other determination" under the Act (1781).

The Commission is authorized to control the disposal of wastes into the waters of the state by municipalities, industries, and public and private persons; to establish pollution standards for such waters; to restrain the discharge of waste material or polluting substances into state waters; and to issue rules, regulations, and orders in carrying out these functions (1782).

As yet, no standards or objectives have been established. Any disposal of sewage or industrial wastes is subject to a permit issued by the Water Pollution Control Commission.

The Arkansas Game and Fish Commission has authority in the field of water pollution parallel to that of the Water Pollution Control Commission.

CALIFORNIA

The background and philosophy of water-pollution control in California are described in Chapter I. Primary responsibility for protection of the quality of fresh and saline waters rests with the State Water Pollution Control Board, which is intended by law to coordinate the interests of other state agencies, such as the Department of Public Health, Department of Fish and Game, Department of Water Resources, and Department of Agriculture. While the State Water Pollution Control Board establishes overall policy, budgets and distributes funds (including federal allotments under P.L. 660), sponsors research and investigations, publishes reports, and generally administers the program, the specific con-

trol measures are carried out by nine Regional WPC Boards.

With considerable freedom to conduct water-pollution abatement in accordance with local conditions and needs, each regional board has developed its own pattern of general "objectives" for the maintenance and protection of the major receiving waters in the region and has promulgated specific "requirements" for each existing or proposed discharge of municipal or industrial wastes. The general objectives relate to the quality to be maintained in the receiving waters (stream, lake, groundwater basin, estuary, or open ocean) but the specific requirements may govern the amount or concentration of pollutant in the effluent as well as the quality of receiving water. To reproduce, tabulate, collate, or otherwise describe the hundreds of objectives and requirements issued by the nine regional boards would be tedious and perhaps unwise. Instead, one example will be cited for objectives and one for requirements. These examples are not necessarily typical, nor should they be considered as models. Indeed, a major feature of the California program of water-pollution control is the individual case-bycase analysis of each specific problem, a feature that militates against typical or model solutions.

Objectives have been promulgated by the Santa Ana Regional Water Pollution Control Board (No. 8) for the quality of exported and sub-surface outflow of ground water from the Bunker Hill Basin, a fairly well-defined ground-water body underlying the City of San Bernardino and contiguous areas. These objectives, reproduced as Appendix A-1 of this report, are intended to prevent the degradation by sewage or industrial wastes of this extensive water resource and the downstream groundwater basins into which it discharges. Although they do not relate to any specific dicharge, the objectives are used as guidelines in establishing requirements for present and future waste effluents in this area.

An example of requirements for a specific disposal situation is given by Resolution No. 60-76 of the Los Angeles Regional WPC Board (No. 4), reproduced herein as Appendix A-2. This resolution prescribes requirements for the disposal of effluent from an activated-sludge plant to be used for reclamation of water at Whittier Narrows, in the County of Los Angeles. After recitation of background information and findings, the resolution specifies the maximum limit of 14 constituents in the effluent, the location of sampling stations, the type, frequency and technique of sampling and analysis, the records and reports to be maintained and submitted, and the establishment of monitoring wells to determine the effect, if any, that the spreading of discharged wastes will have on underground receiving waters.

Objectives and requirements issued by the nine regional WPC boards in California are subject to frequent review and revision in the light of new findings and improved techniques of analysis. For this reason, any interested reader should check with the responsible regional board for the most recent version relating to any specific situation.

COLORADO

The agency that has primary responsibility concerning water-pollution control is the State Department of Public Health. However, the City and County of Denver have authority to control pollution on the South Platte River and tributaries above Clear Creek, such control to keep the waters safe for domestic purposes (1783).

Changes in the State Health Department Laws include

a 1955 amendment:

"The state department of public health shall establish and enforce minimum general sanitary standards as to the quality of water supplied to the public and as to the quality of the effluent of sewerage systems and trade wastes discharged upon the land or into the surface or ground waters.

"The phrase 'minimum general sanitary standards' as used in this section shall mean the minimum standards reasonably consistent with protection of the public health, and in the case of minimum general sanitary standards as to the quality of water supplied to the public, the same shall in no event be less than the drinking water standards of the United States Public Health Service. The word 'standards' as used in this section shall mean standards reasonably designed to promote and protect the public health. . . .

"To enforce the public policy of the state of Colorado with reference to the pollution of waters of the state by human excreta as herein expressed, it is hereby declared that the health, safety, and welfare of the inhabitants of the state of Colorado require that the streams, lakes, and other waters of the state be kept free of pollution by human wastes, and it is therefore declared to be the public policy of this state that no discharge which contains human excreta shall be permitted to flow in the streams, lakes, or other waters of this state, unless such discharge shall comply with all standards of the state board of health adopted pursuant to law; and in addition thereto the following standard shall apply:

The coliform count shall not average more than 1000/ml based upon not less than four samples taken at the rate of at least one sample per day over a period of four consecutive days" (1784).

In 1959, the Health Department Law was amended to include:

"Minimum standards shall be not more than 0.5 ml/l for settleable organic matter, not more than 75 mg/l for suspended organic matter, and not more than 50 mg/l for the combined suspended and dissolved organic matter when measured in terms of 5-day, 20°C BOD" (1784).

In addition, State Board of Health Regulations specify that:

- "1. The effluent of sewerage systems or trade wastes shall not contain substances in quantities toxic to man.
- "2. No floating matter shall be discharged in the effluent of sewerage systems or trade wastes.
- "3. If the effluent of sewerage systems or trade wastes are discharged into a watercourse used downstream in Colorado as a surface source of public domestic water supply, the dissolved or suspended matter shall not exceed 30 mg/l when measured in terms of 5-day 20°C BOD" (1785).

CONNECTICUT

The control of water pollution in Connecticut rests largely with the State Water Resources Commission, but the State Department of Health has specific powers relating to water-pollution control as it affects public health (1786). Since Connecticut is a member of both the Interstate Sanitation Commission and the New England Interstate Water Pollution Control Commission, some of her waters are subject to certain standards and classifications of those commissions (46), as described hereinafter. The Commission adopts some standards on a river-valley basis and others on individual plants and specific discharges.

In September 1952 the Commission adopted a pollution-abatement policy in the Quinnipiac River Valley which established the following effluent standards (1787):

- "1. All sewage or sanitary wastes before discharge to the Quinnipiac River or its tributaries shall be treated in an adequately designed and operated plant which will produce an effluent of a quality equal to that usually produced in a treatment process including high rate trickling filters and chlorination.
- "2. All water borne industrial wastes, before being discharged to the Quinnipiac River and its tributaries shall be treated in an adequately designed and operated plant which will produce an effluent which, upon laboratory tests, will meet the following standards:
 - a. pH between 6.5 and 8.5
 - b. Color and turbidity not over 50 ppm.
 - c. Suspended solids not over 30 ppm.
 - d. B.O.D. not over 25 ppm.
 - e. Metals (dissolved) each not over 5 ppm.
 - f. Oils and greases not over 20 ppm.
 - g. Any water borne wastes of unusual character or volume not covered by the preceding standards will be considered as individual problems."

For the Hockanum River Valley the following effluent standards were established by a policy statement of the State Water Commission in March 1953 (1788):

- "1. All sewage or sanitary wastes, before they are discharged into the Hockanum River and its tributaries, shall receive a degree of treatment equal to that ordinarily expected from a well designed and well operated plant including high rate trickling filters and chlorination.
- "2. All industrial wastes, before they are discharged into the Hockanum River and its tributaries, shall receive a degree of treatment which will produce an effluent having a quality falling within the following standards:
 - a. pH between 6.5 and 8.5
 - b. Suspended solids not over 30 ppm.
 - c. Biochemical Oxygen Demand not over 30 ppm.
 - d. Color and turbidity shall not increase by more than 5 ppm. the amount present in the receiv-

- ing stream sampled above any industrial waste outlet.
- e. Any water borne wastes containing substances of a toxic, unusual, or peculiar character and volume not specifically covered by the above items shall be subject to specific standards."

In 1961, the definition of "water" was considerably

expanded (45).

The Commission and the oil industry in the state endeavor, cooperatively, to control pollution of surface waters by gasoline, oils, and other petroleum products (1431).

DELAWARE

In 1949 the State of Delaware created a Water Pollution Commission with general power to supervise all laws relating to pollution of the waters of the state. The State Board of Health also exercises some functions relating to the protection of public water supplies and the disposal of wastes by public authorities and individuals (1790). The Commission considers each instance individually, specifying the improvements necessary in terms of (1) maximum acceptable amounts of important constituents, (2) percentage reduction of significant pollutants, or (3) the type or degree of treatment required (1791).

Although Delaware is a member of the Interstate Commission on the Delaware River Basin and of the new Delaware River Basin Compact Commission, and the former Commission has promulgated minimum standards for the Delaware River within the state, no statewide water-quality standards have been formulated and an-

nounced (47).

FLORIDA

The State Board of Health has the primary responsibility for water-pollution control in Florida. The Board has general control and supervision over all waters insofar as their pollution may affect the public health or impair the interest of the public or persons lawfully using them (1794). No specific water-quality standards or classifications have been adopted. Florida has never attempted stream classification because, with few exceptions, every stream would be classified for recreational use regardless of its industrial load (1795).

In the State Sanitary Code, the following general conditions are declared to menace the health of persons, fish, or livestock and therefore are unlawful (1754):

"(a) When raw sewage or incompletely treated sewage, or wastes deleterious to a drinking water or to a water treatment plant, are discharged into a stream or body of water from which a public water supply is derived.

"(b) When raw or incompletely treated sewage is discharged into a water so as to cause an unsafe concentration of bacteria from human excreta in waters where shellfish are taken, or where there are bathing beaches established and operating.

"(c) When sewage or wastes are discharged in such concentrations as to reduce the dissolved oxygen below

the natural oxygen balance.

"(d) When acids, alkalies, or other chemicals, or deleterious substances are discharged into waters so as

to interfere with the biochemical functioning of the stream or waters, or where such wastes kill or interfere with the normal development of fish or other foods derived from waters" (51).

In 1957, an amendment was made to the Sanitary Code to provide for both temporary and permanent injunctive relief in the abatement of pollution (1775).

GEORGIA

On July 1, 1957, the "Georgia Water Quality Control Act" went into effect. This Act gave the State Board of Health extensive responsibility for controlling the pollution of the state's waters. It also created a "Water Quality Council" for the purpose of "making recommendations to the Board regarding rules, regulations, procedures, policies, standards, waste disposal certificates, and for the conduct of hearings in review of orders or actions of the Board" (1780).

The Board is authorized "to establish such standards of quality for any waters in relation to the reasonable and proper use thereof as it deems necessary, and to establish such general policies and standards relating to any existing or future pollution of such waters as it deems necessary, and to modify, amend, or revoke any such standards or policies so established."

No specific standards have been promulgated (1789).

However, Section 6 of the Act states:

- "(a) It shall be unlawful for any person to discharge or permit to be discharged into any of the waters of this State any sewage, industrial wastes, or other wastes which would adversely affect the health of the people of the State or any segment of such people through:
 - (1) The spread of contagious or infectious diseases;
 - (2) The dissemination of toxic or radioactive substances;

without having first provided treatment facilities or works for the treatment of such wastes approved as to methods of treatment, plans and specifications for the construction of facilities or works, and/or operation thereof, by the Board' (1792).

- "(b) It shall also be unlawful to use any waters of the State for the disposal of sewage, industrial wastes, or other wastes so as to render such waters unsuitable for their then current uses except in such a manner as to conform to and comply with all rules, regulations, certificates and orders established under the provisions of this Act and applicable to the waters involved.
- "(c) It shall also be unlawful for any person to erect, construct, enlarge, extend, open, reopen, or operate any public or community water supply system, including storage, distribution, purification treatment facilities or works, without having first secured from the Board approval of: the source of water supply; the means and methods of treating, purifying and storing water; plans and specifications for the construction of facilities or works; and the operation thereof.
- "(d) Anything to the contrary notwithstanding, nothing shall prohibit a person, firm or corporation from discharging its sewage, industrial wastes or other wastes into any non-navigable stream or other non-navigable waters of this State, if

- (1) Such person, firm or corporation owns all the lands immediately adjacent to such streams or waters lying between the point of entry of such sewage, industrial wastes or other wastes into such streams or waters and the point of its junction with other waters lying adjacent to lands belonging to others if at such point of junction the quality of water does not adversely affect the health of the people of the State as defined in the preceding paragraph of this Section, or
- (2) Such person, firm or corporation has acquired an easement, either by express grant or prescription, to discharge such sewage, industrial wastes, or other wastes into such waters of this State provided that the water of such stream at a point not more than 3 miles from the point of entry of such sewage, industrial wastes, or other wastes, and within limits of said easement, does not adversely affect the health of the people of the State as defined by the preceding paragraph of Section 6" (1789).

HAWAII

The State Department of Health exercises primary control in the area of water pollution. Its activities in this area are administered by the Division of Environmental Health (1796). The Department of Land and Natural Resources through the Director of the Division of Fish and Game is authorized to enforce all laws relating to the protection of fish and fishing within the state. Also, the Harbors Division of the Department of Transportation is authorized to make rules and regulations to prevent the throwing into the waters of the state of garbage or other substances liable to make such waters unsightly, unhealthful, or unclean and to prevent the escape of fuel or other oils into such waters either from vessels, pipes, or storage tanks upon the land (1797).

Water-quality standards are under consideration but have not yet been adopted. The Department of Health is authorized to adopt and establish rules and regulations and will adopt water-quality standards when deemed necessary. Each case at present is handled on its merits (1798).

IDAHO

The State Board of Health, created in 1955, is the agency that has the primary function of controlling water pollution caused by sewage or sewage effluents and any other pollution that may affect the public health. It has authority to establish and enforce minimum sanitary standards (52, 1799).

In addition to the regulations of the State Board of Health, there are certain types of pollution control that may be enforced by the State Fish and Game Department. Also, wastes from dredge mining are controlled

by the State Land Department (52).

The State Board of Health has the power to administer and enforce all state health laws and regulations and to establish and enforce minimum sanitary standards for "the quality of water supplied to the public and as to the quality of the effluent of sewerage systems, sewage treatment plants, and discharges upon the land or into the surface or ground waters" (1800).

On May 11, 1959, the State Board of Health adopted

regulations which state, in part:

"1. All wastes discharged to waters of the state shall be subjected to such treatment that they shall not create a health hazard or nuisance and such wastes shall not impair the quality or interfere, either directly or indirectly, with the treatment processes of any public water supply. Waters of the state shall include surface waters and underground waters.

Minimum acceptable treatment for any waste shall be equivalent to the removal of readily settleable and floatable solids. Minimum treatment for waste containing domestic sewage shall include removal of readily settleable and floatable solids and effective disinfection.

"2. The Department of Health shall adopt sewage works design standards, water quality objectives, and subsurface sewage disposal standards to be used as a guide in determining adequacy of proposed treatment and to be used as a guide in the review of plans for proposed treatment facilities. Plans for waste treatment and sewage facilities shall be submitted to the Department of Health for review and approval before construction is begun" (1801).

In promulgating the above regulations, the Department of Health adopted the standards previously developed by the Northwest Pollution Control Council as described hereinafter (52).

ILLINOIS

The Sanitary Water Board has the authority to develop a comprehensive plan for controlling water pollution in the state. Its authority, however, does not extend over any sanitary district having a population of one million or more.

The Department of Public Health exercises supervision over adequacy and quality of public water supplies. The Department of Mines and Minerals has authority to make rules and regulations for the prevention of pollution of fresh-water supplies by oil, gas, or salt water (1802).

The common-law water rights doctrine has been interpreted in Illinois by the theories of natural flow and reasonable use (1803). As a signator of the Ohio River Valley Water Sanitation Commission, the state subscribes to the following requirements for effluents discharged to the Illinois, Ohio, Mississippi, and Wabash Rivers:

"Industrial wastes shall be treated or otherwise modified prior to discharge so as to maintain the following conditions in the receiving waters:

- Freedom from anything that will settle to form putrescent or otherwise objectionable sludge deposits which interfere with reasonable water uses.
- 2. Freedom from floating debris, seum and other floating materials in amounts sufficient to be unsightly or deleterious.
- Freedom from materials producing color or odor in such degree as to create a nuisance.

4. Freedom from substances in concentrations or combinations which are toxic or harmful to human, animal or aquatic life.

"These conditions to be maintained in the receiving waters following the discharge of industrial-waste effluents, are basic or minimum requirements" (1804).

The questionnaire from Illinois indicated that the above requirements apply equally to municipal wastes and also that "these are not standards nor rules and regulations but upon decision can be and would be embodied in rules and regulations" (54).

Illinois is also a member of the Bi-State Development Agency and the Great Lakes Commission.

INDIANA

Functions relating to the control of water pollution in Indiana are primarily delegated to the Stream Pollution Control Board. The functions of the State Board of Health relate to public water supplies and sewagetreatment works (1825).

Indiana law states that:

"The Stream Pollution Control Board shall have jurisdiction to control and prevent pollution in the waters of this State with any substance which is deleterious to the public health or to the prosecution of any industry or lawful occupation, or whereby any fish life or any beneficial animal or vegetable life may be destroyed, or the growth or propagation thereof prevented or injuriously affected.

"The Stream Pollution Control Board shall have the power to determine what qualities and properties of water shall indicate a polluted condition of such water, in any of the streams or waters of this State, that shall be deleterious to the public health or to the prosecution of any industry or lawful occupation for which or in which any such waters may be lawfully used or employed, or whereby the carrying on of any agricultural, floricultural or horticultural pursuit may be or shall be injuriously affected, or whereby the lawful conduct of any livestock industry, or the use of any such waters for domestic animals may be prevented, injuriously affected or impaired, or whereby any lawful use of any such waters by the State of Indiana, or by any political subdivision, corporation, municipal corporation, association, partnership, person, or any other legal entity, may be lessened or impaired or materially interfered with, or whereby any fish life or any beneficial animal or vegetable life in said waters may be destroyed, the growth or propagation thereof prevented or injuriously affected" (1805).

The above law was broadened in 1957 to include ground waters (1806).

Regulation SPC 1, promulgated by the Stream Pollution Control Board in accordance with the above laws in 1945, is still very much in effect:

"WHEREAS, the Stream Pollution Control Board of the State of Indiana has the power under Section 7, Chapter 214, Acts of 1943, to determine what qualities and properties of water shall indicate a polluted condition of such water in any of the streams or waters of this State, and "WHEREAS, the Board recognizes the fact that the character of all surface water is affected by the mode of life of the people and the activities of industry, and that both the people and industry are dependent on said surface water to a greater or lesser extent, and

"WHEREAS, it is recognized that concentrations of population may exist on small streams where diluting water is insufficient to maintain suitable concentrations of oxygen by the use of known and reasonable methods of waste treatment, and

"WHEREAS, there is a fair economic balance between cost of treatment of waste and benefits received beyond which it is not reasonable to expend money for treatment, and the cost of treatment and the benefits to be derived must be considered in determining the extent of corrective treatment to be applied, and

"WHEREAS, natural purifying agencies in the stream should be reasonably utilized, these agencies consisting primarily of the biology of the stream which is affected by the depth of the water, the velocity of the current, etc., and

"WHEREAS, the necessary degree of purity of surface waters depends on the subsequent use which varies on different watersheds and at different points on the same watershed, and

"WHEREAS, for the above-named reasons, each stream presents a separate problem and standards may need to be modified to fit specific cases,

"BE IT RESOLVED, that in general the following regulations and standards shall be applicable to all receiving waters and any water which does not meet such standards and properties shall be deemed and considered as in a polluted condition.

- 1. Floating material including grease and oil shall not be discharged into any surface water in deleterious amounts, or in amounts sufficient to affect injuriously fish life, fur bearing or domestic animals, or the general biology of the water, or plant life in or in the vicinity of such water.
- Waste which is discharged into any water shall contain nothing which will deposit in a stream or a
 lake to form putrescent or otherwise objectionable
 sludge banks.
- 3. Waste which is discharged into any water shall contain no materials in concentrations sufficiently high to affect adversely public health, fish life, fur bearing or domestic animals, or plant life in or in the vicinity of such water.
- 4. Generally the oxygen content of the receiving water, after being mixed with and affected by the waste, shall be no less than 50 per cent saturation. A lower concentration will be tolerated temporarily, but only so long as it is not injurious to aquatic life, and in no case shall it fall below 25 per cent saturation.
- 5. Receiving waters shall be considered unsuitable for bathing if the coliform concentration exceeds 1000 per 100 ml. (MPN.) If the receiving water is used as a source of water supply, a coliform density greater than 5000 per 100 ml. (MPN.) shall not exist at or in the vicinity of the intake. Also in the

case of wastes, bearing or producing substances objectionable from a taste or odor standpoint, which are discharged into waters which are used as a source of water supply such wastes shall be so treated as to render them unobjectionable before discharge into the stream or lake" (1807).

Indiana is a member of the Ohio River Valley Water Sanitation Commission and the Great Lakes Commission.

IOWA

The State Department of Health is the agency that has the primary responsibility for controlling water pollution. The State Board of Health acts in an advisory capacity to the State Department of Health.

The Iowa Natural Resources Council is authorized to make plans and recommendations for the development, protection, and preservation of the water resources of the state. A permit must be obtained from the Iowa Natural Resources Council for the diversion of water or any material from the surface directly into any underground watercourse or basin (1808).

Water use in Iowa was formerly controlled by riparian doctrine, but since the enactment of Chapter 455A of the Code of Iowa, as amended in 1957, the principle of reasonable use has been adopted (1809).

The Iowa Stream and Lake Pollution Law states:

"The department is empowered to adopt and enforce rules and regulations consistent with and not different from the provisions of this chapter restricting the polluting content of any waste material and polluting substances discharged or sought to be discharged into any of the waters of the state" (1810).

No rules and regulations have been published but the polluting content discharged or sought to be discharged is controlled by orders requiring abatement of existing pollution and the issuing of permits for new sewage and waste outlets. The polluting content is restricted in accordance with downstream water uses and the public health aspects.

Iowa has nonofficial affiliations with:

- Great Lakes Upper Mississippi River Board of State Sanitary Engineers
- 2. Joint Resolution of Illinois, Wisconsin, and Iowa Water Pollution Control Agencies for Control of Pollution of Mississippi River
- 3. Missouri River Basin Engineering Health Council
- 4. Five State Agreement of South Dakota, Nebraska, Iowa, Missouri, and Kansas Water Pollution Control Agencies for Control of Pollution of Missouri River" (56).

KANSAS

The State Board of Health has the responsibility of controlling water pollution. The Board is authorized to make rules and regulations necessary for the protection of the surface and subsurface water from pollution by oil, gas, salt water injection wells, or underground storage reservoirs, and to govern the disposal of domestic, industrial, and sewage wastes by municipalities, corporations, companies, or individuals (1775).

"The water-pollution control program of the Kansas State Board of Health stems primarily from a system of continuous state-wide surveillance of stream, oil field waste disposal methods, and waste treatment plant conditions by field personnel; and by the use of a permit system for new waste sources. Since permits are required for the discharge of wastes into the waters of the state, new sources of water pollution are largely controlled prior to their origination. These policies pertain to both municipal and industrial waste sources" (1811).

In certain river basins where pollution problems have been widespread, overall basin studies have been conducted which have resulted in the adoption of basin-wide pollution abatement policies. The State Board of Health has adopted the following policy, applicable to both sewage and industrial wastes:

"Throughout the Arkansas River basin below Great Bend—including the major tributaries, Cow Creek and the Little Arkansas River, but not including the Ninnescah and Walnut rivers and Rattlesnake, Slate and Walnut creeks or the streams which join the Arkansas River in Oklahoma.

- A. At minimum stream flows the biochemical oxygen demand exerted on any section of the stream shall not reduce the dissolved oxygen content below 4 ppm.
- B. Treatment practice will be aimed at reducing the coliform concentration in the streams to less than 20,000 organisms per 100 milliliters.
- C. In addition to item A, industrial wastes should be substantially free of toxic substances, including metallic ions, phenolic compounds, chemical or immediate oxygen demand, oils, alkalies, and acids, before they are discharged to a watercourse.
- D. Primary treatment of sewage and industrial wastes is the minimum degree of treatment which will be acceptable. Additional treatment will be necessary in many instances to maintain water quality in the streams as indicated under items A, B and C.
- E. Oil storage facilities so located that a tank failure or surface runoff from the area could quickly contaminate a watercourse shall be surrounded by an earthen dike providing a capacity equal to the storage tank contents plus a freeboard of 1.5 feet.
- F. All brine shall be disposed of in such a way that fresh water is not polluted.
- G. All industrial wastes discharged to municipal sewerage systems shall be pretreated to an extent which will assure that the wastes will not adversely affect the sewage treatment process.

"The pollution abatement policy is uniform in its intent that all polluters begin planning immediately and that they start construction of waste treatment works or disposal facilities quickly. Because the Little Arkansas River is a potential source of public water supply and is used for recreational purposes the early elimination of bacterial pollution is essential. Chemical and other types of pollution of the Little Arkansas River are equally important but because of their amount and complexity more time must be allowed for planning and constructing the necessary facilities" (1811).

The criteria established for the Kansas River Basin in 1950 continues in effect:

"The Kansas State Board of Health, after giving careful consideration to the data collected and its responsibilities is adopting the following policy which is believed to be in the best public interest. This policy will apply to sewage and industrial, organic or inorganic pollution throughout the Kansas River Basin.

1. That at minimum stream flows the biochemical oxygen demand exerted on any one section of a stream shall not reduce the dissolved oxygen content below 5

parts per million.

- 2. That at minimum stream flows the goal for coliform bacteria is 20,000 organisms or less per 100 milliliters (this quality should not be confused with the number of coliform organisms present during heavy runoff, since at such a time they may be primarily soil organisms not indicative of sewage pollution).
- 3. That the primary treatment of sewage is the minimum amount which will be acceptable.
- 4. Where oil pollution is concerned, all above-ground oil storage tanks shall be surrounded by an earth dike with a capacity equal to the contents of the tank plus a free board of 1.5 feet.
- 5. All brine ponds and waste oil ponds shall be operated in such a manner that 2.5 feet is provided above the maximum brine level.
- 6. That no brines from any field in the river basin shall continue to be stored in ponds, or discharged directly or through seepage to a fresh water course, either surface or subsurface, after July 1, 1951, which date has previously been set by the Kansas State Board of Health. However, in no case will there be any deviations from the policy in such matters, as outlined in the Board's letter dated February 15, 1950'' (62, 1811).

Quality standards have also been adopted for radionuclides in water. These Basic Standards utilize the Recommendations of the National Committee on Radiation Protection and Measurements as published in Handbooks of the National Bureau of Standards as guides or as bases for calculations. Section 28-35-11, "Maximum Permissable Dose and Concentrations" as well as the specific isotopes, are quoted in Appendix B (1812).

KENTUCKY

The Water Pollution Control Commission is charged with the responsibility for developing a comprehensive program for the prevention, control, and abatement of water pollution throughout the Commonwealth. The Commission is contained within the Department of Health. The Commission is authorized to establish or modify, after public hearing, water-quality standards for the waters of the Commonwealth according to their uses (1813).

Water-quality standards have not yet been adopted. Kentucky is a member of the Ohio River Valley Water

Sanitation Commission.

LOUISIANA

The Stream Control Commission has the primary function of controlling water pollution. It also establishes pollution standards for the waters of the state, and controls all waste disposal into such waters. The State Board of Health exercises jurisdiction over the water supplies of the state. The Department of Conservation is responsible for the protection of fresh-water sands from pollution by oil-well drilling and production wastes (1814), and the Commissioner of Wildlife and Fisheries supervises the drainage of all salt water and other noxious substances into natural streams.

No one may discharge into state waters any pollution of any kind that will tend to destroy fish, other aquatic life, wild or domestic animals or fowls, or be injurious to the public health or against the public welfare in violation of any rule, order, or regulation of the Commission (1815).

The Commission promulgated the following criteria on 1 September 1955 with respect to the discharge of sugar-mill wastes:

- "I. No acid, acid water, alkali water, mill washdown water, effects condensate, filter press mud or liquid from filter press mud shall be discharged into state waters or drains or pipes leading to state waters during the grinding season.
- "II. No wastes impounded during the grinding season will be discharged until stabilization has taken place, until the biochemical oxygen demand has been satisfied, and then only into water volumes capable of assimilating such waste waters.
- "III. That all cane wash water shall be impounded for a period of not less than thirty days prior to discharge.
- "IV. That all cane wash water impoundments be compartmented so that the first compartment shall act as a settling basin. The design of the impoundments shall be approved in writing by the Stream Control Commission.
- "V. That, except in cases where specific orders applicable to individual mills have been issued, that condensor water, that water used in barometric condensors, can be discharged into state waters provided first that not more than fifty parts per million of 5 day, twenty degree centigrade biochemical oxygen demand is added to the waters while being pumped through the condensors, and second that the condensor water not cause a serious oxygen depletion to take place in the receiving stream" (1817).

Correspondence with Louisiana indicates no change in the exercise of water-pollution-control administration within the state since 1953 (65). In 1955, O'Neill stated that the 1954 revision of the Louisiana State Sanitary Code contains no quantitative requirements, thereby giving the State Board of Health some degree of flexibility in the application of requirements (1818). In 1959, a court ruled against the state because the statute (in question) only generally characterized or denounced the offense for which the defendant was being prosecuted. And in 1960, the Commission attemped to have new legislation passed, but it failed (65).

Louisiana has a Waterworks Warning Network on the Lower Mississippi River to notify waterworks operators of spills of industrial waste.

MAINE

The Water Improvement Commission became, in 1955, the agency exercising primary control of water pollution

(67). The Revised Statutes state:

"It shall be the duty of the Commission to study, investigate, and from time to time recommend to the persons responsible for the conditions, ways and means, so far as practicable and consistent with the public interest, of controlling the pollution of the rivers, waters and coastal flats of the state by the deposit therein or thereon of municipal sewage, industrial waste and other substances and materials insofar as the same are detrimental to the public health or to animal, fish or aquatic life, or to the practicable and beneficial use of said rivers, waters and coastal flats. The Commission shall make recommendations to each subsequent legislature with respect to the classification of the rivers, waters and coastal flats and sections thereof within the state, based upon reasonable standards of quality and use.

"The Commission shall make recommendations to each legislature with respect to abatement of pollution of the rivers, waters and coastal flats and sections thereof within the State for the purpose of raising the classifications thereof to the highest possible classification so far as economically feasible; such recommendations to relate to methods, costs and the setting of time limits for com-

"The Commission shall have 4 standards for the classi-

fication of surface waters and tidal flats.

"Class A shall be the highest classification and shall be of such quality that it can be used for bathing and for public water supplies after disinfection, and the dissolved oxygen content of such waters shall not be less than 75% saturation and contain not more than 100 coliform bacteria per 100 milliliters.

"There shall be no discharge of sewage or other wastes into water of this classification and no deposits of such material on the banks of such waters in such a manner that transfer of the material into the waters is likely. Such waters may be used for log driving or other commercial purposes which will not lower its classification.

"Class B, the second highest classification, shall be di-

vided into two designated groups as B-1 and B-2.

"B-1. Waters of this class shall be considered the higher quality of the Class B group and shall be acceptable for recreational purposes and after adequate treatment for use as a potable water supply. The dissolved oxygen of such waters shall be not less than 75% of saturation and contain no more than 300 coliform bacteria per 100 milliliters.

"There shall be no disposal of sewage or industrial wastes in such waters except those which have received adequate treatment to prevent lowering of the standards for this classification, nor shall such disposal of sewage or waste be injurious to aquatic life or render such dan-

gerous for human consumption.

"B-2. Waters of this class shall be acceptable for recreational boating, fishing, industrial and potable water supplies after adequate treatment. The dissolved

oxygen of such waters shall not be less than 60% of saturation and contain no more than 1,000 coliform bacteria per 100 milliliters.

"There shall be no disposal of sewage or industrial waste in such waters to lower its classification nor shall such disposal of sewage or waste be injurious to aquatic

life or dangerous for human consumption.

"Class C, the third highest classification, shall be of such a quality as to be satisfactory for recreational boating, fishing and other uses except potable water supplies and swimming, unless adequately treated to meet standards.

"Waters of this classification shall be free from scums, slicks, odors and objectionable floating solids, and shall be free from chemicals and other conditions inimical to aquatic life. The dissolved oxygen content of such waters shall not be less than 5 parts per million for trout and salmon waters and not less than 4 parts per million for non-trout and non-salmon waters.

"The Commission may take such action as may be appropriate for the best interests of the public when it finds that a "C" classification is temporarily lowered due to abnormal conditions of temperature and stream

flow for that season involved.

'Class D waters, the lowest classification, shall be considered as primarily devoted to the transportation of sewage and industrial wastes without causing a public nuisance as defined in Chapter 141, Section 6, by the creation of odor producing sludge banks and deposits or other nuisance condition and such waters shall contain dissolved oxygen at all times. During a period of temporary reduction in the dissolved oxygen content in this class water, due to abnormal conditions of temperature of stream flow for the particular season involved, the Commission, provided a nuisance condition has not been created in such water and in the opinion of the Commission is not likely to be created during such season, shall take no action to reduce the amount of pollution from any source which is allowed in such class water under normal conditions.

"With respect to "C" and "D" classifications, the number of coliform bacteria, or amounts of toxic wastes or chemicals discharged into said waters shall be only those amounts which will not, in the determination of the Commission, be harmful to the public health"

(1819).

The Department of Health and Welfare and the Public Utilities Commission also have functions in waterpollution control relating primarily to water supply and to sewage disposal affecting water supplies (1820).

Maine is a member of the New England Interstate Water Pollution Control Commission and has informal working arrangements with the Province of New Brunswick.

MARYLAND

Both the Maryland Water Pollution Control Commission and the State Board of Health have functions relating to the abatement of water pollution. The Commission is authorized to recommend standards for sewage or waste effluents discharged into waters of the state and to establish such reasonable water-quality standards or criteria, keeping in mind the public use to which they are or may be put. The Board has general supervision and control over waters insofar as their sanitary and physical condition affect the public health or comfort (1821, 1822).

The Commission requires that its Regulation IV apply to all industries:

"No industrial wastes shall be placed or permitted to be placed or discharged or permitted to flow into any of the waters of the State in any manner by any person unless the industrial wastes after treatment or untreated shall meet with the nine industrial waste requirements established by the Water Pollution Control Commission before being discharged into any waters of the State. These nine industrial waste requirements are as follows:

1. Solids

- A. Solids in the effluent—Must not exceed particle size than can pass Tyler designation 20 mesh screen. Grinding, maceration or any other waste treatment or handling operation intended to reduce the size of oversize solids in the effluent to pass Tyler designation 20 mesh screen, will not be permitted or approved.
- B. Total suspended solids—Must not exceed 400 ppm.
- C. Dissolved solids-Must not exceed 1500 ppm.
- D. Total solids-Must not exceed 1900 ppm.
- 2. Turbidity—Must transmit 10% of light through 12 inches of sample in a 3 inch column or not to exceed 300 ppm, as determined by the Jackson candle turbidimeter.
- 3. Biochemical Oxygen Demand:
 - A. The Biochemical Oxygen Demand—The 5 day, 20° C. Biochemical Oxygen Demand in the effluent must not exceed 100 ppm.

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- B. The Dissolved Oxygen in the waste receiving waters must not be depleted beyond 50% of normal saturation.
- 4. Toxicity or toxic compounds—Eliminate, or reduce to limits of tolerance, substances toxic to humans, livestock, fish, aquatic and wildlife.
- Color—Color intensity regardless of light frequency must not exceed 400 ppm. on the chloroplatinate scale.
- 6. pH-Must not range below 5.5 or above 8.5.
- 7. Temperature—Must be below 100°F. in the stream within 50 feet from waste outlet.
- 8. Oils and grease in the effluent—Must not exceed 30 ppm.
- Taste and odor—Effluent must not exceed threshold odor number of 1000. Mixture of the waste and receiving waters shall have a threshold odor number not in excess of 80.

"These nine industrial waste requirements are generally applicable values but are not absolutely fixed

values. They can be made more stringent if a survey of the waste receiving waters indicates they are still polluted or are continuing to be degraded, or in any instance where the Water Pollution Control Commission, after due study and deliberation, deems that more stringent requirements are necessary. They can be made more liberal only by formal action of the Commission on the basis of satisfactory evidence and proof that waste receiving waters are sufficient in quantity and quality to not be affected adversely by a particular industrial waste effluent having values in excess of those stated above" (1822).

In the Baltimore Harbor Area, the Commission has adopted the following Regulation (IV-A) and standard of quality:

"A-Receiving Water Quality Standards

Item:

1. Floating solids, settleable solids, sludge deposits

2. pH

3. Toxic wastes, oil, deleterious substances, colored wastes and other wastes

4. Water quality in waters bordering the Baltimore Harbor Area Specification:

None which are readily visible and attributable to industrial wastes or other wastes or which deleteriously increase the amounts of these constituents in the receiving waters.

Must not range below 5.5 or above 8.5.

None alone or in combination with other substances or wastes in sufficient amounts to prevent survival of fish or aquatic life, to damage marine structures, create a nuisance and/or impair the use of these waters for industrial water supply and navigation.

The quality of any waters receiving industrial wastes or other wastes shall be such that no impairment of the best usage of waters in any area bordering but outside the designated Baltimore Harbor Area shall occur by reason of such discharge of industrial wastes or other wastes.

"B-Desirable Effluent Characteristics

- Solids not to exceed particle size that can pass Tyler designation 20 mesh screen. Grinding, maceration or any other waste treatment or handling operation intended to reduce the size of oversize solids to pass Tyler designation 20 mesh screen not to be used.
- 2. Total suspended solids not to exceed 400 ppm.
- Toxicity or compounds toxic to fish, aquatic and wildlife to be eliminated or reduced to limits of tolerance.
- 4. pH not to range below 5.0 or above 9.0.
- 5. Oils and greases not to exceed 30 ppm" (1822).

On July 1, 1961, the Maryland Department of Health (concurred in by the Water Pollution Control Commission) established restrictions upon the disposal of commercial laundry wastes containing detergents. The requirements for treatment of these waste waters:

"1. No wastes shall be discharged or permitted to flow into the waters of the state in any manner unless the effluent characteristics meet the requirements of the Water Pollution Control Commission's Regulation IV.

- "2. The treated wastes must be sufficiently free of foam-producing materials or chemicals, and the physical appearance must be such, so as not to produce a nuisance in the receiving waters.
- "3. Permission will not be granted for the discharge of treated or untreated wastes into subsurface drainage or disposal systems. No new subsurface disposal system shall be permitted, and no existing subsurface systems shall be extended, or connected thereto, for this purpose.
- "4. Permission will not be granted for the discharge of untreated wastes into a municipal sanitary sewerage system where there is no sanitary sewage treatment or where the degree of treatment is insufficient to properly treat such wastes" (1823).

Maryland is a member of the Interstate Commission on the Potomac River Basin and the Washington Metropolitan Regional Sanitary Board.

MASSACHUSETTS

The Water Pollution Control Agency for the Commonwealth of Massachusetts is the Department of Public Health (1824). Rules and regulations have been adopted by the Department which prohibit the discharge of sewage and wastes, except under conditions and with treatment for which approval is required. As a member of the New England Interstate Water Pollution Control Commission, Massachusetts has adopted a program for the classification of its interstate streams using the classifications and standards of quality for interstate waters as adopted by the New England Interstate Water Pollution Control Commission.

The Department of Public Health has adopted rules and regulations with respect to the protection of surface water supplies. However, such rules and regulations do not apply to the Connecticut River, the Merrimack River, the Concord River, the Ipswich River, or the Saugus River (73).

MICHIGAN

The Water Resources Commission and the State Departments of Health, Conservation, Agriculture, and Highways, whose heads constitute four of the seven members of the Commission, exercise their separately authorized controls of water pollution coordinated where pertinent with activity of the Commission. None of this control takes place, however, under established statewide water-quality standards.

Section 6 of the Commission Act establishes, in effect, water-quality criteria for the state in declaring unlawful the discharge into its waters of "any substance which is injurious to the public health or to the conducting of any industrial enterprise or other lawful occupation; or whereby any fish or migratory bird life or any wild animal or aquatic life may be destroyed or the growth or propagation thereof be prevented or injuriously affected or the value of lawfully taken fish or game be destroyed or impaired as the consequence of said pollution."

Boundary waters between the U.S. and Canada (St. Marys, St. Clair and Detroit Rivers, and Lake St. Clair)

are subject to objectives for quality control adopted by the International Joint Commission in October 1950.

Many Commission orders have been adopted setting effluent restrictions and conditions controlling individual uses so designed as to prevent unlawful pollution as above defined.

Michigan is a member of the Great Lakes Commission (75).

MINNESOTA

The primary function for controlling water pollution rests with the Water Pollution Control Commission. The State Board of Health exercises functions relating to water-pollution control insofar as public health and water supply used for domestic purposes are concerned (1826).

The Commission is empowered to make such classification of waters as it deems advisable, and to establish and alter such reasonable pollution standards for any waters of the state in relation to the public use to which they

are or may be put (1827).

The Water Pollution Control Commission has not established any general pollution standards or made any broad classifications of the waters of the state. Recent legislation has been provided for the creation of sanitary districts (77). Minnesota is a member of the Great Lakes Commission and the Tri-State Water Commission.

MISSISSIPPI

The control of water pollution created by municipal and industrial wastes is the responsibility of the Game and Fish Commission, but control of the contamination caused by domestic sewage is the responsibility of the State Board of Health (79). The State Board of Health has been designated as the official Water Pollution Control Agency of the state.

The State Oil and Gas Board is authorized to make rules and regulations for the prevention of pollution of fresh water supplies by oil, gas, or salt water. The State Game and Fish Commisson is empowered to set effluent standards, but does not have jurisdiction over lakes or other waters that are wholly land-locked and privately owned or the Mississippi River or its tributaries (1828).

The Commission has adopted the following standards

(9):

"4. The degree of treatment of industrial wastes or sewage required shall be based upon the chemical and biological condition of the receiving waters. The minimum standards required in the receiving waters one thousand feet (1000') below the industrial waste outfall shall be:

a. There shall be no noticeable floating solids, scum,

oil, grease or sleek.

b. The degree of acidity and the degree of alkalinity as expressed by pH values shall average in the range of 6.5 to 8.4, and any single sample shall not be below pH 5.0 or above pH 9.5, during the prescribed sampling period.

c. The increased salt concentration shall not exceed one thousand (1000) parts per million of sodium

chloride.

d. The industrial waste after dispersion in the receiving waters, or not more than one thousand (1000)

feet below or above the point of discharge, shall not reduce the dissolved oxygen in the receiving waters below an average of 4.5 parts per million, and no sample taken from the receiving water at the point designated shall contain less than 2.5 parts per million dissolved oxygen during the prescribed sampling period.

e. No poisons or deleterious substances shall be present in sufficient quantities to cause injury or death

to fish or wildlife.

f. No substances shall be present which may cause distinct foreign tastes in fish. Sampling place and sampling—The sampling place shall be chosen after the waste has been dispersed in the receiving waters and not more than one thousand (1000) feet below or above the waste or sewage outfall. Samples shall be collected over a minimum period of four (4) hours; the samples shall be taken approximately every thirty (30) minutes, or a minimum total of eight (8) samples. The samples collected in a stream shall be taken normally in mid-channel at mid-depth, or in such a manner as to obtain samples representing the average conditions of the stream."

MISSOURI

The 1957 Legislature enacted a new water-pollution law for the state and placed its administration in a newly created Water Pollution Board within the Division of Health of the Department of Public Health and Welfare. The Board is empowered to establish and revise standards of water purity that specify the maximum degree of pollution permissible in accordance with public interest in water supply, the conservation of fish, game, and aquatic life, and agricultural, industrial and recreational uses (1829).

The Missouri Water Pollution Board has not set standards, but has adopted water quality objectives for the Missouri, Mississippi, and Blue Rivers (81). These objectives are described in Appendix C. Missouri is a member of the Bi-State Development Agency.

MONTANA

The 1955 Legislature enacted a comprehensive water-pollution law and created a Water Pollution Council with responsibility for overall policy. The responsibility for administering the Act is placed in the State Board of Health. The Board may modify the policy only when public health is involved (1830, 1831).

The Council is authorized and directed "to formulate standards of water purity and classification of water according to the most beneficial uses of such water" (1832). Accordingly, the Council has adopted the water-quality objectives shown in Table 3-1.

NEBRASKA

The 1957 Legislature passed a new Water Pollution Control Act which was amended in 1961. The Act provided a Water Pollution Control Council within the Department of Health. This Council is authorized to develop effluent standards and standards of water quality, and also to classify the waters of the state (1833, 83).

As of January 1962, a committee was in the process of preparing water-quality standards to be used in accomplishing the following water-quality objectives. These objectives were adopted by the Council to be used as a guide in all future work relating to the disposal of wastes into Nebraska waters:

- "1. Toxic substances including metallic ions, phenolic compounds, oils, alkalies, and acids should be virtually eliminated from sewage effluents.
- "2. Removal of settleable and floating solids to prevent sludge banks, floating materials, and nuisance conditions should be required as the minimum acceptable treatment.
- "3. For industrial wastes similar in nature to municipal wastes, treatment should be based on the same premise as recommended for municipalities. For industrial wastes not comparable to municipal wastes, treatment should be provided as necessary to prevent deterioration of water quality for beneficial uses in the receiving stream.
- "4. Additional treatment over that specified in item 2 above should be provided as necessary to protect downstream water uses. Quality objectives for certain water uses are:
 - (a) For water serving as a source of domestic supply, raw water bacteriological quality should conform to that recommended in 'Manual of Recommended Water Sanitation Practices, 1946, Public Health Service Bulletin No. 296,' pages 11-13.
 - (b) For bathing or swimming waters, monthly arithmetical average 'most probable number' of coliform organisms should not exceed 1,000 per 100 ml during any month of the recreation season; nor exceed this number in more than 20 percent of the samples examined during any such month; nor exceed 2,400 per 100 ml on any day. For non-bathing or non-swimming waters, the monthly arithmetical average 'most probable number' of coliform organisms should not exceed 5,000 per 100 ml in any month of the recreational season, nor should exceed this number in more than 20 percent of the samples examined during any such month.
 - (c) For fish and aquatic life a minimum oxygen concentration of 5.0 ppm. is desirable in waters otherwise offering suitable fishery habitat, with 6.0 ppm. for trout streams.
 - (d) For bacteriological quality of irrigation water:
 - Sewage used for irrigation of forage crops should be given treatment insuring a consistent reduction in coliform bacteria of not less than 90 percent.
 - (2) Sewage used for irrigation of human food crops should be given treatment insuring a consistent reduction (a) in suspended solids of not less than 75%, (b) in 5 day 20°C. B.O.D. of not less than 75% and (c) in coliform bacteria

STATE OF MONTANA WATER POLLUTION COUNCIL STREAM CRITERIA FOR WASTE DISCHARGES

Water Quality Objectives and Minimum Treatment Requirements for Montana Surface and Underground Waters

		WATI	ER QUALITY C			1.1
Minimum treatment requirements for domestic sewage	Primary treatment and effective disinfection except in sponda case as determined by the State Board of Heath. Sewage agoon treatment will neet his requirement.	Sano as for use 'A' above.	Same as for use "A" above		Same as for use "D" above.	
High temporature wastes	Not in sufficient quantities slone or in combination with other wastes to interfere with the use indicated.	Same as for use "A". above.	Same as for use "A" above.	Not in sufficient quantity as to increase the temperature of the receiving water beyond that optimum for the normal aquatic life of the speutic water.	Same as for use "A" above.	
- 5	None	None detectable	Same as for use "B" above,	Same as for use "B" above	Same as for use "B" above	
Phenolic compounds	Less than five (6) parks per billion	"A" above.	hyo (25) parts per hyo (25) parts per hillion or none in sufficient amounts as to impart a residual taste to recreational or commercial fish or obther aquatic forms	Same as for 1196 "C" above.	None in sufficient quantity as to make reesiving water unsuitable for use indicated.	
Toxic, colored, or other deleterious substances	None alone or in combination with combination with or other substances or wastes in sufficient amounts or of such making water unseaso unsuitable for use indicated (U. S. Pt. H. S. Skds)	Same as for use "A" above.	1	None alone or in combination with other substances or wastes in sufficient amount or of such character as to make receiving waters unsafe for use indicated.		
Hd	Hydrogen ion oon- centration ex- pressed as pH should be main- tained between 6.5 and 8.5.	Same as for use	"A" above.	Зате ва for use "А" above.	Hydrogen ion con- centration contrasion expressed as pH should be main- tained between 8.0 and 9.5.	
Dissolved	Greater than five (5) parts per mi- lion, except for underground waters.	Same as for use	Greater than five (5) parts per mil- lion,	Same as for use	Greater than three (3) parts per mil- flon.	
Taste or odor producing substances	None attributable to sewage, industrial wastes or other wastes.	None attributable to servage, industrial wastes or other wastes which, after reasonable dilution and mixture, will increase the threshold color number above eight (3).	None attributable to sarage, industrial wastes or other wastes of dilution and dilution and mixture, will interfere with the best use of these waters for the purpose indicated.	None attributable to esewage, industrial servage, industrial wastes which will interfere with the paglatability or propagation of recentional or commercial fish or other edible soutstic forms.	None attributable to sewage, industrial wastes or other wastes which will adversely affect the marketability of agricultural or indus- trial produce.	
Floating, suspended settleable solids and sludge deposits	None attributable to servage, industrial wastes, or other wastes which, after reasonable dilution and mixture with reverying waters, inferier with the best use of these waters for the purpose indicated.	(Same as for use "A" above).	Same as for use "A" above.	Same as for use "A" shove.	Same as for use "A" above.	
Organisims of the coliform group	Most probable number (MPN) colifora bac- ferial content of a rep- resentative number of samples should aver- age less than 50 per 100 ml, in any month.	MPN coniform bacterial content of a representative to under of amples about average less than 2000 per 100 ml. and should over exceed this number in more than 20 percent of samples examined in any month where assertiated with domestic sewage.	MPN coliform bacterial pontent of a representation of repr	See note under "C" above.		· · · · · · · · · · · · · · · · · · ·
Water quality Water uses	(A) WATER SUPPLY, DRINKING, CULL. DRINKING, CULL. PROCESSING, Without treatment other with a simple distriction and removal of naturally present impurities.	(B) WATER SUPPLY, DRINKING, CULL-NARY, AND PRODD PROCESSING. With treatment equal to coagulation, sedimentation, and any additional treatment necessary for removing naturally present impurities.	(C) BATHING, SWIM-MING, AND RECRE-ATION. Notes: When waters are used for recreational purposes such as fahing and bossing, exclusive of and bossing, exclusive of and bossing, exclusive of the number "1000" may be substituted for "240" in statement of collicern objectives.	(D) GROWTH AND PROPAGATION OF PISH AND OFHER AGUATIC LIPE, Including waterfowl, fur- squasic and other aquasic and eemi- aquasic life.	(E) AGRICULTURAL WATER SUPPLY WATER SUPPLY WITHOUT treatment exposple for the removal of natural impurities to make special quality requirements order than those classified under Note: Permissible limits of total consontration percent sodium, boron, ellorides, and sulphates of receive facilities is less study, suggested value for percent sodium is less than 40. Percent sodium computed as the ratio of puted as the ratio of	expressed in equivalent weights Cabulated from the formula: Na X 100 + Na + + Ca + Mg when Na, Ca, K, and Mg are expressed in equivalents.

Water quality Objectives of a watercourse will apply at the point of discharge of a waste except in special cases where the sampling points will be determined by the Montana Water Poliution Council.

Determinations in the above table will be in accordance with "Standard Methods for the Examination of Water, Sewage and Industrial Wastes".

Adopted tentatively Feb. 28, 1950 Revised April, 1958 Reviewed Sept. 2, 1958 of not less than 98 percent, unless discharged into a stream where the volume of dilution water, available during the low flow periods during which irrigation diversions may occur, is at least 10 times greater than the anticipated maximum daily volume of sewage, in which case a bacterial reduction of 90 percent may be acceptable.

Provided, however, that where the time of passage from plant discharge to irrigation diversion is such as to permit the normal death rate of bacteria as evidenced by the die-away curve to provide equivalent bacterial reduction, the requirements of (1) and (2) above may be appropriately modified" (83).

Nebraska is a member of the Missouri Basin Engineer-

ing Health Council.

NEVADA

The State Board of Health has the primary function of controlling water pollution. Legislation enacted in 1957 and amended in 1959 authorizes the Division of Public Health Engineering, under the direction and supervision of the Board, to develop a system of classification of the waters of the state (1834, 1835, 1836).

No standards or classifications have been promulgated,

as yet.

NEW HAMPSHIRE

Both the Water Pollution Commission, established in 1947, and the State Board of Health have functions relating to the control of water pollution (1837). Surface waters of the state are classified by the Legislature. The Water Pollution Commission has the duty of enforcement of such classification. Control of pollution of unclassified surface waters is accomplished by a permit system administered by the Commission (87).

Waters are to be classified as follows:

- "I. Class A waters shall be of the highest quality and shall contain not more than fifty coliform bacteria per one hundred milliliters. There shall be no discharge of any sewage or waste into waters of this classification. The waters of this classification shall be considered as being potentially acceptable for water supply uses after disinfection.
- "II. Class B waters shall be of the second highest quality and shall be divided into two parts as follows:
 - (a) Class B-1 waters shall have no objectionable physical characteristics, shall be near saturation for dissolved oxygen, and shall contain not more than two hundred forty coliform bacteria per one hundred milliliters. There shall be no disposal of sewage or industrial waste into said waters except those which have received adequate treatment to prevent the lowering of the physical, chemical or bacteriological characteristics below those given above, nor shall such disposal of sewage or waste be inimical to fish life or to the maintenance of fish life

in said receiving waters. The waters of this classification shall be considered as being acceptable for bathing and other recreational purposes and, after adequate treatment, for use as water supplies.

- (b) Class B-2 waters shall have no objectionable physical characteristics, shall be near saturation for dissolved oxygen, and shall contain not more than one thousand coliform bacteria per one hundred milliliters. The waters of this classification shall be considered as being acceptable for recreational boating, fishing and for industrial purposes, and, after adequate treatment, for use as water supplies.
- "III. Class C waters shall be of the third highest quality and shall be free from slick, odors, and surface-floating solids of unreasonable kind or quantity, shall contain not less than five parts per million of dissolved oxygen; shall have a hydrogen ion concentration within the range of pH 5.0 to 8.5; and shall be free from chemicals and other materials and conditions inimical to fish life or the maintenance of fish life. The waters of this classification shall be considered as being acceptable for recreational boating, fishing or for industrial water supply uses either with or without treatment depending upon individual requirements.
- "IV. Class D waters shall be of the lowest classification and shall be free from slick, odors and surface-floating solids of unreasonable kind, quantity or duration, taking into consideration the necessities of the industries involved, and shall contain dissolved oxygen at all times. The waters of this classification shall be considered as being devoted primarily to the transportation of sewage or industrial wastes, or both, without nuisance.
- "V. All tests and samplings for the purposes of examination of waters shall be performed and carried out in a reasonable manner and whenever practicable, in accordance with the current edition of the Standard Methods for the Examination of Water and Sewage as published jointly by the American Public Health Association and the American Water Works Association. Near saturation for dissolved oxygen shall mean a dissolved oxygen content of at least seventy-five percentum of saturation. The waters in each classification shall satisfy all the provisions of all lower classifications.
- "VI. Nothing contained herein shall be construed to prohibit, under such terms and conditions as the commission may direct, the use of rotenone or similar compounds by the fish and game department in the conduct of its program to reclaim the public waters of the state for game fishing" (1838).

After adoption of a classification by the Legislature, the Commission may on its own motion or on petition of not less than 100 inhabitants of the county or counties in which such water in question is situated, reinvestigate the conditions of pollution and make recommendations to the Legislature for reclassification. Persons aggrieved by the classification adopted by the Legislature may petition the Superior Court of the county in which the pollution is occurring for a variance in the classification as applied to his specific case.

The State Board of Health is authorized to establish such regulations as it deems necessary for the protection from contamination of public water or ice supplies (1837). Recent legislation (1961) has not been concerned

with standards or classifications (87).

New Hampshire is a member of the New England Interstate Water Pollution Control Commission.

NEW JERSEY

The State Department of Health is the legally constituted water pollution control agency of the state. It is authorized, among other things, to issue orders to abate legal violations and to make and enforce rules and regulations concerning the design and operation of all public water supplies, and of sewerage systems and disposal plants for treatment of wastes discharged into any of the waters of the state (1796).

Effluent or stream specifications, especially the former, are used in New Jersey as guides. They are not law and not intended to be law, and are primarily administrative tools (1749). Effluent specifications are patterned to meet the needs in each valley or stream situation. A typical effluent specification on an inland stream is as follows (89):

- "1. The effluent shall contain no free acidity; that is, all titratable acidity shall be neutralized.
- "2. The effluent shall be free of noticeable floating solids, scum, oil, grease, or sleek.
- "3. The effluent shall be sufficiently free of color or turbidity, or both, so that after dispersion in the receiving waters, or not more than one thousand (1,000) feet above or below the point of effluent discharge, it will not noticeably discolor or add to the turbidity of the receiving waters.
- "4. The effluent shall be free of caustic alkalinity or other toxic or deleterious substances.
- "5. The effluent shall be free of offensive odors.
- "6. The effluent shall have a biochemical oxygen demand not exceeding in the average over any four (4) hour period of a day thirty (30) parts per million and not exceeding at any time forty (40) parts per million.
- "7. The effluent shall contain a chlorine residual of at least one (1.0) part per million at all times."

An example of an effluent standard as applied to an industry discharging into a tributary of the Rockaway River which supplies the Boonton Reservoir is as follows: "... The pH... shall be between 5.0 and 8.5, ... free of phenol and phenol-like substances, and must be free of toxic or deleterious substances and in particular cyanides, cyanates, trivalent chromium and hexavalent chromium. Chemical substances must not exceed the fol-

lowing concentration in parts per million: sodium, 285; chloride, 210; fluoride, trace; sulfate, 85; and nitrate, 45" (1839).

New Jersey is a member of the Interstate Commission on the Delaware River Basin, the Interstate Sanitation Commission, and the new Delaware River Basin Commission.

NEW MEXICO

The State Board of Public Health has the primary function of controlling water pollution. It establishes policies, rules, and regulations for the New Mexico Department of Public Health. The Oil Conservation Commission is authorized to make rules and regulations for the prevention of pollution by wastes from oil and gas wells. The Department of Game and Fish is authorized to protect game, fish, and spawning waters (1840). In addition, the Plumbing Administrative Board, Office of the State Engineer, and the Interstate Stream Commission have functions that relate to water pollution (90). No water-quality criteria are contained in the legislation and none have been promulgated by the various boards and commissions.

NEW YORK

Effective 1 January 1962, the Water Pollution Control Board was abolished. The functions of the Board were transferred in part to the State Commissioner of Health and in part to the Water Resources Commission. The Water Resources Commission has the authority to classify waters and establish standards. The State Commissioner of Health has the responsibility of enforcing the law.

The extensive system of classification of fresh, tidal, and ground water that appeared as Appendix B in the first edition of WATER QUALITY CRITERIA (1952) has been maintained (91). It is again reproduced in this report as Appendix D and includes several new, special classes, namely, Class A-Special (International Boundary Waters), Class AA-Special (Lake Champlain Drainage Basin), and Special Class (Lower Genessee River).

New York is a member of the Interstate Sanitation Commission, the Interstate Commission on the Delaware River Basin, the Ohio River Valley Water Sanitation Commission, the New England Interstate Water Pollution Control Commission, the Great Lakes Commission, and the new Delaware River Basin Commission.

NORTH CAROLINA

The State Stream Sanitation Committee, created by legislation enacted in 1951, is responsible for the control and abatement of water pollution in North Carolina. The original act established the Committee within the State Board of Health; however, amendments by the General Assembly of 1959 transferred the Committee to the new Department of Water Resources and established therein a Division of Stream Sanitation and Hydrology to serve as administrative agent for the Committee.

The Committee acting under authority of the Statute, adopted a comprehensive series of Water-Quality Standards on 19 November 1953. These standards, are reproduced in full and included as Appendix E (1841).

Pertinent sections of the enabling act (94) are quoted below:

- "(a) Duties of Committee Under This Section: The committee is hereby directed and empowered, as rapidly as possible with the limits of funds and facilities available to it, and subject to the procedural requirements of this Article:
- (1) To develop and adopt, after proper study, a series of classifications and the standards applicable to each such classification, which will be appropriate for the purpose of classifying each of the waters of the State in such a way as to promote the policy and purposes of this Article most effectively;
- (2) To survey all the waters of the State and to separately identify all such waters as the committee believes ought to be classified separately in order to promote the policy and purposes of this Article, omitting only such waters as, in the opinion of the committee, are insufficiently important to justify classification or control under this Article; and
- (3) To assign to each identified water of the State such classification, from the series adopted as specified above, as the committee deems proper in order to promote the policy and purposes of this Article most effectively.
- "(b) Criteria for Classification: In developing and adopting classifications, and the standards applicable to each, the committee shall recognize that a number of different classifications should be provided for (with different standards applicable to each) so as to give effect to the need for balancing conflicting consideration as to usage and other variable factors; that different classifications with different standards applicable thereto may frequently be appropriate for different segments of the same water; and that each classification and the standards applicable thereto should be adopted with primary reference to an existing or a contemplated best usage to be made of the waters to which such classification will be assigned.
- "(c) Criteria for Standards: In establishing the standards applicable to each classification, the committee shall consider, and the standards when finally adopted and published shall state: The extent to which any physical, chemical, or biological properties should be prescribed as essential to the contemplated best usage.
- "(d) Criteria for Assignment of Classifications: In assigning to each identified water the appropriate classification (with its accompanying standards), the committee shall consider, and the decision of the committee when finally adopted and published shall contain its conclusions with respect to the following factors as related to such identified waters:
- (1) The size, depth, surface area covered, volume, direction and rate of flow, stream gradient and temperature of the water;
- (2) The character of the district bordering said water, including any peculiar suitability such district may have or any dominant economic interest or development which has become established in relation to or by reason of any particular use of such water;

- (3) The uses which have been made, are being made, or may in the future be made, of such water for transportation, domestic consumption, industrial consumption, bathing, fishing, and fish culture, fire prevention, the disposal of sewage, industrial wastes and other wastes, or any other uses;
- (4) The extent to which such water is already receiving sewage, industrial waste, or other waste as a result of present or past usage of the water, and the relative economic values involved in improving or attempting to improve the condition of such water."

NORTH DAKOTA

The State Water Conservation Commission and the State Department of Health act jointly in controlling water pollution in the state. The Industrial Commission, through the State Geologist, is authorized to prevent the pollution of fresh-water supplies by oil, gas, or salt water.

The State Water Conservation Commission is authorized to establish rules and regulations for the control of pollution in watercourses. Commission approval is required for municipal or industrial-waste disposal facility or municipal waterworks construction. Before the Commission grants approval, however, plans must first be approved by the State Department of Health. The Commission cannot declare waters to be polluted without a finding to that effect by the State Department of Health (1842).

No statewide standards of water quality have been promulgated by the Department of Health or the Water Conservation Commission (95). North Dakota is a mem-

ber of the Tri-State Water Commission.

OHIO

The Water Pollution Control Board and the Division of Sanitary Engineering, both of which are established within Ohio Department of Health, have functions relating to the control of water pollution. The Water Pollution Control Act of Ohio passed in 1951 created the Board with administrative, regulatory, and quasi-judicial powers. Membership of the Board includes the Directors of the State Departments of Health, Commerce, and Natural Resources as well as two appointive members that represent municipalities and industry.

The Board has the authority to develop programs for the prevention, control, and abatement of water pollution. Studies and recommendations with respect to such programs are carried out by the Division of Sanitary Engineering. A major portion of the programs of the Board is carried out through the granting of permits for the discharge of wastes to waters of the state. Such permits are issued for a specific period of time and their renewal is granted upon compliance with certain conditions that are affixed to the permit. Failure to comply with the conditions results in formal hearing and possible Board action.

General supervision of public water supplies and waterworks, as well as of the disposal of wastes and waste treatment works is carried out by the Division of Sanitary Engineering.

Previous printings of WATER QUALITY CRITERIA (1952 and 1954) have included water-quality objectives

for the Miami and Maumee River Basins, and also of the objectives of the Lake Erie Pollution Survey Report. Since then, objectives have been promulgated for the Muskingum, Cuyahoga, Mahoning, and Scioto River Basins. All of these objectives are reproduced in Appendix F.

Ohio is a member of the Ohio River Valley Water Sani-

tation Commission (98).

OKLAHOMA

The Oklahoma State Department of Health has primary responsibility for protecting the municipal and domestic water supplies from pollution. In addition, the Department has the authority to control pollution resulting from municipal or domestic sewage or any pollution affecting municipal, domestic and/or recreational waters.

The Oklahoma Water Resources Board, created in 1957, coordinates the activities of the other pollution control agencies in the state and is responsible for industrial waste discharges (1843). It is also responsible for adopting and promulgating standards of quality of the

waters of the state (1844).

The Oklahoma State Corporation Commission has responsibility for controlling pollution resulting from oil and gas production and/or processing. The Oklahoma State Department of Wildlife Conservation is responsible for maintaining water quality at levels suitable for sustaining and propagating fish and wildlife (1843).

The Bureau of Water Resources Research, University of Oklahoma, has prepared an extensive listing of water-quality criteria for the various cooperating agencies to be used as guidelines for acceptable quality of state waters. These criteria are not intended to be utilized as inflexible standards. They are summarized in Table 3-2 (1845).

OREGON

The State Sanitary Authority, created within the State Board of Health in 1939, has the primary responsibility for the control of water pollution in Oregon (101, 1846). Among the Sanitary Authority's powers and duties are the following: to encourage "... restoring and preserving the quality and purity of waters of the State in accordance with standards established by the Sanitary Authority ...", to "... amend or cancel rules and regulations pertaining to minimum requirements for disposal of sewage and industrial wastes ...", and to "... establish, modify or amend standards of quality and purity of the various waters of the State ..." The Statutes defines standards as "... such measure of quality or purity for any waters in relation to their reasonable and necessary use ..." The Statutes also identify certain pollutants in association with standards:

"Section 11. The Sanitary Authority is authorized and empowered to establish standards of quality and purity of the waters of this state in accordance with the public policy of the state of Oregon and in establishing such standards, consideration shall be given the following factors:

(a) The extent, if any, to which floating solids may be permitted in the water;

TABLE 3-2
SUGGESTED CRITERIA OF RAW WATER QUALITY
FOR THE STATE OF OKLAHOMA (1845)

	Water use			
Ion, organism or substance	Municipal	Industrial	Agricultural	Recreation- fish, wildlife
Algae—Std. Units	1000 Std. Units	1000	000 Absence of toxic algae	
Vol.	Vol.			ı
Alkalinity—ppm	120	50-150		
Ammonia—ppm	0.1			0.3
Biochemical Oxygen	Max. 1.0-3.0			
Demand—ppm	Ave. 0.75-1.5			See D. O.
Bicarbonates—ppm	150	3-100		
Boron—ppm	1		0.2 - 0.5	
Cadmium-ppm	0	0	0	0
Calcium—ppm			40	
Carbon Dioxide—ppm			20-40	i
Carbonates—ppm		200-400	10	
Chloride—ppm	50	20-250	100	10.0
Chromium—ppm Coliform-MPN/100 ml	0	0.05	0	500-1000
Coliform-MPN/100 ml	50	100-1000		200-1000
Color	20-70	100-1000	0.2	1.5
Copper—ppm	3.0		0.2 0	1.0
Cyanides—ppm	0	0	0.2	over 4
D.O.—ppm	over 4.0	0.2-2.0	0.2	Over 4
Floating solids	0	, v	U	5.0
Fluoride—ppm Hydrogen Ion Concentration-pH	1.5	1.0	i	5.0-9.5
Hydrogen Ion Concentration-pH_	6.5-8.5	6.0-9.6	l	4
Iron—ppm	0.3	u.a	20*	
Magnesiumppm			20	44
Nitrate-ppm	10	-ñ	-6	0.3
Oil—ppm	0	.001010	.005020	0.2-1.0
Phenolic compounds—ppm	Background	Background	Background	Background
Radioactivity—uuc/1	0-10	50	10	Distriction
Sodium-ppm	250	100-250	190	1 77
Sulfates—ppm Suspended Solids—ppm	4-570	100 200		ludge deposit
Total Dissolved Solids—ppm	1000	100-1000	1	
Temperature—°F. (desirable)		60	60	32-95
Total Nitrogen—ppm	10	""		10
Turbidity—ppm	0-40	10-50	1	2000
I mmmel hbm	, , , ,	1	1	

*SAR values show the inter-relationship.

(b) The extent to which suspended solids, settleable solids, colloids or a combination of solids with other substances suspended in water may be permitted;

(c) The extent to which organisms of the coliform group, and other bacteriological organisms or viruses may be permitted in the waters;

(d) The extent of the oxygen demand which may be permitted in the receiving waters;

(e) The minimum dissolved oxygen content that shall be maintained;

(f) The limits of other physical, chemical, biological or radiological properties that may be necessary for preserving the purity of the waters of the state;

(g) The extent to which any substance must be excluded for the protection and preservation of

public health; and

(h) The value of stability and the public rights to rely upon standards as adopted for a reasonable period of time to permit institutions, municipalities, commerce, industries and others to plan, schedule, finance and operate improvements in an orderly and practical manner" (1847).

Specific standards and classifications are included in Appendix G unchanged from that which appeared in the 1952 edition (101, 1848).

Oregon is a member of the Klamath River Compact Commission and the Pollution Control Council, Pacific Northwest Area.

PENNSYLVANIA

The Sanitary Water Board in the Department of Health has the primary function of controlling water pollution in the Commonwealth. The Department of Health acts as the enforcement agent for the Board, and exercises control over water supplied to the public (1849).

The control of water pollution in Pennsylvania is unique in several respects. The Sanitary Water Board established one of the first comprehensive plans for the rehabilitation of polluted streams. In an attempt to deal fairly with all municipalities, the Board has classified all streams of the Commonwealth as: (a) those into which all wastes that are discharged shall be given complete treatment or its equivalent, e.g., 85 percent BOD reduction, (b) those into which all wastes that are discharged shall be given primary treatment, e.g., settling, grease removal, and chlorination, (c) acid-impregnated streams that, for the present, require no treatment of wastes received thereby, and (d) those into which a degree of treatment somewhere between primary and complete is required. This fourth category may apply to particular reaches of a stream. The degree of treatment is specified for each particular case.

In a further attempt at an equitable handling of industrial wastes, the Sanitary Water Board has encouraged industry-wide committees to formulate specific regulations and effluent standards for each industry and for each type of waste normally discharged by such industry. Rules and regulations, including standards, have already been promulgated for five types of industries, viz., wastes from pulp and paper mills (104), wastes from milk plants (105), acid pickling wastes from metallurgical plants (106), wastes from oil and natural-gas wells (107), and wastes from wells other than oil and natural gas (108). By setting up normal values for the strength of such wastes and then requiring a certain percentage removal of polluting materials therefrom, the Board recognized that the wastes frequently can be reduced in quantity and pollutional strength by improved operation and equipment, and by good "housekeeping" methods, as well as by waste-treatment works.

The Sanitary Water Board has also adopted rules and regulations with respect to the disposal of wastes into underground strata and also disposal of heated wastes. These rules and regulations are reproduced in Appendix H (103).

Pennsylvania has also adopted policies and standards with respect to radioactive discharges. Radioactive wastes have been classified as industrial wastes. The permit granted for the Shippingport reactor is subject to certain Special Conditions, some of which are noted in Appendix H (1850, 1851).

Where the Sanitary Water Board requires the removal of BOD it specifies percentage removals equivalent to that obtained by sewage treatment. This requirement amounts to 35 percent for primary treatment and 85 percent for complete treatment (1852). Pennsylvania is a member of the new Delaware River Basin Commission, the Great Lakes Commission, the Interstate Commission on the Delaware River Basin, the Interstate Commission

on the Potomac River Basin, and the Ohio River Valley Water Sanitation Commission.

RHODE ISLAND

The Department of Health has primary responsibility for the control of water pollution in the State of Rhode Island. The Division of Sanitary Engineering in the Department of Health enforces the water pollution laws of the state (1853). Although Rhode Island has promulgated no standards of its own, it subscribes to those of the New England Interstate Water Pollution Control Commission of which is it a member (109).

SOUTH CAROLINA

In 1950, the Water Pollution Control Authority was created within the State Health Department. The Authority was assigned the responsibility of preparing a general comprehensive program for the abatement and prevention of water pollution (110, 1854).

The Authority is empowered to classify the designated waters. Standards of quality and purity for each such classification are related to public use or benefit and may be later modified.

The resulting system of classifications and standards were listed in the appendices of previous printings of WATER QUALITY CRITERIA. They are again reproduced unchanged in this edition as Appendix I (110).

SOUTH DAKOTA

The Committee on Water Pollution, working through the Division of Sanitary Engineering of the State Department of Health, has the primary responsibility for water-pollution control in South Dakota (1855). No specific effluent standards are in effect, but each installation is evaluated individually. Streams have been classified as indicated by the pertinent sections of the enabling statute (113) quoted below (from Laws pertaining to Water Pollution 1960 Supplement to South Dakota Code—1939):

"61.0145 Classification of Waters. It shall be the duty of the Committee to classify the public waters of this State, or parts thereof, into classes which shall be known as 'Class A' waters and 'Class B' waters, 'Class A' waters shall be those waters, or parts thereof, in which the pollution or corruption entering such waters can be so controlled that the waters receiving such pollution and corruption shall not be unwholesome or unfit for domestic use, or unsafe as a source of public water supply, or deleterious to fish or plant life, or shall not cause a public nuisance. 'Class B' waters shall be those waters, or parts thereof, which are more important to the welfare of the people of the state as carriers of waste, providing such wastes are not detrimental to the public health. (No person, firm or corporation shall discharge or cause to be discharged in 'Class A' waters of this state any new pollution or corruption in the form of sewage, industrial or other wastes, liquid or solid, without first having applied for and received a permit from the Water Pollution Committee for such discharge. In issuing the permit, the Committee shall prescribe the standards of water quality and purity of such sewage, industrial or other wastes necessary to maintain the receiving water as 'Class A' water of this state as defined in Section 61.0145, 1960 Supplement to South Dakota Code of 1939. The Committee shall have authority to require the applicant for the permit to furnish such technical information and data as may be necessary to judge the character of the waste and the degree of treatment required to maintain the necessary standards of purity.)"

South Dakota is a member of the Tri-State Water Commission.

TENNESSEE

The Stream Pollution Control Board is charged with the primary responsibility of controlling water pollution. The Department of Public Health also exercises some functions relating to water pollution, primarily in the construction of public water supply and sewerage systems (1856).

The Tennessee Stream Pollution Act of 1945, as amended in 1951 (115), gives the Board the duty and authority "... To establish such standards of quality for any waters in relation to their reasonable and necessary use as it shall deem to be in the public interest." The original standards or any changes therein can be promulgated by the Board only after public hearings.

Acting in accordance with the statute, the Board issued the following criteria to be used as guides (1857):

"Criteria of Water Conditions

1. Solids, Floating Materials, and Deposits

There shall be no distinctly visible solids, seum, foam, oily sleek, or the formation of slimes, bottom deposits or sludge banks of such size or character as may be detrimental to public health, fish and other aquatic life, recreation, industry, or other reasonable and necessary uses of the waters.

2. Temperature

The temperature of the receiving waters shall not be raised or lowered to such an extent as to interfere with the reasonable and necessary uses of the waters.

3. Turbidity or Color

There shall be no turbidity or color added in amounts or of such character as interferes with the reasonable and necessary uses of the waters, or that cannot be reduced to acceptable concentrations by modern water treatment processes as commonly employed, or that result in an objectionable appearance of the waters.

4. Taste or Odor

There shall be no substances added which will result in taste or odor that prevent the production of potable water by modern water treatment processes as commonly employed, or imparts unpalatable flavor to food fish, or result in noticeable offensive odors in the vicinity of the waters, or otherwise interfere with the reasonable and necessary uses of the waters.

5. Acidity or Alkalinity

There shall be no substances added which will make the waters acid or alkaline to such an extent as to interfere with the reasonable and necessary uses of the waters.

6. Hardness or Mineral Compounds

There shall be no substances added to the waters which will increase the hardness or the mineral content of the waters to such an extent as to appreciably impair the usefulness of the waters as a source of water supply or interfere with other reasonable and necessary uses of the waters.

7. Dissolved Oxygen

The dissolved oxygen shall not be depleted to an extent that will interfere unduly with the reasonable and necessary uses of the waters.

8. Bacteria

No disease-producing bacteria or other objectionable organisms shall be added to surface waters which will result in the contamination of said waters to such an extent as to render the water unsuitable as sources of domestic water supply after treatment with currently existing methods or otherwise increase the bacterial content to such an extent as to render said waters unsuitable for other reasonable and necessary uses.

9. Toxic Substances

There shall be no substances added to the waters that may produce toxic conditions that materially affect man, animals, or aquatic life, or impair the safety of a treated water supply, or adversely affect other reasonable and necessary uses.

10. Other Pollutants

Other pollutants shall not be added to the waters in quantities which may be detrimental to public health, fish or aquatic life, recreation, or other reasonable and necessary uses of the waters' (114, 1857).

Tennessee is a member of the Tennessee River Basin Water Pollution Control Compact, but as of 1 January 1962 this Compact had not been activated.

TEXAS

The Texas Water Pollution Control Law, passed by the 57th Legislature in 1961, was the first change in water pollution control in Texas since 1953. This act created the State Water Pollution Control Board, which has the authority to abate and prevent pollution of the waters of the state.

Streams are not classified formally nor have standards of water quality been promulgated, although streams or other bodies of water used as the raw water supply to a public water treatment plant must conform to standards established by the Department of Health which has adopted the U. S. Public Health Service standards (116). Although the act does not mention standards per se, Section 4 states, in part:

The Board "after notice to the parties affected and after a public hearing if ... (deemed) ... to be in the public interest, may issue permits for the discharge of waste into or adjacent to the waters of this State. Each such permit shall set forth the conditions upon which it is issued by the Board, including, but without limiting such conditions, to the duration of such permit, the maximum quantity of waste which may be discharged thereunder at any time and from time to time,

and the quality, purity and character of waste which may be discharged thereunder... The Board shall adopt, prescribe, promulgate and enforce rules and regulations reasonably required to effectuate the provisions of this Act' (1858).

UTAH

In 1953 the Utah State Water Pollution Control Board was established with strong powers to control, prevent, and abate the pollution of surface and underground waters. The Water Pollution Control Act did not alter the powers of other state agencies also functioning in water-pollution control, namely, the State Health Department, the Fish and Game Department, and the State Engineer (118, 1859).

Among the powers and duties that the Board shall have and may exercise under Section 4 of the act is the following: "To adopt, modify or repeal and promulgate standards of quality of the waters of the state and classify such waters according to their reasonable uses in the interest of the public under such conditions as the board may prescribe for the preservation, control and abatement of pollution." Section 6 of the same act states:

"In order to effectuate a program for the prevention, control and abatement of pollution of the waters of the state, the board is authorized to group the waters of the state into classes according to their present most reasonable uses. Subject to the approval of the Legislature the board is authorized to upgrade and reclassify from time to time the waters of the state to the extent that is practical and in the public interest.

"The board is authorized to establish standards of quality for each classification consistent with most reasonable present and future use of such waters, and such standards may be modified or changed from time to time. Prior to classifying waters, setting standards or modifying or repealing them the board shall conduct public hearings in connection therewith. Notice of public hearing for the consideration, adoption, or amendment of the classifications of waters and standards of purity and quality thereof shall specify the waters concerning which a classification is sought to be made or for which standards are sought to be adopted and the time, date, and place of such hearing. Such notice shall be published at least twice in a newspaper of general circulation in the area affected and shall be mailed at least twenty days before such public hearing to the chief executive of each political subdivision of the area affected and to such other persons as the board has reason to believe will be affected by such classification and the setting of such standards.

"The adoption of standards of quality of the waters of the state and classification of such waters or any modification or change thereof shall be effectuated by an order of the board which shall be published in a newspaper of general circulation in the area affected. In classifying waters and setting standards of water quality or making any modification or change thereof, the board shall allow and announce a reasonable time for persons discharging wastes into the waters of the state to comply with such classification or standards. "Any discharge in accord with such classification or standards shall not be deemed to be pollution for the purpose of this act" (1860).

In accordance with these powers, the Utah Water Pollution Control Board has officially adopted the system of classification with water quality standards as shown in Appendix J (118).

VERMONT

The Vermont Water Resources Board, formerly known as the State Water Conservation Board, had its name changed by an act of the General Assembly of the State of Vermont in 1961 (119). The Water Resources Board has the primary responsibility of controlling water pollution in all surface waters. The State Health Commission also exercises some functions dealing with water pollution. These functions relate primarily to public water and ice supplies and advice concerning the disposal of drainage or sewage (1861). The Vermont Water Resources Board administers the state grant-in-aid program whereby 20 percent of the total eligible costs for necessary pollution-control facilities is paid by the state. In administering this grant-in-aid program, the Board is responsible for establishing standards of treatment and reviewing and approving plans for these facilities. Its duties also include review of sewer extension plans, issuing of permits for these extensions for new sources, and the initiation of enforcement activities when needed.

The Water Resources Board is authorized to classify waters not already classified by the Legislature, and to determine the degree of purity that should be obtained and maintained in such waters in the future. The 1961 General Assembly also amended Section 902 of the water-pollution-control laws on classification. It now reads (1862):

"S902. Classification of waters.

The State of Vermont hereby adopts, for purposes of classifying its waters, the following classes and definitions thereof:

- Class A. Suitable for public water supply. Character uniformly excellent.
- Class B. Suitable for bathing and recreation, irrigation and agricultural uses; good fish habitat; good aesthetic value, acceptable for public water supply with filtration and disinfection.
- Class C. Suitable for recreational boating, irrigation of crops not used for consumption without cooking; habitat for wild life and for common food and game fishes indigenous to the region; and such industrial uses as are consistent with other class "C" uses.
- Class D. Suitable for transportation of sewage and industrial wastes without nuisance, and for power, navigation and other industrial uses."

The above classes correspond essentially to those of the New England Interstate Water Pollution Control Commission of which Vermont is a member. The Water Resources Board utilizes the standards of this Commission (119).

VIRGINIA

The State Water Control Board has the primary function of controlling water pollution in the state. The State Board of Health has general supervision and control over all water supplies and waterworks in the state insofar as the sanitary and physical quality of water furnished may affect the public health (1863).

The State Water Control Board is charged "to establish such standards of quality for any waters in relation to the reasonable and necessary use thereof as it deems to be in public interest, and such general policies relating to existing or proposed future pollution as it deems necessary to accomplish the purposes of this chapter, to modify, amend or cancel any such standards or policies established and to take all appropriate steps to prevent pollution contrary to the public interest or to standards and policies thus established" (1864).

The water-quality aspects of each case involving a waste discharge to state waters is considered on its own merits, taking into consideration the downstream water uses and the assimilative capacity of the receiving stream. In this consideration the Board utilizes a guide of general objectives for the setting of water-quality standards. In effect, therefore, stream quality standards, either expressed or implied, exist for each stretch of stream below a point of waste discharge. Moreover, each certificate (permit) granted contains a section making at least a general reference to stream quality.

The general criteria used by the Board as a guide in recommending standards of quality are:

- "1. Solids which may settle to form detrimental sludge deposits in the quieter sections of streams should not be permitted.
 - 2. Oil, grease, scum or floating solids which are unsightly, may be deposited on the shores, interfere with re-oxygenation of the water, or are otherwise detrimental should not be permitted.
 - 3. pH in the stream should be maintained within specified limits.
 - 4. Inorganic dissolved solids in the stream should be kept within concentration limits so that water is not rendered unfit for an industrial or domestic water supply, as an environment for aquatic life, or for other uses.
 - Materials in the stream toxic to fish and other aquatic life, or to man or animals using the water, should be kept at or below specified maximum concentrations.
 - Dissolved oxygen should be kept at specified levels in the stream below the point of any waste discharge, so indigenous aquatic life may be maintained.
 - Discoloration and turbidity of the stream should be kept within specified limits.
 - 8. The most probable numbers of coliform bacteria in the stream should be kept within specified limits.
 - Radioactivity levels should be kept within specified limits.
- 10. Temperature should be kept within specified limits.

11. Specifications for other constituents in the stream will be set in individual cases" (120).

An example of a certificate (permit) stipulation re-

lating to water quality is the following:

- "After adequate mixing of the industrial wastes referred to in this certificate with receiving State waters, the following general conditions shall be maintained:
- (a) No appreciable change in existing color.
- (b) No appreciable settleable or floatable solids.

(e) No grease or oil films.

(d) Natural pH value of stream not changed more than one pH unit.

(e) Biochemical oxygen demand of waste sufficiently low to prevent depressing the dissolved oxygen content at any time or at any location below parts per million.

(f) Potentially toxic substances substantially below toxicity thresholds for aquatic or other life"

(120).

Virginia is a member of the Interstate Commission on the Potomic River Basin, the Ohio River Valley Water Sanitation Commission, and the Washington Metropolitan Regional Sanitary Board.

WASHINGTON

The Pollution Control Commission has been responsible for administering and enforcing the State Water Pollution Control Act since 1945. The Commission has broad authority under the Act to control and prevent pollution of state water, including the setting of standards. Other state agencies that have roles concerning certain aspects of water pollution include the State Department of Health, the State Department of Conservation and Development (Division of Water Resources), the Director of Fisheries and the Director of Game, and the State Oil and Gas Conservation Committee (1865).

The Pollution Control Commission has adopted the

following standards (1866):

"1. No sewage or industrial waste shall be discharged into any of the waters of the state that will cause:

(a) The reduction of the dissolved oxygen content to less than five parts per million (5 p.p.m.)

(b) The hydrogen-ion concentration (pH) to be outside of the range of 6.5 to 8.5.

- (c) The liberation of dissolved gases, such as carbon dioxide, hydrogen sulphide or any other gases in sufficient quantities to be deleterious to fishes or related forms.
- (d) The development of fungi or other growth having a deleterious effect on stream bottoms, fishes and related forms, or be injurious to health, recreation or industry.

(e) Toxic conditions that are deleterious to fishes and related forms or affect the potability of drinking

water.

(f) The formation of organic or inorganic deposits detrimental to fishes and related forms, or be injurious to health, recreation or industry.

(g) Discoloration, turbidity, scum, oily sleek, floating solids, or coat the aquatic life with oily films, or be injurious to health, recreation or industry.

(h) The temperature to be raised above the limit of tolerance of fishes and related forms.

"2. In those waters which are used or reasonably suitable for use as drinking water supplies, shellfish culture, bathing, or in other instances where its use presents a definite public health hazard by presence or potential presence of disease-producing organisms, the median bacteriological content of a representative number of samples shall not show the presence of coliform organisms in excess of 50 per 100 ml. expressed in terms of the most probable number, provided that the sanitary survey reveals that bacterial content is of human origin. In other instances where the use of water presents a public health hazard by the presence or potential presence of diseaseproducing organisms, the median bacteriological content of a representative number of samples shall not show the presence of coliform organisms in excess of 240 (M. P. N.) per 100 ml provided that the sanitary survey reveals that the bacteriological content is of human origin."

As a member of the Pollution Control Council of the Pacific Northwest Area, the Washington Commission utilizes the water-quality objectives of this interstate agency.

WEST VIRGINIA

The State Water Resources Commission, named in 1959, was incorporated in the newly formed Department of Natural Resources in 1961. This Commission has the primary responsibility of controlling water pollution in the State of West Virginia (1867).

Minimum Water Quality Objectives adopted by the Commission, as amended in 1959, conform with objectives of the Ohio River Valley Water Sanitation Commission of which West Virginia is a member. This document states (126):

"That the State Water Commission adopt as a general guide the following minimum water quality objectives, applicable to all waters of the state, that is to say:

"No sewage, industrial wastes or other substances allowed to enter any of the waters of the state shall cause therein or materially contribute to any of the following conditions thereof:

- Distinctly visible floating or settleable solids, scum, foam or oily sleeks of unreasonable kind or quantity;
- (2) Objectionable bottom deposits or sludge banks;
- (3) Objectionable odors in the vicinity of the waters;
- (4) Objectionable taste or odor in municipal water supplies;
- (5) Poisonous to man, animal or fish life;
- (6) Dissolved oxygen concentration to be less than 3.0 parts per million at the point of maximum oxygen depletion;
- (7) Objectionable color;
- (8) Requiring an unreasonable degree of treatment for the protection of potable water by modern water treatment processes as commonly employed; and, be it

Further Resolved, that with respect to sewage under the control of any municipal or private corporation, any county court, government institution, agency or political subdivision, these objectives be interpreted to require at least sufficient treatment to provide substantially complete removal of settleable solids and removal of not less than 45 percent of the total suspended solids, and, be it

Further Resolved, that chlorination of sewage treatment plant effluents will be required where deemed necessary, and, be it

Further Resolved, that nothing contained herein shall be construed to be antagonistic to or interfere with the obligations incurred by the State of West Virginia as a signator to the Ohio River Valley Water Sanitation Compact; and, be it

Further Resolved, that higher or additional water quality objectives may be established by the Commission at its discretion, or exceptions may be made to these objectives in individual cases where justified."

Although the above guides are to be followed in all state streams, more stringent measures can be applied to certain streams.

West Virginia is also a member of the Interstate Commission on the Potomac River Basin.

WISCONSIN

In Wisconsin, the Committee on Water Pollution, the State Board of Health, and the Conservation Department exercise functions relating to water pollution. The Committee exercises general supervision over the administration and enforcement of all laws relating to the pollution of the surface waters of the state (1868). Changes in the statutes since 1953 have not involved water-quality criteria.

No water-quality standards have been established; each pollution problem is considered individually. The Committee has, however, adopted the policy that at least primary treatment with chlorination should be provided for all sewage discharged into surface waters, and that industrial-waste-treatment plants should provide equivalent reduction in BOD to that attained in the treatment of sewage for any given location (127).

Wisconsin is a member of the Great Lakes Commission.

WYOMING

The State Department of Health has general supervision over water-pollution control in the state. The Stream Pollution Advisory Counsel assists the Department in the development of a comprehensive program for the prevention, abatement, and control of water pollution. The State Engineer is responsible for the control of pollution of underground waters. The Oil and Gas Conservation Commission also has responsibilities concerned with prevention of pollution of fresh-water supplies by oil, gas, or salt water (1869).

The Wyoming State Board of Health has adopted criteria set forth by the Missouri Basin Engineering Health Council, of which the Wyoming Department of Public Health is a member. These criteria are as described hereinafter (128).

BI-STATE DEVELOPMENT AGENCY

The States of Illinois and Missouri created by compact in 1949 the Bi-State Development Agency which has

general planning authority only with respect to water supply (St. Louis metropolitan area). Under this authority, the Agency, in 1954 and in conjunction with other agencies, sponsored a water-pollution investigation of the Mississippi River (1870).

Among the recommendations made were that all wastes discharged into the river shall be in a condition

which shall not cause:

- a) excessive bacterial, physical, or chemical contamination;
- b) unnatural deposits in the stream;
- objectionable colors, tastes, or odors to water used for domestic or industrial purposes; and
- d) shall be free from floating materials, such as oils, grease, sewage solids, or other refuse.

For sanitary sewage and storm water, it is recommended that treatment be sufficient for adequate removal or reduction of solids, bacteria, and chemical constituents that may interfere with the use of the water, such as substantially complete removal of floating and settleable solids, and not less than 45 percent of the suspended solids. Phenol wastes shall not produce a concentration exceeding a monthly average of 2 micrograms per liter or a maximum of 5 micrograms per liter at any point. The pH of the waters shall not be less than 6.7 nor more than 8.5. Odor-producing substances in the effluent shall be reduced so that after the final dilution, the mixture does not have a monthly threshold odor number in excess of 10 and a maximum daily odor number in excess of 30. Oils and floating solids shall be reduced to a point such that the stream is free from noticeable floating solids, oil, grease, and sleek. Highly toxic wastes should be eliminated or reduced to safe limits. Deoxygenating wastes should be suitably treated (1871).

DELAWARE RIVER BASIN COMMISSION

This new agency came into existence on 27 October 1961 as an interstate-federal compact. The Federal Government will participate with the States of New York, New Jersey, Pennsylvania, and Delaware in the planning, regulation, and execution of water-resources projects and programs in the Delaware River Basin. The new agency will probably supplant the Interstate Commission on the Delaware River Basin and absorb much of the latter's progress in and activities concerning the setting of standards (133).

Section 3.6 of the Compact authorizes the Commission to "Establish standards of planning, design and operation of all projects and facilities in the basin which affect its water resources. ..." Section 4.2 allows the Commission power "to acquire, operate and control projects and facilities for the protection of public health, stream quality control, economic development, improvement of fisheries, recreation, dilution and abatement of pollution, the prevention of undue salinity and other purposes. .." Also, Section 5.2 states "The commission may assume jurisdiction to control future pollution and abate existing pollution in the waters of the basin, whenever t determines after investigation and public hearing upon due notice that the effectuation of the comprehensive plan so requires. The standard of such control shall

be that pollution by sewage or industrial or other waste originating within a signatory state shall not injuriously affect waters of the basin as contemplated by the comprehensive plan. The commission, after such public hearing may classify the waters of the basin and establish standards of treatment of sewage, industrial or other waste, according to such classes including allowance for the variable factors of surface and ground water such as size of the stream, flow, movement, location, character, self-purification, and usage of the waters affected. After such investigation, notice and hearing the commission may adopt and from time to time amend and repeal rules, regulations and standards to control such future pollution and abate existing pollution, and to require such treatment of sewage, industrial or other waste within a time reasonable for the construction of the necessary works as may be required to protect the public health or to preserve the waters of the basin for uses in accordance with the comprehensive plan" (1872).

GREAT LAKES COMMISSION

The Great Lakes Commission is an agency created by a 1955 interstate compact among seven Great Lakes States, and serves as their joint advisory agency on Great Lakes water-resource programs. The State of Ohio is the only state eligible for membership that is not now participating in the Commission's program. Also, Congress has not yet given its consent to the Compact. Nevertheless, the member States of Illinois, Indiana, Michigan, Minnesota, New York, Pennsylvania, and Wisconsin continue to recognize the Commission as their joint agency.

Article VII of the Great Lakes Basin Compact lists "measures for combating pollution" among the subjects to be considered by the Commission. In the exercise of its powers under the Compact, which limits the Commission's authority to advisory powers, the Commission to date has not recommended any water-quality standards for the Great Lakes (1873).

INTERNATIONAL BOUNDARY AND WATER COMMISSION

The 1944 Water Treaty between the United States and Mexico set forth, among other things, the jurisdiction and functions of this Commission. Article 3 of the Treaty states that "all of the (water) uses shall be subject to any sanitary measures or works which may be mutually agreed upon by the two Governments, which hereby agree to give preferential attention to the solution of all border sanitation problems." Consequently, two international sewage treatment works have been jointly constructed, the operation and maintenance of which are under Commission supervision. The Commission does not promulgate its own standards of water quality. Instead, it is guided by the regulations of the border states involved in consultation with the federal public health agency of each country (1874).

INTERNATIONAL JOINT COMMISSION

The International Joint Commission was created by the Boundary Waters Treaty, signed in 1909, between the United States and Great Britain "Relating to Boundary Waters and Questions arising Between the United States and Canada." It was agreed in the Treaty that boundary waters and waters flowing across the boundary "... shall not be polluted on either side to the injury of health or property on the other ..." (130). The Treaty did not designate specific procedures to ensure compliance with this agreement. Hence, waterpollution problems have been handled under the general provisions of Article IX, under which considerations of any kind can be referred to the Commission for investigation, report, and recommendation (1875).

In 1946, the two governments directed the Commission to investigate conditions of Lake St. Clair and of the St. Clair and Detroit Rivers (130). Eventually, the Commission's investigation was broadened to include sections of Lakes Superior, Huron, Erie, and Ontario. A Board of Technical Advisors, assisting the Commission in the investigation, developed a series of objectives for quality control of the boundary waters (131). These

objectives appear in Appendix L.

A feature of these objectives (1876) is their combination of recommendations for stream quality with suggestions for effluent concentrations, e.g., an objective of 0.3 mg/l of iron in the receiving waters "will probably be attained if plant effluents are limited to 17 ppm of iron in terms of Fe." Similar expressions are given for phenols, pH, odors, and oils. Ontario, Canada, makes use of a similar system of objectives plus effluent concentration recommendations (1877).

The International Joint Commission has established an international warning system for notifying downstream water users following industrial waste spills (1875). Louisiana utilizes a similar warning system

along the Mississippi River.

INTERNATIONAL WATER SUPPLY ASSOCIATION

In June 1947, representatives from Great Britain, France, and the Netherlands met in England to discuss the formation of an International Water Supply Association. The general purposes of the new group would be to enable men engaged in water supply in all parts of the world to exchange information, to meet to discuss problems of common interest, and eventually to pool ideas and to carry out research on an international basis. The decision was made to convene an International Water Supply Congress in Amsterdam in 1949 and there to set up a new Association and adopt a constitution (1878).

Each third year commencing with 1949 the Association holds an International Water Supply Congress. The United States became a member at the time of the 1961 Congress held in Berlin. Current membership now in-

cludes 32 corporate members (nations).

Also at the 1961 Congress, the Association's Technical Commission on Pollution of Surface Waters presented recommended limits of pollution of surface waters (1879) as follows:

"1. The increasing population of the world, the rising standard of life and the increase in the demand for wholesome water supplies will make it necessary to resort more and more to surface waters for drinking water. The Commission is therefore alarmed at the extent to which pollution is allowed in rivers which are or will be used for drinking water.

- "2. The Commission therefore recommends that the following principles be adopted:
 - (a) Rivers which are at present clean shall be preserved free from pollution.

(b) Rivers which are already polluted shall not be made worse by further pollution but shall

be improved wherever possible.

(c) Rivers polluted beyond the following limits shall be improved in accordance with a definite programme aimed at reducing the pollution to the following limits measured at the point of intake.

(1) Physical Characteristics

Temperature: Permissible increase to be fixed by each country pending international agreement.

Taste and odour: No disagreeable taste and odour.

Suspended matter: Permissible increase to be fixed by each country pending international agreement. pH range: 6.5 to 8.7

(2) Chemical Characteristics

Biochemical oxygen demand: Five days at 20°C; not greater than 4 mg/l Dissolved oxygen content: Not less than 70% saturation

Free ammonia as N: Not greater than 0.5 mg/l

Chlorides as Cl: Desirable limit 200 mg/l

Phenols: Not greater than 0.001 mg/l Oils and fats: No oils or fats to be allowed

(3) Toxic Substances

Not greater than the concentrations set out in the "International Standards of Drinking Water Quality" published by the World Health Organization in Geneva in 1958, namely:

	Maximum allowable
Substance	concentrations
Lead (as Pb)	$0.1 \mathrm{mg/l}$
Selenium (as Se)	$0.05 \mathrm{mg/l}$
Arsenic (as As)	0.2 mg/l
Chromate (as Cr)	0.05 mg/l
Cyanide (as CN)	0.01 mg/l

(4) Radioactivity

The limits fixed by the World Health Organization from time to time. The present figures are:

Alpha emitters—not greater than 1 micro-microcurie per litre.

Beta emitters —not greater than 10 micro-microcuries per litre over and above the naturally occurring radioisotope Potassium 40.

- "3. The principles set out in paragraph 2 above apply with equal force to lakes. The Commission is to consider whether any amendment is required in the detailed application of these principles to lakes.
- "4. The detailed figures set out in paragraph 2 above may require to be altered, added to, and completed in the light of further knowledge and investigation. The Commission will continue its studies and will publish a new report or reports as and when necessary.
- "5. The Commission also intends to study and to make recommendations on practical measures to be taken to assist in achieving the objects set out in paragraph 2 above."

INTERSTATE COMMISSION ON THE DELAWARE RIVER BASIN (INCODEL)

Correspondence with the Interstate Commission on the Delaware River Basin (133) indicated that the information presented in the earlier printings of WATER QUALITY CRITERIA is still applicable. Therefore, most of this information is repeated.

Recognizing that the growing problem of pollution along the Delaware River was of interstate origin and concern, Delaware, New Jersey, New York, and Pennsylvania joined in a reciprocal agreement for the correction and control of such pollution. In the original agreement (132) the areas of the basin were classified into zones according to the principal uses of the water and minimum quality requirements for effluents discharged into each zone were promulgated. In this manner, Incodel combined effluent standards with stream classification. Pertinent sections of the reciprocal agreement, dealing with zones and standards, have been excerpted and included herewith as Appendix N.

However, Incodel will soon be supplanted by a new agency. On 27 September 1961, President Kennedy signed an interstate-federal compact under which the Federal Government will participate with the States of New York, New Jersey, Pennsylvania, and Delaware in the planning, regulation, and execution of water-resources projects and programs in the Delaware River Basin. This co-operation will be accomplished under the aegis of a new agency endowed with broad and strong powers over all aspects of water development, including water-pollution control. The new agency officially came into existence on 27 October 1961, a month after the authorizing compact was signed by the President.

While an effective job has thus far been done in coping with pollution in the Delaware River Basin, it has become apparent that the water-quality standards must soon be up-graded in order to keep pace with the rapid growth in industry and population. In the past few years, Incodel has been conducting studies to establish bases upon which the new standards should be founded. It is sure the new Commission will continue these tasks at an accelerated rate (133). This new Commission is to be known as the Delaware River Basin Commission and is described separately.

INTERSTATE COMMISSION ON THE POTOMAC RIVER BASIN

A compact entered into by Maryland, Virginia, Pennsylvania, West Virginia, and the District of Columbia created the Potomac Valley Conservancy District, comprising the drainage basin of the Potomac River and its main and tributary streams. The compact also established the Interstate Commission on the Potomac River Basin as a co-ordinating body for the purpose of "regulating, controlling, preventing, or otherwise rendering unobjectionable and harmless the pollution of the waters of said Potomac drainage area by sewage and industrial and other wastes..." (134).

Among its duties and powers, the commission is authorized "To make and, if needful from time to time, revise and to recommend to the signatory bodies, reasonable, minimum standards for the treatment of sewage and industrial or other wastes now discharged or to be discharged in the future to the streams of the Conservancy District, and also, for cleanliness of the various streams in the Conservancy District" (134).

Water-quality criteria promulgated by the Commission in 1946 and recommended to the states of the basin for their use are included in Appendix O. Also, in January 1958, the Commission adopted criteria for the Potomac River in the Washington Metropolitan area. These latter criteria are included in Appendix K.

An amended compact is currently being negotiated. Since an important aspect of the new compact concerns standards and classifications, the part concerning such in Article II, Section F2 is quoted:

"To establish reasonable physical, chemical and bacteriological standards of water quality satisfactory for various classifications of use. It is agreed that each of the signatory bodies through appropriate agencies will prepare a classification of its interstate waters in the District in entirety or by portions according to present and proposed highest use, and for this purpose technical experts employed by appropriate state water pollution control agencies are authorized to confer on questions relating to classification of interstate waters affecting two or more states. Each signatory body agrees to submit its classification of its interstate waters to the Commission with its recommendations thereon.

"The Commission shall review such classification and recommendations and accept or return the same with its comments. In the event of return, the signatory body will consider the comments of the Commission and resubmit the classification proposal, with or without amendment, with any additional comments for further action by the Commission.

"It is agreed that after acceptance of such classification, the signatory body through its appropriate state water pollution control agencies will work to establish programs of treatment of sewage and industrial wastes which will meet or exceed standards established by the Commission for classified waters. The Commission may from time to time make such changes in definitions of classifications and in standards as may be required by changed conditions or as may be necessary for uniformity and in a manner similar to that in which these standards and classifications were originally established. "It is recognized, owing to such variable factors as location, size, character and flow and the many varied uses of the waters subject to the terms of this Compact, that no single standard of sewage and waste treatment and no single standard of quality of receiving waters is practical and that the degree of treatment of sewage and industrial wastes should take into account the classification of the receiving waters according to present and proposed highest use, such as for drinking water supply, bathing and other recreational purposes, maintenance and propagation of fish life, industrial and agricultural uses, navigation and disposal of wastes" (1880).

INTERSTATE SANITATION COMMISSION

The information concerning the Interstate Sanitation Commission that appeared in earlier printings of WATER QUALITY CRITERIA is still unchanged (1881).

The Tri-State Treaty Commission was created in 1931 jointly by New York, New Jersey, and Connecticut to study the existing conditions of pollution of the harbor and coastal waters of the New York metropolitan area and to recommend methods for the abatement of the pollution. The Treaty Commission recommended the adoption of the Tri-State Compact which established the Interstate Sanitation District and the Interstate Sanitation Commission (135).

The compact, signed by New York and New Jersey in 1936 and by Connecticut in 1941, delimited the areas and waters to be included within the district, defined two classes of water, and enumerated the quality requirements of effluents to be discharged into waters of each classification. The two pertinent articles of this compact are reproduced below (1882):

"Article VI

1. It is recognized by the signatory States that, where tidal waters are used for such varied purposes as bathing, navigation, shellfish culture, and the development of fish life and the disposal of wastes, no single standard of purity is practicable in all parts of the district. In order to attain the objects of this compact, the commission, after proper study and after conducting public hearings upon due notice, shall group the designated waters of the district into classes. Where local conditions shall have changed in the future to such an extent that changes in classification become necessary, the commission may, after conducting public hearings upon due notice, adopt such changes.

Two general classifications shall be used:

- Class "A", in which the designated water areas are expected to be used primarily for recreational purposes, shellfish culture or the development of fish life;
- (2) Class "B", in which the designated water areas are not expected to be used primarily for recreational purposes, shellfish culture or the development of fish life."

"Article VII

1. It is agreed between the signatory States that no sewage or other polluting matters shall be discharged or permitted to flow into, or placed in, or permitted to fall or move into tidal waters of the district, except under the following conditions and restrictions:

- (1) All sewage discharged or permitted to flow into Class "A" waters of the district shall first have been treated so as—
 - (a) to remove all floating solids and at least sixty per centum (60%) of the suspended solids;
 - (b) to effect a reduction of organisms of the B. coli group (intestinal bacilli) so that the probable number of such organisms shall not exceed one per cubic centimeter in more than fifty per centum (50%) of the samples of sewage effluent tested by the partially confirmed test; provided, however, that in the case of discharge into waters used primarily for bathing this bacterial standard need not be required except during the bathing season; and
 - (c) to effect a reduction in the oxygen demand of the sewage effluent sufficient to maintain an average dissolved oxygen content in the tidal waters of the district and in the general vicinity of the point of discharge of the sewage into those waters, at a depth of about five feet below the surface, of not less than fifty per centum (50%) saturation during any week of the year.
- (2) All sewage discharged or permitted to flow into Class "B" waters of the district shall first have been so treated as—
 - (a) to remove all floating solids and at least ten per centum (10%) of the suspended solids, or such additional percentage as may by reason of local conditions be necessary to avoid the formation of sludge deposits in the Class "B" waters of the district; and
 - (b) to effect a reduction in the oxygen demand of the sewage effluent sufficient to maintain an average dissolved oxygen content in the tidal waters of the district and in the general vicinity of the point of discharge of the sewage into those waters, at a depth of about five feet below the surface, of not less than thirty per centum (30%) saturation during any week of the year."

Correspondence with the Commission indicated that in recent months the Commission has placed more emphasis on the abatement of industrial wastes. In order to clarify the industrial-waste standards required by the Tri-State Compact, the following requirements have been established (1881):

"Industrial Waste Standards Required by Tri-Sate Compact

- Remove all floating matter such as oil, grease or solids.
- Remove settleable solids so as to prevent the formation of sludge deposits along the shores or in the waterways.
- 3. Remove toxic materials, color, taste or odors that would interfere with the maintenance of fish life,

- shellfish and marine life in waters designated Class 'A' or creates a condition in any District waters which is obnoxious or causes a nuisance.
- 4. pH-No corrections or neutralization required unless it causes a condition which violates one of the preceding standards or creates a condition which is obnoxious or causes a nuisance.
- 5. Reduction in oxygen demand sufficient to maintain. an average dissolved oxygen content in the waters of not less than 50 percent saturation during any week of the year in Class 'A' waters and 30 percent saturation during any week of the year in Class 'B'

It is to be noted that these are not new standards or regulations, and have been issued only to re-emphasize the requirements that have always been covered by the

original Compact (1881).

It should be pointed out that Standard No. 3 is basically for Class "A" waters where certain materials might interfere with maintenance of fish life, shellfish, and marine life, but also would apply to "B" waters if they flow into and affect Class "A" waters. There is some flexibility to these standards as may be found under No. 5. This standard allows a determination to be made of an industrial plant on the basis of its location. For example, if a plant discharges waste with a soluble BOD and the water area into which it discharges has sufficient DO, no reduction in the BOD would be necessary. However, in an area with deficent DO, the industry would be required to reduce the oxygen demand of its wastes (1883).

KLAMATH RIVER COMPACT COMMISSION

In 1957, the Klamath River Basin Compact between the States of Oregon and California created the Klamath River Compact Commission. Article VII of the Compact states that, in order to aid in pollution abatement and control, the Commission shall have the duty and power "to cooperate with the states or agencies thereof or other entities and with the United States for the purpose of promoting effective laws and the adoption of effective regulations for abatement and control of pollution of the waters of the Klamath River Basin, and from time to time to recommend to the governments reasonable minimum standards for the quality of such waters.

The basic data to support minimum water-quality standards has been collected. However, the character of development within the area and the existing water quality has not required action by the Commission to

establish minimum requirements (1884).

MISSOURI BASIN ENGINEERING HEALTH COUNCIL

The Missouri Basin Engineering Health Council consists of the chief sanitary engineers of the ten Basin States (Colorado, Iowa, Kansas, Minnesota, Missouri, Montana, Nebraska, North Dakota, South Dakota, and Wyoming) who meet yearly to discuss common engineering health programs. As an organization, it is not an interstate agency for adoption or administration of water-pollution-control laws (1885).

In 1952 this group adopted tentative objectives for water-pollution-control programs in the Basin. The state engineers recognize that the objectives are guides only

and that changes in conditions, particularly as they affect water uses, may require modifications thereof. In 1954, the Council reviewed and reaffirmed these objectives, eliminating the qualification "tentative" (1886). The objectives are quoted in Appendix P.

NEW ENGLAND INTERSTATE WATER POLLUTION CONTROL COMMISSION

Following a recommendation of the New England Conference of State Sanitary Engineers in 1946, the several New England States negotiated a compact for the control of pollution of interstate streams. The New England Interstate Water Pollution Control Compact was ratified by the States of Connecticut, Massachusetts, and Rhode Island and approved by Congress. Since the creation of the Commission, New York, Vermont, New Hampshire, and Maine have also become members. All eligible states are now members (1887).

"The New England Interstate Water Pollution Control Compact is built around a classification of interstate waters according to their highest use based on physical, chemical and bacterial standards adopted by the Commission. Under the Compact, each signatory State agrees to submit classifications of its interstate waters to the Commission for approval, and then to establish programs of treatment of sewage and industrial wastes to bring about the improvements required to meet the approved

classifications, (137).

The establishment of standards for water classification has involved extensive studies. The former "Tentative Plan for Classification of Water" has been revised as "Classification and Standards of Quality for Interstate Waters" and appears in Table 3-3 (1887).

OHIO RIVER VALLEY WATER SANITATION COMMISSION (ORSANCO)

The following material on the Ohio River Valle, Water Sanitation Commission has been taken from a publication of the Commission (1888), which is rather

inclusive with respect to water-quality criteria.

"The Ohio River Valley Water Sanitation Commission, created by the Ohio River Valley Water Sanitation Compact which became effective on June 30, 1948, is an agency representing the states of Illinois, Indiana, Kentucky, New York, Ohio, Pennsylvania, Virginia and West Virginia. The Commission is charged with the responsibility of administering the provisions of the Compact . . .

This "Compact establishes basic standards for the treatment of wastes and empowers the Commission to supplement these standards. In addition, the Commission is empowered to prescribe and promulgate rules and regulations for the enforcement of treatment standards and for the administration of the provisions of the Compact . . . Primary enforcement of regulatory controls is sought through the appropriate state regulatory

agencies . . .

"Compact provisions-The express objective of the Compact is to place and maintain the waters of the Ohio River basin in a satisfactory sanitary condition, available for safe and satisfactory use as public and industrial water supplies after reasonable treatment, suitable for recreational usage, capable of maintaining fish and

other aquatic life, free from unsightly or malodorous nuisances due to floating solids or sludge deposits, and adaptable to such other uses as may be legitimate.

"The Compact contains the following guides and specific-performance requirements regarding control of waste discharges:

- 1. All sewage discharged to those portions of the Ohio River and its tributaries which form boundaries between, or are contiguous to two or more signatory states, or which flow from one signatory state into another signatory state shall be so treated as to provide for substantially complete removal of settleable solids and the removal of not less than forty-five percent of the total suspended solids, and to such higher degree as may be determined to be necessary by the Commission after investigation, due notice and hearing.
- 2. All industrial wastes discharged to waters under Compact jurisdiction shall be modified or treated, in order to protect the public health or to preserve the waters for other legitimate purposes, to such degree as may be determined to be necessary by the Commission after investigation, due notice and hearing.
- 3. All sewage and industrial wastes discharged to waters situated wholly within one state shall be treated to that extent necessary to maintain such waters in a sanitary and satisfactory condition at least equal to the condition of the waters of the interstate stream immediately above the confluence.

"Water-Quality objectives—As a guide in establishing sewage-treatment requirements and in evaluating water-quality conditions, the Commission on April 4, 1951 adopted objectives regarding the concentration of coliform bacteria." These objectives are presented in Appendix M.

"Sewage-treatment standards—The Commission, in the exercise of the authority granted it by the Compact, has promulgated seven sewage-treatment standards, each applying to a particular stretch of the Ohio River." These standards are also shown in Appendix M.

"Recommendations regarding pollution-abatement needs for interstate tributaries—In cooperation with state agencies, the Commission has investigated pollution-abatement needs for the Wabash River between Terre Haute, Indiana and Vincennes, Indiana and for the West Fork and Monongahela Rivers between Weston, West Virginia and Pittsburgh, Pennsylvania. The results of these investigations have not been transposed into formal treatment standards, . . . but conclusions have been reached and recommendations made regarding degrees of treatment needed in these areas to maintain quality conditions that would be acceptable from an interstate point of view." These conclusions and recommendations are presented in Appendix M.

"Basic industrial-waste requirements—Minimum or basic requirements for the treatment and control of industrial wastes in the Compact District were promulgated on April 6, 1955. These requirements, designated as IW-1, were derived from an interpretation of Compact provisions requiring that all waters are to be free from unsightly or malodorous nuisances due to floating solids or sludge deposits. On September 13, 1958, the basic requirements were amended by the addition of restrictions on the discharge of toxic substances.

"The basic requirements were enunciated as part of a statement of policy and procedure regarding industrial-waste control, which statement represents an agreement on basic principles among the eight states signatory to the Compact and establishes the frame-work within which additional waste-control measures are to be developed. Waste-control measures adopted in accordance with this statement of policy and procedure may be transposed into formal treatment standards when furtherance of the objectives of the compact warrants or requires." The industrial-waste requirements (IW-1) and also Orsanco's chloride-control resolutions appear in Appendix M.

Publications by the Commission have been extensive. They include the Annual Summaries, the Progress Reports of the Aquatic Life Advisory Committee, the Physiological (and other) Studies by the Kettering Laboratory on specific pollutants, including fluoride, lead, chloride, phenol, common inorganic salts, copper, cadmium, iron, cyanide and thiocyanates, cresol, cobalt, and a comprehensive evaluation of river-quality conditions during a 16-week shutdown of upper Ohio River Valley steel mills, as well as numerous articles dealing with aspects beyond the scope of WATER QUALITY CRITERIA.

Many of the above reports terminate with recommendations to the Commission regarding the specific pollutant involved. Such recommendations are included hereinafter under the write-up of each pollutant.

POLLUTION CONTROL COUNCIL, PACIFIC NORTHWEST AREA

This council is an informal organization of the sanitary engineers in direct charge of water-pollution-control programs in Alaska, British Columbia, Idaho, Montana, Oregon, and Washington, with representation of the Canadian Department of National Health and Welfare and the U. S. Public Health Service. The group was organized in May 1949 for the purpose of standardizing pollution-control activities in the Pacific Northwest area. A number of committees were appointed, including a Committee on Water Quality Objectives, which submitted a report on 10 September 1952. The table of water-quality objectives and minimum treatment requirements contained in this report appears in Table 3-4.

The members of the Pollution Control Council were reported to have used these water-quality objectives effectively since their adoption in 1952, in carrying out their individual pollution-control programs. In recent years, Montana and Idaho have formally adopted comparable objectives to guide their state programs. Oregon and Washington, together with the U. S. Public Health Service, have adopted an action program on the interstate boundary waters of the Lower Columbia River in keeping with these objectives. Similarly, Oregon and Washington have consistently aimed their programs at the same goals.

TABLE 3-3

CLASSIFICATION AND STANDARDS OF QUALITY FOR INTERSTATE WATERS NEW ENGLAND INTERSTATE WATER POLLUTION CONTROL COMMISSION

(As Revised and Adopted October 1, 1959)

CLASS B

CLASS C

CLASS D

		SUITABILITY FOR USE		The state of the s
	Suitable for any water use. Character uniformly excellent,	Suitable for bathing and recreation, irrigation and sgricultural uses, good fish habitat; good seathetic value, Accopable for public water supply with filtration and dismfection.	Suitable for recreational boating, irrigation of orous not used for communityfon without cooking; habitat for wildlife and common food and game fishes indigencus to the region; industrial cooking and most industrial process uses.	Suitable for transportation of sewage and industrial wastes without nuisance, and for power, navigation and certain industrial uses.
		STANDARDS OF QUALITY	Å	
Dissolved oxygen	Not less than 75% sat.	Not less than 75% sat.	Not less than 5 n m	Present of all times
Oil and grease	None	No appreciable amount	Not objectionable	A recent as an utities
Odor, soum, floating solids, or debris	None	None	None	NOT THE TENT
Sludge deposits	None	None	N	aleganons for
Color and turbidity	M		NOR	Not objectionable
	None	Not objectionable	Not objectionable	Not objectionable
Phenois or other taste producing substances	None	None	None	
Substances potentially toxic	None	None		
- 17 · · · · · · · · · · · · · · · · · ·		STORY.	Not in toxic concentrations or combinations	Not in toxic concentrations or combinations
Free Bods of alkalics	None	None	None	Not in objectionable amounts
Radioactivity	Within limits approved by the a	Within limits approved by the appropriate State agency with consideration of possible adverse effects in downstream waters from discharge of radioactive wastes; limits in a particular watershed to be resolved.	rse effects in downstream waters from discharge of radios fter consultation between States involved.	active wastes; limits in a particular watershed to be
Coliform bacteria	*Within limits approved by State Department of Health for uses involved.	Bacterial content of bathing waters shall meet limits approved by State Department of Health and accoptability will depend on sanitary survey.		

Sea waters used for the taking of market shellfish shall not have a median coliform content in excess of 70 per 100 ml.
 NOTE: Waters falling below these descriptions are considered as unsatisfactory and as Class E.
 These standards do not apply to conditions brought about by natural causes.
 For purpose of distinction as to use, waters used or proposed for public water supply shall be so designated.

The Pollution Control Council, during 1959, reviewed these water-quality objectives and found them sound, important, and of continuing value in conserving the quality of the water resources of the Pacific Northwest. The Council, at its October 1959 meeting in Portland, Oregon, re-adopted the objectives for the purpose of bringing them up to date and insuring their continued use (1889).

TRI-STATE WATER COMMISSION

A compact among the States of Minnesota, North Dakota and South Dakota created the Tri-State Water Commission. Although Congress approved the Compact in 1938, the Commission has been inactive since 1953 and it is doubtful that it will function again as an organized group (1890).

WASHINGTON METROPOLITAN REGIONAL SANITARY BOARD

The Washington Metropolitan Regional Sanitary Board was organized on 16 July 1959, through efforts initiated by the Water Supply and Pollution Abatement Committee of the Washington Metropolitan Regional Conference, a voluntary organization of elected representatives of jurisdictions in the region. These jurisdictions include, in addition to Washington, D. C., the Counties of Loudoun, Fairfax, Arlington, and Prince William in Virginia, and Montgomery, Charles, and Prince Georges in Maryland (1891).

This voluntary Conference, to which the Board is subordinated, has accepted water-quality objectives (with some minor differences) based on those promulgated by the Interstate Commission on the Potomac River Basin (1892). These objectives appear in Appendix K.

WATER QUALITY CRITERIA

WATER QUALITY OBJECTIVES AND MINIMUM TREATMENT REQUIREMENTS

TABLE 3-4

Water Quality Objectives, Applicable to Receiving Waters, for Salt and Fresh Surface Waters and Underground Waters

		WATER	R QUALITY CR	ITERIA	63
Minimum treatment requirements for domostic sewage	Sedimentation and effective disinfection	Sedimentation and offoctive disinfection	Sedimentation and effective disinfection	Sedimentation for all uses under this group but distriction required in addition only if discharged into waters used for the growth & propagation of shelish, either our nertial or recreations!	Sedimentation and effective disinfection
High temperature	Not in sufficient quantities alone or in com- bination with other wastes to interfere with the use indicated	Same as for use "A" above	Same as for use "A" above	None in sufficient guantity as to be in- jurious to or interfere with the normal propagation of fish, shellish, or other squado life	Same as for use "A" sboye
П	None	None alone or in com- bination with other substances or wastes as or wastes as receiving water unfit or unate for the use	Same as for use "13" above	Same as for use "B" above	Same as for use "By" above
Phenolic	Less than five (5) parts per billion	Less than five (5)	Less than 25 parts per billion or none in sufficient amounts and as amounts to recreational rest to recreational fish, shellish, of other aquatic forms	Come as for use	None in sufficient quantity as to make receiving water unsuitable for use indicated
Toxic, cofored, or other defeterious substances	None alone or in combination with other substances or wastes in sufficient nature as to make receiving water unsafe or unsuitable for use indicated for use indicated (U.B.P. H.S. Soke.)	Same as for use "A" above	Same as for Use "A" shove	None alone or in combination with other substances or wastes to sufficient amount of cold such character as to make receiving waters unsuitable for use indicated or use indicated	Same as for use "A" above
Hd	Hydrogen ion con- centration ex- pressed as pH shined between 6.5 and 8.6	Same as for use	Bame as for Use	Same as for use	Hydrogen ion con- centration ex- pressed as pH should be main- tained between 6.0 & 9.5
Dissolved	Greater than five (5) parts per mil- lion except for underground waters	Greater than five (b) parts per million except for underground waters	Greater than five (5) parts per million	Greater than six (6) parks per million	Greater than three (3) parks per million
Taste or odor- producing substances	None attributable to Bewage, industrial wastes, or other wastes	None attributable to sewage, industrial sewage, or other wastes, which, after reasonable dilution & mixture, will increase the threshold odor number above eight (9)	None attributable to sewage, industrial wafter, or other waste- which, after reasonable dilution & mixim, will interfere with the best use of these waters for the purpose indi- cated	None attributable to sewage, industrial wastes, or other wastes which will incercee with the matcheability or propagation of ree- restional or commercial fish, shellifan, or other etible aquasic forms	None attributable to sewage, mulustrial wastes, or other wastes ye which the ladversely a flott the ladversely of agricultural or industrial produce
Floating, suspended & settleable solids & settleable solids	None attributable to sewage, industrial wasteen or other wasteen or which, after reasonable dilution & mixture with receiving waters, inderfore with the best use of these waters for the purpose indicated	Same as for use "A" above	Same as for use "A" above	Same as for use "A" above	Same as for use "A" sbove
Organisims of the coliform group	Most probable number colliform bacterial con- terite of a representative bumber of samiles should average less than 50 per 100 mi.	M.P.N. coliform bac- fernial cortent when as- sociated with domestic servage of a represen- dative number of sam- ples should average less than 2000 per 100 ml, and should not ex- eed this number in more than 20 per cent of samples examined in any month.	Coliform bacterial con- tents of a representative number of samples should average less than 240 per 100 mil. And should not exceed this number in more than 20 per out of samples examined when associated with dome- tic servage (see note under "C" at left)	Collorm bacterial con- tent of a representative number of samples should not have a median concentration greater than 70 per 100 ml. in waters used for the growth & prop- agasion of shellfish	
Water quality >	A. WATER SUPPLY, DRINKING, CULIN, ARY & FOOD PRO- CESSING Without test treat other than simple disnifection and removal of neturally present impurities	B. WATER SUPPLY, DRINKING, CULL. NARY & FOOD PRO- CESSING, With rement equal to coegulation, sedimenta- tion, fiftration, distinct- tion, first and any additional treatment necessary for removing maturally present impurities	C. BATHING, SWIM-MING AND RECREATION Note: When waters are used for crowstonal purposes such as fabring the bathing of swimming the number '11000'' may the number '11000'' may the number '1100'' may the number of coliform objective	D. GROWTH & PROPACTION OF PIECE SHELL/PIECE OTHER AGUATIC LIFE	E. AGRICULTURAL WAND INDUGERIAL WAND INDUGERIAL WAND SUPPLY Without treatment ex- eept for the removal of makural impurities to meet special quality re- quirements other than those classified under "A" above. Note: For agricultural water supply, saliuity and softlum hasarda ave determined by electrical conductivity (EC × 109) ratio (SAR). Waters determined by electrical conductivity (EC × 109) ratio for irrigation purposes, (Ece * classifi- sedton and use of ririgat- softlum waters, divular softlum waters, divular softlum waters, divular No. 969, U. Depart- ment of Agriculture, November, 1986)

CHAPTER IV

JUDICIAL EXPRESSION

By PAUL R. FREEMAN, B.A., LI.B.*

The object of this chapter is to marshal the judicial decisions that illustrate the principles adopted by the courts in the application and evaluation of water-quality criteria to the solution of legal problems in the field of water pollution. A brief resume of the research techniques followed may be of some value to the lay reader in understanding how legal research is accomplished.

Broadly speaking, there are two general avenues of examination employed in searching for the law on any particular subject. One is to search in indices, digests, treatises, etc., for the subject matter under its topical arrangement. In some instances, it is the only approach that can be used. Every lawyer has a working familiarity with the main topics, classifications, or titles of law that are found in legal encyclopedias, digests, compilations, and texts. He needs no assistance to help him find general information on Contracts, Criminal Law, Vendor and Purchaser, Corporations, Evidence, Code Pleading, Fish and Game, etc.; but very often he is in a field that may be related to or discussed in many categories of the same legal topic. Under such circumstances, the second method, that of examining the cases in the subject field, may furnish a better means for beginning a search. Such a method may not be available in all situations. Yet, it has the peculiar advantage that one need not stop to consider what classification or topic to examine. Its use is limited to instances where one can start with some particular decision bearing on the question he wishes to investigate. Then, by citation reference, he can go directly to the volumes and pages of all the reports where that case has been cited and find everything that the courts have said about it. The later cases will tell whether the case in question has been approved, disapproved, limited, distinguished, or in any way weakened or overruled. Very often by this process one can quickly gather all the legal authorities needed. Then, by following these authorities through the application of the principle of the case, he can find the very decision sought. The fountainhead of the law is the decision of the courts as contained in the reported cases. Even the effects of the statutory rules of law is dependent on judicial decisions. Judicial decisions do two things: (a) they declare the law on points not covered by the statute, and (b) they determine by judicial construction of statutes, rules, regulations, and administrative findings their ultimate effect.

In this study the textbooks, digests, and legal encyclopedias were used not so much as a source of information in themselves, but rather as a means of finding the decisions in which water pollution was a facet of the case. It is impossible in a review of this general character to go into detail as to the precise method employed in

searching for the cases in which there was judicial expression relative to criteria for determining water quality. Suffice it to say, however, that an exhaustive search was made not only of the most likely topics or subdivision of topics where cases dealing with water pollution were cited, but in every place where there was a possibility of a case in point having been digested or referenced, and where there was a possibility that a cross reference might open a new avenue of research. Thus, for example, many cases that were examined came to the attention of the writer under such diverse headings and classifications as Actions, Appeals, Courts, Costs, Compromise, Criminal Law, Damages, Drains, Eminent Domain, Equity, Evidence, Fish, Parties, Navigable Waters, Trial, Towns, Barters, Pleadings, Pollution, Negligence and Nuisance, Health, Injunction, Limitation of Action, Master and Servant, Mines, Landlord and Tenant, Judgments, Municipal, Corporation, Waters, Watercourse, and Witness.

While this review of legal decisions is concerned primarily with those cases in which the courts have considered water-quality criteria, keeping in mind the ultimate objective of determining the validity of such criteria through judicial acceptance, it is nevertheless necessary and appropriate to include briefly a summarization of the legal principles that have been developed in water-pollution cases even though the quality of the water per se was not the issue in the case.

This summarization becomes apparent in view of the fact that there has been no significant case discovered to date in which specific water-quality criteria have been discussed from the purely scientific approach. While the criteria and standards promulgated have been discussed, as will be seen, their reasonableness or scientific accuracy as such has never alone been determinative of the legal issues involved in the particular case. It is indeed a rare situation when the litigation concerns itself only with the quality of the water, since so many times the polluted condition of the water is presumed to exist from the extrinsic facts and the question for decision is solely whether the condition imposes a remediable situation in one party and liability in the other.

It is recognized, moreover, that the acuteness of the water-pollution problem for any given area may be measured in terms of the availability of water, and that the attitudes of courts and juries must certainly be influenced by and reflect the abundance or paucity of the supply. Thus, subconsciously, standards for decisions that serve as guides for the judge or jury are formulated, based on the existence or non-existence of certain rudimentary factors, and these influences are translated into decisions in the tribunal. A brief review of the cases in which such extrinsic factors have indirectly affected the outcome of a water-pollution case may aid

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in a clearer understanding of the rules being sought and will help possibly in reconciling the opposing positions that courts in different jurisdictions have sometimes

Despite the examination of well over 1,200 cases dealing with some aspect of water pollution, this writer is not presumptuous enough to imply he has found every case that contained some expression of the court relative to water-quality criteria or that all such cases have been reported or cited herein. The principles developed by the cases are comparatively few but their applications are very numerous. The manner in which these principles are applied can only be learned through an examination and comparison of judicial decisions. It is the aim of this chapter to bring these principles into focus, thereby aiding the reader in understanding some of the principles that will be applied by the courts. Also, thereby, he will be provided with some foreknowledge of the questions with which he may have to deal and methods needed to assist the courts in finding the true rule of the case.

INDIRECT NON-TECHNICAL CRITERIA

Sections 1831 and 1832, California Code of Civil Procedure, state that direct evidence proves a fact without inference, while indirect evidence, usually termed circumstantial evidence, tends to establish one fact by proving another. People v. Goldstein (1956) 139 C.A. (2d) 146, 293 Pac. (2d) 495 contains an excellent delineation of the difference between the two.

"The terms 'indirect evidence' and 'circumstantial evidence' are interchangeable and synonymous (18 Cal. Jur. 2d 434, Sec. 12). Direct evidence is that which is applied to the fact to be proved, immediately and directly, and without the aid of any intervening fact or process: as where, on a trial for murder, a witness positively testifies he saw the accused inflict the mortal wound, or administer the poison. Circumstantial evidence is that which is applied to the principal fact, indirectly, or through the medium of other facts, from which the principal fact is inferred. The characteristics of circumstantial evidence, as distinguished from that which is direct, are, first, the existence and presentation of one or more evidentiary facts; and, second, a process of inference, by which these facts are so connected with the fact sought, as to tend to produce a persuasion of its truth (Burrill on Circumstantial Evidence, 4, 5). An inference is a conclusion as to the existence of a material fact that a trier of fact may properly draw from the existence of certain primary facts (Blank *. Coffin, 20 Cal. (2d) 457, 126 Pac. (2d) 868). Inferences drawn from physical facts amount to circumstantial evidence (McCready v. Atlantic Coast Line R. Co., 212 S.C. 449, 48 S.E. (2d) 193). It has been said that circumstantial evidence, as distinguished from direct evidence, is testimony not based on actual personal knowledge or observation of the facts in controversy, but of other facts from which deductions are drawn, showing indirectly the facts sought to be proved (Aday v. State, 28 Okla. Crim. 201, 230 Pac.

In the preponderance of cases dealing with water pollution, the existence of a polluted body of water is

established not by the introduction of direct evidence as to its quality as determined by actual testing of the chemical quality of the water but rather by the introduction of circumstantial evidence from which the inference is made that the water must be polluted. In several cases, this circumstantial evidence relates to the effect of the water upon fish, livestock, or even humans. It might be reasoned, therefore, that such evidence represents a form of bio-assay, albeit not standardized.

In Albough v. Mt. Shasta Power Corporation (1937) Cal. (2d) 751, 73 Pac. (2d) 217, the circumstantial evidence of the growth of weeds, the foul odor that emanated from a pool, and the preference of cattle and horses for other bodies of water were sufficient to cause the jury to conclude that the water was in fact polluted. This decision was reached despite the contrary evidence

of chemical analyses:

"It is true that appellant introduced more evidence and new theories on the present trials on the issue of pollution than had been presented by it on the prior trials. Two chemists were produced who testified that from a chemical analysis the water in the pool was fit to drink. Scores of photographs showing horses and cattle apparently drinking from the pool after the diversion were introduced. This, and other evidence introduced by appellant on this issue, did nothing more than create a conflict in the evidence, which was resolved by the jury contrary to appellant's contentions. There can be no doubt, in fact, appellant admits, that the evidence thoroughly establishes that since the diversion there has been a marked increase in the weed growth (and that) in the summer months the pool has been covered with weeds, slime, and moss.

"Appellant contends, however, that these conditions were due not to the diversion but to many years of subnormal run-off of Pit River. This argument is necessarily predicted on appellant's contention, already refuted, that before the diversion the Fall River water did not mingle with the Pit River water in the pool. The argument totally ignores the permissible inference that the Fall River water freshened the pool. Considerable credible evidence was introduced that since the diversion foul odor has emanated from the pool. Various witnesses for respondents testified as to the preference of cattle and horses for other fresh and nonstagnant water. Several witnesses living on the pool testified that in the years since the diversion they have never seen cattle drink from the pool. As already held on the prior appeals, the juries were amply justified in inferring that these conditions were caused by the diversion and the construction of the dam, and that such changed conditions caused a material depreciation in the market value of respondents'

In Knopp v. State (1936) 59 Okla. Cr. 143, 56 Pac. (2d) 1193, the defendant was convicted of contaminating a stream by placing, allowing, and causing to be run into its waters, oil, cement cuttings, slush, and waste from an oil well, and was sentenced to pay a fine of \$200. In upholding the lower court, the Appellate Court stated:

"There is evidence that the slush pits of this well were permitted to overflow and run into the stream, and that it became murky and muddy from such contamination; that sediment settled on the stones in the creek; that numerous fish could be seen in the creek before this, and none after. This was ample proof of pollution of the stream and the judgment is fully sustained by the evidence . . . "

In Conley et al. v. Amalgamated Sugar Co. (1953) 74 Idaho 416, 263 Pac. (2d) 705, an action by grocers against a sugar-beet factory to recover damages to a grocery business and building allegedly caused by the offensive odor of a creek polluted by the factory, the circumstantial evidence was sufficient to sustain the trial court's finding that the grocers' loss was due to the odor of beet pulp. This finding was sustained despite the introduction of expert testimony to the contrary.

"... Apellant countered respondents' evidence with expert and lay testimony and documentary evidence that no odor of beet pulp persisted or could persist down the stream from where the waste products of appellant's plant entered into Indian Creek, as far as respondents' store, and if odors emanated from the Creek, they were from other sources entirely disconnected from appellant's business. Also, that the amount of offensive effluent from appellant's plant was so small in proportion to the regular flow of the Creek, sometimes one to 200 cubic feet per second, it was so diluted that all offending odors therefrom were dissipated before reaching respondents' place of business. All this evidence merely created a conflict, resolved by the trial court against appellant . . . "

Eckart v. City of Belleville (1938) 294 Ill. App. 144, 13 N.E. (2d) 641 involved an action brought by a farmer to enjoin the city from polluting a creek adjacent to his farm by discharging raw and contaminated sewage therein. The finding of a polluted condition was predicated on the existence of tubifex worms in the water and on the foul odor that emanated from the creek. The court stated:

"... In November of the same year he (referring to a sanitary engineer who had testified at the trial) made another inspection and found that a quarter of a mile south of septic tank No. 1, the creek was full of suspended matter, heavy sludge deposits, and foul odors, and that for a distance of approximately twenty miles south of the tank, the water in the creek was dark and the stream was lined with tubifex worms. Tubifex worms live only in polluted streams. Samples of the water taken from the creek on this inspection were present and exhibited at the trial of this case.

"Much contradictory testimony appears in this record, and plaintiffs and their witnesses testifying to the above foregoing conditions and the terrible effects thereof on their homes and their comforts, and also to the effect upon their livestock; the defendant's wit-

nesses denying that such conditions exist.

"The defendant city has brought the record here on appeal, assigning many errors, three only of which are argued. The first is that the finding and judgment of the court is against the manifest weight of the evidence. A reference to this record at once meets this objection. The evidence shows not only that the court

was warranted in the action that it took, but that the conditions existing in the premises described are most shocking. The least that can be said is that the testimony raises a question of fact for the court who heard the witnesses and saw them testify. A striking incident appeared in this trial as it is described by the trial court; that is, that one of the witnesses for the defendant smelled and drank some of this water in court. The court in its opinion says that this is true, but that this witness did not impress the court either with his intelligence or his integrity. This but illustrates the wisdom of the rule that the tribunal which first hears the facts and hears them from the witnesses themselves is in a better position to judge of the credit due such witnesses than is an appellate tribunal which is only concerned with the record. . ."

A rather humorous instance of testing by taste is related in the decision in Town of Smithfield v. City of Raleigh (1935) 207 No. Car. 597, 178 S.E. 114, in which the court stated:

". . . Indeed, it seems that the trial judge subjected the question to 'trial by water,' because the record discloses that his Honor 'had drunk of the water, bathed in it, and suffered no ill effects." The ancient mode of trial by water was aforetime deemed efficacious in determining the guilt or innocence of witches and by applying the practice of the ancient law the distinguished jurist has found the waters of the Leuse River not guilty. . ."

In Bumbarger v. Walker (1958) 393 Pa. 143, 142 A. (2d) 171. (Supreme Court of Pennsylvania—May 26, 1958, Rehearing denied June 20, 1958), an action was brought by a lower landowner against persons purportedly in charge of an open-pit mining operation on upper land for damages for contamination of plaintiff's spring. The Court of Common Pleas entered judgment for plaintiff against one of the defendants and he appealed. The Supreme Court held that the evidence presented a question for the jury as to whether contamination of plaintiff's spring was due to defendant's action in discharging drainage waters accompanying his mining operations onto plaintiff's land, or to some other cause for which defendant was not responsible. The judgment was affirmed for the plaintiff, the court stating:

". . . The plaintiff, Harvey Bumbarger, owns a farm in Graham Township, Clearfield County, which, until 1955, was enriched with a spring which supplied all his domestic needs with pure potable water but which, by October of that year became wholly useless because of certain chemical infiltrations which rendered it unfit for drinking, cooking, or cleansing purposes. The plaintiff's wife testified that, after the chemical invasion, the water made a precarious bathing agent because, 'it would burn the skin off you almost.' Allowing her a little latitude for over-zealous exaggeration, there would still seem to be no doubt from the record that the water underwent a drastic transformation. Whereas originally it had a 'good taste,' it now became sour; whereas, before it was odorless, it was now offensive in smell; whereas theretofore it flowed easily and innocuously through pipes

and fixtures, it now corroded and otherwise damaged

its copper, brass and lead containers.

"As no change in nature's manifestations occurs without the intervention of some force, put into effect either by man or cosmic energy, there had to be a reason for the deterioration in Bumbarger's spring. Bumbarger contended that this deterioration, which made it necessary for him to obtain water elsewhere at considerable expense and inconvenience, was due to the discharging into his spring of drainage from an open pit mining operation on an adjoining property which was owned by one Albert Smith. He brought suit against Ray S. Walker and Robert Bailey, purportedly in charge of the strip mining in question. The jury returned a verdict in favor of Bumbarger in the sum of \$10,000 against Ray S. Walker, but exonerated Robert Bailey from any liability in the premises.

"The defendant maintains that even if, arguendo, Bumbarger's spring became unusable, it was not proved conclusively that he was responsible for the resulting damage since there were seven other mining operations in the area: four deep mines and three open pit mines. Walker maintains in this connection that the jury was allowed to guess as to which mine was responsible for the befouling muck which penetrated Bumbarger's spring. But this argument is refuted by the size and content of the record which covers 450 printed pages. Landowners, chemists, civil engineers, sanitary engineers, coal operators, pathologists, coal analysts and farmers testified to every possible phrase of the controversy and it was for the jury to decide whether the plaintiff met the burden of proof of showing that the worm of corruption and contamination in the spring, which at one time contributed to life, health, and cleanliness on the Bumbarger farm but which now generated only the germs of decomposition and decay, got into the spring through the conduit originating in the mine workings on the Smith lands.

"The jury's verdict here established that the damage was not necessary and was avoidable, and that it was sufficiently obvious to have been foreseen and preventable by reasonable care and expenditure. Hence, any further discussion of the case would be like digging a channel after the river has reached the sea.

Judgment affirmed."

In Klassen v. Central Kansas Coop. Creamery Association of Hillsboro (1946) 160 Kan. 697, 165 Pac. (2d) 601, an action was brought against a creamery association that permitted waste products to escape from its plants and injure a farm tenant by polluting a stream and underground water supply. In disposing of the defense that no evidence of pollution had been introduced, the court stated:

"Hogs and chickens do not die from drinking water unless there is something the matter with it. It is not necessary that there be a chemical analysis as to whether the water was polluted to make a case go to the jury. There was ample evidence that the water in the stream was polluted. . . What better proof could there be than the fact that the stock had not died before the pollution came even though they drank

water from these wells, that they died after the pollution came, and that after the rest of the stock began to use water from a different source the losses stopped."

The case of Cartwright v. Stanolind Oil & Gas Company (1948) 200 Okla. 633, 198 Pac. (2d) 737 aptly states the rule of circumstantial evidence:

"The plaintiffs, suing for damages to their land and personalty allegedly resulting from oil and other deleterious substances which defendant permitted to escape from defendant's adjoining land and flow over plaintiffs land, had the burden of proving that the oil and other substances were of such nature and character as to cause damage, and also had the burden of proving, in absence of proof that oil which escaped was crude, that the oil was deleterious, and such burden could be sustained by proving effect of oil, and the plaintiffs were not required to produce direct evidence of identity or qualities of the oil and other substances. . .

"In support of the assignment of the insufficiency of the evidence to sustain the judgment, it is urged that it was incumbent upon the plaintiffs to prove that the oil as well as any other substances included in the allegation were of such nature and character as to cause the resulting damage. Also, that there is no evidence of any substance escaping other than the oil floating upon the water and that no chemical analysis was made to show that the oil so floating was poisonous. There is cited 29 O.S. 1941 273, inhibiting the escape of 'crude oil or other deleterious substance. It is urged that the statutory recognition of the deleterious character of oil applies only to crude oil and that, since there is no proof that the oil which escaped was crude oil, it was incumbent upon plaintiffs to prove that the oil was deleterious and that, independently thereof, there is no foundation for the jury's verdict other than conjecture.

"It is true that such burden rests upon the plaintiffs. But it does not necessarily follow it can be sustained only by direct evidence of the identity or qualities of the substance. Such is true because a cause may be proven by the effect thereof. Such additional method of proof is recognized in Prest-O-Lite Co. v. Howery, 169 Okla. 408, 37 Pac. (2d) 303, as follows: 'If it had been proved that at the time the injuries were incurred there were poisonous or deleterious substances in the water, harmful to animal life, or if it had been proved that the animals and fowls died as a result of drinking the water, a different situation would prevail, but the failure to prove one of these circumstances is fatal to plaintiff's right of recovery.'"

In Rusch v. Phillips Petroleum Co. (1947) 163 Kan. 11, 180 Pac. (2d) 270, an action was brought against certain oil companies and others for damages caused by pollution of water. Proof of chemical analysis was not necessary where other evidence showed that water was injurious to livestock. The court stated:

"Appellants contend there was no evidence of a chemical examination of the water in 1942. That is

true. It was not imperative that there should be proof of pollution by chemical analysis (Klassen v. Creamery Co., 160 Kan. 697, 165 Pac. (2d) 601). There was evidence the water was tasted and found to be salty in 1942 and that the stock would not drink it; that the stock drank some of the polluted water in 1943 and lost stated amounts of weight in 1942 and 1943."

The case quoted Donley v. Amerada Petroleum Corp. (1945) 152 Kan. 518, 106 Pac. (2d) 652:

"It may, also, be noted, that appellees were not obliged to exclude every possible source of pollution after establishing facts from which it reasonably could be inferred that appellants had polluted the stream. The fact that appellants polluted the stream could, of course, be shown by circumstantial evidence."

In Divelbiss v. Phillips Petroleum Company (1954) 272 S.W. (2d) 839, a Missouri case arising out of the poisoning of plaintiff's cows by drinking water allegedly polluted by the defendant oil company, the existence of pollution was determined in an unusual manner:

"On November 18, 1950, Mr. Divelbiss, Sr., and five of his neighbors, who were also farmers, went to plaintiffs' pasture. They saw dead frogs and minnows in the branch. They dipped water from the branch at several locations. Part of the sample taken was poured out on the ground and ignited. Mr. Divelbiss and these neighbors testified that they traced the oil and gasoline to a pipe coming out from defendant's pumping station and emptying into an open ditch, which connected with the branch running across plaintiffs' pasture."

In Hillhouse v. City of Aurora (1958) 316 S.W. Pac. (2d) 883, an action by a landowner against a Missouri city for pollution of a stream because of the discharge of effluent from the city's sewerage system, the quality of the water was determined from the following testimony of plaintiff's witness:

"... that about 1946-47 the water in the creek began to darken, a foul odor first became apparent and fish disappeared from the stream; and that thereafter the water gradually darkened in color until it became black, grayish, slimy looking, and the odor gradually became more pungent and offensive until it was similar to a toilet..."

Stekoll v. Wilson (1952) 207 Okla. 456, 250 Pac. (2d) 454 was an action for injuries to cattle allegedly caused by drinking salt water produced by the defendants' oil well and permitted to run into the plaintiff's creek. The court stated:

"Defendants urge two propositions for reversal. The first is that the court permitted incompetent and irrelevant evidence to be admitted; and second, that the trial court erred in overruling the defendant's demurrer to the evidence and motion for judgment. As to defendants' first proposition, plaintiff's Exhibits 1 and 2, two three-ounce bottles of water, were admitted; these bottles had labels on them showing their salt content. Plaintiff's Exhibit 3 was a letter from the Oklahoma State Health Department Bureau of Labo-

ratories to A. S. Booten, a veterinarian in Okemah, signed by H. E. Maxey, Chemist, but unauthenticated in any way, which gave the chemical analysis of the contents of the two three-ounce bottles. In our opinion it was error for the trial court to admit these exhibits without testimony by the chemist, but we think that this error was harmless in view of the other evidence offered by the plaintiff, which in our opinion was sufficient to authorize the trial court to overrule a demurrer to the evidence. It was unquestioned that the well of the defendant Stekoll produced a little more than ten gallons of salt water every second. The plaintiff's evidence showed that this salt water seeped into the only stream of water on plaintiff's land from which the cattle could drink, and also that in times of high water large quantities of salt water flowed into this stream. There was also testimony by a veterinarian that the cattle of the plaintiff had sustained injuries and that the injuries were the result of drinking salt water, and other witnesses testified that the only salt water available came from the well of defendant Stekoll and that defendant Stekoll had not used proper methods to prevent the salt water from escaping."

In two Oklahoma cases, the court was unwilling to accept the circumstantial evidence as decisive and ruled in favor of the defendants:

"Defendants contend that there is no evidence whatever tending to show pollution of the 'north well.' In this connection plaintiff testified that his hogs and chickens drank the water from that well and a number of them were killed and others were injured. There was other evidence to the effect that the water from the well had a 'queer' taste. It also appeared that a bottle of the water was introduced in evidence and examined by the jury but no evidence was introduced by the plaintiff showing an analysis of the water; therefore, neither the jury nor this court was informed as to the nature of the claimed pollution of the water. An examination of all the evidence on this point, together with all the conclusions reasonably deducible therefrom, fails to disclose any evidence to the effect · that the north well was in fact polluted. What we have said in discussing the question of causal connection in relation to the south well is likewise applicable here. In this connection the plaintiff points out the proximity of a pond in the vicinity of the north well but it does not appear that a pond contained polluted water or that any pollutive substance escaped therefrom into the fresh water strata which supplied plaintiff's well." Shell Petroleum Corporation v. Blubaugh (1940) 187 Okla. 198, 102 Pac. (2d) 163.

"The . . . conclusion of the witnesses that the salt water destroyed the fish and timber was based entirely on the assumption that the salt content was sufficient to bring about that result. That assumption was wholly without foundation in actual experience of the witnesses, or knowledge of the salt content of the water, and without the aid of visible effects peculiarly associated with salt water damage that would in some acceptable degree distinguish the asserted cause of destruction from any number of other possible causes.

"The mere fact that water tasted salty will not support an inference of evidential verity that dead fish found in such water, and dead trees near by were destroyed as a result of the salt content of the water. Nor will the courts take judicial notice that such result will follow. Shell Petroleum Corp. v. Worley 185 Okla. 265, 91 Pac. (2d) 679, 680."

In Tyrrell-Combest Realty Co. v. Adams (1927) Tex. Civ. 291 S.W. 252, the Texas court rejected the theory of circumstantial evidence as determinative of the condition of the water. In its decision the court stated:

"Whether water is contaminated with impurities, or contains ingredients rendering it hurtful, and maybe dangerous to the human system, and unfit for domestic use, if used continuously, is a matter for scientific investigation and analysis, and cannot be correctly determined other than by such scientific investigations as will disclose its elements and their effect when used for the purposes in question or by such continued use as will demonstrate its safe and suitable adaptability to same, or the contrary."

SCIENTIFIC EVIDENCE

Scientific evidence is a non-technical term sometimes used to refer to evidence produced by the use of expert scientific techniques and experimental methods. A considerable body of case law has been built up in which there has been expressed approval of certain techniques, criticism of others, and expression of a need for a more extensive reliance on such evidence.

Evidence of experiments and scientific tests is usually produced and offered in court by an expert witness. The following cases are illustrative of the inclination of the courts to accept scientific testimony as controlling the outcome of the litigation:

Commonwealth of Kentucky v. G. & H. Cattle Co. (1950) 312 Ky. 314, 227 S.W. (2d) 420:

"The testimony of Drs. Gibbs and Lyen that in their opinion the effluent entering the river from the drain would pollute the water three miles down stream and after flowing over two dams was not incompetent, but it had no probative value in view of the three chemical analyses of the water just mentioned, all of which show there was no pollution of the water. This case is much like City of Durham v. Eno Cotton Mills, 141 N.C. 615, 54 S.E. 453, 7 L.R.A., N.S., 321, where the court said, on page 328, that it would have been an easy matter for the city to have shown by a chemical or bacteriological analysis of the water at the intake whether or not it had been polluted by sewage and waste material deposited in the stream at defendant's mill. Instead of so doing, the city contented itself with introducing several physicians and two laymen who gave their opinions that the water was polluted at the intake, just as the Commonwealth did in the case at bar, and the North Carolina Court said such testimony was of little value where the fact in dispute could have been ascertained accurately by a scientific analysis of the water."

Hoke v. Sun Oil Co. (1946) 197 Okla. 261, 169 Pac. (2d) 753, an action for injury to livestock caused by

drinking polluted water in which the scientific evidence of the pollution was damaging to the defendant:

"A sample of the water which drained into plaintiff's fresh water pond was taken at a point on the drain several feet from its entrance into the lake. This sample was submitted to Dr. V. G. Heller, chemist at the A & M College at Stillwater, and his report of its analysis was made by letter to the plaintiff in the following language:

"'A partial analysis of the sample of water submitted for you by Judge Simcoe reveals that the water is slightly alkaline having a pH of 7.4. The total amount of soluble solids present amounts to 59,858 p.p.m. The chloride content of the soluble material calculated as sodium chloride amounts to 55,600 p.p.m. A considerable part of this chloride is present as calcium chloride.'

"On cross examination with reference to this report of his analysis the following questions and answers appear:

"'Q. Well, you testified on direct examination did you not that some of this water was harmful to cattle? A. Yes, sir.

"'Q. Why did you conclude it was harmful to cattle? A. Our experiments show if a cow would drink a water such as this containing 58,000 p.p.m., it would kill her, undoubtedly."

Nash & Windfohr v. Edens (1937) Tex. Civ. App. 109 S.W. (2d) 496:

"An action for damages caused by alleged seepage of salt water from stream used by plaintiff for irrigation purposes and allegedly polluted by defendants, evidence respecting alleged seepage of salt water through the soil, destroying plaintiff's pecan trees, without any showing as to salt content of water at any time, was insufficient to authorize recovery.

"... Furthermore, we desire to say that we do not believe the evidence introduced for the purpose of establishing the fact that salt water in this creek seeped through the soil and soaked into appellee's lands and killed his pecan trees is sufficient to raise such an issue. No effort was made to show that the salt water overflowed the banks of the stream and covered the soil over the roots of these trees. And no effort was made to show the salt content in the water at any time, and we are of opinion that under such circumstances a mere layman, such as is appellee, cannot give, as his opinion, a statement that salty water flowing along or standing in a stream actually soaks into the soil for a distance of from 10 to 40 feet in sufficient quantities to kill a pecan tree, and thereby raise an issue of fact as to the death of such pecan trees from the salt water . . . ''

In a recent Oklahoma case, Burge v. Sunray Oil Corporation (1954) 269 Pac. (2d) 782, livestock raisers brought an action against a manufacturer of petroleum products to recover for damages to land and livestock because of the pollution of a stream with allegedly poisonous chemicals. The District Court entered judgment adverse to the manufacturer, and the manufacturer ap-

pealed. The Supreme Court held that the evidence was insufficient to sustain a verdict for the livestock raisers. The Court relied heavily and based its judgment primarily on the scientific evidence.

"Although plaintiffs allege that defendant in the operation of its refinery used chemicals and substances that were harmful to animals, which substances defendant permitted to drain into Cow Creek, plaintiffs offered no evidence to support this allegation. On the contrary, the proof is without contradiction that the refinery maintained pits for impounding its effluent water so that by a process of oxidation the sulfides and sulfates would become free sulphur, which in the latter state, when commingled with the flowing water in Cow and Beaver Creeks, would not be injurious to livestock. Furthermore, the evidence discloses that the bad odor of the streams was attributable to organic matter in the raw sewage, and not from any chemical content in the water. The evidence is further without contradiction that enormous amounts of oil field brine from producing wells within the watershed below defendant's refinery contaminated the waters in these two streams, as has been indicated by reference to the evidence, supra.

"Although the witnesses Crawford and Sparks, the Game Rangers, had taken samples of water coming from the defendant's refinery as it entered Cow Creek, plaintiffs made no proof of the chemical contents

thereof.

"The Chief Chemist of the defendant, as well as Dr. Heller, of A & M College, discloses that various samples of water taken from Cow Creek below the refinery, had substantial quantities of sodium chloride (common salt) but did not contain any other chemicals in sufficient quantities to be harmful or injurious or toxic to livestock.

"If the evidence thus produced by plaintiffs may be said to raise an inference or presumption that the defendant's effluent waters resulted in harmful pollution of the streams, then with like force it may be said the evidence that raw sewage in the streams also raises an inference or presumption that organic matter was the cause of plaintiffs' complaint. Likewise, the evidence with equal force presents an inference or presumption that the pollution of the streams was occasioned by oil producing wells making salt brine which drained into the streams.

"The fact that defendant's effluent water drained into Cow Creek, standing alone, does not create an inference that the water contained poisonous elements injurious to livestock. In view of the further evidence that defendant impounded its effluent water in pits until the sulfides and sulfates therein by a process of oxidation became free sulphur, wholly fails to sustain plaintiffs' contention that the refinery water resulted in the injury to plaintiffs' livestock when it passed through the stream on plaintiffs' farm twenty-five miles below the refinery. Furthermore, the evidence of the chemist stands uncontradicted that the water coming from the defendant's refinery did not contain any chemical properties injurious to livestock. Furthermore, plaintiffs' own evidence is to the effect that they

lost one cow in 1949 from Bangs disease, and that cattle abort from many causes other than the drinking

of polluted water.

"Where evidence fails to establish with reasonable certainty that damage resulted from some act of commission or omission by a defendant so charged, or that such acts resulted in the damage or injury complained of, a verdict and judgment thereon is not sustained by sufficient evidence and is therefore contrary to law."

In Magnolia Petroleum Company v. Glen A. Stinson (1957) 230 Miss. 533, 93 So. (2d) 815, an action against an upstream oil-well operator for damage to sheep, cattle, and pasture from the alleged pollution of a creek, the court relied completely on expert testimony as to the quality of the water.

"O. U. Walling, chemist at State College, testified that he received a bottle containing a liquid content from Doctor Peters on April 28, 1954. The breakdown

of his analysis was as follows:

"'Well, I found it to be essentially a solution of sodium dihydrogen phosphate. I found 24.20% sodium dihydrogen phosphate in the water. That was based on the determination of the phosphate. The pH of the water was 5.2, which is indicative of a slightly acidic condition, and it had a specific gravity of approximately 1.223 which, of course, would indicate quite a bit of dissolved substances in it. I found phosphorus present and when expressing the (phosphorus) as P_2O_5 it analyzes 14.32% and (as) sodium dihydrogen

phosphate it becomes 24.20%.

"When asked if the chemicals, shown by his analysis, were the chemicals used in drilling muds, he said that he could not be certain, but 'I know that a compound of salt is used to bring up the gravity of the mud. Whether this is always used, or commonly used, I could not say.' He said that the specific gravity of the water was 1.223 and was indicative of a high concentration in the water. He said that most any compound of salt in excessive amounts is toxic. When asked if the contents, which he found, would be poisonous to sheep, he did not wish to pose as an expert on that question. However, when counsel for the defendant asked if he would say that this was in excessive amounts, he replied, 'In my opinion, it is.'

" . . . 'Q. Now doctor, if the drinking water in a stream contained a pH of 5.2, indicative of a slightly acid condition, and had a specific gravity of approximately 1.223, which was indicative that there was quite a bit of dissolved substance in the water, and the phosphorus as P₂O₅, which analyzed, is 14.32, of (sodium) dihydrogen phosphate, it becomes 24.20% if consumed by sheep, in your opinion, would it be fatal in the event that the sheep drank this and later died? A. That, of course, would depend on the amount that they drank. Ruminants ordinarily drink great volumes of water. I should think yes, it's perfectly capable of causing death. Q. Assume that there were approximately one hundred sheep in the herd, heavy burdened with lambs, which were almost ready to be born, and they consumed the same contents and the same water. and later all aborted, now do you have an opinion as to whether the water they drank containing the substances that I have set out, would be the cause of their aborting? A. In my opinion, it certainly would be, because one of the things that we learned early in medicine, is that acid is abortive. That would be true, it would seem.'

". . . For the defense, William G. Spence, a chemist with the Game and Fish Commission, in charge of water pollution, testified that he checked the water for its acid and alkaline condition on February 22, 1952. At that time it was normal. He said that he made an examination of material in a sack at Stinson's milk barn and found it on the acid side. He examined the location at the McShane No. 1 well and found it sloppy. He saw a couple of sacks containing material that appeared to be caustic. There was a number of empty sacks around the place in the mud. In the pits he found a conglomeration of mud and water. He did not test the pH of the pits. While he did not go around the pits on all sides, he saw that the little pit had sloshed over at the end at the time of his visit. He ran a pH on the sacks that looked to be caustic, and said that whether this substance, washing down stream for half a mile, would have a pH of more than 7 would depend on the amount of the water with which it was mixed and the amount of the substance. He, of course, could not say that the contents of the other sacks had not washed down the stream before his visit."

T. H. McCasland v. Debert Burton (1956) 292 Pac. (2d) 396, an Oklahoma case, involved an action by a land-surface owner against the owners of an oil and gas lease on a portion of land for damages allegedly suffered by the escape of salt water from an oil well on the lease, which water was allegedly drunk by plaintiff's cattle and caused death and abortions of such cattle. The judgment was for the plaintiff.

"The gist of defendants' arguments is that the evidence is insufficient to show by a preponderance thereof, that the salt water which concededly escaped from the salt water pits on their lease was the proximate cause of the death of four of plaintiff's cattle that died and the abortions that seven others suffered. Their counsel say that, in order to sustain the verdict, it must be assumed: First, that the water escaping from the pits contained sufficient amount of salt to be injurious to cattle; and, Second, that if such water was so injurious, the livestock drank sufficient of it to cause the deaths and abortions.

"As to the question involved in the first of the claimed assumptions, the uncontradicted evidence shows that plaintiff, in the company of Dr. Ryan, a veterinarian, took samples of water from the salt water pit on the premises and delivered one of them to Jack Womack, Sanitarian of the Stephens County Health Department, who in turn, mailed it to Mr. A. G. Maxey, Assistant State Chemist of the State Health Department at Oklahoma City, to be analyzed. Mr. Maxey testified that this sample contained 7.09% of 'calculated' salt, or 7.09 pounds of salt to every twelve gallons of water, and that such salt content was excessive for drinking purposes. Dr. Ryan, who was called by plaintiff to examine his cattle, stated that they were definitely sick and emaciated and had diarrhea. He

further testified that he believed it had been proven that '3.3 to about $6\frac{1}{2}$ pounds of salt (to 12 gallons of water) is a fatal dose to a cow. . . .' He further testified that a cow drinks 10 to 15 gallons of water per day, and that in his opinion, if a cow should drink as much as 7.09 pounds of salt in 12 gallons of water 'she would die.' He further testified that he was familiar with the symptoms of salt water poisoning in cattle, described what they are, and then answered, in the affirmative, the question: 'Did you see any of Mr. Burton's cows that had any of those symptoms?' "

The necessity for scientific analysis of the suspect water was discussed in Pure Oil Company v. Renton (1952) Sup. Ct. of Okla. 248 Pac. (2d) 580. This was an action by Johnston Renton, and wife, against the Pure Oil Company, for the pollution of a stream. The Superior Court, Seminole County, entered judgment for plaintiffs and defendant appealed. The Supreme Court held that evidence was insufficient to support award of damages that could properly be measured only by depreciation in usable value of realty. The decisive question urged by the defendant is that the evidence was insufficient to support the judgment of the court. This contention was sustained by the Appellate Court.

"While plaintiffs and other witnesses testified that the water in the creek was salt(y) and the evidence showed that a considerable amount of salt water per day was dumped into the creek by defendant, there was no analysis of the water and the only evidence produced by plaintiffs as to its effect on livestock was the testimony of plaintiff, Johnston Renton, that two years before, and while the salt water easement was in effect, two of his cattle had died from drinking salt water, and his further testimony that it would kill his hogs if he . . . (let them have) access to it."

The need for expert testimony and evidence based on scientific data was again expressed in Reynolds Metal Co. v. Ball (1950) Sup. Ct. of Ark. #4-9108, 232 S. W. (2d) 441. Fred H. Ball brought an action against the Reynolds Metal Company to recover damages for injury to his land alleged to have been caused by deposits of sediment containing poisonous substance from defendant's plant. The Circuit Court, Saline County, entered judgment for the plaintiff, and the defendant appealed. The Supreme Court held that the evidence was insufficient to sustain the verdict, but that the circumstances justified remanding the case for a new trial.

"... Defendant Reynolds denied that any substantial amount of the sediment came from its plant, and also denied that any poisonous or harmful substances whatever were allowed to flow from its plant into the creek at any time. Reynolds introduced the testimony of expert witnesses, chemists who stated that they had analyzed the chemical content of the sediment and found nothing in it that would be poisonous or otherwise harmful to vegetation, apart from the obvious effect of choking the vegetation out by covering it up. Plaintiff introduced no expert evidence as to the chemical content of the sediment. The plaintiff and some of his witnesses gave their opinions that the sediment was poisonous, but these were unscientific

statements of lay opinion, based on observations from which it might also have been concluded that the vegetation was merely choked out. Substantial proof that the sediment included chemical constituents that were

poisonous to vegetation was lacking.

"We are forced to conclude that the record does not contain substantial evidence that Reynolds discharged from its plant into the creek deleterious or poisonous substances which caused the damage of which plaintiff complains. The judgment based upon the jury's verdict in the Circuit Court must therefore be reversed."

Dohany v. City of Birmingham et al. (1942) 301 Mich. 30, 2 N.W. (2d) 907, was a suit to enjoin the city from discharging raw sewage into a watercourse crossing the plaintiff's land outside the city. The evidence was held to establish the plaintiff's right to a permanent injunction against the continuance of the nuisance by the city.

"Some six months after the dam and pumping station were put into operation plaintiff obtained samples of the sewage discharged across his land. These samples were taken each week for a period of 12 consecutive weeks during the months of April, May and June. The samples were analyzed and brought into court as evidence. Three different chemists testified that these samples contained all of the usual elements of sewage,—abundant chlorides, hydrogen sulphide, active bacilli coli, ammonia and insoluble solids. At that time human excrement was still being deposited on plaintiff's land. The stench continued and was such that a nearby resident was at times, compelled to keep the windows of his house closed."

REJECTION OF STANDARDS ON EXPERT TESTIMONY

While there have been no significant cases discovered in which the courts have seen fit to reject standards that have been promulgated through appropriate legislative actions, there have been some cases in which the courts have at least indicated that they are not bound by the testimony of the experts. They may, if they see fit, draw their own conclusions where there is a conflict in the testimony, and, influentially, accept non-expert testimony as the rule in the case.

Illustrative of such a situation is the Texas case of Barakis v. American Cyanamid Co. (1958) 161 F. Supp. 25. It was brought by a tenant of land abutting on a river and leased from the county water-control district against an upstream owner discharging industrial wastes into the river. The evidence failed to establish any damages to crops attributed to the effluent from the defendant's plant despite expert testimony. The court stated:

"The preponderance of the evidence does not show that the water flowing by the plaintiff's tract was essentially useless for irrigation. The analysis of the content of the Trinity River at the plaintiff's pump site as introduced in evidence by the plaintiff was approximately 1,500 parts per million of sodium. The testimony of Dr. Gray, plaintiff's expert witness from Midwestern University, was to the effect that this content was not so high as to cause him to condemn the water for irrigation purposes on that basis. He condemned the water because its Soluble Sodium Per-

centage (S.S.P.) was in excess of 60% and he stated that the standard of 60% was obtained by him from the Handbook published by the Riverside California Experimental Station. However, his testimony did not establish that this was an essential standard by which irrigation waters generally might be judged. The testimony of Dr. Edward Stiber established that water of a much higher sodium content and with a much higher S.S.P. was being used successfully, commercially, in the Rio Grande Valley, and also both the Brazos and Bosque Rivers. Mr. Valentine of the Dalworth Soil Conservation District, a witness for plaintiff, testified that he, in his official capacity, started getting complaints about the irrigation waters of the Trinity River in 1956. For over 12 years the defendant had been discharging its effluent into the River and Mr. Valentine had heard no complaints. His testimony that it was not customary to even test the waters of the Trinity River would indicate that the effluent discharge had not made the waters of the Trinity unsuitable for irrigation.

"The testimony of plaintiff's witness, Leonard Lamp, of the Texas Game, Fish and Oyster Commission, made it evident that the Commission was aware of the situation that existed in and along the Trinity River during the period in question. His testimony further showed that the Commission had been diligent in the prosecution of salt water pollution cases. However, it is to be noted that the Commission had taken no action against the defendant for the pollution of the Trinity River. Witness Lamp did not purport to know anything about agricultural pollution, and his testimony cannot be interpreted as authority for the proposition that the waters of the Trinity River were then, or are now, unfit for irrigation.

"The uncontroverted fact that plant growth along the banks of the River and down to the edge of the water was dense and luxuriant is evidence that the water of the River had no serious deleterious effect upon plant life generally. Plaintiff Barakis' testimony that he pumped water from the River and onto his land many times without suspecting any detrimental qualities is convincing that the water was no more polluted or contaminated or less suited to the ordinary domestic needs, including irrigation, than is the water of most any stream similarly situated in Texas."

Thompson v. Globe Aircraft Corporation (1947) Tex. Civ. 203 S.W. (2d) 865 related an action by B. G. Thompson against the Globe Aircraft Corporation for death and injury to the plaintiff's cows allegedly caused by chromic-acid poisoning because of defendant's alleged negligence in causing the creek on plaintiff's land to become polluted with chromic acid. From an adverse judgment, the defendant appealed. The court was unwilling to base its reversal on the failure to show that there was insufficient evidence of quantity of chromic acid in the water but preferred to find other grounds to reverse and remand the cause for a new trial.

"First, it is argued that the court should have instructed a verdict for defendant because there was no testimony showing that there was sufficient chromic acid in the waters of the creek to cause injury to plaintiff's cattle. Plaintiff undoubtedly tried the case in the court below, and still contends here, that his cattle began to suffer injury from the pollution of the creek within a short time after he moved onto the leased land in April of 1944. A sample of water was taken from the creek in April of 1945 and other samples were taken in June and later in the summer of that year. Those samples were analyzed by chemists, and found to contain chromic acid. The least chromic acid content shown by the analyses was 7.8 parts of acid to one million parts of water, the greatest content was 31 parts of acid to one million parts of water. Some of the expert witnesses testified that chromic acid was poisonous, but none of them testified as to the amount of acid which would be required to render the water injurious to the cattle. In other words, there is no expert testimony that water with chromic acid content of the amount shown by the chemical analyses would be injurious to cattle. Opposed to defendant's argument is the theory advanced by plaintiff to the effect that the poisonous nature of the polluted water may reasonably be inferred from the known fact that chromic acid was in the water, from the fact that the cattle suffered injury, and from the fact that the evidence excludes the likelihood of injury from any other cause. Since we have concluded that the judgment of the trial court must be reversed for other reasons, and since the proof may not be the same on another trial, we shall forego further discussion of this question except to say that we are unwilling, in view of the entire record, to render judgment for defendant on this ground."

Where the injurious effect upon soil and plant life of excess salt in water overflowing land is known, where the evidence shows that salt water actually overflowed the land, where the plaintiff's analysis of the soil and water showed the presence of excess salt, where lay experts testified to the observable effect of excess salt and described that effect as present, and where no other cause or reason for the loss of fertility of the soil was advanced, it was held that plaintiff had introduced sufficient evidence to justify submitting the issue to the jury (Magnolia Petroleum Co. v. Norton (1942) 189 Okla. 166, 116 Pac. (2d) 893):

"Given the admitted fact that excess salt produces such conditions, and barring the fact that a 'layexpert' made an examination from which he was qualified to express an opinion, the jury was in as good position as the 'lay-expert' witness to draw a conclusion whether the excess salt (if they believed it present) caused the injuries. We do not believe this is an instance where a so-called technical expert, scientific expert, Wigmore, supra, vol. 2, page 635, sec. 556, was required. It is well known, and the parties all assume, that the presence of salt in water and soil above tested levels is injurious to plant life. Each party had an analysis of the soil and water made, and the report of plaintiff's analyst showed far more than enough salt to injure plant life. The lay-experts did not qualify themselves to give more than their observation of the effect of salt on soil and plant life. Having proved the presence of salt in injurious proportions, plus the admitted fact of its injurious effect in such proportions, plus the description of the soil and plant life by competent observers, there was no necessity for the use of a technical expert. This is especially so where the defendant did not resort to the evidence of technical experts to ascribe the loss of the fertility of the soil to any other cause. This is not applicable to the trees. Defendant did introduce an expert witness who ascribed the death of the trees to borers."

The rule that a conflict in the evidence presents a factual problem for determination is succinctly stated in Burr v. Adam Eidemiller, Inc. (1956) 386 Pa. 416, 126 A. (2d) 403. It involved an action in trespass against a road construction company for damages arising out of subterranean contamination of plaintiffs' water supply. The court stated:

"The plaintiffs introduced evidence by a chemist to the effect that the acid condition of the water was the cause of the destruction of the heating and plumbing system owned by the plaintiffs as well as the loss of the use of their sewage system. While the defendant offered evidence to the contrary this was an issue of fact for the jury to determine which was resolved in the plaintiffs' favor."

Hutchinson v. Rock Island Oil and Refining Co. (1953) 208 Okla. 259, 255 Pac. (2d) 234 was an action to recover damages for the loss of livestock alleged to have resulted from the drinking of polluted water out of Cow Creek. The plaintiffs, owners of the stock, contended that the injury and resulting damages arose out of the defendants' operation of some oil refineries located several miles south of the plaintiffs land. Judgment for the plaintiff was affirmed in spite of the defendants apparently expert evidence.

"Defendants then introduced the deposition of V. G. Heller, Professor of Biological Chemistry at the Oklahoma A & M College. He testified that H. M. Marney mailed him two samples of water; one taken from Cow Creek and the other from the well on the Mize farm on Feb. 3, 1949, and from these samples he found and so advised Mr. Marney as follows:

"I seriously doubt if it would be advantageous to make a quantitative determination of the exact amount of inorganic materials present so long as we know the total amount would not be injurious. I think the only chemical analysis that is going to help you is to find when there are sulfides or similar compounds present that are truly toxic. We can certify to the bad physical appearance, bad odor, and to the unsavory flavor, but we have to admit that there is none of the usual oil field brines, acids, or alkalies present in toxic quantities. In your waters we are dealing with a different type of material. The total amount of dissolved materials present would definitely not be toxic to either man or animal. The amount of salts present are in the form of sodium chloride, calcium chloride, or magnesium chloride, so often found in oil well brines and which are poisonous in large quantities either to plants or animals, is not present in your water. Neither do we find the presence of alkalies as are sometimes found

about refineries or do we find any free acid, so from the standpoint of all these normally discussed materials in waters, I think you would have no case for damages.'''

COLIFORM BACTERIA AS EVIDENCE OF FECAL POLLUTION

The decisions are numerous in which the courts have found that the presence of coliform organisms in water is evidence of its polluted condition. A few such cases are cited and quoted to illustrate the courts' line of thought. Board of Health of the State of Maryland v. Edward

J. Crew (1957) 212 Md. 229, 129 A. (2d) 115:

"The testimony showed that the order to Crew to discontinue the use of his well was issued after Dr. Gordon had determined, and the Health Department agreed, that a danger to health existed in the use of a private well in the Willoughby Beach area. Dr. Gordon explained that sewage from septic tanks and cesspools has to be purified by seeping through the ground. A soil that thus purifies the sewage gradually becomes contaminated itself, no longer acts as a purifier. The rate of absorption and the value of the soil as a purifier vary with the nature of the soil. Crew had testified the soil on his place was clay for a depth of seven or eight feet under several feet of top soil. A Health Department witness had tested the soil on a place adjoining Crew's and found it clay, with poor absorptive powers. Dr. Gordon's testimony was that since a clay soil will not absorb sewage, it does not act as a purifying agent and that wells in an area where the soil is clay are likely to become contaminated. An entire area may become contaminated and the contamination may reach any or all of the wells of the area, particularly where the wells are shallow. Dr. Gordon would fix no definite time as to when this contamination might occur but said, in essence, that it could be the next day, the next week or next year. 'A well is considered to be contaminated when bacteria called coliform organisms, derived from warm blooded animals, including man, are found in the water. Dysentery can result from such organisms as well as typhoid fever.' "

Looney v. Panther Coal Co. (1946) 185 Va. 758, 40 S. E. (2d) 298 described an action for the pollution of a stream by a lower riparian owner against an upper riparian owner engaged in coal mining. The judgment for the plaintiff was reversed, for it was shown that the plaintiff's wells, rather than the stream, were the object of pollution:

"The testimony for the defendant was in sharp conflict with that for the plaintiff. That testimony was to the effect that the trouble with plaintiff's sawmill was old age and improper care and operation; that stock would drink out of the branch; that soap would lather in the water from the well, and that the water would wash clothes clean, and would make good tea, and would not turn black when boiled, and that rice cooked in it would not turn black, as claimed. Experiments were made before the jury to show that these things were true, and the results of some of the experiments are before us as original exhibits. Water was

brought from the wells during the trial, tasted by four witnesses, all of whom testified that so far as taste, look, and smell, were concerned, it was good drinking water. These witnesses included J. G. Burch, health officer of the county, who said that so far as taste was concerned this water was above the average of what he was used to drinking in the county...

"It is not surprising, therefore, that when the plaintiff's wife had this water from the wells analyzed by J. G. Burch, a sanitation officer for the State Health Department, and a witness for the defendant, as noted above, he found the water in both wells badly polluted with B-coli bacteria and unfit and unsafe for use."

Borough of Westville v. Whitney Home Builders, Inc. (1956) 40 N. J. Sup. Ct. 62, 122 A. (2d) 233 was a case involving an action by the borough against a house builder and town to enjoin the operation of a sewage-treatment plant discharging effluent into a stream that ran into a pond which was in the borough recreational park and which was used for fishing, skating, and wading. The Superior Court, 32 N. J. 538, 108 A. (2d) 660, entered judgment denying injunctive relief, and the borough appealed. The Superior Court, Appellate Division, held that evidence on the issue of reasonable use of waters did not make denial of injunctive relief erroneous. The judgment was affirmed:

"Water pollution is generally measured in important degree in terms of bacteria count and index of coliform micro-organisms (B-coli), the latter reflecting the degree of animal (including human) excrement. Analysis of the waters of the ditch and pond by an expert for defendants prior to the construction of the plant, on July 27, 1954, showed 'gross pollution' at points above and below the proposed site of the sewage plant and in the pond, in terms both of bacteria and B-coli. The measure of dissolved oxygen at the mouth of the pond was 1.9 parts per million in July, 1954, an indication of the beginning of putrefaction. All the witnesses testified that the polluted condition of the ditch and pond stemmed from the normal floatage of impurities on surface waters in such a semiurban area.

"Tests made April 7, 1955, after three months of operation of the plant, showed a bacteria count for the effluent vastly lower than for the water at various locations in the stream and pond, and this was also true as to the B-coli index. Substantially similar results were indicated by analysis of samples taken May 16, 1955, and also by analyses made by one of the expert chemists, Corson, who testified for plaintiff. There were indications that the chlorine in the effluent had the beneficial effect of reducing the bacteria count of the stream for some distance below the point of discharge.

"The analysis of the effluent also showed a lower (more favorable) B.O.D. (0.4 P.P.M. as compared with the Incodel maximum of 50.0) than in the samples from the watercourse, in ditch and pond. The remainder of the chemical analyses of the effluent made by defendants' expert chemist showed what he described as good, or very good, conditions, in comparison with treated sewage effluent, generally. The

amount of residual solids was such as to lead him to describe the effluent as 'rather dilute.'

"Plaintiff's experts, Boyd, a sanitary engineer, and Corson, a chemist in the public health field, testified that some disease-bearing viruses or organisms found in human feces might survive the effect of the chlorination and treatment of the average sewage plant. Polio, hepatitis and typhoid were cited as examples. Neither of these experts was a bacteriologist. Corson conceded it would occur 'extremely infrequently.' Boyd admitted that on the basis of the amount of residual chlorine in the effluent, the possibility of escape of harmful bacteria was remote, and that he did not consider himself 'an expert on viruses.' Lanning testified he considered the survival of harmful bacteria of fecal origin in the effluent as highly improbable.

"The only other tangible, rather than psychological, objection advanced by plaintiff was to the possibilities of odor or stench. There was some evidence that when the plant operates at full capacity and there is simultaneously a period of low natural flow in the ditch, the volume of effluent may be expected to exceed that of the natural stream flow. Corson stated that at such times there would be stench in the pond, attributable to depletion of dissolved oxygen in the sewage. But this is seen to be without warrant, in view of the unchallenged results of the tests made by defendants' chemist, Beltz, which showed the effluent to have substantially lowered B.O.D. than the waters of the stream and pond and quite similar proportions of dissolved oxygen. Boyd offered a different thesis for prognosticating an 'odor of decay.' It was that the chemicals in the effluent would cause 'lushness of vegetation' in the pond and that such vegetation would 'smell' in dry periods. Both Beltz and Lanning testified there would not be increased plant growth. The evidence is that there generally is considerable plant life in the pond in summer and that no odors have ever emanated therefrom. The conclusion of the trial court that the evidence of potential odors from vegetation or putrescence is speculative seems to us a fair characterization, on the present record."

Board of Health of the State of New Jersey v. Borough of Vineland (1906) 72 N.J. Eq. 289, 65 A. 174:

"If coli are found to exist in considerable numbers the conditions are believed to be conducive to the propagation of pathogenic organisms. The coli are, in themselves, harmless, and the number that may safely exist in water are not entirely certain, one thousand coli to the cubic centimeter is believed to disclose a dangerous condition of the water."

City of New York v. Blum (1913) 208 N.Y. 337, 101 N.E. 869:

"The presence of colon bacilli in water indicates the presence of fecal matter from warm-blooded animals and renders the water unwholesome and unfit for human consumption."

Hamilton v. Madison Water Co. (1917) 116 Me. 157, 100 A. 659:

"... showed 30 colon bacilli to the ounce, while the samples taken at the mouth of Getchell Brook showed 300 to the ounce. This high percentage did not of itself signify the presence of typhoid germs, but of the existence of a large quantity of sewage. Colon bacilli are normally present in the intestines while the typhoid germ is a parasite. The presence of a large quantity of colon bacilli in water indicates therefore sewage pollution, and naturally the greater the percentage the greater likelihood of the existence of the typhoid germ."

Pennsylvania Railroad Co. et al. v. Lincoln Trust Co. Administrator (1929) 91 Ind. App. 28, 167 N.E. 721:

"... several samples of water were taken and found to contain gas formers and colon bacilli, the bacteria count being 2,700 colonies per cubic centimeter; the presence of colon bacilli indicated sewage pollution; the greater the bacterial count, the greater the danger from typhoid bacilli."

John Wiesner, Jr. v. City of Albany (1928) 250 N.Y. 551, 116 N.E. 320:

"The presence of colon bacilli in water indicates contamination from human sources. Many types are harmless in the sense that they do not furnish the origin of the disease. The typhoid bacilli (scientifically known as 'B-typhosus') are the well recognized cause of typhoid fever. While they are difficult of isolation they belong to the colon groups, and the presence of colon bacilli in the water indicates that there is grave danger that the typhoid bacilli are also present; and this becomes a practical certainty when there is an outbreak of typhoid fever, not directly traceable to other sources of infection."

Highly significant was the affirmed ruling for the plaintiff in People v. City of Los Angeles (1948) 83 Cal. App. (2d) 627, 189 Pac. (2d) 489, 335 U. S. 852, 93 L. E. 400, 69 S. C. 80, which restrained the city from maintaining sewers without permits from the State Board of Public Health, part of which stated:

"The quality of water along the beach was not safe and suitable for bathing purposes as a result of such discharge and the bacterial count of escherichia coli had exceeded 10 per cubic centimeter."

Mary Hayes v. Torrington Water Co. (1914) 88 Conn. 609, 92 A. 406:

"... that laboratory examination of the Crystal Lake water, made while the epidemic was in progress, disclosed a persistent appearance of colon bacilli, indicating the possibility that the water was infected with typhoid germs also."

A significant case occurred in Mayor and Aldermen of Jersey City v. Jersey City Water Supply Co. (1918) 90 N.J. Eq. 14, 105 A. 494, in which the court held that on review consideration of new evidence was not possible, for the court cannot wait for the latest of scientific developments. In speaking of the evidence that was not accepted the court stated:

"This evidence is that since the trial, bacteriologists have discovered that a bacillus known as B. welchii, if present in water in considerable numbers, is productive of intestinal disorders; that this bacillus has recently been found in the Jersey City water . . ."

The foregoing cases illustrate judicial acceptance of the sanitary bacteriologists' use of coliform organisms as indicators of fecal contamination. One exception, however; occurred in People v. Bowen (1941) 376 Ill. 317, 33 N.E. (2d) 587. Here Bowen, the Director of the Department of Public Welfare of the State of Illinois, was indicted and found guilty by the trial court of palpable omission of duty for failing to take proper measures to render drinking water at a state hospital safe. As a result, an epidemic of typhoid fever resulted with much illness and many deaths. On appeal, the Supreme Court of Illinois, reversed the decision and stated:

"... the most that can be said for any of the 158 exhibits, is that it showed the water to be either positive or negative as to coli aerogenes. It appears from the record that coli aerogenes or colon bacillus may be friendly or inimical, and that the mere presence of the colon bacillus in water proves exactly nothing as far as typhoid fever is concerned. The tests seem to have been made by a method of broth fermentation, and determined nothing more that the presence or absence of some kind of colon bacillus. It further appears that this type of bacillus is present in the air one breathes, in milk, on fruits and practically everywhere.

"... It is further apparent that colon bacillus may be of the fecal or non-fecal types and that so far as typhoid is concerned, it is only the fecal type from man alone (not from animals) that can spread the disease. The typhoid bacillus could not possibly have been identified by the Laboratory means used in any of these reports and none of them is of any value to the People in an attempt to prove the guilt of the defendant

"... Even if these reports were of any probative value they would necessarily tend to disprove, rather than prove, a case against the defendant. The water from these wells was consumed by all inhabitants of Manteno for more than eight years prior to this epidemic. This test over a period of eight years, if looked upon as a laboratory experiment, would go a long way toward proving that the water actually was safe for human consumption, because there is no evidence of any abnormal condition as to typhoid occurring during that period of time..."

It is interesting to note that, among the advances of the past decade, certain pathogenic forms of the coliform group of organisms have been identified. See Chapter VII, Coliform Bacteria. Such late progress, however, would not constitute sufficient grounds for reopening the Illinois case cited above.

JUDICIAL NOTICE

Under the doctrine of judicial notice, certain matters are assumed to be indisputably true and the formal in-

troduction of evidence to prove them is not required. Judicial notice is thus a substitute for formal proof (9 Wigmore on Evidence, Sec. 2565 et seq). This method of deciding questions of fact was in current use in the English Common Law Courts and today the increasing tendency of the judges to recognize the significance of various types of facts demonstrates that they are striving to keep pace with the rapidly growing complexity of problems with which they have to deal. Thus, the doctrine that matters of common knowledge, in addition to matters recognized at common law, need not be proved before the court has found application in a variety of situations.

The application of the principle was early seen in an action in which the plaintiff-landowner sought an injunction to prevent the discharge of effluent into a stream which crossed the plaintiff's land. The court stated in Hayes v. Village of Dwight (1894) 150 III. 273, 37 N.E. 218:

"Despite witnesses' testimony that in their opinion the proposed discharge of sewage would not have the affect of materially polluting the stream, the court held that little weight is to be given to the testimony of witnesses who attempt to swear contrary to known and established natural laws. That the sewage of a village of 1600 inhabitants, discharged into a small stream will materially pollute the waters of the stream and render it unfit for domestic use, for at least a few rods below the point of discharge, is a proposition too plain and too thoroughly verified by ordinary experience and observation to admit of reasonable doubt."

In Kent v. Shell Petroleum Corporation (1940) 187 Okla. 637, 105 Pac. (2d) 230, the plaintiff sought to recover damages for alleged pollution to his water supply by reason of the defendant's pollution of a creek which traversed the farm. From an adverse judgment the defendant appealed. In the decision affirming the judgment of the lower court, the Appellate Court stated:

"A portion of our opinion in Oklahoma City v. Page, 153 Okla. 285, 6 Pac. (2d) 1033, clearly demonstrates the fallacy of confusing the character of a stream's contamination in regard to permanency with the character of the injuries resulting therefrom. From the judicial pronouncements referred to it will also be noted that a stream may be considered 'permanently' polluted from a legal standpoint, when neither the condition itself nor the injuries flowing therefrom are everlasting in character. To deny that a stream once regarded as permanently polluted can thereafter become relatively pure is to disregard the operation of natural forces. It is only reasonable that when the proportion of fresh water to salt water in a polluted stream increases (whether from a curtailment of the flow of salt water or an increase in the flow of fresh water into it) the aggregate body of water therein becomes more suitable for drinking purposes. There is evidence in the present case which tends to show that this is what was occurring in Black Bear Creek during a period that may be variously estimated at from several months to three or four years preceding July, 1935, so that by the latter date, some of the farmers living along the stream in the vicinity

of plaintiff's farm were using it for watering their livestock. For the reasons we have mentioned, the evidence cited by defense counsel showing that the stream was polluted for several years before this transformation cannot be considered fatal to the plaintiffs' cause of action for damages they sustained when its salt water content again became so great that it was once more harmful to animals drinking therefrom."

In an Alabama case involving a proceeding to restrain the pollution of a stream resulting from a quarrying operation, the court took judicial notice of the economic factors involved.

"'The court will take notice of the fact that in the development of the mineral interests in this state, recently made, very large sums of money have been invested. The utilization of these ores, which must be washed before using, necessitates, in some measures, the placing of sediment where it may flow into streams which constitute the natural drainage of the section where the ore banks are situated. This must cause a deposit of sediment on the lands below; and while this invasion of the rights of the lower riparian owner may produce injury, entitling him to redress, the great public interests and benefits to flow from the conversion of these ores into pig metal should not be lost sight of."

"We approve the following principle extracted from Sanderson v. Pennsylvania Coal Co., 86 Pa. 401, 27 Am. St. Rep. 711: 'The exigencies of the great industrial interests must be kept standing in view; the property of large and useful interests should not be hampered or hindered for frivolous or trifling causes. For slight inconveniences or occasional annoyances, they ought not to be held responsible, and, in dealing with such complaints, juries should be held with a steady hand." Montgomery Limestone Co. v. Bearden (1951) 256 Ala. 269, 54 So. (2d) 571.

The Texas Court in Rudco Oil & Gas Co. v. Lemasters (1940) Tex. Civ. App., 146 S.W. (2d) 806, pp. 811 took judicial notice of the polluting potential of refinery wastes.

"As to the point that the court should have instructed a verdict because 'there was no evidence to show that the oil, gasoline, waste material and drip oil was of such character and content as would inflict the damage to plaintiff's property complained of' there certainly was evidence tending to show that damage was inflicted from such cause which necessarily includes evidence of the damaging characteristics of such substances.

"Besides, we think we must take judicial knowledge that oil, waste material (from a refinery), drip oil or gasoline may pollute water used for domestic purposes and damage land."

Daniels v. Bethlehem Mines Corporation (1958) 391 Pa. 195, 137 A. (2d) 304, is illustrative of the court taking judicial notice in a situation involving the quality of water flowing from mines:

"In the coal mining industry, whether in the anthracite or bituminous field, the elimination of water from the mines presents a very serious problem. Its

elimination is an absolute necessity if mining is to continue and, yet, its elimination by discharging it into streams and creeks grievously affects lower riparian owners along these streams and creeks, and, in some instances, the public. Waters which have their source in a coal mine, of necessity, contain deleterious substances as a result of contact with the coal and its various chemical compounds. Any mine water—that is, water which comes from a mine—upon discharge into a stream deteriorates and destroys, in varying degrees, the purity and cleanliness of the natural waters of the stream."

The ability of a veterinarian to testify as to salt condition of water through having tasted it was a matter of judicial knowledge in Greis v. Mitchell (1939) 185 Okla. 136, 90 Pac. (2d) 894. The court stated:

"Complaint is also made of the admission of an identified bottle of salt water from the creek because the degree of salt therein was not definitely shown. The complaint goes to the probative force of the evidence which was for the jury and not to the admissibility thereof which would have presented a question of law for the court. We apprehend that a veterinarian familiar with salt water and its effect on stock can by taste determine with a reasonable degree of certainty whether the water is sufficiently saturated to cause injury or death to stock. Testimony to that effect was presented in this case."

The rapid growth of technical knowledge in so many branches of water pollution has removed many factual situations from the realm of judicial knowledge, and thus we see a reluctance on the part of the judiciary to rely on the convenient expediency of judicial knowledge where other persuasive and more technical evidence is available. Thus in Christensen v. Northern States Power Co. of Wisconsin (1946) 222 Min. 474, 25 N.W. (2d) 659, the court rejected the theory of judicial notice.

"The real question presented for decision is whether there is sufficient evidence that either the electrical current or the dynamite killed the fish. The testimony was that the ice was under such pressure that it had sheared off one of the three steel supports of the tower and that for a period of four seconds electricity may have discharged into the tower. It is the claim of plaintiff that the electricity escaped into the water and killed the fish in the lake. However, the record is silent on the effect this might have had. Any conclusion a jury would reach would be mere conjecture and could not be sustained. No connection as cause between the alleged escape of electricity and the death of the fish is established. What effect, if any, the electricity would have is a matter of which this court cannot take judicial notice, for the simple reason that it is not a matter of common knowledge."

In State v. Heller (1937) 123 Conn. 492, 196 A. 337, the court distinguished the factual situations in which it could take judicial notice.

"While the established scientific fact that water can serve as a carrier of disease germs to one drinking ... is one within judicial notice (State v. Morse, 84

Vt. 387, 80 A. 189, 194, 34 L.R.A., N.S., 190, Ann. Cas. 1913B, 218), what the conditions essential to the destruction of such germs in water of a flowing stream may be, is not. But, aside from this, the tendency of such pollution to produce public injury, even though no actual injury occurs, affords ground sufficient to sustain the Legislature's act. State v. Wheeler, supra, 44 N.J.L. 88, 92; Dunham v. New Britain, 55 Conn. 378, 384, 11 A. 354. Upon the record before us we cannot hold that bathing in a tributary of a reservoir might not have such a tendency to endanger the health of users of the water that the Legislature might not reasonably prohibit it. It is our conclusion that the statute by its terms is not of such broad scope that it fails to bear a rational relation to the protection of the public health, thus constituting an unreasonable exercise of the police power."

In De Garza v. Magnolia Petroleum Co. (1937) Tex. Civ. App., 107 S.W. (2d) 1078, the court said:

"Furthermore, this court does not know judicially that salt water is poisonous or harmful to cattle. It occurs to us it would depend on the amount of salt in the water. The evidence shows that the tank had twenty-three times as much salt at one time, as it had previously had, but this does not establish the fact that the water was poisonous or harmful to the cattle. The fact that the cattle did not like the salt water proves nothing; from the evidence, they must have lived on the water for some six months."

To the same effect, see Shell Petroleum Corp. v. Worley (1939) 185 Okla. 265, 91 Pac. (2d) 679 cited hereinbefore under "Indirect Non-Technical Criteria."

It becomes apparent from a reading of the cases, however, that when complex scientific information is necessary or available, the courts are not reluctant to discard the vehicle of judicial notice. The increasing frequency with which courts resort to other sources for factual information rather than to their own impressions is very reassuring. In addition to pointing up the recognition by the courts themselves of the limitations of this method of proof, the use of technical data lends encouragement to the fact that, as scientific techniques for the detection and prevention of pollution are improved and additional criteria for determining water quality are established, the outcome of litigation will be more predictable with a greater degree of certainty. Such use is certainly to be preferred rather than subservience to the economic and social philosophy of the court where it may have been compelled to act from a minimal factual situation, relying on its own particular knowledge or lack of knowledge.

EXPERIMENTAL EVIDENCE

The principal use of experimental evidence is in the testing of theories of the case by the performance of controlled experiments out of court followed by an expert testifying as to the results. The experiment is thus merely the basis of the expert testimony as to the facts and opinions, and demonstrative evidence is only incidentally involved, as where the expert offers in evidence physical objects connected with the experiment. (See generally McCormick on Evidence, p. 359; 2 Wigmore, Sections

441 et seq.; 2 Belli, Sections 179 et seq.) Since experiments may be conducted under dissimilar conditions and often without notice to the other side, the courts have a broad discretion to admit or exclude experimental evidence.

In Southland Co. v. Aaron (1954) 221 Miss. 59, 72 S. (2d) 161, an action for damages sustained by the plaintiff as a result of pollution by the defendants of the waters of a creek, the testimony of the expert who had collected samples of the water was shown to have some weaknesses.

"J. B. Price, of the Chemistry Department of Millsaps College, testified that he had collected a sample of the water in McGill's Branch, at a point below the refinery, and samples of the water in Boguehoma Creek, above and below the mouth of McGill's Branch. The sample taken from McGill's Branch showed 114 parts per million of sodium chloride. The sample taken from Boguehoma Creek, a short distance above the mouth of McGill's Branch, showed 1510 parts per million of sodium chloride, and the sample taken from the creek just below the land owned by the plaintiffs showed 1368 parts per million of sodium chloride. The witness stated that he did not observe the presence of any petroleum products in McGill's Branch or in Boguehoma Creek. He saw no evidence of oil deposits on the roots of trees on Dr. Copeland's land, which adjoined the land of the plaintiffs. He admitted, however, that the samples of water that he had taken were taken below the surface, and that oil would not go down and mix with water."

It should be pointed out, however, that the requirement is not always that of identity of condition to establish the validity of the experiment but in some cases only substantial similarity is necessary (to wit see Pickens v. Harrison (1952) 151 Tex. 562, 252 S.W. (2d) 575).

CONSTITUTIONALITY OF CRITERIA ESTABLISHED THROUGH LEGISLATION

The courts have uniformly held that the abatement and prevention of water pollution is a matter of state concern, and legislation designed to regulate and control such pollution is within the scope of the state's police power. City of Utica v. Water Pollution Control Board (1959) 5 N.Y. (2d) 164, 156 N.E. (2d) 301.

The problem has been considered primarily from the standpoint of how far state legislation can go without violating the prohibitions in the Federal Constitution against arbitrary and unreasonable classification of all persons and things. From the legal standpoint there appears to be no constitutional limitation that would prevent a satisfactory solution. It has been well settled that any provision of a statute or ordinance regulating a nuisance, such as a pollution nuisance, is valid insofar as the due process clause of the 14th Amendment of the United States Constitution is concerned, if it is reasonably necessary for the accomplishment of the purpose and for the public welfare generally, and if it is not unduly oppressive nor arbitrarily interferes with private business or imposes unusual or unnecessary restrictions upon a lawful business.

It becomes largely a question of fact as to whether or not the regulations and standards are reasonable. No hard and fast rule can be established for all cases. It depends upon the facts and circumstances of each case. A law is not invalid solely because it may put a particular establishment out of business or require the expenditure of large sums of money to comply with the terms of the law. In some situations it amounts to a weighing of the advantages and disadvantages although the doctrine is not placed on that ground. A slight inconvenience to the public will not justify an unnecessary destruction of property rights.

To some extent and particularly in the case of private nuisance, the rule is based on the maxim of jurisprudence as stated in the California Civil Code, Sec. 3514: "One must so use his own rights as not to infringe upon the rights of another."

The rule of law is aptly stated in City of Huntington v. State Water Commission (1953) 137 W. Va. 786, 78 S.E. (2d) 833. In this action the City of Huntington brought proceedings against the State Water Commission to review an order of the commission requiring the city to cease and desist from polluting certain rivers. The Circuit Court entered judgment dismissing the proceeding, and the city brought error. The Supreme Court of Appeals held that the evidence sustained the finding that the waters of these rivers were polluted by untreated sewage of the city in violation of the act creating the commission. The judgment was affirmed, the court stating as follows:

"The uncontradicted evidence introduced at the hearing held by the Commission, on August 15, 1949, clearly shows that the waters of the Guyandotte River and the Ohio River are polluted by untreated sewage from the City of Huntington which is discharged and flows into those streams; and the finding to that effect by the Commission is neither arbitrary nor in excess of its statutory powers. The findings of the Commission is expressly authorized by Section 6, Article 11, Chapter 16, 1931, as amended by Chapter 6, Section 6, Acts of the Legislature, 1933, Regular Session, which provides, in part that: 'After a full hearing the commission shall make its findings of facts, and if it finds that any person is polluting any of the waters of the state, it shall make and enter an order directing such person to cease such pollution and such person shall have thirty days after notice of the entry of such final order to notify the commission that he will comply therewith or will install, use and operate some practical and reasonable system or means which will reduce, control or eliminate or reduce to a harmless minimum such pollution, having regard for the rights and interests of all persons concerned.'

"The question of the force and the effect of an order of an administrative board or tribunal, and particularly the force and the effect of an order of the Public Service Commission of this State, has been frequently considered by this Court. In Town of Harrisville v. Public Service Commission, 103 W. Va. 526, 138 S.E. 99, this Court held, in the syllabus, that: 'The findings of the Public Service Commission, based upon substantial evidence, will not be reviewed by this

Court.' In the opinion in that case, with respect to the findings of the Commission, this Court said:

"'Its findings are presumed to be reasonable, lawful and correct, and will not be set aside by this Court if based upon substantial evidence. Findings of fact by the Public Service Commission, based upon evidence to support them, generally will not be reviewed by this Court.' United Fuel Gas Co. v. Public Service Commission, 73 W. Va. 571, 80 S.E. 931; Mill Creek Coal (& Coke) Co. v. Public Service Commission, 84 W. Va. 662, 100 S.E. 557, 7 A.L.R. 108; City of Charleston v. Public Service Commission, 86 W. Va. 536, 103 S.E. 673; City of Huntington v. Public Service Commission, 89 W. Va. 703, 110 S.E. 192; Baltimore & Ohio Railroad Co. v. Public Service Commission, 90 W. Va. 1, 110 S.E. 475."

PRESUMPTION OF POLLUTION FROM VIOLATION OF STATUTE

In the case of C. L. McMahon v. Smith (1941) 189 Okla. 579, 118 Pac. (2d) 1022-23, the defendant appealed from a verdict for the plaintiff alleging that an instruction to the jury that a violation of statutory law was actionable negligence was prejudicial to his defense. The statute in question reads as follows:

"'No inflammable product from any oil or gas well shall be permitted to run into any tank, pool or stream used for watering stock; and all waste of oil and refuse from tanks or wells shall be drained into proper receptacles at a safe distance from the tanks, wells or buildings, and be immediately burned or transported from the premises, and in no case shall it be permitted to flow over the land. Salt water shall not be allowed to flow over the surface of the land." 52 Okla. St. Ann. Sec. 296.

"'A violation of this statutory law is actionable negligence."

The court stated:

"While the instruction is technically defective, in that by the use of the word 'actionable' in the last sentence it eliminates causal connection as an element of liability, this defect was cured by subsequent instructions in which the trial court positively and repeatedly told the jury that plaintiff's right to recover existed only if the injuries to his livestock were caused or contributed to by the negligent acts of defendant, so that the error was harmless. Oklahoma City-Ada-Atoka Ry. Co. v. Riddle, 183 Okla. 318, 82 Pac. (2d) 304; Marathon Oil Co. v. Sanders, 180 Okla. 642, 71 Pac. (2d) 956.

"Defendant does not contend that the use of the word 'actionable' in instruction No. 4 in any way prejudiced him, but asserts that it amounts to a peremptory instruction for plaintiff, as it in effect made the defendant liable for damages resulting from the escape of salt water and oil from its lease, regardless of whether the escape of such substance was due to causes beyond its control, and it was in fact guilty of no negligence.

"An instruction quoting the language of the statute, and telling the jury that a violation thereof is negli-

gence, is proper. Devonian Oil Corp. v. Hurt, 169 Okla. 114, 36 Pac. (2d) 24. And if the statute is violated, and injury results therefrom, the liability attaches. The violation of the statute is negligence per se. Comanche Drilling Co. v. Shamrock Oil & Gas Co., 122 Okla. 253, 254 p20; Owen-Osage Oil & Gas Co. v. Long, 104 Okla. 242, 231 p296. Affirmed."

In Magnolia Petroleum Co. v. Ford (1938) 183 Okla. 14, 79 Pac. (2d) 588, the court held that a violation of statute requiring an oil lessee to prevent waste oil and refuse from flowing over surface of land is negligence per se, and no other negligence need be pleaded or proved in an action for damages caused by violation of the statute. While the courts have not hesitated to rule that a violation of statutory law or officially adopted standards are prima facie evidence of negligence and indicative of pollution, they have hesitated to adopt the same attitude with respect to activities that apparently bear the seal of approval of some regulatory body or administrative agency.

Thus, the following recent cases may be considered decisive of the factual situations there presented. N. C. Ginther, H. C. Warren and W. L. Ginther, d/b/a Ginther, Warren & Ginther, and R. B. Lynn v. Arthur W.

Long (1956) 227 Miss. 885, 87 So. (2d) 286.

"In an action for damages to plaintiff's land and timber thereon because of salt water and oil flowing from defendants' oil well on adjacent land into a creek and thence onto plaintiff's land, Game and Fish Commission's retroactive certificate, issued after infliction of damages, that defendants had complied with Commission's anti-pollution regulations on date prior to occurrence of damages, was properly excluded from evidence on plaintiff's objection. Assuming that the certificate had been issued on January 1, 1951, it did not constitute a perpetual license to the appellants to discharge its deleterious effluents upon the land of the appellee and thereby cause damage. Masonite Corp. v. Guy, Miss., 77 So. (2d) 720. To hold otherwise would be to grant to the State Game and Fish Commission the right to make an ex parte retroactive finding as to pollution or non-pollution, which retroactive finding would be conclusive upon private parties in an action for damages such as this. We think there was no error in the action of the trial court in sustaining the objection to the introduction in evidence of the certificate."

In C. H. Guy v. Masonite Corporation (1955) 223 Miss. 8, 77 So. (2d) 720, it was shown by appellant that pursuant to the provisions of Chapter 381, Laws of 1946, there was issued to appellant on November 26, 1946, a certificate of the State Game and Fish Commission, as follows:

"'This is to certify that Masonite Corporation of the City of Laurel, County of Jones, is complying this date with the Rules and Regulations of The State Game and Fish Commission on Industrial Waste Effluent.' It is contended that this certificate of 1946 is conclusive evidence that appellant did not pollute these streams in 1950 and 1953. With that position we do not agree. The fact that appellant constructed its settling ponds in accordance with the regulations of the commission and agreed not to release its effluent therefrom except in times of high water and then only in such quantities as not to injure fish life does not grant a perpetual license to violate its agreement with immunity, and the evidence here is sufficient to show that it did release its effluent in such quantities as to pollute these streams, and to make a jury issue on that question."

In B. E. Massey v. Masonite Corp. (1955) 219 Fed. (2d) 586, an action was brought for alleged pollution by defendant of plaintiff's allegedly privately owned lake. The lower court issued summary judgment for defendant finding that the water could not have been polluted by defendant since it had a certificate of compliance from the Mississippi State Game and Fish Commission.

The Appellate Court ruled that this was insufficient

proof:

"We are of the opinion that a certificate of compliance issued by the State Game and Fish Commission, which only has jurisdiction over the waters of the State, exclusive of lakes or other waters which are wholly landlocked and privately owned, and over industrial concerns using such waters for the discharge of waste, is not a legal bar to a private suit for damages for the pollution of a privately owned lake. There is a genuine issue of fact as to whether the appellant's lake was private or landlocked, and whether Masonite's effluents killed the fish in the lake. We think it was error for the court to enter a summary judgment based upon the certificate of compliance, and the judgment appealed from is reversed. Masonite Corporation v. Guy, Miss., 77 So. (2d) 720. Reversed."

In Ellison Bros. Oyster Co. v. Rayonier Incorporated (1957) 156 F. Supp. 214, the court enuniciated the principle that adherence to the terms of a permit was an effective shield against actionable nuisance arising from a discharge of pollutants.

"Actions by tideland owners against pulp and cellulose mill for alleged wrongful pollution of state waters resulting in deterioration and death of plaintiffs' oysters. Defendants moved to dismiss. The District Court, Boldt, J., held that under doctrine of primary jurisdiction Washington Water Pollution Control Commission had primary jurisdiction to control and prevent undue pollution of all tideland waters of state and if mill had been operated pursuant to commission permit from time required, if rules, regulations and standards for such operation had been established by commission which were not arbitrary, capricious or unreasonable and if effluents had not been discharged in violation of standards prescribed, discharge of waste was not unlawful or unreasonable and recovery could not be granted on either trespass or nuisance theory."

MISCELLANEOUS

It may be helpful to enumerate briefly some instances of civil litigation in which the pollution of a water supply has been the focal issue and where a principal of law has evolved through the decisions in the cases which could serve as a precedent in future similar factual situations. This situation arises despite the compliance or failure to comply with promulgated standards.

COMPARATIVE INJURY DOCTRINE

The doctrine of comparative injury, or as it is sometimes called "balancing the equities" has been discussed in a number of cases in the field of water pollution. Based on equitable principles, it would seem to be properly applicable in cases of undue hardship. Yet, the reasoning in the case of its denial is difficult to answer since, insofar as the plaintiff is denied a decree enjoining an actual nuisance arising out of the pollution of the waters, the defendant in effect is given an easement over the plaintiff's land. This action amounts to a taking of property for private use in violation of the Constitution. Where the defendant is required to pay the plaintiff, the reasonable value of his property or the interest therein which is damaged, the effect is condemnation for the benefit of a private individual who does not possess the power of eminent domain.

In American Cyanamid Co. v. Commonwealth (1948) 187 Va. 831, 48 S.E. (2d) 279, an action to enjoin the defendants, the company operated a chemical plant and in the course of its operations in producing titanium dioxide discharged dilute sulphuric acid. The action was brought to enjoin the defendants' activities. The Appellate Court in this state sustained a ruling for the defendant stating:

"The end desired is to keep the clean waters clean and to reduce the pollution in the unclean waters. Some of this pollution comes from industrial waste. discharged by industries invited into the State and furnishing employment to some of its people. The problem is to be dealt with so as to give fair treatment to the industries, to its employees and to the public. That requires a measure and balancing of the interests involved. Some waters should be kept pure. A measure of pollution in others is necessary. Not all pollution can be abruptly stopped. On the agreed facts here, for example, this industry would have to shut down if immediately required to cease discharging its acid waste into the river. The aesthetic and recreational features involved in the pollution problem are important, but the opportunity to make a living may be even more so."

The complaint against the defendant was dismissed. Barber v. School District No. 51, Clay County, Missouri (1960) Kansas City Ct. of App's., 335 S.W. (2d) 527 was an action by owners of adjoining real estate for damages and an injunction restraining a school district from discharging water from its sewage-disposal system upon plaintiff's land.

The plaintiff's land was 25 feet from the sewagelisposal system. The septic tank had overflowed onto the farm and photographs of the water were received in evidence. The plaintiff had testified that the water had an offensive odor and that he had seen his cattle start to drink it and "turn up their noses."

The public-health engineers testified that the system was working adequately, that the water had only a slight dor, and that it would not destroy grass.

The court held that although plaintiff's property rights were technically violated by the sewer discharge and plaintiff received some nominal damages, in view of the fact that he did not suffer substantial damage and the granting of the injunction would result in great injury to the school, to the community and the public, without a great advantage to plaintiff, injunctive relief would not be granted. The court appealed the doctrine of comparative injury. To the same effect, see Johnson v. Independent School District No. 1 (1947) 239 Mo. App. 749, 199 S.W. (2d) 421.

People ex rel. Stream Control Commission v. City of Port Huron et al. (1943) 305 Mich. 153, 9 N.W. (2d) 41 states the rule as follows:

"The doctrine of 'comparative injury' should be confined to those situations where the plaintiff can be substantially compensated. This principle is distinguished in City of Harrisonville v. W. S. Dickey Clay Mfg. Co., 289 U. S. 334, 53 S. Ct. 602, 603, 77 L. Ed. 1208, where Mr. Justice Brandeis said:

"The discharge of the effluent into the creek is a tort; and the nuisance, being continuous or recurrent, is an injury for which an injunction may be granted. Thus, the question is whether, upon the facts found, an injunction is the appropriate remedy. For an injunction is not a remedy which issues as of course. Where substantial redress can be afforded by the payment of money and issuance of an injunction would subject the defendant to grossly disproportionate hardship, equitable relief may be denied although the nuisance is indisputable. This is true even if the conflict is between interests which are primarily private.' "See, also, Edwards v. Allourez Mining Co., 38 Mich. 46, 31 Am.Rep. 301; Monroe Carp Pond Co. v. River Raisin Paper Co., 240 Mich. 279, 215 N.W. 325; and authorities annotated in 77 L.Ed. 1222."

In Sanderson v. Pennsylvania Coal Co. (1878) 86 Pa. 401, 27 Am. St. Rep. 711, the court stated:

"... The exigencies of the great industrial interests must be kept standing in view; the property of large and useful interests should not be hampered or hindered for frivolous or trifling causes. For slight inconveniences or occasional annoyances, they ought not to be held responsible, and, in dealing with such complaints, juries should be held with a steady hand.

"It is certainly true that owing to the want, if not the necessities, of the present age,—of agriculture, of manufactures, of commerce, of invention and of the arts and sciences,—some changes must be tolerated in the channels in which water naturally flows, and in its adaptation to beneficial uses. Reasonable diminution of its quantity, in gratifying and meeting customary wants, has always been permitted. So its temporary detention for manufacturing purposes, followed by its release in increased volume, is a necessary consequence of its utilization as a propelling force. Nor must we shut our eyes to the tendency—the inevitable tendency—of these and other uses, in which water is an indispensable element, to detract somewhat from its normal purity. These modifications of individual right must be submitted to, in order that the greater good

of the public be conserved and promoted. But there is a limit to this duty to yield, to this claim and right to to expect and demand. The water course must not be diverted from its channel, or so diminished in volume, or so corrupted and polluted as practically to destroy or greatly impair its value to the lower riparian proprietor. 'Sic utere tuo' in such conditions is enjoined by social obligation and by law. It is difficult if not impossible, to declare a rule in language so clear and precise, as that it can be applied with certainty to every case that may arise. See Mississippi Mills Co. v. Smith, 69 Miss. 299, 11 So. 26, 30 Am.St.Rep. 546, 100 Ala. at pages 258-261, 14 So. at page 169, 46 Am.St.Rep. 46."

In Ravndal v. Northfork Placers (1939) 60 Idaho 305, 91 Pac. (2d) 368, an action was commenced for damages to land claimed to have been caused by mud and silt being dumped into a river by defendant's placer mining operations and washed into irrigation ditches upon the plaintiffs' lands. The defendant appealed from a judgment for the plaintiff. The court in affirming the judgment stated:

"Numerous authorities announce the doctrine that while a proper use of the water of a stream for mining purposes necessarily contaminates it to some extent, such contamination or deterioration of the quality of the water cannot be carried to such a degree as to inflict substantial injury upon another user of the waters of said stream. Montana Co. v. Gehring, 9 Cir., 75 F. 384: . . . Salstrom v. Orleans Bar Gold Min. Co., 153 Cal. 551, 96 p. 292; Luama v. Bunker Hill & Sullivan Mining & Concentrating Co., 9 Cir., 41 F. (2d) 358; ... We believe the rule stated in Arizona Copper Co. v. Gillespie, 12 Ariz. 190, 100 P. 465, 470; Id. 230 U.S. 46, 33 S. Ct. 1004, 57 L.Ed. 1384, is controlling in this case, namely: 'We do not mean to say that the agriculturist may captiously complain of a reasonable use of water by the miner higher up the stream, although it pollutes and makes the water slightly less desirable, nor that a court of equity should interfere with mining industries because they cause slight inconveniences or occasional annoyances, or even some degree of interference, so long as such do no substantial damage.' "

In Otley v. City of Kewanee (1903) 204 III. 402, 37 N.E. 218, a bill to enjoin pollution of a stream alleged that defendant city had constructed drains which discharged polluted water on plaintiff's land and in the stream flowing thereon rendering it unsuitable for the purposes to which it was adapted, namely pasturage, cultivation, and building lots for residences; that said lands are arable lands and were used for farming purposes and for pasturages; and that lots laid out thereon were suitable for building purposes, and would be valuable therefore but for the nuisance created by the sewage which occasioned complainant great loss and irreparable injury. The court found:

". . . that the city had constructed drains and sewers which discharge upon plaintiff's lands certain noxious, filthy and polluted waters, in which are carried great quantities of poisonous acids and greasy and oily substances, defiling said stream and rendering it unfit and unsuitable for the purposes aforesaid, and emitting noxious, injurious and offensive odors so as to create a nuisance . . .; that the water from the said sewer injuriously affected cattle and hogs . . .

"The cases held that equity jurisdiction is properly invoked to afford relief to a lower riparian owner where an upper proprietor defiles or corrupts a stream to such a degree as to impair its purity and to prevent its use for any reasonable purpose to which running water may be applied.

"The pollution of a stream constitutes the taking of property which may not be done without compen-

sation."

In an action to restrain the operation of a village sewage-treatment plant in such manner as to cause obnoxious odors, and for damages, the court directed that the village correct the offensive condition or, if correction could not be effected, that it cease and desist from operation of the equipment or appurtenance creating that condition. The Supreme Court, Appellate Division, held that in view of the important public purpose served by the plant, the property owner was not entitled to an injunction unless the condition could be remedied without undue hardship.

"Though obnoxious odors from village sewer plant (sic) constituted nuisance to a property owner, she was not entitled to injunction unless condition could be remedied without undue hardship on village, and if correction could not be so made, she was entitled only to permanent damages, in view of important public purpose served by the plant." Esphyr Slobodkina, Resp. v. Village of Great Neck, App. (1955) 285 App. Div. 908, 138 L.Y.S. (2d) 28.

In Slide Mines, Inc. v. Left Hand Ditch Co. et al. (1938) 102 Colo. 69, 77 Pac. (2d) 125, the court had to consider whether to deny an injunction against the pollution of a stream by a mining company on the ground that the plaintiffs did not come into court with "clean hands" because of their act in turning into the stream water from a reservoir carrying extraneous substances. The court ruled:

"In support of its position, the mining company cites a number of cases in which an injunction was denied a complainant who, himself, was guilty of the same wrongful acts against which his suit was directed. Under the record in the case at bar, these authorities have no bearing. In the Wilmore Case, supra, in the majority opinion on rehearing, the word 'pollution' is defined as meaning 'an impairment, with attendant injury, to the use of the water that plaintiffs are entitled to make. Unless the introduction of extraneous matter so unfavorably affects such use, the condition created is short of pollution.' Here the trial court factually determined that such extraneous matter as the farmers introduced into the stream, not only did not unfavorably affect the use of the water they were entitled to make but was beneficial to it, and hence caused no pollution in a legal sense. The farmers having been adjudged guiltless, no basis is presented for the application of the principle advanced by the mining company."

Where the evidence is not clear and satisfactory but is conflicting as to any obnoxious odors arising from the effluent from a disposal plant which are alleged to create a nuisance, an injunction will not be granted, but reasonable time may be given to improve the operation of a plant. The courts consider, among other things, whether an injunction would not destroy the sewer system of a city and subject the public to serious inconvenience and danger. In Hall v. City of Friend (1938) 134 Neb. 652, 279 N.W. 346, the court stated:

". . . The facts present a case wherein the principle of the greatest good to the greatest number must be permitted to operate and private interests must yield to public good, and if the erection has been skillfully performed and without negligence, and in a way to do the least mischief, it must be held to be a lawful exercise of power that equity will not restrain. The construction of sewers and outlets is sanctioned by law, and what the law grants will not constitute a nuisance per se, public or private, and if the law is obeyed no actionable wrong will result."

Although there are decisions apparently to the contrary, the general rule, as supported by the weight of authorities, seems to be that when the issuance of an injunction will cause serious public inconvenience or loss without a correspondingly great advantage to the complainant, no injunction will be granted. So, while there is some authority apparently to the contrary, it is generally held that if the injunction would have the effect of greatly injuring or inconveniencing the public, it may be refused even though as against a defendant the complainant would be entitled to its issuance. The general rule under consideration has been applied where the allowance of an injunction would seriously interfere with or work detriment to public works or works of public benefit, where the issuance of the injunction asked would prevent the necessary disposal of sewage. 32 C.J. 81, Sec. 66; 43 C.J.S., Injunctions, Sec. 31, p. 465; State v. Pearcy, 328 Mo. 550, loc. cit. 574, 41 S.W. (2d) 403, loc. cit. 409; Johnson v. Independent School Dist. No. 1, Buffalo (1947) 239 Mo. App. 749, 199 S.W. (2d) 421.

In Butler v. Village of White Plains (1901) 59 App. Div. 30, New York, the defendant village operated a sewage-treatment plant the effluent of which discharged into a river on which the plaintiff was a lower riparian owner. It was held that the injury was a continuing one and the plaintiff was entitled to injunctive relief. The court stated:

"The court finds that such discharge does produce at times a foul and offensive odor over the lands of the plaintiff and that such effluent adds to the discolorment and pollution of the waters of the stream, and the courts have held that, to warrant an injunction against odors and gases from an offensive business, it is not necessary that the odors should be noxious, and if they are so offensive and disagreeable so as to render life uncomfortable, equity may interfere, and the fact that the nuisance recurs only when the wind is in a given direction, or that the nuisance complained of is surrounded by other nuisances does not deprive plaintiff of their right to relief."

Jessup & Moore Paper Co. v. Zeitler (1942) 180 Md. 395, 24 A. (2d) 788 was a suit in equity for an injunction against emptying waste from defendants' paper mills into a creek flowing through complainants' lands. The court considers the synergistic effects of individual pollutants and states:

"The locality of the nuisance is the common point, like the point of convergence in an hourglass, upon which the previously aggregated results of the originally independent acts of the several defendants concentrate, and jointly operate, and from which the joint effects again radiate and distribute themselves upon all within the reach of their influence. This view was also followed in United States v. Luce, C. C., 141 F. 385, 411, where it was held that, even though there was no business connection between two defendant factories, and even though the odors from either of them alone would not so contaminate the air as to create a nuisance, nevertheless if the combined odors from both have the effect of producing the nuisance, the two factories cooperate in fact in the creation of the nuisance, and under these circumstances the managers of either or both of the factories may be enjoined from contributing to the maintenance of the nuisance."

FLUORIDATION

Although arguments ranging from the right of each individual to be free to treat his health as he pleases, to the right of freedom of religion have been raised against the introduction of fluorides into the water supply, the cases appear to hold uniformly that the fluoridation of public water supplies does not infringe on the constitutional liberties of the individual, and in more than ten states including California (De Aryan v. City of San Diego (1953) 119 C. A. (2d) 674, 260 Pac. (2d) 98) where the issue has been brought to the courts the decisions have been in favor of the public body (Murdoch).

This concurrence of judicial opinions would indicate that the water-quality standards promulgated for fluorides have met legal acceptance and where such fluorides are introduced in the quantity permitted they will not adversely affect the condition of the water supply.

POLLUTION OF GROUND WATER

Phillips v. Sun Oil Co. (1954) 307 N.Y. 328, 121 N.E. (2d) 249 was an action in trespass arising out of alleged underground travel of gasoline from defendant's land into plaintiff's waterwell. The chemist testified that gasoline in the plaintiff's well was the same brand as that dispensed by the defendant, and the representative of the defendant testified that they had found only a small leak in an underground tank, but there was no evidence that the defendant knew or should have known that gasoline would flow to the plaintiff's land. In finding for the defendant the court stated:

"The application of the above-stated rule, in the few pertinent New York cases, to damage claims arising from the underground movements of noxious fluids, produces this conclusion: that, even when the polluting material has been deliberately put onto or into defendant's land, he is not liable for his neighbor's

damage therefrom, unless he (defendant) had good reason to know or expect that subterranean and other conditions were such that there would be passage from defendant's to plaintiff's land. Dillon v. Acme Oil Co., 49 Hun, 565, 2 N.Y.S. 289; Elsey v. Adirondack & St. Laurence R. Co., 97 Misc. 273, 161 N.Y.S. 391; Thompson v. Board of Education of Union Free School Dist. No. 2, Town of Newfield, 124 Misc. 840, 209 N.Y.S. 362. The leading New York decision seems to be Dillon v. Acme Oil Co., supra, where, in the absence of knowledge or notice, an oil refining company was held not liable for discharging, onto its own land, water containing chemicals which somehow soaked down into and through the soil, polluting a well on adjoining property. In the suit we have before us, plaintiff's position is weaker than was Dillon's, since Dillon's defendant intentionally poured, on the ground, the substance which seeped and percolated into Dillon's well."

EMINENT DOMAIN

Article I, Sec. 14 of the California Constitution provides that: "Private property shall not be taken or damaged for public use without just compensation having first been made to, or paid into Court for, the owner. . "The Fifth and Fourteenth Amendments to the U.S. Constitution provide additional safeguards. These are the guarantees that are applicable to the usual situation of condemnation by the state, county, city, school district, or other instrumentality of the governing body. The courts have held that the pollution of a water supply is in effect a taking of private property under some circumstances.

In Clinard v. Town of Kernersville (1939) 215 N.C. 745, 3 S.E. (2d) 267, the court stated:

"The liability of the town is not to be determined by any negligent conduct on its part in the operation of its disposal plant. If in so doing it in fact discharges foul matter upon the lands of the plaintiffs, or it so pollutes the water of the stream which crosses plaintiffs' land that foul and noxious odors emanate therefrom it is liable for the resulting damage, even though in so doing it is exercising a governmental function. An action by a landowner against a muncipality or corporation possessing the right of condemnation for the maintenance of a continuing nuisance which adversely affects the value of plaintiffs' land is, by the demand for permanent damage either by the plaintiff or by the defendant, converted into an action in the nature of a condemnation proceeding for the assessment of damages for the value of the land or easement taken. The assessment of permanent damages for the maintenance of a continuing nuisance as here alleged and the payment of such damages vests the defendant with an easement entitling it to a continued use of the property in the same manner. No matter how urgent the demands of the public may be or how necessary to the progress of the country, no man's property may be taken without compensation. In those cases wherein the right is asserted to pollute streams or otherwise appropriate or subject lands to an additional burden the question of negligence is not involved. Courts uniformly hold that where the action

is for damages by way of compensation, which when paid, secures an easement, the owner of the property is entitled to recover. The pollution of a stream is equivalent to a taking and an appropriation in part. Stanton v. R. R., 111 N.C. 278, 16 S.E. 181, 17 L.R.A. 838; Thomason v. R. R., 142 N.C. 318, 55 S.E. 205; Beach v. R. R., 120 N.C. 498, 26 S.E. 703; Lassiter v. R. R., 126 N.C. 509, 36 S.E. 48. The law permits the acquisition of the easement in such cases by the payment of permanent damages, the judgment having that effect. Brown v. Power Co., 140 N.C. 333, 52 S.E. 954, 3 L.R.A., N.S., 912; Thomason v. R. R., supra."

Cases in other jurisdictions have made the same rule of law.

Snavely et ux. v. City of Goldendale et al. (1941) 10 Wash. (2d) 453, 117 Pac. (2d) 221:

"Generally, polluting a stream is tortious, but, if a municipality pollutes a stream on such scale as to create a public nuisance, municipality's action may assume the character of a 'taking' or 'damaging' of property within the contemplation of the constitutional guaranty that no private property shall be taken or damaged for public or private use without just compensation having first been made. Const. Art. 1, Sec. 16."

Quoting Platt Bros. & Co. v. Waterbury (1900) 72 Conn. 531, 45 A. 154, the court states:

"The right to pour into the river surface drainage does not include the right to mix with that drainage noxious substances in such quantities that the river cannot dilute them, nor safely carry them off without injury to the property of others. The later act is in effect an appropriation of the bed of the river as an open sewer, and the proposition that it may become lawful by reason of necessity is inconsistent with undoubted axioms of jurisprudence. The appropriation of the river to carry such substances to the property of another is an invasion of his right of property. When done for a private purpose, it is an unjustifiable wrong. When done for a public purpose, it may become justifiable, but only upon payment of compensation for the property thus taken. Public necessity may justify the taking, but cannot justify the taking without compensation. It may be necessary for a city to thus mix with its drainage such substances, but it is not necessary to pour such mixture into the river without purification. Indeed the purification is coming to be recognzed as a necessity. But, however great the necessity may be, it can have no effect on the right to compensation for property taken. The mandate of the Constitution is intended to express a universally accepted principle of justice, and should receive a construction in accordance with that principle, broad enough to enable the court to protect every person in the rights of property thus secured by fundamental law."

A decision rendered in Barber v. State (1938) 135 Fla. 637, 185 So. 319 stated that although a city may not be compelled to erect a treatment plant, the discharge of effluent so as to ruin oyster leases is a "taking" of private property and is compensable. To the same effect

see Douglass v. City of Lakeland (1940) 143 Fla. 771, 197 So. 467.

FRESH WATER-TIDAL WATER

There is a marked and well-defined distinction between the pollution of a small nonnavigable stream and the pollution of large tidal navigable bodies of salt water, for the reason that in the first case the bed of the stream and the waters are owned by the riparian owners, while in the latter case the bed of the navigable, tidal salt water and the waters themselves are owned and controlled by the state, for the use and benefit of all the public. It is for the state to say what uses shall be made thereof and by whom, subject always to the right of the public, and for the state, through the legislative branch of the government, to say how much pollution it will permit to be emptied into and upon its waters, so long as the owners of the land between low-water and highwater marks are not injured.

In Squaw Island Freight Terminal Co., Inc. v. City of Buffalo (1937) 273 N.Y. 119, 7 N.E. (2d) 10, the rule

was stated:

"The general rule is that a riparian owner in a nonnavigable fresh water stream is entitled to have the water that passes his land free from pollution. Such riparian owners, therefore, are entitled to an injunction against a city which pollutes the water of such a stream. Sammons v. City of Gloversville, 175 N.Y. 346, 67 N.E. 622. As to tidal waters, the rule is that riparian owners are not entitled to have such waters free from pollution. Seaman v. City of New York, 176 App.Div. 608, 161 N.Y.S. 1002, affirmed, 227 N.Y. 572, 124 N.E. 901; Darling v. City of Newport News, 249 U.S. 540, 39 S.Ct. 371, 63 L.Ed. 759. The underlying basis for this exception as to tidal waters is that the state is the absolute owner of the bed of the stream and may grant rights therein of benefit to the public, subject only to the right of the public to use the waters for purposes of navigation. 9 R.C.L. 682. . . "

United States v. Republic Steel Corp. et al. (1960) 362 U. S. 482 was a suit by the United States to enjoin Republic Steel Corporation, Interlake Iron Corporation, and International Harvester Company from depositing industrial solids in the Calumet River (which derives flow from Lake Michigan and connects eventually with the Mississippi River) without first obtaining a permit from the Chief of Engineers of the Army. The District Court found that the defendants, who operate mills for the production of iron and related products, discharged through sewers into a navigable river of the United States industrial-wastes solids which, on settling out, had substantially reduced the depth of the channel. The court enjoined the companies from continuing this disposal practice and ordered them to restore the depth of the channel by removing the deposits. The U. S. Supreme Court in a close decision held that the discharge into a navigable river of industrial solids which reduces the depth of a channel creates an "obstruction" to the "navigable capacity" of the river within the meaning of Section 10 of the Rivers and Harbor Act of 1899. The Supreme Court held further that the discharge of such industrial solids suspended in water flowing into a river

through sewers is a discharge forbidden by Section 13 of the above Act, and is not exempted as "refuse matter" flowing from sewers and passing therefrom in a liquid state.

MEASURE OF DAMAGES

The scope of recovery of damages in actions for the pollution of water is governed by the same legal principles that apply in most fields of the law, i.e., that the person injured by the pollution is entitled only to recover damages sufficient to compensate him for the injury done. Cases in various jurisdictions have applied this rule.

Oates v. Algodon Mfg. Co. (1940) 217 N.C. 488, 8 S.E. (2d) 605:

"In an action to abate a nuisance and to recover damages allegedly caused by the wrongful pollution of a stream flowing through plaintiff's farm, an instruction that the measure of damages would be the difference between the reasonable market value of the land immediately before and after the injury was erroneous. Where damages to land is due to a cause that may be removed or a nuisance that may be abated, such as the flooding of land, the measure of damage is not the difference in the market value of the land before and after the injury, but is estimated by comparing its productiveness before and after the flooding."

Oklahoma City v. Tyetenicz (1935) 175 Okla. 228, 52 Pac. (2d) 849:

"It is a general rule that where an upper riparian owner has caused the pollution of a water course to the injury of a lower riparian owner and the injury resulting from the pollution is of a temporary character and constitutes a nuisance abatable, the measure of damages is the difference between the rental or usable value of the property free from and subject to the nuisance, together with such special damages as may be established."

Newkirk v. City of Tipton (1939) 234 Mo. App. 920, 136 S.W. (2d) 147:

"The appropriation by city of use of stream for sewer purposes does not deprive a lower riparian owner of his right to compensation for damages suffered by him as result thereof, and measure of damages to which city must respond in case either of condemnation or appropriation without condemnation is a diminution in market value of land damaged thereby."

United States v. Fixico (1940) 115 F. (2d) 389:

"In one of the cases which was reviewed plaintiff seeks past and future damages for permanent injury to his restricted allotted land by pollution arising out of the operation of oil wells, it being alleged, among other things, that the fertility of the soil has been permanently impaired; and in the other case plaintiffs seek damage for the depositing of sewage at such place and in such manner that it ran and runs upon and across the restricted allotted land, it being alleged, among other things, that the land has become impregnated with the sewage, that a water course traversing

the land has become infected and polluted so that it will poison livestock drinking the water, that a well on the land has become polluted, that if a new well were dug it would be likewise polluted, that offensive, noxious and poisonous gases are generated, that a stench arises which renders their home unfit for habitation, and that such conditions prevent the use of the land as a farm. Ordinarily in a case where the source or cause of the pollution is not abatable the measure of recovery is the difference in value of the land immediately before and immediately after the injury occurs. Sinclair Oil & Gas Co. v. Allen, 143 Okla. 290, 288 Pac. 981; Mid-Continent Petroleum Corp. v. Fisher, 183 Okla. 638, 84 Pac. (2d) 22. And where the injury is permanent in nature, plaintiff may recover judgment for such damages as he has already suffered, and in addition such further damages as he will sustain in the future. Comar Oil Co. v. Hackney, 119 Okla. 285, 250 Pac. 93; H. F. Wilcox Oil & Gas Co. v. Murphy, 186 Okla. 188, 97 Pac. (2d) 84. The rendition and discharge of such a judgment creates or recognizes the existence of a right somewhat difficult to define with precision but which is measurably akin to that of an easement. Luama v. Bunker Hill & Sullivan Mining & Concentrating Co., 9 Cir., 41 F. (2d) 358. And in Oklahoma an easement granting certain rights over land is an interest in the land. Missouri State Life Ins. Co. v. Whisman, 181 Okla. 168, 73 Pac. (2d) 130."

Masonite Corporation v. Steede (1945) 198 Miss. 530, 21 So. (2d) 463:

"Where the number of patrons of the fishing resort of a riparian owner was reduced by the killing of the fish in the stream by wood fiber effluent from a manufacturing plant, the owner of the fishing resort can recover from the owner of the manufacturing plant profits he claims to have lost by reason thereof only, if at all, when it clearly appears that because of the killing of the fish his profits from the business thereafter were less than they would have been had the fish not been killed."

POLLUTION FROM CEMETERIES

Two Texas cases and one Washington case have had the occasion to consider the effect of the burial of the dead on the pollution of ground waters. In Clark v. Sunset Hills Memorial Park (1954) 273 Pac. (2d) 645, the Washington case, an action was brought to enjoin the operation of a cemetery located in the vicinity of residences of the plaintiffs. The evidence sustained the finding that the fear of plaintiffs that burial of the dead in the cemetery would pollute the water in wells on the realty of plaintiffs was wholly unfounded. The court stated:

"Appellants next contend that, irrespective of the statutory questions involved in this case, the maintenance of the respondents' cemetery constitutes a nuisance which should be abated. At the trial, appellants sought to show that the existence of the cemetery on high ground above the sites of their several water wells created a danger of pollution and contamination. In this connection, the trial court made the following finding of fact:

"'That the land of each of the plaintiffs, except the plaintiffs Love and Hardgrove, is supplied with water from wells situated upon their property. That the evidence overwhelmingly established that the maintenance and use of the property described in paragraph II, above, owned or under option to the defendants, as a cemetery or for cemetery purposes, or for the burial of dead human remains therein, will not contaminate or pollute the wells of the plaintiffs, or other persons similarly situated, nor render the water of said wells unfit for human or animal consumption, and that the fears, if any, claimed by some of the plaintiffs in that regard are wholly unfounded."

"This finding is strongly supported in its entirety by the expert testimony of a professor of sanitary engineering at the University of Washington, a public health engineer employed by the Washington State Health Department, the Supervisor of Sanitation for King County, and an eminently qualified pathologist."

This ruling was also adopted in Eternal Cemetery Corp. v. Tammen (1959) 324 S.W. (2d) 562 (Texas) in which the court held that the evidence introduced was insufficient to support plaintiffs contention that the burial of human bodies would contaminate the water wells and stock tanks. The Court also cited the earlier case of Jones v. Highland Memorial Park (1951) 242 S.W. (2d) 250 (Texas) where, although the possibility of pollution of underground waters by the presence of human bodies was not ruled out, the court held that the evidence was insufficient to establish firmly that the proposed cemetery would be operated in such a manner as to cause irreparable injury.

PROXIMATE CAUSE

To establish liability of defendants for damages resulting from the pollution of a stream, there must be evidence reasonably tending to prove that the defendants either caused the pollution or contributed to it.

". . . An examination of the record reveals that there was abundant proof of the fact that the plaintiff's crop was damaged and destroyed by flood water containing oil, salt water, and refuse deposited upon plaintiff's premises by an overflow of the North Canadian river at the time alleged in the plaintiff's petition. There was also evidence that the defendants, with the exception of Skelly Oil Company and Amerada Petroleum Corporation, were operating producing oil wells in the drainage basin of the North Canadian river and that said wells were located about ten miles upstream from the land of the plaintiff. However, the record shows that the only evidence which sought to connect the defendants with the pollution of the stream was that of one witness to the effect that some of the pollution was known to come from the Oklahoma City Oil field and of another to the effect that all producing oil and gas wells have more or less oil, salt water, and waste and refuse around them. There was no evidence to show directly or immediately that any oil, salt water, waste, or refuse had been permitted to escape from the wells and premises of the defendants or either of them. The most that can be said of the plaintiff's evidence

in this respect is that it establishes the possibility that some of the pollution might have come from the wells of the defendants. This was insufficient to charge the defendants with liability. As said in Magnolia Pet. Co. et al. v. Dexter, 177 Okla. 153, 57 Pac. (2d) 1155: 'Where there are several oil leases on a section of land that drains into a stream, and the stream is polluted, no lessee can be held liable without showing that polluting materials from its lease went into the stream.'' Indian Territory Illuminating Oil Co. v. Henning (1937) 179 Okla. 462, 66 Pac. (2d) 83.

In Magnolia Petroleum Co. v. Dexter (1936) 177 Okla. 153, 57 Pac. (2d) 1155, the rule was thusly stated:

"The principal question and one determinative of the case, relates to the sufficiency of the evidence to show that either of the companies contributed to the pollution. The law is definitely settled in this jurisdiction that all persons who participate in a pollution are jointly and severally liable, although there is no concurrence in action, but it is equally as well settled that a party cannot be held liable unless he contributes to the pollution. Tidal Oil Co. v. Pease, 153 Okla. 137, 5 Pac. (2d) 389; Comar Oil Co. v. Sipe, 133 Okla. 222, 271 p. 1010. In the instant case there was not a word of evidence to show that any polluting material from the lease of any one defendant entered into the stream. As far as the Texas Company and Skelly Oil Company were concerned, they were not even mentioned in the evidence, and yet their demurrers to the evidence and motions for directed verdicts were overruled and judgment rendered against them. As to the other companies, the plaintiff testified that they had wells on section 6, and that the drainage from the section was to the streams that were polluted. Plaintiff said he had been on section 6, but did not fix the time. There is testimony that the streams were polluted. Plaintiff said that there was drainage from this section into the stream, but there is not a word of testimony showing that polluting materials came from any particular lease. There is nothing to show that other companies did not have leases in the section; only the fact that the Magnolia, Carter, Coline, and Roxana had leases there at some unknown time in the past. There is nothing to show that either company polluted the streams.'

In Cities Service Gas Co. v. Eggers (1940) 186 Okla. 466, 98 Pac. (2d) 1114, the court stated:

"In action by owner of farm for pollution of subterranean waters by seepage from creek into which deleterious substances from oil and gas wells had been discharged, petition alleging that defendants brought to surface crude oil, salt water, basic sediment, and other deleterious substances and permitted them to accumulate and escape from their premises into the creek, was sufficient to allege commingling of salt water by the various defendants, so as to authorize instruction that, where separate independent acts or negligence of several persons combined to produce directly a single injury, each is responsible for the entire result. "It is common knowledge that salt water entering a stream from various sources will commingle therein and thus combine to cause any resulting injury."

SUMMARY AND CONCLUSIONS

Water pollution has become a matter of gravest public and private concern. As seen in the cases mentioned herein, important private and public interests in a wide variety of circumstances are in seeming conflict and require consideration of ultimate state public policy in determining the extent and character of water pollution to be permitted in general and specific cases. Such determination involves extremely technical, complicated, and scientific problems that reasonably might be thought more suitable for resolution by administrative procedures than by the trial of particular damage claims, the varying decisions of which may not always provide specific standards.

While the writer has found no cases in which the courts have accepted one set of standards of quality in preference to another, it is significant to note that there have been many cases in which the courts have stated, expressly or inferentially, that a scientific approach to the problem based on expert evaluation of carefully derived criteria is the most reliable method of arriving at a solution of the problem in the case. Where scientific data have not been available the courts have been obliged to resort to less desirable categories of proof in the form of circumstantial or indirect evidence, judicial notice, and even standards as expressed in criminal statutes.

The courts are ready to accept the constitutionality of water-quality standards or requirements established by public authority and administered through public agencies operating under well-defined procedures best suited for the geographical areas involved. The courts have recognized that the determination of specific issues of pollution is best left with the administrative agency and the courts are content to deal only with the adjudication of individual rights as they become the subjects of lawsuits.

The judiciary appears to be only too anxious to be ousted from the undesired position of having to determine arbitrarily that a condition of pollution exists or does not exist based on the testimony of laymen and influenced by nontechnical, albeit persuasive, indirect evidence. The absence of any litigation or reported cases in which duly promulgated standards or requirements were held up to the searching light of judicial inquiry to determine their reasonableness indicates that the courts are uniformly anxious to have, and have readily adopted, scientifically developed criteria to assist them in their determination.

The existence of definitive criteria, however, is not enough. It is hoped that the delineation of the cases in this chapter will have demonstrated that, while private litigation has its own role to play in the courts, the judiciary can be aided materially in a context of personal litigation through reliance on a proper legal presentation of the data established in determining whether an actionable condition has been proved and how it can best be compensated.

CHAPTER V

QUALITY CRITERIA FOR THE MAJOR BENEFICIAL USES OF WATER

As the most abundant compound on the face of the earth, water is called upon to serve many purposes ranging from internal consumption by living organisms, through agricultural and industrial uses, to the exploitation of its remarkable powers to transport and assimilate the wastes of civilization. The many purposes that water serves in promoting the economic good and well-being of mankind are known as "beneficial uses." They have been listed and cited by Camp (151), Bacon (2323), and others. By combining these references and rephrasing, the following tabulation of the major beneficial uses of water has been established. It should be recognized that these uses are not listed in the order of economic importance nor in the order of increasing or decreasing water quality.

Domestic water supply

Industrial water supply (including cooling water)
Agricultural water supply (irrigation)

Stock and wildlife watering (including refuge for water fowl)

Propagation of fish and other aquatic and marine life

Shellfish culture

Swimming, bathing, and other water-contact sports Boating and esthetic enjoyment

Water power and navigation

Transport, dispersion, and assimilation of wastes.

The relative importance of these beneficial uses for any stream, lake, open ocean, estuary, or ground-water basin depends on the economy of the area and the desires of the inhabitants. Many of the uses, such as domestic water supply and industrial-process water supply, may be compatible within narrow ranges of water quality, whereas the use of a stream for unregulated waste disposal will be at complete variance with its use

for domestic water supply.

It is the intent of this chapter to present the findings and recommendations contained in the principal references dealing with each major beneficial use of water. Only the more significant sources of literature pertaining to each beneficial use have been condensed and summarized. Bits of data from numerous other sources have not been blended into these principal references. Instead, such data are presented under appropriate headings in the chapters that follow. By no means, therefore, should these summaries be considered to be complete with respect to every potential pollutant. There are numerous substances listed in the succeeding chapters (VI, VII, VIII, IX, and X) that are not cross-filed in this chapter. In using and assessing Chapter V, therefore, the reader is urged to make frequent reference to the specific substances in the chapters that follow.

DOMESTIC WATER SUPPLY

The use of water by human beings for drinking and other domestic purposes is conceded generally to be the primary, highest, or most essential use of water. Such water, to be sure, may be given the primary procurement rights and may be afforded the highest degree of sanitary protection, but other beneficial uses may have water-quality requirements that are far more stringent in certain respects than those for drinking water. Many industrial processes, for example, cannot use without further treatment water that is suitable for domestic supplies; softened water from municipal systems is often detrimental for irrigation; and aquatic life in streams and lakes may be destroyed or inhibited by concentrations of copper or zine that are permissible in domestic water.

In evaluating water-quality criteria for domestic use, two conditions of the water must be considered: (a) its quality at the source of supply, be it surface water or ground water, and (b) its quality at the tap or point of use. In former years when water of pristine purity was available from protected watersheds, the two conditions were virtually synonymous, inasmuch as no treatment was provided or deemed necessary. Groundwater supplies, for the most part, still enjoy the luxury of no treatment; but disinfection, softening, carbonate-equilibrium control, and other methods of treatment are gaining favor rapidly, even for supposedly protected supplies.

It is not the intent of this report to deal specifically and thoroughly with the quality of treated water as delivered to the consumer, inasmuch as this study is expected to cover only the quality of water found in natural water courses. Yet, the quality of the treated delivered water is partly relevant to this report, for there are many substances in such water that are not altered readily by present methods of treatment, i.e., their concentration in the treated water is essentially the same as in raw water.

The domestic water-supply industry is caught between two strong trends in water quality. On the one hand, domestic and industrial customers are demanding improved quality and greater uniformity in the water delivered at the tap. Indeed, many water purveyors are leading a crusade towards even higher goals of water quality for the consumers (1745, 1746). On the other hand, the sources of raw water have been deteriorating under the inexorable impacts of modern civilization and may be expected to get worse in future years. The waterworks industry, therefore, must produce a better and more uniform product while drawing upon a poorer and less predictable source of supply. Fortunately, there

are many recent improvements in technology that are capable of bridging the widening gap in quality between raw and finished waters. One of the greatest needs today in water-supply technology is reliable quantitative information relative to the potential harmful effects of trace substances in raw and treated water.

DRINKING WATER STANDARDS (U.S.A.)

The physical, chemical, and bacterial quality of drinking water in the United States is now judged in relation to the Public Health Service Drinking Water Standards of 1962 (2036). Originally promulgated in 1914, these standards were modified and reissued in 1925, 1942, and 1946 prior to the 1962 edition. A comparison of the chemical constituents of these standards is shown in Table 5-1.

Strictly speaking, the USPHS standards apply only to drinking water and water-supply systems used by interstate carriers and others subject to Federal Quarantine Regulations. They have been voluntarily accepted, however, by the American Water Works Association and by most of the state departments of public health as criteria for all public water supplies. The extent to which they can be enforced within any state depends on the state and local laws.

A complete statement of the 1962 standards is contained in public documents (2036) and will not be repeated herein. Instead, the principal provisions dealing with quantitative limits are condensed and summarized below:

- 1. Bacterial quality. The minimum number of samples to be collected from the distribution system and analyzed each month, and the numbers of these samples and portions thereof that may show the presence of coliform organisms are specified. In effect, these requirements limit the average monthly coliform content to a most probable number (MPN) or membrane filter count of one coliform per 100 ml. For a further discussion of bacterial quality in treated and raw waters, see Coliform Bacteria in Chapter VII.
- 2. Physical characteristics. The following limiting concentrations are recommended for water in the distribution system of a water supply:
 - a. Turbidity (silica scale), not to exceed 5 units
 - b. Color (standard cobalt scale), not to exceed 15 units
 - c. Threshold odor number, not to exceed 3
- 3. Chemical characteristics. The limits for chemical elements or compounds in water are divided into mandatory requirements for certain substances and recommended criteria for others. The mandatory limits are shown in the first part of Table 5-1. For further information dealing with the validity or reasonableness of these mandatory limits, reference is made to the specific substances listed in Chapter VI. The rationale by which such standards are established is discussed by Hopkins (2324), by Derby et al. (2062), by Stokinger and Woodward (2325), by Welsh and Thomas (2326), and by the advisory committee (2327).

The non-mandatory but recommended limits for less critical substances are shown also in Table 5-1. For three

substances (arsenic, cyanide, and fluoride) recommended limits are given in addition to the maximum permissible concentrations. Thus, an arsenic limit of 0.01 mg/l is recommended, but a concentration of not more than 0.05 mg/l will be permitted if no alternative source of supply is available.

TABLE 5-1
COMPARISON OF CHEMICAL SUBSTANCES IN USPHS
DRINKING WATER STANDARDS OF 1925,
1942, 1946, AND 1962

	Concentrations in mg/l								
Substance	1925	1942	1946	1962					
A. Maximum permissible concentrations: Arsenic** Barium Cadmium Chromium (hexavaleut) Copper Cyanide** Fluoride** Lead Selenium Silver Zine	0.2 0.1	0.05 0.0 • 1.0 0.1 0.05	0.05 	0.05 1.0 0.01 0.05 * 0.2 1.6-3.4# 0.05 0.01 0.05					
B. Recommended limiting concentrations (provided that other more suitable supplies are or can be made available): Alkyl benzene sulfonates. Arsenic** Carbon chloroform extract. Chloride. Copper. Cyanide** Fluoride* Iron Manganese. Magnessium Nitrate, as NO: Phenolic compounds, as phenol Sulfate. Total dissolved solids. Zinc.	100	250 3.0 0.3 125 0.001 250 500 15.0	250 3.0 0.3 { 125 0.001 250 15.0	0.5 0.01 0.2 250 1.0 0.01 0.8-1.7 0.3 0.05 0.001 250 5.0					

 Maximum permissible concentrations were replaced by recommended limits after the 1925 standards.

**These substances have both recommended limits and maximum permissible concentrations.

Recommended limits and maximum permissible concentrations for fluoride vary with the annual average of maximum daily air temperature, from the lowest concentrations at 79.3-90.5°F to the highest at 50.0-53.7°F.

The changes in each subsequent edition of the standards have not been drastic, but there are certain noticeable trends. With each edition there are more substances that come under the recommended or maximum permissible limitations. In general, moreover, there is a recent tendency to tighten up on the limitations. Zinc, for example, started out at 5.0 mg/l mandatory, changed to 15.0 mg/l recommended, and recently reverted to 5.0 mg/l as a recommended limit. Arsenic was limited in 1942 to 0.05 mg/l maximum and was still at this level in 1962 for the permissible concentrations. It is now recommended, however, that arsenic be restricted to 0.01 mg/l unless an alternative supply is not available. Similarly, the restrictions on copper were relaxed from 0.2 mg/l in 1925 to 3.0 mg/l in 1942 and 1946; but in 1962 the recommended standard was tightened to 1.0 mg/l.

Radioactivity became an official criterion of the USPHS standards for the first time in 1962. In general, water supplies may be approved when "the radioactivity intake from such water supplies when added to that from all other sources is not likely to result in an intake

greater than the radiation protection guidance recommended by the Federal Radiation Council and approved by the President.

"Water supplies shall be approved without further consideration of other sources of radioactivity intake of Radium-226 and Strontium-90 when the water contains these substances in amounts not exceeding 3 and 10 μμc/liter, respectively. When these concentrations are exceeded, a water supply shall be approved by the certifying authority if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action.

"In the known absence of Strontium-90 and alpha emitters, the water supply is acceptable when the gross beta concentrations do not exceed 1,000 μμc/liter. Gross beta concentrations in excess of 1,000 μμc/liter shall be grounds for rejection of supply except when more complete analyses indicate that concentrations of nuclides are not likely to cause exposures greater than the radiation protection guides as approved by the President on recommendation of the Federal Radiation Council" (2036). It is apparent, therefore, that any criteria of radioactivity in drinking-water standards are dependent upon the current decisions of the Federal Radiation Council.

DRINKING WATER STANDARDS (OUTSIDE OF U.S.A)

Except for the United States, only a few countries have published national guidelines for drinking water quality (153, 154, 155, 1457, 1545). Recently, however, the World Health Organization (WHO) has promulgated the 1958 International Standards for Drinking Water and the 1961 European Standards for Drinking Water. The WHO standards arose from the Seminars for European Sanitary Engineers sponsored by the World Health Organization and the Rockefeller Foundation. Corti (1648) discussed circumstances favorable and antagonistic to the development of international standards. He recommended that continuing research be directed along two separate lines; first to define requirements for good drinking water, and second to develop reliable laboratory techniques for adequate quantitation of water quality. The WHO group that met in Geneva in 1956 to consider requirements for water quality believed that the term "standards" should be applied to their suggested criteria even though such standards were tentative and subject to modification after experience in their application. This same group also studied various analytical procedures. Approved methods of analysis are described in the annexes of the WHO International Standards for Drinking Water (2328).

Concurrent with the development of the International Standards, the WHO Regional Office for Europe sponsored meetings in 1956 and 1959 that led to the publication of European Standards for Drinking Water (2329). The preface of this document points out the reasoning by which WHO has issued both international standards and European standards as follows: "International Standards for Drinking-Water proposes minimal standards which are considered to be within the reach of all countries throughout the world at the present time. In view of the different economic and technological capa-

bilities of various countries there will be some areas in which higher standards than those proposed for the world as a whole will be attainable—and these areas should be encouraged to attain such higher standards. It is believed that Europe is such an area and that there is, therefore, nothing illogical in setting higher standards in Europe than internationally. One of the objects of having standards at all is to stimulate improvement in water quality, and it is hoped . . . that improvement in economic and technological resources throughout the world will allow higher standards to be suggested in the future than those at present proposed for the whole world" (2329).

To describe the international standards and European standards in detail is beyond the purview of this report. It is interesting, however, to compare the two WHO standards with the 1962 USPHS standards. Table 5-2 presents this comparison for chemical constituents. In using this table, one should bear in mind that all figures are not directly comparable, for different analytical methods may be involved. Before drawing any conclusions from this table, the reader is advised to consult the original texts.

With respect to bacteriological criteria, the WHO international standards are approximately equal to the USPHS standards in requiring that the arithmetic mean coliform density should not exceed one organism in 100 ml of water. The WHO European standard, however, is considerably stricter, limiting the average coliform density to one organism in two liters of water, or one-twentieth the density in the USPHS and international standards.

The radiological requirements of the WHO standards for drinking water, both international and European, are based upon the recommendations of the International Commission on Radiological Protection. They set the following upper limits in drinking water as supplied to consumers for life-time use for large populations:

alpha-emitters beta-emitters 1 picocurie/liter 10 picocuries/liter

Note that a picocurie is a micromicrocurie; hence the WHO limit for beta-emitters corresponds to the USPHS limit for beta emission from strontium-90. If these limits are not exceeded, no further radiochemical analysis is required by the WHO standards. "Higher figures than those given above are safe for many radionuclides, and a water with a higher total radioactivity than the figures given above may be safe for use if the absence of the more dangerous radionuclides can be confirmed by radiochemistry" (2328, 2329). Neither the WHO nor USPHS standards give permissible limits for short-time use or for small populations.

RAW WATER STANDARDS

Of particular interest to the sanitary engineer engaged in water-pollution control are the standards or criteria that have been promulgated for natural waters used as sources of domestic supply. Such standards have been issued by the U. S. Public Health Service, as well as by several state and interstate agencies, notably the New England Interstate Water Pollution Control Commission, the Interstate Commission on the Potomac River Basin, the Pollution Control Council, Pacific Northwest

TABLE 5-2

COMPARISON OF CHEMICAL CONSTITUENTS IN THE DRINKING WATER STANDARDS OF THE WORLD HEALTH ORGANIZATION AND THE U.S. PUBLIC HEALTH SERVICE	Concentrations In Milligrams Per Liter	WHO International (1958)	Permissible Bacessive Maximum Recommended Tolerance Recommended Maximum onstituent Limit Limit Allowable		0.5 0.5 0.0	1	20.0	007 01	250 600 250	0.00 50.00 1.00	0.01	1,5		125**	in sunate 000		ols) 6.001 - 6.002 - 6.001 - 6.001	0.05	250 400 500 500 500 500 500 500 500 500 5	
			Chemical Constituent	Alkyl benzene sulfonate	Ammonia (NH4)	Barium	Calmium	Carbon chloroform extract	Chloride	Chromium (hexavalent)	Cyanide	Fluoride	Lead	Magnesium Sadium antere	Manganese	Nitrate (as NO ₃)	Oxygen, dissolved (minimum) Phenolic compounds (as phenols)	Selenium	Sulfate	Zinc Zinc

* After 16 hours contact with new pipes; but water entering a distribution system should have less than 0.05 mg/1 of copper, ** If there are 250 mg/1 of sulfate present, magnesium should not exceed 80 mg/1.

Recommended limits and maximum allowable concentrations vary inversely with mean annual temperature. See table 5-1,

Area, and the states of Maine, Montana, New Hampshire, New York, Oklahoma, South Carolina, and Utah. For a complete description or tabulation of the standards or criteria used by each interstate agency or state, see Chapter III and the appropriate appendices. The Public Health Service recommended sanitary requirements for water treatment systems is reproduced herein as Appendix Q.

Inasmuch as these standards tend to follow a pattern, they have been assembled and summarized in Table 5-3, "Ranges of Promulgated Standards for Raw Water Sources of Domestic Water Supply." The table is presented as a summary of current thought on the subject. No attempt is made at evaluation of the reasonableness or unreasonableness of each standard. For further background information relating to each specific pollutant, see Chapters VI and VII.

Earlier studies of the efficacy of water-treatment plants on the removal of bacteria have shown that an average plant using rapid sand filtration and supplying a low chlorine residual by post chlorination could provide a satisfactory drinking water if the average concentration of coliforms in the raw water did not exceed 5000 per 100 ml. At an average concentration of 20,000 per 100 ml, it was found that supplementary treatment, such as prechlorination and double-stage sedimentation, was required (141). Similar studies showed that for waters requiring only simple chlorination, "... the average B. coli index of the raw water, when considered over a similarly long period of time, should not exceed 400 per 100 cc. for more than 5% of the time ..." (156, 157).

INDUSTRIAL WATER SUPPLY

The total use of water in this county by industries for all purposes was estimated in 1950 at 70 billion gallons per day, as compared with 15 billion gallons per day for municipal and rural non-irrigation use and 95 billion gallons per day for irrigation use (158). Industrial demands for water are increasing more rapidly than irrigation requirements, so before long industrial use of water will be the largest category. The great magnitude of the industrial demand demonstrates the extreme importance of water to industry. Water is used as an ingredient with other raw materials in the finished product, as a bouyant transporting medium, as a cleansing agent, as a coolant, and as a source of steam in heating and power production. The quantities of water used per unit of product have been published for many industries (161, 2330, 2331) and predicted for others (2332) but these figures represent averages only. The actual use by an industry in a specific location may be considerably greater or less than these averages. Inasmuch as quality, rather than quantity, is the prime consideration of this report, no attempt will be made to summarize data on quantity requirements.

The ideal quality of water required for industrial use varies widely for the many purposes to which water is put. Needless to say, it is impossible to organize the quality requirements of the waters used for each of the many different industrial processes into a single set of standards. Such quality requirements differ far too much to allow any broad generalization or simplification. Within any industrial plant, water may have several

functions, the quality requirements for which vary markedly. A brewery, for example, needs soft water for bottle washing but can utilize hard water for brewing. Many feed, another quality for cooling towers, and a third quality for production processes.

Industries are generally willing to accept for most processes water that meets drinking-water standards. Where water of higher quality is needed, e.g., for television picture-tube manufacture, certain food and beverage preparation, or for high-pressure boilers, industry recognizes that additional treatment is the responsibility of the water user (2333).

One characteristic, however, is of primary importance for all industries, namely, the concentrations of the various constituents of the water should remain relatively constant. That the water is originally of poor quality for a particular industrial use is probably not as important, once a process is started and the difficulties created by the presence of undesirable constituents in water are eliminated, as having the quality remain constant. Short-time variations in concentrations of substances in the process water require continued attention and added expense (2334, 2335, 2336).

Although many studies have been made of the quality requirements of water for use in certain industries, there remain innumerable other industries for which the requirements of water quality have not been specified in public documents except in a general and qualitative way. Perhaps the most thorough study of the waterquality requirements of various industries has been that conducted by the Committee on Water Quality Tolerances for Industrial Uses, of the New England Water Works Association. The committee presented an extensive report in June, 1940, containing tables of tolerance limits for waters for a number of industries, and text material describing the effects of various harmful substances in water on industrial operations (159). Much of this information is incorporated in the book "Water Quality and Treatment" of the AWWA (152) and many of the data appear under the appropriate sub-heading in this part of Chapter V. The NEWWA table has been reproduced in several other published articles.

In 1953 the American Society for Testing Materials published the first edition of its "Manual on Industrial Water," ASTM Special Technical Publication No. 148 (1654). There have been subsequent printings. In this book, one chapter, entitled "Uses of Industrial Water," refers to the chemical, steel, paper, leather, textile, and food and beverage industries. It tells how water is used by each industry without describing the quality requirements for each industry or each process therein.

Another chapter describes "Difficulties Caused by Water in Industry," noting that "industrially speaking, water is an essential, but troublesome raw material." The three major categories of difficulties, with descriptive subheadings, are presented in this manner:

A. Effect on Product

- 1. Decay, resulting from biological action
- 2. Staining
- 3. Corrosion
- 4. Chemical reaction and contamination

TABLE 5-3
RANGES OF PROMULGATED STANDARDS FOR RAW WATER SOURCES OF DOMESTIC WATER SUPPLY

Constituent	Excellent source of water supply, requiring disinfection only, as treatment	Good source of water supply, requiring usual treatment such as filtration and disinfection	Foor source of water supply, requiring special or auxiliary treatment and disinfection
BOD (5-day) mg/l Monthly average: Maximum day, or sample:	0.75-1.5 1.0-8.0	1.5-2.5	Over 2.5 Over 4.0
Coliform MPN per 100 ml Monthly average:	50-100	50-5,000	Over 5,000
Maximum day, or sample:	Less than 5% over 100	Less than 20% over 5,000	Less than 5% over 20,000
Dissolved Oxygen mg/l average: % saturation:	4.0-7.5 75% or better	4.0-6.5 60% or better	4.0
pH Average:	6.0-8.5	5.0-9.0	3.8-10.5
Chlorides, max. mg/l	50 or less	50-250	Over 250
Fluorides, mg/l	Less than 1.5	1.5-3.0	Over 3.0
Phenolic compounds, max. mg/l	None	0.005	Over 0.005
Color, units	0-20	20-150	Over 150
Turbidity, units	0-10	10.250	Over 250

- B. Deterioration of Equipment
 - 1. Corrosion
 - 2. Erosion
 - 3. Cavitation
 - 4. Water hammer
 - 5. Scale deposition
- C. Reduction of Efficiency or Capacity
 - 1. Tuberculation
 - 2. Sludge formation
 - 3. Scale deposition
 - 4. Foaming
 - 5. Organic growths.

There have been several excellent papers describing the general problems of industrial water quality and giving brief descriptions of the general problems for specific industries (1649, 1650, 1651, 1740, 2331, 2333, 2334, 2335, 2336, 2337, 2338).

In the discussions that follow, consideration has been given to the common and prominent industrial uses of water, where literature relating to water-quality criteria for such industries is available. These uses are listed in alphabetical order by means of sub-headings, with cross-referencing where indicated.

ALUMINUM INDUSTRY

The water requirements of the aluminum industry have been summarized in a comprehensive report by the U. S. Geological Survey (2339) from which the following material has been abstracted. No quantitative criteria of water quality are given in the USGS report.

Aluminum is made in two steps. The first process is the production from the bauxite ore of alumina, a white powder. The second step is the reduction of alumina to metallic aluminum by electrolytic action.

In alumina plants, water of high quality is required for the hydrate wash, which constitutes only about five percent of the total water demand. For other water uses, quality is not a serious consideration. Any impurities introduced in the hydrate wash tend to accumulate in the caustic soda solution and impair its function. Fortunately, modern alumina plants employ multiple-effect evaporators to concentrate the sodium aluminate solution and the vapor from these evaporators can be condensed and recovered for use in the hydrate wash.

In reduction plants, the major need for water is in the sprays used for scrubbing of stack gases to minimize air pollution. Water quality is not a consideration in these sprays. Minor quantities of water are used for boiler feed, engine cooling, and other processes for which high quality is necessary.

BAKING (see also Confectionary, Food Processing)

In addition to being bacteriologically safe, water used in baking should not cause undesirable tastes, odors, colors, or interference with the complex fermentation processes. Inasmuch as calcium is necessary for some yeast actions, hardness is not necessarily a disadvantage for all baking waters. Too much hardness, however, retards the fermentation and too little softens the gluten to produce a soggy bread. For some cake and eracker baking, water of zero hardness is used. The few threshold values that have been recommended in the surveyed

literature are summarized below (152, 159, 160, 161, 162, 2337).

	Range of Recommended
Constituent	Threshold Values in ma/l
Turbidity	10
Color	
	10
Taste and odor	
Iron	0.2
Manganese	0.2
fron and manganese	0.2
Hydrogen sulfide	0.2

BOILER FEED WATER

The problem of make-up or feed water for boilers is common to almost all industries. Its importance and complexity has made it the subject of innumerable technical articles, special studies, and recipes. A thorough review of all such references is beyond the scope of this study inasmuch as they deal mostly with the addition of chemical compounds or with other treatment methods to render the water non-corrosive or non-scale-forming. Insofar as the raw-water supply is concerned, however, the presence of many substances will render boiler feed water more difficult to treat or otherwise to handle. The suggested limits of tolerance for boiler feed waters as recommended by the aforementioned Committee on Water Quality Tolerances for Industrial Uses of the New England Water Works Association (159), are contained in Table 5-4.

For beilers of very high pressure (1000 psi or greater), all hardness must be removed, dissolved oxygen should be less than 0.05 mg/l, and total dissolved solids should be as low as possible, preferably less than 0.5 mg/l. For such purposes, carefully distilled and deaerated water is necessary, for no natural water would meet these conditions (2336, 2338, 2340). Silica is especially troublesome, for it tends to form a hard scale in boilers and boiler tubes. Moreover some of it carries over in the steam and forms troublesome deposits on the blades of steam turbines (2341, 2342). For high-pressure boilers, dissolved silica should not exceed 0.2 mg/l, although 1 to 5 mg/l can be tolerated at low pressures (2341). Aluminum is troublesome, for it also tends to be deposited as scale on boiler tubes. Excessive sodium and/or potassium may contribute to the foaming of boiler water (2342). In sugar refineries, the presence of sugar in boiler feed water has caused foaming and the production of organic acids that contribute to corrosion (2343). Ideally, no ammonia should be present, for it is very damaging to copper parts (1740). Finally, toxic boiler compounds should not be employed where steam is used in the preparation of food.

BREWING (see also Malt Preparation, Fermentation Processes)

An ancient art, brewing has become in the last century increasingly reliant upon scientific principles. The quality of beer depends largely upon the ingredients used in its manufacture, among which water is a major factor. The ions of the water have a marked influence on the brewing, the fermentation, and the quality of the finished product (2344). Indeed, many breweries have been located on the basis of water quality and in earlier days there was a marked association of particular waters with certain characteristic beers, especially in Europe (2345).

In the brewing industry, the use of water is divided into two major categories: production water and process water. Each use has different quality requirements. The water of production is used in brewing and much of it remains as the major ingredient of the beer or ale. Process water is utilized for heating by steam or for pasteurization, for cooling, for clean-up operations, and for bottle washing (2345). The quality requirements for such process water are similar to those for other industries. In general, the process water should be soft, of low mineral content, and bacteriologically safe. (See Boiler Feed Water, Cooling Water, and Food Washing Equipment)

Production water is first used in some breweries to steep grain such as barley. This water must be microbiologically sound to diminish mold germination and it must not contain any substances that inhibit germination (2345).

TABLE 5-4

SUGGESTED LIMITS OF TOLERANCE FOR **BOILER FEED WATERS**

(From Progress Report of the Committee on Water Quality Tolerances for Industrial Uses, NEWWA) (159)

(units are in mg/l except as otherwise noted)

Pressure (psi)	0-150	150-250	250-400	Over 400
Turbidity	20	10	5	1
Color	80	40	5	2
Oxygen consumed	15	10	4	3
Dissolved oxygen**	2.0ª	0.2ª	0.0	0.0
Hydrogen sulfide *	5	3	0	0
Total hardness (CaCO ₃)	80	40	10	2
Sulfate-carbonate ratio	1:1	2:1	3:1	3:1
(ASME)				
$(Na_2SO_4:Na_2CO_3)$				
Aluminum oxide	5	0.5	0.05	0.01
Silica	40 '	20	5	1
Bicarbonate **	50	30	5	0
Carbonate	200	100	40	20
Hydroxide	50	40	30	15
Total solids b30	000–500	2500-500	1500-10	0 50
pH value (Min.)	8.0	8.4	9.0	9.6

^{*} Except when odor in live steam would be objectionable.

** Limits applicable only to feed water entering boiler, not to original water supply.

* Given as ml per liter. Multiply by 0.70 for ppm.

* Depends on design of boiler.

Steeped barley, rice, and/or corn are next crushed and mixed with water at a suitable temperature and for a correct time to allow conversion of starch, by diastase, to a mixture of simpler carbohydrates which can be fermented to alcohol and carbon dioxide by "brewers yeast". The clear sweet wort that drains from this mashing operation is then boiled in copper kettles with hops.

The enzymic reactions at mashing are extremely dependent upon the pH value, which in turn is governed by the buffering action of phosphates and bicarbonates, both of which are affected by the calcium and magnesium content of the water. The enzyme systems operative at mashing have pH optima that range from 4.6 to 5.7. Calcium, and to a lesser extent magnesium, helps to keep the pH low by precipitation of phosphates and carbonates, but this effect is offset by high carbonates or bicarbonates in the brewing water. For this reason, brewers prefer water of low alkalinity and high calcium content (2345). Indeed, calcium chloride and calcium sulfate are generally added to production water to assure optimum

enzyme reactions during mashing. These salts are also advantageous during boiling with hops (2346).

Iron is detrimental in production water because it gives a bad flavor and discolors the beer. Nitrite interferes with the preservation of beer and may be poisonous to the yeast. Nitrates are similarly undesirable, for they are partially reduced to nitrites during fermentation. Nitrogen compounds in general lead to poor or cloudy appearance of bottled beer. In excess of 30 mg/l, magnesum ion has been known to retard saccharification and to impart a reddish tint and acridness to beer (2344). The chloride ion renders the beer more mellow and sweet, but it may be harmful in concentrations of over 100 mg/l (2344) or perhaps over 60 mg/l (2347). Even small amounts of copper appear to cause beer to "gush" from a can immediately upon opening (2333).

Production water should meet the bacteriological requirements of drinking-water standards, inasmuch as light beers have only a slight bactericidal effect (2308). Dark beers and ales are generally strong enough in alcohol to be bactericidal.

Water containing 1.0 mg/l of fluoride ion, from NaF or Na₂SiF₆ has no adverse effect on production of beer (2348) and indeed at concentrations of 1 to 5 mg/l, fluoride appears to stimulate yeast metabolism (2349). At fluoride concentrations of 10 mg/l or higher, inhibitory effects were noted (2348, 2349).

The various threshold or limiting values that have been recommended in numerous references are summarized below:

Range of Recommended Threshold or Limiting Values, in mg/l Constituent 0-10 Color Turbidity ______ 0-10 Taste and odor none-low 500-1500 Total dissolved solids ____ 300 (for any one substance) 6.5-7.0pH value ___ 75-80 (light beer) Alkalinity, as CaCO₃ _____ 80-150 (dark beer) 0.1 - 1.00.1Manganese ______ Iron and manganese _____ 0.1Carbonate _____ 50-68 Nitrite_____ 0 10 Nitrate _____ 60-100 Chloride _____ Silica _____ 50 Hydrogen sulfide 0.2 Fluoride 1.0 Calcium _____ 100-200 (light beer) 200-500 (dark beer) Calcium sulfate _____ 100-500 Calcium chloride _____ 100-200 Magnesium ___ 30 Magnesium sulfate 50-200 Magnesium chloride _____ 50-200 Sodium chloride ______ 275-500Sodium sulfate _____ Sodium carbonate

References: 152, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 2344, 2345, 2346, 2348, 2349

CANNING (see Food Canning and Freezing)

CARBONATED BEVERAGES

In general, the quality requirements for water used in carbonated beverages are more stringent than those for drinking water or domestic supply. Very low concentrations or complete absence of microorganisms, organic matter, turbidity, color, taste and odor, iron, and manganese are desired. Fruit-juice beverages are particularly susceptible to microorganism growth. Because of the acid nature of the product, uniformly low alkalinity is an important requirement. The various threshold values that have been recommended are summarized below:

	Range of Recommende Threshold Values
Constituent	$in\ mg/l$
Turbidity	1.0-2.0
Color	
Taste and odor	None-low
Alkalinity, as CaCOs	
Total dissolved solids	
Hardness, as CaCO ₃	
Iron	0 4 0 0
Manganese	0.2
Iron and manganese	0.1 - 0.5
Chlorides	250
Sulfates	250
Fluoride	0.2-1.0
Hydrogen sulfide	
Organic matter	
Algae and protozoa	
Oxygen consumed	

References: 152, 162, 164, 173, 179, 180, 181, 182, 184, 185, 186, 187, 185, 2350

CARBON BLACK INDUSTRY

The water requirements of the carbon-black industry have been summarized in a comprehensive report by the U. S. Geological Survey (2351) from which the following material has been abstracted.

Carbon black is used chiefly as a reinforcing agent in the rubber-tire industry and as a coloring pigment in ink and paint. It is manufactured from gaseous or liquid hydrocarbons either by partial combustion followed by contact with cold metal, or by thermal decomposition in furnaces or retorts. Prior to World War I, the contact process was dominant, but in recent years over 70 percent of production comes from the furnace process.

The only process water used in the contact method is for pelleting of the finished carbon black to facilitate packaging. At some plants, carbon black is dry pelleted; at others, water is added to form a slurry prior to pelleting. Because this water is incorporated into the product, it should contain very little dissolved mineral matter.

In the furnace processes, carbon black is produced by incomplete combustion of hydrocarbons at 2,200 to 3,000° F. The carbon black is carried by the hot gases to quenching towers and subsequently to electrostatic precipitators and cyclone collectors. Practically all of the water used for gas quenching is lost by evaporation or incorporated into the product. Hence it should have a low content of dissolved solids. The USGS report does not develop quantitative limits of tolerance of dissolved solids either for pelleting or for quenching.

CHEMICAL PROCESS INDUSTRIES

Many and varied are the chemical process industries that employ water directly in the product or as an auxiliary to the process (189). Such industries are listed under separate sub-headings in this chapter. For most of the industries using water as a raw material, there are undoubtedly limiting concentrations of impurities that cannot be exceeded without damaging the product (159), but many such concentrations are so high that they are rarely encountered in normal domestic supplies. In other instances, however, special water treatment is required and sometimes distilled water must be employed. Important as water is to some of the chemical process industries, it is surprising how little information concerning it is available in the technical literature. The few references uncovered in this survey are included under separate sub-headings.

CONCRETE MIXING AND CONCRETE CORROSION

The formation of concrete from cement, sand, gravel, and water represents a chemical reaction in which the quality as well as the quantity of each ingredient is important. It is well known to most engineers that the strength of the concrete is dependent, in part, on the ratio of the water and cement used. Not so thoroughly understood, however, is the effect of polluting substances in the water on the strength and durability of the concrete. The Portland Cement Association has been investigating the effects of water quality on concrete mixing and much of the following discussion has originated from such research.

"Water used for mixing concrete should be free of acids, alkalies, and oil unless tests or experience indicate that water being considered for use and containing any of these materials is satisfactory. Particularly to be avoided are waters containing decayed vegetable matter which may interfere with the setting of the cement. Most specifications require that the mixing water be suitable for drinking; such water is usually satisfactory with the possible exception of that from certain areas where the drinking water contains large amounts of sulfates" (191). Tests have shown that the compressive strength of concrete is only slightly affected by the use of sea water for mixing. With continuous wet curing for a month or more, concrete mixed with sea water has tested 10 to 20 percent lower than similar concrete mixed with fresh water (192).

Although there are reports that lime mortar behaves oppositely, a mortar made from portland cement and sand is considerably weakened by the presence of sugar in a concentration that is equivalent to 3400 mg/l in the mixing water (193). Small-scale tests have demonstrated that the hardness of the mixing water has no effect on the air-entraining qualities of concrete inasmuch as ". . . the hardness of the igneous portion of a concrete mixture is so great as not to be appreciably affected by the hardness of the water supply ... " (194). Some preliminary tests have been made upon the tensile strength of portland cement made with mine waters of both high and low acidity. Apparent increases in strength were noted, but it was not known whether this change was attributable to actual long-time increase in strengths or merely to an acceleration in setting time (195).

The constituents in natural water causing or suppressing corrosion of the concrete are of great importance, inasmuch as many concrete structures are exposed to the action of such waters. Unfortunately, information of the complicated corrosion phenomena is largely of a qualitative rather than quantitative nature. The rate of

flow of corrosive water over concrete surfaces and the porosity of the concrete greatly affect the rates of corrosion. It is known that most acids, both organic and inorganic, attack or at least slowly disintegrate concrete (2352, 2353, 2354). Petroleum oils and many coal-tar distillates have little or no effect on concrete although creosote, cresol, phenol, and many vegetable and animal oils may disintegrate concrete slowly. Algae in contact with submerged concrete blocks have been reported to cause disintegration of the concrete (2233).

The sulfates attack and disintegrate concrete (2355); with sodium and magnesium sulfates the rate of attack seems to be proportional to the concentration up to a steady rate at 10,000 mg/l and 5,000 mg/l respectively. The effect of sulfurous acid solutions upon concrete have been studied (196). "If the SO₃ concentration is less than 25 ppm injury from this source will be mild and inconsequential. When the SO₃ is in the hundreds of ppm it is a possible source of great harm..."

In addition to sulfates in natural waters of streams, lakes, ground-water basins, and bodies of salt water, consideration must be given to the free carbon-dioxide content of the waters. According to Dr. Ruth Terzaghi (197) free carbon dioxide in concentrations exceeding 20 mg/l will attack concrete sufficiently rapidly to require protective action. Such concentrations occur frequently in ground water, in deep lakes, and possibly in marine estuaries (2356). There appears to be a synergistic action between free carbon dioxide and sulfates, and where this combination is present, the use of sulfate-resisting cement is recommended.

Distilled or "lime-hungry" waters, and those having less than 100 mg/l of carbonate hardness, have been reported as being corrosive to concrete under specific conditions of low temperature or continuously renewed water (2357). High concentrations of organic matter in water (e.g., sewage) may, under certain conditions of high temperature and low pH, favor the production and release of hydrogen sulfide. This gas, in turn, may redissolve in condensate on other concrete surfaces, be oxidized to sulfates, and attack the concrete (198, 2355, 2358).

CONFECTIONARY (see also Sugar Making)

Water used in making confections, as that used in other food-making processes, should have a quality suitable for drinking and should be free from constituents that interfere with the complex chemical and physical reactions of the process. Soft waters have been noted as being better for making hard candies; but ordinary distilled water, with a pH value below 7.0, may favor the inversion of the sucrose sugar to produce a sticky candy. Few definite limits of quality for water to be used in confectionaries have been recommended; however, the results of long study of such waters indicate that natural waters with less than 50 or 100 mg/l of the usual dissolved mineral constituents generally are satisfactory. Summarized below are the recommended threshold concentrations of various constituents in waters to be used for making confectionaries:

Constituent	Range of Recommended Threshold Values in mg/l
Taste and odor	_
Iron	0.2
Manganese	0.2
Iron and manganese	0.2
Total solids	50-100
Hydrogen sulfide	0.2
pH	> 7.0
References: 152, 161, 162, 164	

COOLING WATER

Cooling, or the transfer of heat, is a very common and important step in many industrial processes. A large portion of the water utilized by industry is employed for such cooling purposes, there being several systems or methods for using water for cooling (161). The water may be circulated in a closed system, gaining heat as the product or process is cooled and losing heat in a tower or spray pond prior to recirculation. Or the water can be used first as a cooling agent and then either be wasted or be used in subsequent processes.

If a closed or recirculating system is used for cooling an industrial process, the only water added to the system is that needed largely to replace the evaporation and wind-blown or drift losses that occur in cooling towers and spray ponds. Corrosion, deposition of scale, delignification of wooden cooling towers, and the growth of microorganisms are four phenomena particularly detrimental to such cooling systems. The dangers of circulating a water that may corrode the piping and equipment of a cooling system are obvious; but on the other hand use of a water that tends to deposit scale is also detrimental to a cooling system. Not only does scale affect the physical operation of a cooling system by increasing hydraulic friction; it also diminishes the thermal efficiency of the system. The scale acts as an insulator and makes the transfer of heat from the walls to the water far less efficient. The growth of microorganisms that may act as contributors to corrosion, or as formers of slimes that foul the surfaces of cooling towers and piping, is also hazardous. A raw water introduced into such a recirculating system initially should have characteristics tending towards none of these phenomena. The make-up water, too, must be treated to conform with the desirable quality. A gradual but steady increase of undesirable constituents is possible through the continual addition of improperly prepared make-up water. While this report is not concerned with the treatment of boiler feed water or cooling water, it is significant to note the substances that are desirable or undesirable in such waters.

In the case of water used as a coolant and then wasted or then used in subsequent processes, the initial temperature of the water assumes considerable importance. Generally, the lower the initial temperature of such a water, the more desirable it is as a cooling water. Interesting estimates of the value of low-temperature water have been made (199). One of the major sources of such cooling water is ground water, which generally has a lower and more even temperature than surface waters. The U. S. Geological Survey has made thorough studies of the temperatures of the ground water through the country (200). Water is taken from and returned to rivers and lakes, and in coastal areas much cooling water

is taken from the ocean and returned directly to it. In such cases, the prevention of growths of marine organisms and the fouling of conduits and heat-exchange surfaces is desirable. If water is used once for cooling and then wasted, the treatment processes to prevent corrosion, organism-growth, and scaling should be as inexpensive as possible. In case the water is to be used in subsequent processes, the treatment of the water must not add substances that will prove deleterious to its further uses. Sometimes the subsequent use is cooling at higher temperatures. Such step-cooling can give excellent thermodynamic efficiences.

Among the technical papers reviewed in this search of the literature are studies of the deterioration of the timber (delignification) in cooling towers (201). It was found that the destruction of the wood was largely caused by sodium earbonate in the cooling water and it was recommended that the pH be maintained at 6.5-7.5 to afford a more favorable bicarbonate-carbonate equilibrium. Inasmuch as carbonates commonly give trouble by forming scale, the effects of various additives, as well as softening treatments, in preventing scale deposition have been studied (202). Sewage effluents have proved more desirable as cooling waters in some instances than extremely hard ground waters (203). In another instance (2359), treated sewage was the only dependable source of water for a cooling tower. Actually the entire problem of preventing scale formation is extremely complex, common to many other uses of water, and beyond the scope of this study. For details the reader is referred to the comprehensive book by Powell (2360) and to the ASTM Manual on Industrial Water (1654).

A corrosive or aggressive water, the converse of a scale-depositing water, also presents serious problems when used for cooling purposes. The chemical mechanism of corrosion is extremely complex, especially in cooling systems that may comprise dissimilar metals and materials. Many studies have been made of the corrosionsuppressing effects of various additives to cooling water such as silicates, chromates, hexametaphosphates, phosphates, nitrates, hydroxides, quebracho tannins, and many other substances (202, 204, 205, 206, 207, 2337, 2338). As pointed out earlier, an exhaustive study of the problem of corrosion is not pertinent to this report. Many studies too have been made of the use of various chemicals, such as chlorine, in cooling waters to suppress the growth of aquatic plants, algae, diatoms, iron and sulfur bacteria, slime-forming organisms, and the like (208, 209, 210, 211).

Warren (2361) reports that austenitic stainless-steel equipment is subject to stress-corrosion cracking when it is in contact with chloride-bearing cooling water. His laboratory studies showed that chloride concentrations as low as 10 mg/l and temperatures as low as 40° C contribute to cracking of stainless steel.

Industries that utilize cooling water, and especially those that recycle it through cooling towers, are alerted to the need for treating such water to minimize corrosion, scale formation, delignification, and slime growths. Such treatment, however, is dependent upon a steady condition of the make-up water. For this reason, industries are not as concerned about the absolute quality of

the water supply as they are about changes in quality from day to day.

In short, cooling waters should have appropriate initial temperatures and should not deposit scale, be corrosive, or encourage the growth of slimes. Among the constituents of natural water that may prove detrimental to its use for cooling purposes are hardness, suspended solids, dissolved gases, acids, oil and other organic compounds and slime-forming organisms (212). One of the most definitive lists of quality requirements for cooling waters (152) gives the following limiting concentrations:

	_
Turbidity	50 mg/s
Hardness	50 mg/
Iron	0.5 mg/l
Manganese	0.5 mg/l
Iron and manganese	0.5 mg/l

COPPER INDUSTRY

The water requirements of the copper industry have been summarized in a comprehensive report by the U.S. Geological Survey (2362), from which the following material has been abstracted.

About five-sixths of the domestic copper is mined in Arizona, Nevada, New Mexico, and Utah where most natural water supplies are highly mineralized. On the other hand, about two-thirds of the electrolytic refineries are located near New York City, where high-quality water is available.

At the source of the ore, water is used in open-pit mines to control silica dust. Such water may be of poor quality, but it must be free of petroleum products that interfere with subsequent concentration by flotation. Most of the domestic copper ore consists of low-grade copper sulfides that are first concentrated by flotation. Water for this purpose may be highly mineralized, but it should be free of acid, mud, slime, and particularly petroleum products that adhere to ore and change its specific gravity. Copper oxides cannot be separated by flotation, so the copper is usually separated from the ore by a leaching fluid consisting mostly of water to which sulfuric acid is added. The leachate then contains copper sulfate in solution which is later precipitated by passage through beds of sponge iron or iron scrap. For leaching, water of low pH and low alkalinity is desirable.

Copper smelters and electrolytic copper refineries are generally located where water of better quality is available. A by-product of copper smelting is waste heat, which is utilized in the production of steam power, for which high-quality boiler-feed water is needed. Cooling water is also needed, so the water-quality criteria applicable to these two water uses will apply. At electrolytic refineries, copper is transferred from anodes that contain about 98 percent copper and 2 percent impurities to cathode sheets of refined copper in electrolytic baths of high-quality water to which copper sulfate and sulfuric acid have been added. Cathodes are later washed with distilled water or other water of high quality. Refineries also use considerable water for cooling and boiler feed.

About 70,000 gallons of water per ton of finished copper are used in mining and concentrating the ore and about 30,000 gallons per ton for reducing the concentrate to refined copper. Thus, more water is used to produce a

ton of copper, on the average, than to produce a ton of any other major metal (2362).

COTTON PROCESSING (see Textiles)

DAIRY INDUSTRY

Water is used in the dairy industry primarily for the cleaning of pasteurizing equipment, for rinsing and cleaning tank trucks and cans, and for bottle washing. For this reason, according to Bonnet (2344), the water must be bacteriologically potable and free from chemicals that might leave harmful residues. He classifies water as "very good" when it has a total bacterial count of 25 organisms per ml or less, "good" up to 100 per ml, "passable" up to 500 per ml, and "bad" over 500 per ml.

With respect to chemical quality, the water should be free from copper, and very low in iron and manganese, inasmuch as these metals function as catalysts for the oxidation of fatty matter and for the hydrolysis of milk constituents. Hence they may cause fatty, oily, or fishy tastes in the milk products. Bonnet (2344) recommends the following limits for chemical and physical constituents:

less than 500 mg/lDry residue less than 30 mg/lNitrate, as N₂O₅ none Nitrite traces only Ammonia, as NH₃ less than 30 mg/l Chloride less than 60 mg/l Sulfate Organic matter, in terms less than 12 mg/l of KMnO₄ Hardness, as CaCO₃ less than 180 mg/l0.1 to 0.3 mg/IIron 0.03 to 0.1 mg/lManganese none Color none Odor

DISTILLERIES (see Fermentation Processes)

DYEING (see Textiles)

ELECTROPLATING AND METAL FINISHING

Plating-room processes that utilize water include the stripping or pickling operations, cleaning by organic solvents or alkaline solutions, rinsing, and electrochemical plating (2363). For acid stripping or for alkaline cleaning, the quality of water used in the baths is seldom critical, for the added chemicals far outweigh the natural constituents of the water. Hardness of water may be detrimental when soaps or alkaline cleaning agents are used.

For rinsing and for plating, water quality is frequently a major problem. High quality water is of primary importance to assure satisfactory finished work. For decorative plating, water spots and stains may necessitate reworking, wiping, buffing, and other laborious operations. Before the application of any organic corrosion-resistant coating, it is almost a necessity to use demineralized water in the final rinse, in order to achieve adhesion of the coating (2364). A high concentration of dissolved solids is especially detrimental in rinse waters (2365, 2366).

In plating baths, iron, aluminum, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfide, sulfite, sulfate, fluoride, chloride, silicate, copper, and lead have been reported to cause difficulties under certain conditions (161, 213, 214, 2364, 2365, 2367). Considerable evaporation occurs from plating baths and hence the ions present in the make-up water are concentrated to the extent that they are troublesome.

Calcium and magnesium are especially troublesome in plating baths, for they tend to precipitate to form scale on the heated surface or a sludge in the water. There is a probability of these precipitates being included in the electrodeposit, causing pits, porosity, and roughness (213, 2338, 2367). Magnesium may also reduce the "throwing power" in chromium baths (2364), but on the other hand, magnesium sulfate is sometimes added to nickel-plating baths to produce softer deposits, to minimize certain types of pitting, and to increase throwing power (213).

Sodium and potassium are generally not harmful in plating operations, although sodium may cause brittle deposits in nickel baths or reduce the throwing power in chromium solutions (2364). Iron is one of the most troublesome pollutants of many plating operations. In a nickel-sulfate bath, it may cause hazy, streaked, pitted, or brittle deposits; in acid copper solutions it produces rough deposits; in chromium baths it reduces the throwing power; in cadmium cyanide it causes hazy deposits; in silver cyanide stained deposits; and in zinc sulfate baths it lowers the plating efficiency and the protective value of the coating (2364, 2367).

Among the anions, bicarbonates are detrimental in heated alkaline baths, for they tend to be converted to carbonates and accelerate the precipitation of calcium. Moreover, they buffer the water and require higher dosages of acid or alkali to obtain the desired pH value. Chlorides have been reported to cause rough, modular, iridescent, and crystalline deposits in cadmium, copper, silver, and tin baths respectively (2364). Organic substances reduce chromium, and cause rough, hazy, streaked, colored, or pitted deposits under various conditions. Color and turbidity are similarly objectionable (2364).

The articles abstracted herewith give numerous qualitative considerations but no quantitative threshold or limiting concentrations were uncovered.

FERMENTATION PROCESSES (see also Brewing, Malt Preparation)

Closely related to the production of beer is the fermentation of ethyl alcohol from various grains. The water used in preparing the mash for later fermentation by yeast should be free of sediments, tastes, odors, and micro-organisms. Certain mineral constituents, such as calcium and magnesium bicarbonates, in the water may be of advantage in furnishing additional nutrients for the yeast. For use in blending the final product, undistilled water of satisfactory mineral quality is reported to be preferred to distilled water. No lists of quantitatively expressed criteria for quality of water for grainalcohol fermentation were uncovered in the literature (163, 171, 176, 215, 2344).

FOOD CANNING AND FREEZING (see also Food Processing, General and Food Equipment Washing)

A primary consideration for the quality of water used in food canning and especially in freezing processes is its bacerial content. Not only must such water be free of pathogens that may be transmitted to the consumer, but it must also be sterile with respect to saprophytic organisms that may cause spoilage. Many such organisms, to be sure, are destroyed in the canning process or remain dormant in frozen food, but their absence from the process water gives an added factor of safety. The California Department of Public Health has promulgated coliform standards for the water used in fish-canning operations. (See Chapter VII, Coliform Bacteria.)

The effects of chemical pollutants in the water differ for the various foods being processed. Substances that produce tastes, odors, color, deposits, toughening, deterioration of quality or vitamin content, or other detrimental changes in the food are to be avoided. Chlorophenols in a process water, for example, have been reported to have produced tastes in the syrup of canned

pears.

Hardness in the blanching water causes toughening of some vegetables, such as dry beans and peas, coatings or deposits on others, such as beets, and has no effect or may even be beneficial to some, such as cream-style canned corn. Peas and snap beans that had been blanched before freezing with waters containing various concentrations of calcium and magnesium showed a greater loss of ascorbic acid and a greater gain of calcium as the hardness was increased. Compounds of iron, manganese, copper, other minerals, and organic matter have been named as the causes of taste, odor, color, and deposit difficulties. Copper is reported to decrease the shelf life of packaged foods, especially dairy and vegetable oil products. Apparently, fluoride tends to concentrate in spaghetti, baked beans, and cereal (2333).

The various threshold or limiting values that have been recommended are summarized in the following table:

•	Range of Recommended
Constituent	Threshold Values in mg/l
Total dissolved solids	850
Turbidity	1.0-10
Taste and odor	none-low
Hardness, as CaCO ₈	50-85 (general)
	200-400 (peas)
	100-200 (fruits and vegetables)
	25-75 (legumes)
Iron	0.2
Manganese	0.2
Iron and manganese	0.2-0.3
Sodium chloride	1000-1500
pH	not lower than 7.5
Hydrogen sulfide	1.0
Fluoride	1.0
Alkalinity, as CaCO ₃	30-250
Nitrates, as N ₂ O ₅	15
Ammonia, as NH ₃	0.5
ferences: 152, 162, 164, 173, 216 223, 224, 225, 2333, 2337, 2344	, 217, 218, 219, 220, 221, 222,

FOOD EQUIPMENT WASHING (see also Baking, Carbonated Beverages, Food Canning and Freezing, Food Processing, and Ice Manufacture)

The water used to wash and rinse equipment that comes in contact with food should be as safe bacterially as drinking water. In fact, it should also be free from saprophytic organisms that may attack particles of food lodged in hard-to-clean crevices or cracks in the equipment. Constituents in the water that carry or cause tastes and odors or leave deposits or stains on the equipment are to be avoided. Inasmuch as the primary use of these waters is for washing, low hardness is one of the more important qualities to be desired. The various threshold values that have been recommended are summarized below:

DCIOW.	Range of Recommended
Constituent	Threshold Values in mg/l
Turbidity	1.0
Color	5-20
Taste and odor	
Iron and manganese	0.2
Chlorides	250
Hardness, as CaCO ₈	10
Total dissolved solids	850
Organic matter	infinitesimal
Fluoride	1.0
References: 173, 226, 2337	,

FOOD PROCESSING, GENERAL (see also Baking, Carbonated Beverages, Food Canning and Freezing, Food Equipment Washing, Ice Manufacturing)

Although they occur commonly, even in the household kitchen, the chemical reactions and physical changes brought about in commercial processing and preserving foods are extremely complex. Since water is used in nearly all of the processes and is incorporated in many of the products, the various compounds dissolved in the water enter the physical and chemical reactions. The actions of such solutes are not necessarily detrimental; in fact, some are advantageous and desirable.

Owing to the complexity of the reactions and the great number of different foods and dissolved compounds to be considered, it is unlikely that generalizations of required quality or threshold concentrations of food waters, as such, can be made. The threshold concentrations will differ for the various kinds of foods being processed. That the waters used in the process must be bacteriologically safe, at least as potable as drinking water, is one requirement commonly recommended for nearly all types of food processes. In many cases, because of the danger of spoilage or after-growth, precautions must be taken against the presence of microorganisms other than those normally considered to be pathogenic to humans.

Attempts have been made, from time to time, to summarize or generalize the quality requirements of water used for all of the many food products or processes. Inasmuch as detailed threshold values are not available for water used with many foods, the few that have been recommended for general food use are summarized below, although their applicability to any specific problem is necessarily doubtful.

Range of Recommended

*	ivanyo oj recommended
Constituent	Threshold Values in mg/l
Turbidity	1-10
Color	5-10
Taste and odor	Low-barely noticeable
Iron	0.2
Manganese	0.2
Iron and manganese	0.2-0.3
Alkalinity, as CaCO ₃	30-250
Hardness, as CaCO ₃	10-250
Total dissolved solids	850
Fluoride	1.0
References: 152, 162, 2337, 2344, 2368	•

ICE MANUFACTURING (see also Food Equipment Washing and Food Processing, General)

Since manufactured ice should be clear, colorless, tasteless, ordorless, and bacteriologically safe, the water used to make it should have similar qualities. Steam was used for power in the early manufacture of ice and consequently distilled water for making ice was easily and economically available. The very clear, crystal-like appearance of ice produced from such distilled water became associated, in the consumer's mind, with purity and quality. With the advent of electrical power, however, the use of such relative pure water was no longer economical and the effects of various salts dissolved in the natural water had to be considered.

Dissolved salts produce opacity in the ice; hence various methods of treating both the raw water and the freezing water had to be devised. Calcium and magnesium, for example, are troublesome but they can be removed rather easily from the natural water. Several classifications of waters have been made which indicate from the results of a chemical analysis the probable quality of the ice and the treatment required during freezing. In these classifications, the effects of chlorides are weighted 75 percent of the effects of the sulfates; the carbonates, 125 percent. The weighted concentrations, in mg/l, are summed to give a number that will indicate the probable treatment required. The upper threshold values, beyond which it is said that merchantable ice cannot be made, range from 684 to 710 mg/l.

In freezing large blocks of ice, the dissolved minerals tend to concentrate in the central core, making it cloudy (2369). Some ice manufacturers pass the water for ice through an ion-exchange column prior to freezing, for the purpose of reducing the number of times that the core must be removed to get clear ice.

With the wide adoption of electric refrigerators and automatic ice-making equipment, much ice is now made in small units near the point of use, utilizing municipal water of drinking-water quality. Slight cloudiness in ice cubes is seldom noticed or considered to be detrimental.

Depending upon the processes used for the manufacture of ice, the maximum allowable concentrations of dissolved solids that have been recommended range from 170 to 1300 mg/l, with several around 300 mg/l. In Charlotte, North Carolina, an increase in the fluoride content from 0.1 mg/l to about 1.5 mg/l was reported to cause serious brittleness and cracking of ice blocks (152, 162, 164, 168, 173, 183, 227, 228, 229, 230, 231, 232, 233, 234, 235, 2337, 2368, 2369).

IRON AND STEEL MANUFACTURING (see Steel Manufacturing)

LAUNDERING

The most important constituent to be avoided or eliminated in water used for laundering is hardness, because of the wastage of soap and the formation of curds. Also of great detriment is the presence of iron and manganese which, even in low centrations, can cause stains on the materials being laundered. Manganese is especially objectionable in water used in laundry work and textile processing. Concentrations as low as 0.2 mg/l may cause

dark-brown or black stains on fabrics and porcelain fixtures (2342). Leptothrix, Crenothrix, Gallionella, and other iron-depositing organisms are reliable indicators of iron and manganese and of the unsuitability of such water for laundries. High bicarbonate alkalinity, too, may cause staining difficulties.

A summary of the range of recommended threshold and limiting concentrations of various constituents in waters used for laundering processes is presented herewith.

Constituent	Range of Recommended Threshold and Limiting Concentrations in mg/l		
Hardness, as CaCOs	0-50		
Iron and manganese	0.2-1.0		
Iron	0.2-1.0		
Manganese	0.2		
Alkalinity, as CaCOs	60		
Ha	6.0-6.8		

References: 152, 161, 236, 237, 238, 239, 993, 2342

LEATHER PROCESSES (see Tannery Operations)

MALT PREPARATION (see also Brewing, Fermentation Processes)

In the preparation of malt, steeping is the process of soaking grain in water to provide sufficient moisture to start enzyme production and germination which precede the breakdown of cell walls and the hydrolysis of the stored foods. Inasmuch as the steeping solution gradually becomes an excellent medium for the growth of bacteria, it is important that the water used be relatively free of microorganisms.

The tannins, resins, and bitter substances in the husks of coarse barleys are most readily removed by alkaline waters. Water that is too soft may dissolve large proportions of mineral salts and soluble protein derivatives, which are valuable nutrients for yeast. On the other hand, water that is too hard may not remove certain undesirable constituents from the grains. Freedom from objectionable tastes and odors, low contents of nitrate, ammonium salts, and iron, and a uniform temperature of about 13°C are among the characteristics recommended for water used to steep grains for malt production. No lists of quantitatively expressed criteria were uncovered in the literature (172, 175, 176, 240, 2345).

METAL INDUSTRIES (see Aluminum Industry, Copper Industry, Electroplating and Metal Finishing, Steel Manufacturing)

MILK INDUSTRY (see Dairy Industry and Food Processing, General)

OIL WELL FLOODING

For oil-well-flooding operations it has been recommended that the water should not contain more than 0.1 mg/l of iron, should not have a low alkalinity or pH less than 7, and should not be corrosive. The growth of algae in water stored for such operations should be prevented with algicides (349). In many oil-well-flooding situations, it is necessary to filter the water or brine through sand or diatomite units in order to prevent the recharged well from clogging with colloidal particles or microbiological cells.

PAPER MANUFACTURE (see Pulp and Paper Mills)

PHOTOGRAPHIC PROCESSES

Although the photographic processes of developing and fixing images on paper or films involve complicated and sensitive chemical reactions, the quality requirements of the waters used for making up the various solutions and for washing and rinsing are relatively tolerant. An extreme example of this tolerance is the fact that sea water can be used both to wash films and paper if followed with a rinse in fresh water, and to prepare developing and fixing solutions, if the sludge of precipitated chemicals is carefully settled out. For the more usual circumstances, however, hardness in concentrations of more than 200 mg/l usually causes difficulties, whereas in concentrations of less than 100 mg/l difficulties are rare.

Municipal water supplies are generally adequate for most photographic processes. Indeed, they are better in some respects than distilled water, for washing with extremely soft water or distilled water may result in reticulation or softening. The dissolved salts in natural waters prevent reticulation (2370). Most photographic processors are willing to use municipal water provided that it is constant in quality from month to month, so that experience in its use can be developed.

In the mixing of developers, the presence in the water of the chlorides and bromides in excess of 25 mg/l exerts a restraining action, but sodium carbonate tends to speed up the action of a developer. Developers mixed with water containing sodium or potassium sulfides even in small concentrations can cause bad chemical fog. The presence of 100 mg/l of calcium sulfate is reported to cause fogging, as will colloidal sulfur and certain bacteria. High concentrations of calcium and/or magnesium may cause precipitation in alkaline processing solutions. Dissolved solids will crystallize on films and plates when dried unless precautions are taken during drying. Dissolved gases in wash waters can produce blisters on papers. Spots and stains can be caused by iron, manganese, suspended solids, turbidity, and color in the solution and wash waters. Iron in concentrations greater than 0.1 mg/l may cause staining, but some photographic products will tolerate as much as 10 mg/l of ferrous or ferric iron.

Excessive copper causes emulsions to fog. Moreover, 1.0 mg/l of copper results in significant loss of strength of color developer after two weeks and 10 mg/l causes appreciable loss in a few days (2370). Tin, lead, and zinc in concentrations up to 10 mg/l have not proved to be deleterious. Fluoride can also be tolerated up to at least 10 mg/l (161, 239, 241, 242, 2370).

PLASTICS

Plastics have been defined as organic minerals that can be easily molded or shaped by mechanical or chemical action to give tough, non-crystalline substances that are solid at ordinary temperatures. They are made from molding compositions prepared from various raw-material groups such as resin or cellulose derivatives (binders); cellulose, wood flour, cotton fiber, asbestos, mica, or fabrics (fillers); dyes and pigments; and various plasticizers, catalysts, and lubricants.

There are many types of plastics and many complicated processes for manufacturing them. The quantity and quality of water vary in importance, depending on the different manufacturing methods. In general, water of unusual quality is not needed. For special situations, involving only a small proportion of the total water requirement at a plastics manufacturing plant, de-ionized city water is customarily used (152, 162, 189, 2371).

PULP AND PAPER INDUSTRY

The water requirements of the pulp and paper industry have been summarized in a comprehensive report by the U. S. Geological Survey (2372). Much of the material relating to water quality in that report and in the following summary is based upon the publications and specifications of the Technical Association of the Pulp and Paper Industry (TAPPI).

The manufacture of pulp and paper is highly dependent upon an abundant supply of high-quality water. The major purposes for which water is used include the digestion or cooking of wood chips to make pulp, repeated washings of the cellulose pulp, transportation of the pulp and other constituents of paper in a thin slurry through preparatory processes and finally onto the paper machine, boiler feed, and cooling. This section deals only with the process water used for washing of pulp and for paper making. Boiler-feed water and cooling water are covered separately.

Suspended matter is undesirable in process waters because it decreases brightness, affects colors, interferes with texture and uniformity, clogs wire screens, and favors growth of slimes. Hardness gives difficulties by reacting with sizing compounds and causing the precipitation of calcium carbonate. It also tends to form scale on washing screens, the wire of paper machines, and similar equipment. Turbidity and color can cause trouble in the finer-grade products. Dissolved gases in the process waters sometimes cause corrosion of the machinery, and carbon dioxide, in concentrations above 25 mg/l, has been reported to affect adversely the formation of sheets on the paper machines. Iron, manganese, silica, and organic matter are among other undesirable constituents of the process waters (239, 2373).

The presence in the process waters of microorganisms, such as bacteria, algae, and fungi, may lead to difficulties from the growths of slimes, slick spots on the paper, and the development of odors.

In 1940, Miller (243) presented the information in Tables 5-5 and 5-6 to show the ranges of concentration of various substances in process waters used by different paper mills.

Other studies of the desirable quality characteristics of water to be used in paper manufacturing have been made from time to time. Perhaps of greater interest, however, are the specifications for the chemical compositions of several process waters that have been approved, as tentative standards, by the Water Committee of the Technical Association of the Pulp and Paper Industry. These tentative standards, or specifications, are summarized in Table 5-7 and the remarks, definitions, and notes to each are reproduced in the pages immediately following the table. It is understood that paper mills find these specifications to be satisfactory with the possible exception of the limit of 2.0 mg/l for residual chlorine in water used for fine paper. Where dyes are used, they

may be affected by chlorine concentrations in excess of 0.3 mg/l.

RAYON AND ACETATE FIBER INDUSTRIES

The water requirements of the rayon-fiber and acetatefiber industries are described in a comprehensive report by the U. S. Geological Survey (2374) from which much of the following material has been abstracted.

These artificial fibers, resembling silk, are made from purified wood cellulose or cotton linters by one of three processes identified as viscose rayon, euprammonium rayon, or cellulose acetate. The purified cellulose or cotton linters are prepared by methods similar to those used for wood or rag pulp in the fine paper industry. The wash waters for purifying such pulp should be purer than the requirements for fine paper (see Pulp and Paper Industry), and in general should comply with the recommendations in the following tabulation.

The rayon processes, viscose and cuprammonium, produce a filament of regenerated cellulose whereas the cellulose acetate process produces a compound of definite chemical composition. All of the processes involve solution of the cellulose in strong alkali or acid liquors to dissolve undesirable constituents, formation of the threads by filtration and extrusion, air drying, spinning, and finally finishing operations such as bleaching and washing. Process water is used primarily in the initial chemical solutions and in the finishing operations. In quality, it should meet the limits shown in the following tabulation.

In addition to process water, rayon-fiber plants use large quantities of water for power production and air conditioning, inasmuch as many of the processes involving the fine fibers are sensitive to temperature and humidity. Indeed, Mussey (2374) reports an average of 110 gallons of water used to produce a pound of rayon fiber, of which 32 gallons were process water and 78 gallons were used largely for air conditioning and power production (for quality requirements, see Boiler Feed Water and Cooling Water). For the manufacture of a pound of acetate fiber, the average total water use was reported at 170 gallons (2374).

Owing to the fact that rayon and acetate plants require abundant supplies of clean soft water, they are generally located in the eastern area of the United States. Recommended threshold and limiting concentrations of various constituents in water used in the viscose process are summarized below:

Range of Recommended Threshold and Limiting Concentrations in mg/l for Manufacture of Viscose Fayon

	for manufacture of viscose reason			
Constituent	Pulp Production	Manufacture		
Turbidity	5	0.3		
Color	5			
Hardness, as CaCO3		55		
Iron and manganese		0.0		
Manganese		0.0		
Iron	0.0	0.0		
Total solids				
Alkalinity, as CaCOs				
pH		7.8 - 8.3		
Aluminum oxide				
Silica				
Copper	<5			
References: 152, 162, 189, 2374, 2	405			

TABLE 5-5

RANGES OF CONCENTRATION OF VARIOUS SUBSTANCES IN WATER USED BY PULP AND PAPER MILLS

IN WATER COLD DI FOLI ACTO TATALA					
(An	ter Miller) (243)	Number of Mills			
	Range in mg/l	Reporting Process			
Constituent	(except pH)	Water in This Range			
·	0-10	34			
Turbidity	10-50	6			
	50-635	$\overset{\circ}{2}$			
		24			
Color	0-10	13			
	10-50 50-150	8			
		16			
Iron	0-0.1	16 16			
	0.1-0.5	3			
	0.5-1.0	3			
	1.0-1.5	4			
	1.5-4.0				
Manganese, as Mn	0-"trace"	19			
	0.005-0.05	3			
	0.05 - 4.0	6			
Hardness, as CaCO₃	0-25	9			
	25-50	14			
·	50-100	6			
	100-200	9			
	200-300	5 6			
	300-400	1			
	400-766	·			
Alkalinity, total	0-25	19			
	25-50	10			
*	50-100	1			
	100-200	10			
	200-400	3			
Alkalinity, phenolphthalein	0-0.1	19			
• •	0.1-10	4			
	10-80	0			
	80-200	2			
Sulfates	0-10	15			
	10-20	7			
	20-50	8			
	50-100	5			
	100-200	4			
	200-300	1			
Chlorides	0-10	30			
U	10-20	6			
	20-50	9			
	50-100	1			
Total dissolved solids	0-10	0			
Total dissource in	10-50	4			
	50-100	16			
	100-200	6			
·	200-300	6			
4	300-400	. 3			
	400-600	5			
Total solids	0-50	0			
2002	50-100	17			
	100-200	5			
	200-300	. 6			
	300-600	8			
pH value	5.8-6.0	3			
F	6.0-6.5	4			
	6.5-7.0	5			
	7.0-7.5	19			
•	7.5-8.0	3			
	8.2-8.3	5			
•	8.3-9.2	1			

RUBBER (see Synthetic Rubber)

STARCH INDUSTRY

In the manufacture of starch, water should be as soft and mineral-free as possible inasmuch as any precip-

itated salts will accumulate in the starch, which should not leave any ash on ignition. Iron and manganese are especially detrimental in that they give a yellowish discoloration to the starch. A limit of 1.0 mg/l has been recommended for iron (2344).

STEEL MANUFACTURING

About two decades ago, the Bethlehem Steel Company of Sparrows Point, Maryland, required additional sources of water for use in the manufacture of steel products. Large quantities of sea water were used for cooling and condenser purposes but a search was made for a source of fresh water with a minimum safe yield of 50 mgd. Various possible sources of a supply of this magnitude were investigated and the economic and physical requirements soon led to a consideration of the use of the treated effluent from the Back River Sewage Treatment Plant of Baltimore City. According to Wolman (249):

"The quality of water desirable for the various industrial processes was not easily definable, since the exact specifications of water quality for these uses were not known in detail. No unanimity of agreement existed apparently in the steel trade on the characteristics of water harmful or harmless in the individual industrial process.

"These waters for the most part are used for cooling of blast furnaces and open hearths, of rolls in all the rolling mills, of gas washers, of wire machines and for

the quenching and granulating of blast furnace slag and for cleaning of gases. For this reason a number of plant scale experiments were carried out in the various processes and over extended periods, in order to shed some light upon the desirable or objectionable characteristics.

"The local studies, and field observations made elsewhere throughout the country, indicated that the following characteristics determine a desirable quality of water for steel manufacture. They are:

1. Temperature preferably below 75°F. Chlorides preferably below 175 ppm.

3. pH between 6.8 and 7.0.

4. Hardness below 50 ppm.

5. Suspended matter below 25 ppm. Organic content as low as possible.

Corrosion potential at the lowest possible level."

It is interesting to note that, according to the terms of the agreement between the city and the company, the city makes every practicable effort to maintain the following characteristics of the treated effluent:

"(a) The hydrogen ion content shall not exceed 7.8 or fall below 6.5, calculated on the basis of monthly averages.

"(b) The total suspended solids shall not at any time exceed an instantaneous maximum of fifty parts per million and the monthly average of such solids shall not exceed twenty-five parts per million. This requirement shall not apply to effluent discharged from the secondary

TABLE 5-6 PERMISSIBLE UPPER LIMITS OF IMPURITIES IN PROCESS WATER USED IN PAPER MILLS (After Miller) (243)

		(After Mille	er) (243)		
Designation of Mill	Sulfate, mg/l	Chlorides, mg/l	Dissolved Solids, mg/l	Total Solids, mg/l	pН
10 12 15	70 	4.5 30	425 140	425 150 100	7.0-7.2 7.3 6-7
17 19 27	7	0.75 13	59 50 64	250	7.4 7.3 7.0
29	50-200	4-12	153-283	160-290	7.2-7.6 not over
31 43	<u></u>	0			7.1
44	20	10	75	75	6.8-7.3 6.0-7.5

TABLE 5-7 SUMMARY OF SPECIFICATIONS FOR CHEMICAL COMPOSITION OF PROCESS WATERS FOR MANUFACTURE OF VARIOUS PAPERS

Substance Groundwood Paper Sulphate Pulps (See Note C) Fine Paper (See Note C)	· · · · · · · · · · · · · · · · · · ·		HOLVELOVE OL AWKI	OUS PAPERS		
Turbidity as SiO ₂ 50* 50* 25* 40 100 10 10 10 10 10 10 10 10 10 10 10 1	Substance	Paper	Sulphate Pulps			Fine Paner
a series was no profit.	Turbidity as SiO ₂ Color in platinum units Total hardness as CaCO ₃ Calcium hardness as CaCO ₃ Magnesium hardness as CaCO ₃ Alkalinity to methyl orange as CaCO ₃ Iron as Fe Manganese as Mn Silica (soluble as SiO ₂) Total dissolved solids Free carbon dioxide as CO ₂ Chlorides as Cl	50* 30 200 150 0.3 50 500 10	(See Note B) 25* 5 100 50 50 75 0.1 0.05 20 250 10	Bleached 40 25 100 75 0.2 0.1 50 300 10	Unbleached 100 100 200 150 1.0 0.5 100 500	(See Note D) 10 5 100 50 75 0.1 0.05 20 200 10

settling tanks connected with the trickling filter unit, which effluent shall not at any time contain total suspended solids in excess of an instantaneous maximum of eighty parts per million and not exceeding, in monthly average, fifty parts per million.

- "(c) The five-day twenty-degree Centigrade biochemical oxygen demand shall not exceed an instantaneous maximum of forty-five parts per million, and its monthly average shall not exceed twenty-five parts per million. This requirement shall not apply to effluent discharged from the secondary settling tank connected with the trickling filter unit, the five-day twenty-degree Centigrade biochemical oxygen demand of which effluent shall not exceed an instantaneous maximum of eighty parts per million, and the monthly average of which shall not exceed forty parts per million.
- "(d) The chloride content shall not exceed one hundred seventy-five parts per million calculated on the basis of monthly averages" (249).

Perhaps more significant than the use of treated municipal sewage for the manufacture of steel has been recirculation and re-use of water at the Fontana plant of the Kaiser Steel Co. With a make-up of only 2.5% per cycle, water is used about 40 times before being lost through steam or evaporation. Recirculated water is treated to remove accumulations of suspended pollutants

(248). Water-quality requirements were not specified in the surveyed literature.

SUGAR MANUFACTURE

The refining of sucrose sugar from its natural sources in sugar cane or beets is an imporant industry, especially in California. The processes largely involve extracting and concentrating techniques, but care must be exercised to prevent the inversion of sucrose to other related sugars. Relatively little information dealing with the quality requirements of process water for sugar manufacturing was uncovered, although there is no dearth of information relating to the polluting characteristics of sugar-manufacturing wastes, especially from the beetsugar process.

All process water in sugar manufacture should be as free as possible from dissolved solids and completely devoid of suspended solids. Hard water is especially deleterious for it may form precipitates that accumulate in the refined sugar. Process waters should be sterile, not only with respect to coliform bacteria and pathogens but also to saprophytic organisms that may cause destruction of saccharose.

In sugar refineries, great care must be exercised to make sure that no sugar gets into the boiler-feed water, where it is especially detrimental (see Boiler Feed Water).

Note A: Specification E 602 S-48 for Chemical Composition of Process Water for Manufacture of Groundwood Papers (244). "This specification should be considered only as a guide in determining the quality of water to be used in the manufacture of groundwood papers.

"DEFINITION—By groundwood papers are meant coarse papers composed primarily of groundwood fibers such as are used for news, telephone directories, cheaper grades of catalogues, pulp maga-

"LIMITATION-This specification does not apply to process water for groundwood papers made from southern pine, nor to process water to be used for groundwood pulp manufacture.

"NOTES—1. Chlorides are limited to 75 ppm because chloride concentrations in excess of this amount tend to promote corrosion of metal parts in the manufacturing system.

"2. A limit for organic material is not included, since the nature of the organic material is a controlling factor. For some types a much higher limit may be allowable than for others. The limit can color has a limiting effect on some of the more objectionable types of soluble organic matter. In general, organic materials should be kept as low as possible in process water.

Note B: Specification E 603 S-49 for Chemical Composition of Water for Manufacture of Soda and Sulfate Pulps (245). "This specification should be considered only as a guide in determining the quality of water to be used in the production of alkaline pulps.

"DEFINITION—By alkaline pulps are meant those pulps produced by chemical cooking processes known as the soda process and the sulfate or kraft process.

"IIMITATION—This specification for process water applies to pulp manufacture only and not to the subsequent manufacture of papers for alkaline pulps. It is prepared upon the premise that the pulp will be processed in the normal way and without a final treatment to offset the effects of undesirable impurities in the water. Process_water_of less purity is suitable if the pulp undergoes a final corrective treatment.

"This specification is prepared upon the further premise that the pulps may be bleached.

"NOTES-1. Chlorides are limited to 75 ppm because chloride incentrations in excess of this amount tend to promote corrosion of metal parts in the manufacturing system.

"2. Calcium and magnesium compounds are limited to 50 ppm each because of their tendency to form scales upon equipment and precipitates on the pulp where water comes in contact with the highly alkaline chemicals used in process.

"3. Color, iron, and manganese are kept low because of their tendency to be absorbed by and to lessen the brightness of bleached

"4. Silica is kept low because of its tendency to be absorbed by and to increase the ash content of the pulp, and its possible tend-

ency to aggravate scaling in the evaporators and to interfere with the settling of the white liquor."

NOTE C: Specification E 601 S-53 for Chemical Composition of Process Water for Kraft Paper Manufacture (351). "This specification should be considered only as a guide in determining the quality of water to be used in the manufacture of kraft

papers.
"DEFINITION—By kraft papers are meant coarse papers composed of unbleached wood fibers produced by the sulfate process and used primarily for wrapping and other packaging purposes. High-grade sulfate papers, bleached or unbleached, such as condenser tissue, writing, book, file, folder, electrical insulating, and metal wrapping, require water as specified in TAPPI Standard E 600 S-48.

"NOTES—1. Chlorides are limited to 200 ppm because chloride concentrations in excess of this amount are effective in promoting corrosion of metal parts in the manufacturing system.

"2. A limit for organic materials is not included, since the nature of the organic material is a controlling factor. For some types a much higher limit may be allowable than for others. The limit on color has a limiting effect on some of the more objectionable types of soluble organic matter. In general, organic materials should be kept as low as possible in process water.

"3. This specification deals with process water for kraft paper.

"3. This specification deals with process water for kraft paper manufacture. It does not apply to the process water to be used for kraft pulp manufacture."

NOTE D: Specification E 600 S-48 for Chemical Composition of Process Water for Manufacture of Fine Paper. "This specification should be considered only as a guide in determining the quality of water to be used in the manufacture of fine papers. The figures given are believed to be the upper limits of concentration of the significant impurities which are permissible in the manufacture of the general run of fine papers.

'DEFINITION-By fine papers are meant bond, ledger, book, and writing papers.

"NOTES—1. Certain special papers such as facial, cigarette, filter papers, photosensitive papers condenser tissues, may require process water of a greater degree of purity than above specified.

"2. A limit for pH is not included since desirable limits for pH will depend to a large extent upon the particular type and quality of paper being made, the composition of the water, and the condition of operation.

"3. A limit for soluble sulphates and chlorides is not included since these will be limited by the amount of total dissolved solids.

"4. A limit for organic materials is not included since the nature of the organic material is a controlling factor. For some types a much higher limit may be permitted than for others. The limit on color has a limiting effect on the more objectionable types of soluble organic matter. In general, organic materials should be kept as low as possible in process water."

Recommended threshold concentrations of various constituents in water to be used for sugar manufacturing are shown below.

Constituent	Recommended Threshold Values in mg/l
Calcium	
Magnesium	70
Suitate	20
Chloride	20
Bicarbonate, as CaCO ₃	
Iron	01
References: 189, 250, 2343, 2344, 2375	

SYNTHETIC RUBBER

The manufacture of synthetic rubber involves the polymerization of raw materials such as farm-grown carbohydrates, coal, crude petroleum, limestone, salt, water, and air. Large quantities of cooling water and smaller quantities of process water are required. Non-corrosiveness and freedom from suspended matter and algal growths are among the desirable qualities of water reported from a synthetic rubber plant in Pennsylvania. Water having a hardness of more than 50 mg/l and an oxygen demand greater than 3 mg/l, measured by the potassium permanganate test, was found to cause trouble in another plant in West Virigina (189, 251, 252).

TANNING OPERATIONS

An ancient art with a history of several thousand years, tanning involves complex chemical reactions that are not thoroughly understood. Only in the last 50 to 75 years have significant changes been made in the tanning processes, and even now much of the skill depends on "rules-of-thumb." In the last decade, the development of synthetic tanning substances and the extended use of chromium compounds have altered the old arts and processes.

Freedom from iron and manganese, and low concentrations of free carbon dioxide, bicarbonate hardness, color, and turbidity, are among the desirable quality characteristics of waters used in soaking of hides and tanning of leathers. Iron and manganese in such waters are objectionable, for they may cause stains and discolorations.

During the liming process, the presence of bicarbonates and carbon dioxide may cause the deposition of calcium carbonate precipitates which are dye-resistant. High bicarbonates are also reported to cause a swelling of hides (2368). Although hardness in the water may interfere with certain processes, such as leaching tannin extracts, dyeing, and fat liquoring, it apparently does not interfere with chrome tanning or waste dyes in acid baths (161).

A summary of the recommended threshold and limiting concentrations of various constituents in water used for tanning leather is shown below:

	Range of Recommended
	Threshold and Limiting
	Concentrations in mg/l
Turbidity	20
Color	10-100
Hardness, as CaCO ₂	50-513
Alkalinity, as CaCO ₈	128-135
pH	6.0-8.0
Iron and manganese	0.2
Iron	0.1-2.0
Manganese	0.1-0.2
References: 152, 161, 189, 239, 253, 254, 2	368

TELEVISION PICTURE TUBE MANUFACTURE

Several processes in the manufacture of monochrome television picture tubes require distilled or demineralized water. Salts that might contaminate the phosphorus coating or form gas when the tube is hot must be eliminated (2376).

TEXTILE MANUFACTURE (see also Rayon and Acetate Fiber Industries)

For the waters used in the various textile processes, such as wool scouring, cotton, keiring, dyeing, and finishing, the absence of suspended matter, turbidity, color, iron, manganese, hardness, and organic matter is desirable Sufficient concentrations of suspended matter, color, iron, or manganese can cause staining difficulties in textiles. Manganese is especially objectionable in water used for laundry work and in textile processing. Concentrations as low as 0.2 mg/l may cause dark brown or black stains on fabrics and porcelain fixtures. Hardness can interfere with the soaps used in the various washing operations and lead to the deposition of curds on the textiles. Hardness, too, is reported to increase the breakage of silk in reeling and throwing operations. Some hardness has been described as advantageous in waters used for wool scouring. Nitrates and nitrites are reputed to be very injurious in the dyeing of wool and silk. Organic matter and microorganisms in the process water can lead to the development of stains, odors, and growths on the textiles being treated.

A summary of the range of recommended threshold and limiting concentrations of constituents in waters used in the various textile-manufacturing processes is shown below.

·	Range of Recommended
	Threshold and Limiting
Constituent	Concentrations in mg/l
Turbidity	0.3-25
Color	0-70
Iron and Manganese	0.2-1.0
iron	0.1-1.0
Manganese	0.05-1.0
Hardness, as CaCO ₃	0-50
Chemical oxygen demand	8
Heavy metals	none
Calcium	10
Magnesium	5
Sulfate	100
Chloride	100
Bicarbonate, as CaCO ₃	200

References: 152, 161, 162, 250, 255, 256, 257, 258, 259, 260, 261, 2333, 2337, 2342, 2377, 2378

AGRICULTURAL WATER SUPPLY (Irrigation)

When water from irrigation or precipitation is applied to cultivated land some of it may run off as surface flow or be lost by direct surface evaporation, while the remainder infiltrates the soil. Of the infiltrated water, a part is used consumptively, a part is held by the soil for subsequent evapotranspiration, and the remaining surplus, if any, moves downward or laterally through the soil and substrata. The water retained in the soil is known as the "soil solution." It tends to become more concentrated with dissolved constituents as relatively pure water is utilized by plants or lost by upward capil-

lary action and evaporation. The soil solution can only be rendered less saline by dilution with fresh irrigation water or rain, and by downward leaching of excess water.

Absolute limits to the permissible concentrations of salts in irrigation water cannot be fixed, for several reasons (262): (a) It is almost universally true that the soil solution is at least three to eight times as concentrated as the water that replenishes it, because of the evaporation of water from the soil surface, transpiration of plants, and the selective absorption of salts by the plants. (b) There is apparently no definite relationship between the concentration and composition of the irrigation water and those of the soil solution, which in some cases may be as much as 100 times more concentrated than the water (246). (c) Plants very widely in their tolerance of salinity, as well as of specific salt constituents. (d) Soil types, climatic conditions (such as temperature, rainfall and humidity), and irrigation practices may all influence the reactions of the crop to the salt constituents. (e) Interrelationships between and among constituents may be highly significant; the effect of one ion may be modified by the presence of another. (Such antagonistic influences operate between calcium and sodium; boron and nitrates; selenium and sulfates) (263). A comprehensive description of the relationships among irrigation water, soil, and crops is given in Agriculture Handbook No. 60 of the U.S. Department of Agriculture (1642).

Good drainage of the soil may be a more important factor for crop growth than the salts in the irrigation supply. Even when excellent waters are used, poorly drained land may sometimes go out of production; while saline waters, on the other hand, may sometimes be used on open well-drained soils (264). The "leaching requirement" (LR) is defined as the ratio of the equivalent depth of drainage water to the depth of irrigation water,

 $\frac{D_d}{D_i}$ that is required to maintain a given concentration of soil solution at the bottom of the root zone (2379). In effect, it is the percentage of irrigation water applied to soils that must be leached beyond the root zone to maintain soil solution concentrations low enough for good yields (2380).

The concentration of salts in natural irrigation waters is rarely so high as to cause immediate injury to crops. If leaching of the root zone does not take place, however, the concentration of the soil solution at this depth will increase with successive irrigations until it reaches the limit of solubility of each salt. The solubility of many salts (such as borates, chlorides, and sulfates of sodium and magnesium) is beyond the tolerance limit of many plants; consequently these salts can build up to toxic concentrations (265, 266, 267, 268). The slow filling of the soil with salts (resulting in the production of highly concentrated soil solutions) will eventually force the abandonment of an irrigated area (246). This action was probably the cause of failure of many ancient irrigation systems.

In any discussion of the quality of water for irrigation, it is necessary to consider the effects of its constituents on both the plant and the soil. The deleterious effects of salts on plant growth can result from: (a) direct

physical effects of salts in preventing water uptake by plants (osmotic effects); (b) direct chemical effects upon metabolic reactions of plants (toxic effects); and/or (c) indirect effects through changes in soil structure, permeability, and aeration (246).

Owing to the many variable factors, no rigid limits of salinity can be set for irrigation waters. According to authorities in Western Australia (282), water containing up to 1000 mg/l of salinity (dissolved solids) is suitable for growing all types of plants, including the salt-susceptible ones, provided that drainage is good. Water containing up to 2150 mg/l is suitable for most plants except sensitive ones and water containing up to 3150 mg/l has been used for growing tomatoes, cabbages, and other salt-resistant plants. Generally, 3150 mg/l is near the maximum for the safe watering of any plant, and in such instances drainage must be excellent and each watering should permit leaching from the root zone.

The substances most commonly found in natural irrigation waters are often listed under the following three headings, which more or less correspond with the three types of injury just described; (a) total salts, (b) substances found in low or trace concentration, and (c) cations and anions (269). The total salt content, the main effect of which is osmotic, is stated in terms of specific electrical conductance, a measure of concentration of ions per unit of water, and/or in terms of total dissolved solids, in milligrams per liter of water. The substances found in low concentration include compounds of boron, silicon, fluorine, sulfur, phosphorus, iron, and trace elements; nitrite and ammonium ions; hydrogen-ion concentration; and organic matter. These substances contribute to the total osmotic effect; they are often essential, in limited amounts, for plant growth; and they are often toxic above certain concentrations. The cations, Ca++, Mg++, Na+, and K+, and the anions, CO₃-, HCO₃-, SO4-, Cl-, and NO3-, contribute to the total osmotic effect. Moreover, for the most part, they are essential for plant growth; they may be toxic above certain concentrations; and they are additionally important because of their effect upon the character of the soil. Among the trace elements, toxic effects may be produced by chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, and zinc. These metals, as well as the substances in low concentration listed above, are discussed separately in Chapter VI.

Because of all the variables involved, the classification of waters for irrigation use must be somewhat arbitrary and the limits set cannot be too rigid. Many studies, particularly at the University of California and the Rubidoux and Regional Salinity Laboratories of the U.S.D.A., have resulted in the division of irrigation waters into broad categories designated as (a) "excellent to good" or "suitable under most conditions"; (b) "good to injurious" or "harmful to some plants under certain conditions"; and (e) "injurious to unsatisfactory" or "harmful to most plants under most conditions". Occasionally these classes have been further subdivided into groupings labeled "excellent", "good "permissible", "injurious", and "unsatisfactory" (246, 263, 264, 267, 268, 269, 271, 272, 273, 274, 1642, 1733, 1912, 2135, 2381).

For the sake of uniformity, the classifications reviewed for this survey have been reorganized, where necessary, to fit into the three-class system used in Tables 5-9 and 5-10. The characteristics of water, which have been accepted thus far as sufficient to determine its suitability for irrigation, are (a) the total concentration of salts, expressed as mg/l or the specific electrical conductance (EC \times 10°) in micromhos per centimeter at 25°C, (b) the percentage of sodium which is equal to $\frac{\text{Na} \times 100}{\text{Na} + \text{Ca} + \text{Mg} + \text{K}} \text{ when the}$

bases are expressed as milliequivalents per liter, and (c) boron, chloride, and sulfate concentrations. These factors may all vary more or less independently, so that water adequate in several respects may be rendered unsuitable because of a high concentration of one lone constituent, e.g. boron.

According to Doneen (1912), calcium and magnesium carbonates and calcium sulfate should not be considered in establishing standards for total salinity, owing to their limited solubility. He suggests that the remaining soluble salts be termed "effective salinity" and he proposes a tentative classification for this new parameter.

In order to facilitate the determination of water quality for various crops, plants have also been classified according to their tolerance of salinity, and according to their tolerance of boron (246, 267, 274, 1642). The salinity problem, sodium relationship, bicarbonate effect, and boron concentration in relation to the quality of irrigation water are discussed herewith in Chapter V, rather than in the appropriate part of Chapter VI, because they are so important to an understanding of water-quality criteria for irrigation.

The uptake of fission products from irrigation water and from fallout is a problem of increasing concern. According to Bowen (2382), cesium, strontium, barium, and iodine are the only important fission products that are readily absorbed and translocated by plants. As might be expected, strontium and cesium closely resemble calcium and potassium respectively in their behavior in irrigation. For further details of radioactivity in relation to irrigation, see Chapter VIII.

Many other substances whose presence in irrigation water may be undesirable have been investigated, but their limiting concentrations have not yet been fitted into standard routine systems of classification. Some of these occur in natural irrigation waters, but others such as pathogenic bacteria and insecticides are found only when they are added to the water as a result of man's activities. While it might be useful to tabulate all of these substances and their effects on irrigated crops in this section of Chapter V, the resulting tabulation would be cumbersome. Instead, the reader is referred to the effects of various trace constituents of irrigation water, summarized as "potential pollutants", in Chapters VI to X inclusive. For an interesting legal opinion involving the sodium percentage in irrigation water, see Barakis v. American Cyanamid Co. in Chapter IV, Judicial Expres-Sion.

SALINITY PROBLEMS

Certain soluble salts are essential for plant growth, but excessive concentrations of dissolved salts are harmful. In evaluating the effects of salinity on plant growth, it is seldom necessary to determine concentrations of individual salt constituents. A measurement of the osmotic pressure of the soil solution generally suffices. The electrical conductivities (EC) and total dissolved solids contents of soil solutions have been found to be sufficiently well related to their osmotic pressures to permit the substitution of EC for the more involved osmotic pressures (OP) determination. Another simplification involves substitution of the saturation extract of the soil for the more difficult-to-obtain soil solution (2383). Hence,

OP (in atmospheres) =
$$0.36$$
 (EC_e \times 10^3)

Where $EC_e \times 10^3$ is the electrical conductivity of the soil extract in millimhos per cm at 25°C. Also:

Salinity (in mg/l) = 640 (EC_e
$$\times$$
 10³)

The values of EC_e refer to the saturation extract of the soil and not to electrical conductivity in the irrigation water. It must be remembered that salinity of the soil moisture is likely to be five-fold or even ten-fold that of the irrigation water.

Moderate concentrations of chloride in the root zone (700 to 1500 mg/l in the soil moisture) usually cause chloride to accumulate in the leaves to about 1 to 2 percent of dry weight. At such concentrations, marginal leaf burn develops, leading ultimately to leaf drop, twig die-back, and possibly death of the plant. Sodium accumulations in leaves of 0.2-0.3 percent of dry weight produces leaf burns and injury (2383, 2384a).

According to Doneen (2385) the effects of salinity can best be evaluated by the "potential salinity", defined as the chloride concentration plus half of the sulfate concentration, both in meq./1. Chloride salts are highly soluble and toxic to some plants. Half the sulfate is used because this ion is less toxic to plants than chloride and because less salinity will accumulate in the soil from sulfate than from chloride, owing to the precipitation of calcium sulfate. Limiting potential salinities in meq./1 for various soil conditions and for the three classes of irrigation water described in Table 5-8 are shown below:

	Soil Condition 1	Limiting Potential Salinity, me			
		Class I	Class II	Class III	
A	Little leaching, owing to low percolation rates	3	3-5	5	
В	. Some leaching, but restrict Drainage is slow	ted. 5	5-10	10	
C.	Open soils, deep percolati easily accomplished	on 7	7-15	15	

SODIUM RELATIONSHIPS

Calcium and magnesium in the proper proportions maintain soil in good condition of tilth and structure, while the opposite is true when sodium predominates. The effect of potassium on soil is similar to that of sodium, but since the concentration of potassium is generally quite small in water, potassium is often omitted

from calculations or included in figures stated for sodium concentration. In most normal soils in arid or semiarid regions, calcium and magnesium are the principal cations held by the soil in replaceable or exchangeable form, with sodium consisting of a small percentage, i.e., about 3.0 to 7.0 percent (278, 279, 280). Such soils, when not misused, represent a favorable physical condition for root and water penetration. An increase of the exchangeable sodium percentage (ESP) to as much as 12 or 15 percent (or, according to Doneen even to 8.5 percent in some cases) causes the granular soil structure to begin to break down when the soil is moistened. Various changes take place resulting in the sealing of soil pores and a decrease in soil permeability. With further increases in the sodium percentage, the soil continues to deteriorate and its pH increases to the level of alkali soils.

TABLE 5-8 DETAILED CLASSIFICATIONS OF IRRIGATION WATERS

	% Sodium Na × 100				Boron—mg/1			015
References (a)	K + Na + Mg + Ca as meq/l	EC × 10s at 25° C. (b) in micromhos/cm	Total saits mg/l	Sensitive plants	Semi-tolerant	Tolerant	Chlorides meq/liter*	Sulfates meq/liter*
ASS I 263		<500 <500 <750 <750 <1000 <1000 <1000 <750 500-2500 500-2500 750-3000 1000-3000 750-3000	<350 <350 <350 <700 <700 <500 <525 350–1750 300–1750 -700–2000 700–2100 502–520	<0.5 <0.4 <0.5 <0.5 <0.5 < <0.67 0.5-1.12 0.4-1.0 0.5-1.12 0.5-1.12 0.5-1.12 0.5-1.2 0.5-1.2	<1.0 <1.0 <1.0 <1.0 <0.5 <0.5 <1.0 <1.33 1-2.25 1.0-2.25 1.0-2.0 0.5-2.0 0.5-2.0 1-2.25 1.33-2.50	<1.5 <1.0 <1.5 <2.0 <1.5 <2.0 1.5-3.35 1.0-2.0 1.5-3.35 2.0-3.0 1.5-3.35 2.0-3.75	<5.5 <2	<5.5 < 4 <10 <7 5.5-16.0 4-12 10-20 7-20
1733	270 >70 >70 >70 >70 >70 >75 >75 >75	>2500 >2500 >2500 >3000 >3000 >3000 >3000	>1750 >1750 >1750 >2000 >2100 1500-2500 >2100	>1.12 >1.0 >1.12 >1.0 >1.12 >1.12 >1.25	>2.25 >2.25 >2.0 >2.0 >2.0 >2.5 >2.5 >2.5 >2.5	>3.35 >2.35 >3.0 	>16 >6 	>16 >12 >20 >20

[•] meq /liter = mg/l equivalent weight, for example, meq/l of Cl⁻ = $\frac{\text{mg/l Cl}^-}{35.5}$, and meq/l of SO₄⁻⁻ = $\frac{\text{mg/l SO₄}^-}{48}$

TABLE 5-9 SUMMARY OF CLASSIFICATIONS OF IRRIGATION WATERS

_	% Na Na × 100 Na + Ca + Mg + K	Boren, in mg/l	Chlorides in meg/i	Sulfates in meg/l	EC × 10° at 25° C. Specific conductivity (Concentration of ions)	Total salts in mg/l
Class .	as med per liter				Earlier papers suggested limit of about 500,	Up to about 700
I	Less than 30-60% (Most recent work favors a 60% limit)	Boron recommendation for water of this class is generally accepted as less than 0.5 mg/l; however tolerant plants will not be injured by 1-1.5 mg/l.	,	Less than 4-10	but more recently 1000 has been accepted.	
II	30-75%	0.5-2.0 mg/l, although for tolerant plants water with boron up to 3.35 mg/l may be satisfactory	2-16	4-20	500-3000	350-2100 More than 1750
ш	More than 70-75%		More than 6-16	More than 12-20	More than 2500-3000	More than 1100

⁽a) Data from References 263, 268, 269, and 1733 have been changed to fit this table. The original papers set up 5 classes of water.

(b) EC x 10° at 25° C. is a measure of salinity. See text.

(class I Excellent to good, or suitable for most plants under most conditions.

Class II Good to injurious, harmful to some under certain conditions of soil, climate, practices.

Class III Injurious to unsatisfactory, unsuitable under most conditions.

It is easier for calcium to replace sodium in the exchange complex than for sodium to replace calcium, and unless the sodium in the soil solution is considerably in excess of the calcium, no calcium will be replaced. It must be borne in mind that the soil solution is always more concentrated than the irrigation water. If magnesium constitutes a high proportion of the total replaceable cations of the soil, more sodium will be absorbed than if calcium is the only divalent cation present (281). It has been widely recommended

that the percentage of sodium $\left(\frac{\text{Na} \times 100}{\text{Na} + \text{Ca} + \text{Mg} + \text{K}}\right)$ in irrigation water should not exceed 50-60, in order to avoid the deleterious effects on soil which have been described above. Where the soil has a high cation exchange capacity and where the irrigation water is very dilute, values above 50 may be within safe limits (2386).

Aluminum, as well as calcium, in soluble form and in appreciable quantities, has been found to counteract the injurious effects of sodium on clay; and hence applications of these cations may be used to remedy such injury (283, 348).

In 1954 the staff of the U.S. Salinity Laboratory proposed that the sodium (or alkali) hazard of irrigation water can best be expressed in terms of the Sodium Adsorption Ratio, or SAR (1642). This ratio expresses the relative activity of sodium ions in the exchange reactions with soil. It is defined as follows:

$$SAR \, = \, \frac{Na}{[\frac{1}{2}(Ca \, + \, Mg)]^{1/2}}$$

where Na, Ca. and Mg are concentrations of the respective ions in milliequivalents per liter of water. If sodium percentage is defined as

$$Na \% = \frac{100Na}{Na + Ca + Mg}$$

then SAR can be expressed in terms of the milliequivalents per liter of sodium and the sodium percentage as follows.

$$SAR = Na^{1/2} \left[\frac{2Na \%}{100 - Na \%} \right]^{1/2}$$

A thorough description of the SAR and its use is contained in Agricultural Handbook No. 60, U.S. Department of Agriculture (1642). Chapter 5 of this handbook is an excellent treatise on the entire subject of the quality of irrigation water.

Based on a SAR scale from 0 to 30 and conductivity values of 100 to 5000 micromhos per cm at 25° C a diagram has been prepared for classifying irrigation waters with respect to sodium and salinity hazards, taking into account that a given SAR represents a greater hazard when the total concentration of ions is high than when it is low. This diagram appears as Figure 25 of U.S.D.A. Handbook No. 60 and it is reproduced herewith as Figure 5-1.

Water in the Cl-SI area of the diagram can be used on almost all soils and for almost all crops without detri-

mental effects. With increasing salinity, less exchangeable sodium can be tolerated and more leaching will be required to prevent salinity damage. Waters with an SAR value greater than 10 will present an appreciable sodium hazard in fine-textured soil having high cation-exchange capacity, especially as the salinity increases. Water in the S2 range may be used on coarse-textured or organic soils with good permeability (1642, 2387). For further analysis of this diagram, the reader should consult U.S.D.A. Handbook No. 60.

Doneen (2385, 2388) uses the term "sodium index" or "permeability index" to combine the effects of the sodium and bicarbonate ions and the total concentration of cations (c) in the irrigation water, all measured in milliequivalents per liter, thus:

For a water having 5 meq/l of sodium, 4 of bicarbonate, and 8 of total cations, the index would be $\frac{5+2}{8} \times 100$ or 87.5. Doneen (2388) presents curves to show the relation of the permeability index and the total ionic concentration for three types of soil and three classes of irrigation water.

BICARBONATE EFFECTS

The sodium hazard is also increased if the water contains a high concentration of bicarbonate ions, for as the soil solution becomes more concentrated there is a tendency for calcium and magnesium to precipitate as carbonates and for the relative proportion of sodium to be increased as a consequence. Therefore the bicarbonate concentration of the water has been suggested as an additional criterion for irrigation water. It has been found convenient to express the bicarbonate value of the water in terms of the "residual sodium carbonate" (RSC) concentration, a concept devised by Eaton (2406) and defined as follows:

$$RSC = (CO_3^{--} + HCO_3^{-}) - (Ca^{++} + Mg^{++})$$

when the ionic constituents are expressed as milliequivalents (meq.) per liter.

Analyses of irrigation water and soil samples at the Salinity Laboratory have led to the conclusion that waters containing less than 1.25 meq. per liter of residual sodium carbonate are probably safe; those containing 1.25-2.5 meq. per liter are marginal; and those with more than 2.5 meq. per liter are not suitable. Marginal waters might be used successfully where good management practices are followed (1642, 2389).

BORON IN IRRIGATION WATERS

Boron is found in almost all waters used for irrigation in the U.S.A., in concentrations from a trace to over 100 mg/l. It occurs naturally in the form of borax, borates, boric acid, and various borosilicates, such as tourmaline, which are of magmatic origin. It can also be found in fertilizers and certain waste-waters, such as those from citrus washing. In most natural waters, boron probably occurs as almost completely undissociated boric acid (2379, 2390). Although traces of boron are essential for all plant growth, it is doubtful whether more than 0.5 mg/l can be applied continuously to soils without ultimately producing some plant injury (265, 275).

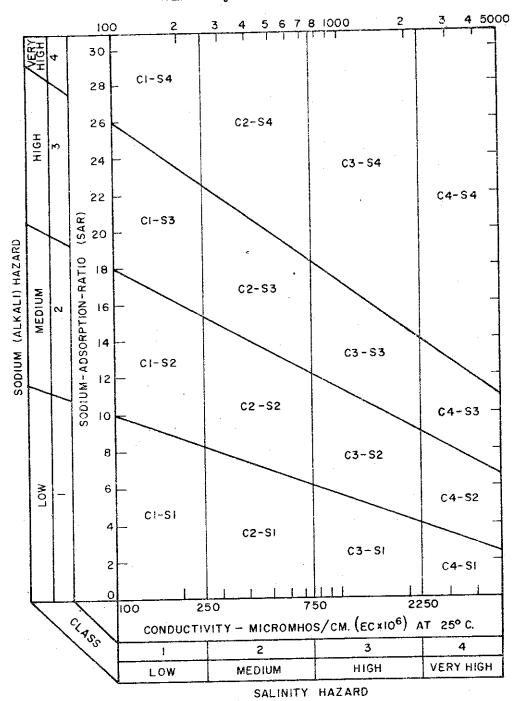


FIGURE 5-1. DIAGRAM FOR THE CLASSIFICATION OF IRRIGATION WATERS (from USDA handbook No. 60)

Agricultural authorities agree that for irrigation water the critical concentration is 0.4 to 0.5 mg/l; but because plants vary in their sensitivity to boron, waters may be classified not only according to their boron content, but also according to the tolerance of the crops to which they are applied. Tables grouping plants in the order to their sensitivity to boron will be found in sev-

eral papers, including the following references (246, 263, 264, 269, 274, 1642, 2391). The most sensitive crops are citrus, nuts, and deciduous fruits; semitolerant are truck crops, cereals, and cotton; most tolerant are lettuce, alfalfa, beets, asparagus, and date palms.

While some crops such as alfalfa and date palms are stated to be uninjured by as much as 20 to 100 mg/l of

boron, it is considered that the maximum concentration safe for even the least sensitive plants is about 4.0 mg/l (276).

Symptoms of boron injury can be distinguished easily from those of most other types of injury, although occasionally they are confused with those of sulfate poisoning. Among trees, advanced damage will result in leafyellowing and burning, premature leaf drop, and reduced yield (276, 277). The quality of soil, drainage, and climatic and other environmental factors, such as the amount of rainfall and total amount of irrigation water applied, can modify the safe concentration limits. However, symptoms of boron injury may not become apparent for as long as several years. They develop more rapidly in light than heavy soils. Concentration of the soil solution owing to evaporation and transpiration tends to accelerate their apearance, but the absorptive capacity of the soil may delay it. Parenthetically, it is essential to remember that when boron in the irrigation water is 0.5 mg/l, its concentration in the soil solution may be more than 4 mg/l (265).

It has been suggested that where the boron concentration in irrigation water is high and cannot be reduced economically, an effort should be made to grow moreresistant crops in the area affected. A widely used classification of water according to its boron concentration is shown in Table 5-10.

STOCK AND WILDLIFE WATERING

Paradoxically, data with respect to the water-quality requirements of animals are both abundant and sparse. There is a wealth of information about the LD₅₀ values of thousands of compounds fed to laboratory animals, mostly rats, mice, and guinea pigs, either in their diet or in their drinking water. Yet, there are very few quantitative data concerning the water-quality tolerances of livestock and poultry. Veterinarians and animal-husbandry personnel in this country do not appear to be particularly concerned over water quality; but in Australia and South Africa, where water for livestock is frequently highly mineralized, considerable attention has been directed to this problem.

Since the total quantities of substances ingested daily are the critical values for animal metabolism, the permissible concentrations of such substances in water will depend, to some extent, on the daily water consumption of the animals. The daily water requirements of animals vary with a number of factors, such as the temperature and humidity of the atmosphere, the water content of the diet, the degree of exertion by the individual with a resulting loss of water as sweat, and the salinity of the available supply (284, 286).

The quantity of water required for livestock and poultry has been estimated as follows (284, 286, 2392):

Animal	Water consumption in gpd per head, except as note		
Beef cattle	7-12		
Dairy cattle	10-16		
Horses	8-12		
Swine	3-5		
Sheep and goats	1-4		
Chickens	8-10 (per 100 birds)		
Turkeys	10-15 (per 100 birds)		

TABLE 5-10

PERMISSIBLE LIMITS FOR CONCENTRATION OF BORON IN SEVERAL CLASSES OF WATER FOR IRRIGATION

(After Scofield) (263)

It has been assumed that water safe for human consumption may be used safely by stock; indeed, it has been recommended that stock, for their highest production, should have such water (284, 285). On the other hand, it appears that animals can tolerate higher salinities than men, and it is conceivable also that they differ in their tolerance of specific substances.

The use of highly mineralized waters can cause among animals, as well as among men, physiological disturbances of varying degrees of severity, such as gastrointestinal symptoms, wasting disease, and death. Among the functions of animals, lactation and reproduction are generally the first to be disturbed by continuous use of waters with unfavorable mineral concentrations, so that milk and egg production are reduced, if not terminated.

It has been stated that no animal will choose to drink saline water if better water is available. Within limits, however, animals can adjust to the use of saline waters that at first were impossible to consume. On the other hand, sudden changes from slightly mineralized to highly mineralized water may cause acute salt poisoning and rapid death (282). The tolerance of animals to salts in water depends also on other independent factors, including their species, age, and physiological condition, the season of year, and the salt content of the diet, as well as the quality and quantity of salts present.

The officers of the Department of Agriculture and the government chemical laboratories of Western Australia (282, 2393) have listed the threshold concentrations of salinity tolerated by livestock in that region. The total salts include the chlorides, sulfates, and bicarbonates of sodium, calcium, and magnesium, with sodium chloride constituting as much as 75 percent of the total salinity. In general, it is stated that waters containing less than 300 grains per Imperial gallon (about 5000 mg/l can be used continuously by all livestock. Sheep are more tolerant than cattle, and cattle are more tolerant than horses or pigs. The standards in use in Western Australia as the safe upper limits for stock are reported as follows:

	Threshold Salinity Concentre	itions in
Animal	grains per Imperial gallon	mg/l
Poultry	200	2860
Pigs	300	4290
Horses	450	6435
Cattle, dairy	500	7150
Cattle, beef	700	10,000
Adult dry sheep	900	12,900

When total salts exceed the above listed concentrations, practical tests are needed to show whether or not the water is safe. When green feed is available, animals can tolerate more saline water than when "bush or scrub" is the only feed. Where feed is low in salt content, water of higher salinity is also tolerable. Sheep have used water containing 18,600 mg/l temporarily, but lambs and ewes should be watched carefully when the water has over 10,000 mg/l. The milk production of cows is reduced by saline waters containing 7150 mg/l or even less.

It has been found that when water is heavily saturated with chlorides, sulfates, carbonates, bicarbonates, sodium, calcium, and/or magnesium, the injury caused represents an osmotic effect of the total salts present rather than a toxic effect of any constituent. The maximum concentration of salts that can be tolerated safely by domestic animals appears to lie between 15,000 and 17,000 mg/l, although it is recognized that this limit may be too high for animals in production (287, 288). Alkali salts were found to be somewhat more injurious than neutral salts, sulfates more harmful than chlorides, and magnesium chloride more harmful than calcium or sodium chloride.

Other investigators have found that concentrations as high as 15,000 mg/l, while safe for limited periods, are dangerous for continuous use (284, 289, 290, 291, 292, 293, 294, 295, 296, 1756, 2394, 2395, 2396, 2397). In areas where the salinity of the water for livestock may be a critical factor for the economic survival of the inhabitants, much lower limiting values have been recommended. For waters in the State of Colorado, a salinity as high as 2500 mg/l is considered acceptable for stock (285). For Montana waters, salt concentrations up to 2500 mg/l are considered good; 2500-3500 mg/l, fair; 3500-4500 mg/l, poor; and above 4500 mg/l, unfit (297).

A South Dakota bulletin (2398) classifies water for livestock as excellent (0-1000 mg/l), good (1000-4000 mg/l), satisfactory (4000-7000 mg/l), and unsatisfactory (over 7000 mg/l). These data were derived from feeding experiments with rats, cattle, swine, and poultry.

Apart from the total salt concentration, some salts are specifically toxic to animals, even in very low concentrations, and their presence in the water may render it dangerous for use. Studies of the effects of excesses of various chemicals on animal physiology are numerous for laboratory animals, but most results deal with the diet rather than in water. Among the compounds causing concern in water are nitrates, fluorides, and the salts of selenium and molybdenum (298). The literature dealing with specific chemical substances has been summarized in Chapter VI and will not be repeated here.

It is reasonable to assume, a priori, that bacterial diseases may be transmitted to livestock as well as to men by infected water. However, the practical significance of water as a vector of animal disease has not yet been established. Several independent investigators report that cattle and swine to which sewage, sewage effluents, and polluted water have been fed over long periods (six months to two years) have shown no signs of bacterial infection (299, 300, 301, 302, 2399, 2400, 2401) even when virulent disease organisms could be isolated from samples of the fluids administered. The risk remains, however, that the udders of cows having access to polluted water or sewage-irrigated fields may become infected by typhoid or tuberculosis bacteria.

More work should be done to determine whether cattle can be infected by bacteria in the concentrations found in sewage effluents. Until more basic data can be furnished it has been recommended that water with bacterial contamination be treated completely for use by cattle (301). On the other hand it has been suggested that water should be condemned for cattle use only when bacteria known to be pathogenic to cattle can be isolated (303). The spread of beef tapeworms through sewage must also be considered; for a discussion of this problem, see Worms, Parasitic in Chapter VII.

According to the section on animal diseases in the 1956 Yearbook of Agriculture (2402), the following diseases may possibly be transmitted through contaminated drinking water: brucellosis, bovine tuberculosis, leptospirosis, listerosis, coccidiosis, and pullorum. While water is implicated as a possible route of infection it is not a primary or major source. Waste waters from slaughter houses and dairies have also been suspect as a pathway for the transmission of animal diseases, but this method of infection has not been proved (2403, 2404).

Of far greater concern are toxic algae and/or protozoa in water consumed by livestock, poultry, and wild birds. Although no quantitative evaluation of the concentration of toxic algae is given, there are numerous citations in the literature of animal deaths attributable to the consumption of such water. The subject of toxic algae is covered in detail in Chapter VII.

Oily substances may possibly be detrimental to livestock, although the strong odor and disagreeable taste of hydrocarbons are likely to prevent animals from consuming water that is heavily polluted with oil products. Waterfowl, however, have suffered heavy losses from contact with oil that sticks to their feathers and interferes with their buoyancy in water. The entire subject of the effects of oily substances on stock and wildlife is covered in Chapter VI.

PROPAGATION OF FISH AND OTHER AQUATIC AND MARINE LIFE

The number of references dealing with the effects of various pollutants on fish and other aquatic life far exceeds those pertaining to any other beneficial use of water. A large proportion of such references has been covered by this survey, but any attempt to condense such information in this part of Chapter V was deemed to be futile; instead the effects of each potential pollutant are described in Chapters VI to X inclusive. Certain general considerations and fundamental concepts are presented at this point, however, and tentative guides for threshold concentrations in fresh and saline water are suggested.

Not only are the references dealing with fish innumerable; they are also individualistic in their approaches to the problem. The conditions under which the many investigators conducted their experiments varied widely and until recently were seldom standardized. Hence, the results by several investigators of the same pollutant may not compare closely. This wide discrepancy arises from variations in the species of fish or other organism used, its prior handling, the temperature, the season, the dissolved-oxygen content, synergistic and antagonistic substances, the hardness and other mineral content of the water, and the time of exposure (2407, 2408). These effects are described in greater detail below.

Perhaps the most variable and most confusing aspect of the numerous references is the nomenclature used to

describe terminal effects. Some authors refer to threshold and limiting concentrations in much the same manner as they are used in this report, i.e., a "threshold" concentration is a point at which a physiological effect begins to be produced or a point at which the use is not damaged to any significant degree by pollution but slight effects are noticeable; and a "limiting" concentration is one at which the quality of water for a beneficial use is markedly impaired. Some investigators measure distress as indicated by the frequency of gill action, others by feeding or the absence thereof, and others by the reflexes of the fish or their response to stimulants. Some refer to "minimum lethal concentration" or "minimum lethal dose" with or without defining the time of the test and whether one or all of the test animals succumbed. The term that is appearing in recent literature and generally approved by fish toxicologists is TLm, the median tolerance limit, or the dosage required to kill 50 percent of the test animals within a specified period, such as 24 or 48 hours. Sometimes vague terms such as toxic concentration or lethal dose are used without further definition.

The time-concentration relationship is very important in all studies of tolerances of aquatic and marine life toward pollutants. Thus, an organism may withstand a 10-minute exposure to 200 mg/l of a certain substance, followed by a return to clear water, without any apparent deleterious effect; yet the same organism may succumb to repeated 10-minute exposures of that concentration or to a continuous exposure to only 20 mg/l of the same substance. On the other hand, by continuous exposure to gradually increasing concentrations, the organism may build up a tolerance to concentrations that would be toxic to a non-acclimated organism. The effects of long-term exposures of fish populations to very low sub-lethal concentrations are not clearly understood.

This relationship of concentration and time of exposure is extremely important in considering the effect of a slug of waste on the aquatic life of a stream. Normally a slug would be more deleterious than a steady uniform discharge with adequate mixing, but in some instances the concentrated slug may be less detrimental than the steady weak pollution. Or, perhaps the lack of lateral or longitudinal mixing in a stream or tidal estuary may be advantageous if it produces a local concentration into which fish may swim accidentally, but from which they can escape to clear water in a few minutes without permanent injury.

A unique concept relating to the effect of pollutants on fish has been presented by Hiatt, Naughton, and Matthews (1737, 1738). The objective of their studies was to find whether or not certain chemical compounds in highly dilute solution would effect a dispersal of schooling fish. Tests were conducted in 50-liter aquaria in which a small school (4 or 5) of Kuhlia sandvicensis was exposed to chemicals dispersed or dissolved in sea water. In the standard 2-minute span of observation, responses varied from mild to violent. Respiratory poisons induced gulping, swimming at surface, and depressed activity. Certain substances caused tetanic or flaccid paralysis, fin or operculum distension, disorientation, or convulsions. Insecticides of the irritant type were effective in dispersing schools but respiratory poisons such as cyanides were only moderately effective. The authors studied 87 compounds and presented a table describing the irritant activity of these substances. It is possible that the dispersal of schooling fish, even without other deleterious effects, might have an economic significance or modify the natural regime of the water course.

It is impossible to set up rigid quality standards or limiting concentrations for broad general application over a wide area, because the many variable factors, both physiological and environmental, can alter the responses of fish to specific constitutents of the water. Some of the most significant of these variables are considered in the paragraphs below.

a The effects of harmful substances upon fish life vary with species, size, age, and physiological condition of the individuals. Water favorable for some species may not necessarily be adequate for others that have been adapted to somewhat different conditions.

b. The effects of deleterious substances upon fish vary with the physical and chemical composition of the water supply; for example, in soft water the damaging effects of poisons are generally greater than in hard water. In distilled water, very low concentrations of some pollutants are deleterious. Decreased oxygen concentrations and increased temperatures tend to increase the susceptibility of fish to toxicants. Interrelationships between the dissolved constituents of the water supply are also extremely important. By synergistic action, the combined influence of several substances simultaneously may result in greater damage to fish life than the sum of the individual effects taken independently. For example, a combination of sulfates of cadmium and zinc, or nickel and cobalt, are additive in effect, but combinations of sulfates of copper and zinc, copper and cadmium, or nickel and zine can produce up to five times the reaction that would be expected if the effect were simply additive. On the other hand, certain combinations of salts act antagonistically to reduce the injurious effects of each. For example, mixtures of salts have become progressively less toxic when to sodium chloride solution has been added calcium chloride, then potassium chloride, and finally magnesium chloride (304, 305, 306, 307, 1459, 2407, 2408, 2409, 2410, 2411, 2412).

c. Hydrographical features of water courses and fluctuating water levels, particularly in impoundments, may also act to modify the effects of pollutants on fish in their natural habitats (308, 309).

d. In surveying the literature it is often difficult, if not impossible, to determine whether concentrations are reported for pure compounds, or with water of hydration.

For reasons such as these, as well as because of the complexity of many effluents, chemical and physical data alone may be insufficient to predict the results of pollution upon the aquatic life of a body of water (305, 311, 312, 343, 1459, 2410). While probable safe limits of concentrations of various materials can serve as a helpful guide for waste discharges, it is generally a good policy to conduct supplemental biological tests, or bioassays, upon the organisms involved, or upon suitable indicator organisms. Recently, attention has been given increasingly to the use of bioassays in or near the industrial plants whose effluents are potentially hazardous for fish (310, 343, 1734, 1735, 2412).

Bioassay procedures for the evaluation of acute toxicity of specific substances and mixed industrial wastes were developed in 1951 by a sub-committee of the Federation of Sewage and Industrial Waste Associations, under the chairmanship of Doudoroff (2413). These procedures, with appropriate extensions and modifications, have been incorporated into the 11th Edition of Standard Methods for the Examination of Water and Wastewater (469). The test was designed to determine whether or not a mixed industrial discharge is toxic (and if so at what concentration and in what period of time) when evaluated in water comparable to the quality of the actual receiving stream and with local fish. While reasonable uniformity of experimental procedure and the manner of presenting results is desirable, rigid standardization of the quality of water used and the test fish would defeat the purpose of the experiment.

Since the widespread adoption of this standard method, there has been a marked improvement in the bioassay results reported in the literature. These results are now expressed as the 24-, 48-, and sometimes 96-hour TL_m values, with a specified fish and recorded temperature. They indicate the concentration of waste required to kill 50 percent of the test animals in the specified time; but they do not reveal a "safe" or threshold concentration at which little or no deleterious effect will occur. Application factors for converting TL_m values to safe concentrations have been suggested, but as of 1961 no suitable factor or formula had been found (2038, 2412).

Extensive bioassay work has been performed to determine the effects on fish and other aquatic or marine animals and plants of dissolved oxygen, pH range, temperature, free carbon dioxide, ammonia, suspended and dissolved solids, turbidity, detergents, pesticides, oily substances, other biota, and hundreds of other specific organic and inorganic substances as well as mixed industrial wastes. These results have been summarized under the appropriate headings in Chapters VI-X inclusive.

Attention is invited especially to the subject of radioactivity and the fact that radionuclides can be concentrated by factors of 10⁵ to 10⁶ in the aquatic and marine food chains. This problem is discussed in detail in Chapter VIII and also under the next section of this chapter dealing with shellfish. It is important here to note that fish, as the end product of the aquatic or marine food chain, tend to accumulate the radioactive substances concentrated by algae, protozoa, crustacea, larvae, insects, and other links in the food chain.

CRITERIA GUIDES FOR EVALUATING THE QUALITY OF WATER USED FOR PROPAGATION OF FISH

Criteria for the quality of fresh water that will support a good mixed fish fauna were first presented by Ellis et al. (247, 313, 347) who proposed the following limits:

- Dissolved oxygen, not less than 5 mg/l;
- 2. pH, approximately 6.7 to 8.6, with an extreme range of 6.3 to 9.0;

- 3. Specific conductance at 25° C, 150 to 500 mho \times 10⁻⁶, with a maximum of 1000 to 2000 mho \times 10⁻⁶ permissible for streams in western alkaline areas;
- 4. Free carbon dioxide, not over 3 cc per liter;
- 5. Ammonia, not over 1.5 mg/l;
- 6. Suspended solids such that the millionth intensity level for light penetration will not be less than 5 meters.

In the absence of toxic substances or pollutants, the water described above is favorable, and not merely sublethal, for a mixed warm-water fish population and its food organisms. It must not, however, be assumed that fish are not found or cannot survive in waters with concentrations beyond these limits.

A review of the general quality of water required for the maintenance of aquatic flora and fauna was presented by Stander (1736) but this publication does not differ significantly from the thorough reports by Ellis.

A most thorough analysis of water-quality criteria for fish and related organisms has been conducted by the Aquatic Life Advisory Committee of the Ohio River Valley Water Sanitation Commission, as presented in its first three progress reports (2109, 2408, 2414).

SHELLFISH CULTURE

The water-quality criteria for the growing of shellfish are sufficiently different from those for fish and other aquatic or marine life to warrant special attention as a major beneficial use of water. This section, however, is limited to the bivalve mollusks: oysters, clams, and mussels. After they have passed through the larval stage, most shellfish are non-motile benthic organisms that are incapable of changing location to avoid an unfavorable environment. The bivalve mollusks, by the very nature of their feeding mechanism, tend to concentrate and accumulate viruses and bacteria, including pathogens, from the overlying water. Moreover, unlike other marine life, these forms are frequently eaten raw. In addition to bacteria, the bivalve mollusks also serve to concentrate radionuclides and paralytic poisons, as described later in this section.

OYSTERS AND CLAMS

It is generally recognized that all good oyster beds are in the estuaries of rivers or in sounds, where they are influenced to a large extent by tidal action, topography, and bottom conditions. Tidal action controls the flushing of an estuary and combines with stream flow to govern the salinity. Along with topography, it influences the cleansing of beds, the removal or deposition of silt, and the supply of food (2415). Clams, on the other hand, live in beach sands along the open ocean as well as in mud flats of estuaries and bays. The requirements for good yields of marine shellfish include favorable bottom, adequate food, and proper water quality. The bottom must be firm enough to give support to the spat and keep the adults from sinking. Shifting sands, soft mud, slimecovered debris, and sedimentary deposits are undesirable for shellfish culture (314, 315, 316, 317, 1448, 2415, 2416). The characteristics of water that are important for shellfish production include temperature, salinity, pH, oxygen concentration, copper content, and the presence of substances deleterious for shellfish development or hazardous to shellfish consumers.

Oysters and clams will tolerate wide variations in temperature, from freezing to 30° C, or perhaps to 35° C for hardier species. At water temperatures below 5° C, however, these shellfiish are almost dormant, with little or no feeding and very slow metabolism (2416). Moreover, they will not spawn in the summer if temperatures do not rise to a critical level, e.g., 13° to 18° C for Olympia oysters (Ostrea lurida) and 18° C or above for Pacific oysters (Crassostrea gigas). At higher temperatures, oysters metabolize their stored reserves of glycogen and consequently deteriorate in quality. Above 22° C, they are very poor (2415).

Oysters grow in brackish waters and can tolerate a broad range of salinities, which differs with species. They have been found at salinites from about 7,000 mg/l to 35,000 mg/l (314, 315, 318, 319, 320, 321) but salinities as low as 5,000 mg/l have caused death after several days (322). According to Churchill (315), the most favorable salt concentrations are between 18,500 and 34,000 mg/l and salinities below 13,000 mg/l can be tolerated for only brief periods. Salinities lower than 12,000 mg/l are definitely detrimental, for the oysters become watery and lose weight (2415). Other "most favorable" salinity ranges reported are 8,750 to 12,250 mg/l (320), 10,000 to 27,000 mg/l (318), and 30,800 mg/l (314).

The gaper clam appears to be restricted to a minimum salinity of about 27,000 mg/l while the softshell clam is found in a wide range of salinities, almost into fresh water (2417). Asiatic clams, which have become troublesome in western water supplies and irrigation systems, prefer fresh water (2418, 2419, 2420, 2421).

Oysters generally grow in neutral or slightly alkaline water. They may be injured by a pH lower than 6.5 (323) and they have been killed by a pH value as high as 9.1 (324).

Adequate dissolved-oxygen concentrations are essential. The minimum oxygen requirement of oysters at 25° C has been found to vary with the season, salinity, and pH. Minimum dissolved-oxygen utilization ranges from 1.1 to 5.8 ml per hour (325). Oysters have been found to be fairly tolerant of temporary oxygen deficiencies (326, 327).

For setting, oyster larvae require a copper concentration around 0.05 to 0.06 mg/l (328), but concentrations above 0.1 to 0.5 mg/l are toxic (329). The 96-hour TL_m value of copper to oysters was estimated at 1.9 mg/l, but such concentrations are not likely to occur in natural water. Oysters in water containing 0.13 to 0.50 mg/l of copper deposited so much copper in their tissues that they were unfit for food (2422).

Certain pesticides (DDT, toxaphene, aldrin, dieldrin) have been found to be deleterious to oysters in low concentrations (2423, 2515). For further details, see Chapter IX.

Oysters and clams feed by straining the water and extracting the plankton organisms. They are capable of pumping up to 50 liters per hour. The rate of pumping varies with the temperature, salinity, silt content of the water, and the concentration of organisms in the water.

It was formerly believed that the diet of oysters consisted chiefly of diatoms, but recent findings indicate that nannoplankton, especially the small flagellates, constitute the major source of sustenance (2415). Bacteria are strained out of the water along with the flagellates, diatoms, and other higher forms of marine life, but bacteria are not believed to be a significant dietary component. Owing to the fact that oysters and claims live on plankton, any change in water quality that will alter the plankton is bound to have an effect on the shellfish (314, 315, 316, 317, 1448, 2415).

Oysters are subject to competition, diseases, and predators. Indeed, it has been estimated that only one out of every million oyster eggs survives to reach adulthood. Competition occurs in crowded oyster beds, from limpets, and from plants such as watermilfoil (2424). Among major predators are drills, flatworms, and starfish. Sponges may also be detrimental (2425). Diseases are caused by a fungus (Dermocystidium marinum), a flagellate protozoan (Hexamita), a copepod parasite (Mytilicola orientalis), and possibly by dinoflagellates such as Gonyaulax scrippsae (see also Chapter VII—Fungi). Any changes in water quality that favor the development of any of its enemies are bound to have a detrimental effect on the oyster (2415).

Considerable research has been conducted to determine the tolerance of oysters to industrial pollutants such as sulfite waste liquor and oily substances. For details of these bioassays, see the specific potential pollutant in Chapter VI.

MUSSELS

Several hundred species of fresh-water mussels are known, adapted to special environmental conditions and inhabiting lakes and rivers, shallow or deep, cold or warm. For natural occurrence they require the entry and survival of fish that serve as hosts for the young mussels during a part of their development. Mussels are often a nuisance in domestic and industrial water systems (2418, 2419, 2420, 2421, 2426).

Neither marine nor fresh-water mussels can survive on a shifting bottom; however, from clean sand or soft silt to coarse gravel and boulders, a variety of bottoms are suitable for various species. Mussels are found at various depths and under different conditions of light penetration. While some suspended organic materials may serve as food, excessive turbidity or heavy silting can smother mussels or stop their feeding movements, and contribute to oxygen depletion by blanketing decaying material having an oxygen demand. Adult mussels have become inactive when the oxygen tension of the water was reduced to 20 percent of saturation, and the young are even more sensitive to oxygen deficiency. Silt and chemical pollutants constitute a threat to the survival of fresh-water mussels (331, 332). Marine mussels are especially susceptible to the accumulation of paralytic toxic plankton, as described below.

PARALYTIC SHELLFISH POISONING

The marine armored flagellate, Gonyaulax catenella, contains an alkaloid toxin which is not harmful to the flagellate nor to shellfish that feed upon it and concentrate the toxin; but it is ten times as potent toward

mice as strychnine (2427), and it can cause a paralytic effect, serious illness, and even death in humans (2428). The public-health significance of paralytic shellfish poisoning is throughly described by McFarren et al. (2429) in a comprehensive monograph on this subject.

Toxicities for this substance are expressed as mouse units (m.u.). The mouse unit is defined in terms of the amount of toxin in a shellfish extract that will cause the death with paralytic symptoms of a standard 20-gram mouse in 15 minutes from the time of injection. It is a variable unit depending on the resistance to the toxin of the mice used in the tests, but one m.u. is generally equivalent to about 0.2 micrograms of purified toxin. For toxicity tests, 100 grams of shellfish meat are extracted with 100 ml of dilute hydrochloric acid. The clear extract is separated from the meat by decantation or centrifugation. If an injection of 1 ml of this extract kills a 20-gram mouse in just 15 minutes, the toxicity of the shellfish is said to be 200 m.u. Where the shellfish are highly toxic, dilutions of the extract are used (2430).

A toxicity of 200 m.u. or less is considered harmless. When toxicity exceeds 400 m.u., the collecting of shell-fish is generally banned. Experience along the Pacific Coast has demonstrated that the mussel, Mytilus californianus, accumulates the toxin to excessive amounts during summer months; consequently the collection of mussels is generally banned during warm weather. The 1959 Manual of Recommended Practice for the Sanitary Control of the Shellfish Industry, published by the U.S. Public Health Service, specifies that "If the poison content reaches 80 micrograms per 100 grams of the edible portions of raw shellfish meat, the area shall be closed to the taking of the species of shellfish in which the poison has been found" (2431).

Oysters and clams have also been implicated in the paralytic shellfish poisoning of humans (2428, 2432, 2433). When exposed to the same water, however, the California mussel attains high toxicity levels much more quickly than oysters or clams. Oysters are least susceptible. Moreover, when the flagellate leaves the overlying water, oysters lose their toxicity most rapidly and mussels appear to retain it for the longer time (2434).

ACCUMULATION OF RADIONUCLIDES BY SHELLFISH

Radionuclides may become associated with aquatic or marine organisms in three ways: (a) through adsorption to surface areas, (b) through absorption from the surrounding medium, and (c) through ingestion as food. In some instances, especially in those tiny organisms that have a large ratio of surface to volume, adsorption is the most important mechanism (2435, 2436, 2437). Clams and oysters have been shown to accumulate and concentrate significant amounts of certain radionuclides, both in their shell and in their meat. Most of this accumulation occurs from the ingestion of nannoplankton that have adsorbed or absorbed the radio-elements, although some of the radioactivity of the shell may be attributed to direct adsorption (2438).

Mollusks, as invertebrate animals, are capable of withstanding high concentrations of radioactivity without apparent harm. A dose of 5000 to 20,000 roentgens is required to cause a 50-percent mortality in mollusks, and up to 50,000 roentgens are needed for 100-percent mortality.

tality (2439). Consequently, they can accumulate considerable amounts of radioactivity that may be harmful to human beings without being deleterious to the shell-fish themselves.

It has been demonstrated by several investigators that plankton concentrate certain elements, whether radioactive or not, from the surrounding waters. These concentration factors have been evaluated for many organisms and for many elements. They range from less than 1.0 (i.e., the concentration of the element is less in the organism than in the surrounding water) to over 100,000. Moreover, the accumulation factor is different for the shell, test, or skeleton than for the organism proper, and in higher forms it varies from organ to organ. Iodine, for example, concentrates in the thyroid whereas calcium, strontium, and iron concentrate in the shell or skeleton (2435, 2436, 2440, 2441, 2442, 2443, 2444). Inasmuch as they feed on primary accumulators of radioactivity, shellfish act as secondary concentrators. For a more detailed review of this problem, see Chapter VIII.

The USPHS has recognized the potential danger associated with accumulation of radionuclides by shellfish in the 1959 Manual of Recommended Practice for the Sanitary Control of the Shellfish Industry (2431) by making low radioactivity one of the three criteria for approved shellfish areas.

Oysters appear to be especially adept at accumulating zinc from surrounding waters (2445). It has been estimated that oysters concentrate Zn-65 by a factor of about 20,000 from their environment (2446), whereas the concentration factor for Sr-89 is approximately unity (2431). The diatom Nitzschia closterium apparently concentrates Zn-65 very effectively and hence acts as one of the steps in accumulation by shellfish (2447).

BACTERIAL AND VIRAL CONTAMINATION OF SHELLFISH

Shellfish have long been implicated as significant vectors of typhoid fever and other enteric diseases. Recently, they have been demonstrated as the transmitting agent for infectious hepatitis. Owing to the fact that they strain bacteria as well as plankton from the surrounding water, they serve as concentrators and carriers of pathogens.

The bacterial content of the meat and shell liquor of shellfish will generally reflect the bacterial quality of the water in which the animals have grown. The relationship, however, is subject to many variable factors. For example, the soft shell clam shows a consistently higher coliform content than do other species harvested from waters of similar coliform concentration. Eastern oysters harvested from the Gulf areas have higher coliform contents than those from Middle Atlantic states. Finally, there is also a marked seasonal variation (2431). Nevertheless, it can be expected that the coliform content of shellfish, as MPN per 100 grams, will be from one to ten times as high as the MPN per 100 ml of the water from which they were taken. Furthermore, Salmonella organisms as well as coliforms will survive in shell liquor of harvested shellfish for 15 to 60 days, although there is little evidence that they will multiply in shellfish (2448).

The aforementioned USPHS Manual of Recommended Practice (2431) classifies shellfish growing areas into four categories: approved, conditionally approved, re-

stricted, and prohibited areas. To be fully approved, an area must meet these three criteria:

- a. The area must not be so contaminated with fecal material that consumption of the shellfish might be hazardous. (The proximity of sewer discharges, even from secondary treatment plants, would be considered a hazard.)
- b. The area must not be so contaminated with radionuclides or industrial wastes that consumption of the shell-fish might be hazardous. (The level of radioactivity and quantitative criteria for industrial wastes are not specified.)
- c. The coliform median MPN of the water must not exceed 70 per 100 ml and not more that 10 percent of the samples may exceed an MPN of 230 per 100 ml. These limits need not be applied if it can be shown by detailed study that the coliforms are not of direct fecal origin and do not constitute a public-health hazard.

A conditionally approved area is one that meets the water-quality requirements of an approved area, but the attainment is dependent upon the proper performance of a sewage treatment plant discharging effluent directly or indirectly to the area.

An area may be classified as restricted when a sanitary survey indicates a limited degree of pollution that would make it unsafe to harvest the shellfish for direct marketing. Shellfish from such areas may be marketed after self-purification in mildly chlorinated water, or after transplantation in clean water for a suitable period. For a restricted area, the coliform median MPN must not exceed 700 per 100 ml and not more than 10 percent should exceed an MPN of 2300 per 100 ml. Otherwise, the criteria are the same as for approved areas.

If an area is so contaminated with radionuclides or industrial wastes that consumption of the shellfish might be hazardous and/or if the coliform content exceeds a median value of 700 per 100 ml or a 10 percent value of 2300 per 100 ml, the area is classified as prohibited (2431).

No bacteriological criteria have been formally established in the U.S.A. for shellfish as marketed and consumed. In 1956, however, the Shellfish Sanitation Workshop (2449), sponsored by the USPHS, adopted two-year interim bacterial standards for marketed shucked oysters with three classes as follows:

Class	Description	Coliform MPN per 100 ml	Standard Plate Count per ml
2 Ac	ceptable ceptable on condition ejectable	Not over 16,000 n* Not over 160,000 Over 160,000	Not over 50,000 Not over 1,000,000 Over 1,000,000
the	originating state will m		sh sanitation authority in s of the producer's plant acy in the market area.

In 1951, Canada adopted a similar system of classification except that the MPN limit on the acceptable class was set at 2400 per 100 ml.

It is certainly incongruous that the USPHS Drinking Water Standards restrict the coliform content of potable water to one per 100 ml, yet oysters containing 16,000 coliforms per 100 ml are considered to be acceptable. Most persons, to be sure, consume over 16,000 times as much water as oysters. Nevertheless, a significant number of people frequently eat a dozen raw oysters or clams on the half shell. It is not surprising, therefore, that shell-

fish constitute one of the weakest links in our defense against enteric infection, whether bacterial or viral.

In 1958-1959, a study was undertaken to evaluate the interim standards for shucked oysters. This study (2450) and subsequent work by Kelly et al. of the USPHS Shellfish Sanitation Laboratory (2451, 2452) have indicated that the entire coliform group of organisms is not a meaningful indicator of pollution in shucked oysters at the market. Instead, they recommended the adoption of a new interim standard based on densities of Escherichia coli. A satisfactory sample of shucked oysters should show a fecal coliform density (MPN) of not more than 78 per 100 ml and a plate count of not more than 100,000 per ml (Class Ia); except that a fecal coliform density up to and including 230 per 100 ml and/or a plate count up to and including 500,000 per ml will be acceptable in occasional samples (Class Ib). Unsatisfactory samples (Class II) are those that exceed 230 fecal coliforms per 100 ml or a plate count of 500,000 per ml.

While the bacterial quality of shucked oysters is not directly related to water-quality criteria for shellfish growing areas, an understanding of the entire problem should lead to a better evaluation of this beneficial use of water.

The role of oysters as vehicles for the transmission of hepatitis from sewage-polluted waters was demonstrated firmly during an epidemic in Sweden in 1955-56 (2453). Outbreaks of infectious hepatitis in Pascagoula, Mississippi, and in Troy and Mobile, Alabama, in January 1961, were definitely traced to oysters harvested from sewage-polluted waters near Pascagoula (2454). Finally, there is strong epidemiological evidence that much of the endemic occurrence of hepatitis along the eastern seaboard is attributable to the consumption of raw or partially cooked clams. Crovari (2455) has demonstrated that mussels may be regarded as possible vehicles for the dissemination of poliovirus. Mussels will accumulate poliovirus from seawater and passage of the virus through this mollusk does not affect its pathogenicity. It appears, therefore, that shellfish are capable of transmitting enteric viruses as well as bacteria.

SWIMMING AND BATHING WATERS

To be acceptable to the public and the regulatory authorities, waters that are used for swimming and bathing must conform to three general conditions: (a) they must be esthetically enjoyable, i.e., free from obnoxious floating or suspended substances, objectionable color, and foul odors; (b) they must contain no substances that are toxic upon ingestion or irritating to the skin of human beings; and (c) they must be reasonably free from pathogenic organisms (333).

Stream standards that have been promulgated by various state and interstate agencies (see Chapter III) seldom attempt to define the first two conditions in any but general terms, i.e., the standards are qualitative and descriptive without being quantitative. Occasionally limits are set for temperature, pH, color, and turbidity inasmuch as these parameters are easy to determine. For a further discussion of the effects of potential physical and chemical pollutants on bathing-water quality, see the specific substances as listed in Chapter VI.

The third condition given above, viz, that swimming and bathing waters be reasonably free from pathogenic organisms, has been subject to strict and definitive bacterial standards in many states and regions. It is agreed by most investigators that the bacterial quality of water for bathing need not be as high as that for drinking, but that natural bathing water should be maintained reasonably free of bacteria of known sewage origin. Present knowledge and technical procedures are not sufficient to permit the development of precise quantitative standards to distinguish between bathing beaches that are safe and those that are not safe. Despite this limitation, many state and interstate agencies have promulgated bathing-water standards.

Garber (2456) has collated and evaluated the bacterial standards for bathing water from several state and municipal agencies. He and others have noted that the coliform concentration of acceptable bathing areas vary widely from 50 to 3000 bacteria per 100 ml (330, 333, 334, 335, 2456, 2457). This observation is confirmed by a review of Chapter III of this report and its appendices. Moreover, standards are sometimes expressed in terms of the arithmetical mean, the geometrical mean, or the median of monthly samples. Occasionally, the maximum concentration is specified. Frequently, the percentage of samples that may exceed a stated concentration is indicated.

Perhaps the most restrictive standards are those of the states of Utah and Washington (see Chapter III) which limit the median coliform content of a representative number of samples to 50 per 100 ml (336). Utah further specifies that not more than 5 percent of samples should exceed 100 coliform bacteria per 100 ml. Several states limit the mean coliform density to 240 per 100 ml (see Chapter III and appendices). The most widely utilized criterion is patterned after the ORSANCO objective that the arithmetical mean coliform density not exceed 1000 per 100 ml and that this concentration not be exceeded in more than 20 percent of the samples in any one month. Some agencies add the further restriction that the average of the samples taken on any day shall not exceed 2400 coliforms per 100 ml. For proper interpretation, bacterial results should always be supplemented by sanitary surveys and local epidemiological statistics (334, 335, 337, 338, 339, 340, 341, 342, 345, 2456, 2457, 2458, 2459, 2460, 2461, 2462)

It is interesting to compare the promulgated standards with coliform concentrations that actually exist in bathing waters. Scott (2463) reported results of a comprehensive survey in 1955 and 1956 of bathing waters along the entire Connecticut coastline and also along some tidal rivers. A total of 1150 samples were examined. The total mileage of shoreline was divided into four classes, with the following results: coliform densities were equal or less than 50 per 100 ml along 27.6 percent of the shoreline, equal or less than 500 per 100 ml along 80.1 percent, and equal or less than 1000 per 100 ml along 94.5 percent. Concentrations exceeding 1000 per ml were found only at 5.5 percent of the shoreline. On the basis of these results, a standard of 1000 coliforms per 100 ml for a mean monthly density would not appear to be unduly restrictive.

THE RATIONALE OF BACTERIAL STANDARDS FOR SWIMMING AND BATHING WATERS

Insofar as this survey has been able to determine, all of the bacterial standards for bathing waters as promulgated by state, interstate, and local agencies have been established arbitrarily on the basis of esthetic considerations and ability of compliance. None are founded on sound epidemiological evidence that bacterial infections have been spread by contact with contaminated water. Yet, there must be some rationale for determining bacterial criteria for bathing waters, based on the probability of infection. Certainly the possibility of infection exists, especially in swimming pools and fresh natural waters where some of the water may be swallowed. The possibility is more remote in saline water, but it may still exist.

Two approaches have been used to assess the relationship between the bacterial quality of bathing water and the incidence of illnesses in swimmers, as compared with non-swimmers. One approach, described by Streeter (141), is based on the incidence of typhoid and paratyphoid in a region, the morbidity-mortality ratio, the relationship between these diseases and other enteric infections, the ratio of coliforms to pathogens, the frequency of swimming, the assumption that 10 ml of water will be swallowed by each bather each day, and the probability that this ingestion will cause illness. Streeter calculated that the chance of contracting typhoid fever from swimming daily for a 90-day season in the Ohio River (if it contained 1000 coliform bacteria per 100 ml) would be 1 to 950. Furthermore, the chances of contracting diarrhea-enteritis would be about 1 in 50. Streeter concluded that in this area, bathing in this water would involve no great hazard for the individual bather, although a standard of 1000 coliforms per 100 ml is admittedly a compromise between that which would be desirable and that which is practicable.

The second approach involves an epidemiological and statistical study of populations that have been bathing or swimming in contaminated waters in contrast with those who have not been in such waters or have been exposed only to water of excellent bacterial quality. If Streeter's assumptions are correct, then a statistical study of the population along the Ohio River should reveal a higher incidence of enteric infection among those who swam in polluted water than among other populations. A study of this type was made for the U.S. Public Health Service by Stevenson and his associates (532, 1655, 1656). They undertook a series of field studies of selected population groups swimming in waters of different bacterial quality, to determine the relationship between incidence of illness among swimmers and the coliform density of the water. Table 5-11 summarizes some of the basic data collected (1655).

The results indicated that illness occurred more frequently among swimmers than non-swimmers. This observation is not surprising in view of the fact that water is an abnormal habitat for man, regardless of its quality. The results also showed that when total illnesses among swimmers and non-swimmers were compared, there appeared to be no significant correlation between illness incidence and quality of the water in the areas studied.

TABLE 5-11

SUMMARY OF DATA FROM STUDIES OF BATHING WATER QUALITY

	(After Stevenson) (1655)		
Beach		Coliform Concentr MPN per 100 1		esses per 1000 en-Days
Lake Michigan, at Chicago, I Lake Michigan, at Chicago, II Ohio River, Kentucky Pool, Kentucky Tidal Water, New Rochelle, N.Y. Tidal Water, Mamaroneck, N.Y.	610	Minimum 9.1 23 230 <30 <30	Maximum 3,500 24,000 160,000 460,000 460,000	Among Non-Swimmers 3.7 5.6 7.4 3.3 3.3

It might also be of interest to note that among swimmers, eye, ear, nose, and throat ailments represented more than half of all the illnesses recorded, gastrointestinal disturbances about 20 percent, and skin irritations the remainder. Eye, ear, nose, and throat ailments represented an even higher percentage, 68 percent, of pool-swimmer illnesses.

Stevenson actually found a specific correlation between illness incidence and the quality of water in two instances. In the first case, rates were measured for several days following 3-day periods of high and low bacterial concentrations at one beach on Lake Michigan. It was observed that illness frequency was significantly higher among swimmers when the water had an average coliform density of 2300 per 100 ml than when the average density was 43 per 100 ml. In the second instance, swimming in the Ohio River when the "median coliform density" was 2700 per 100 ml appeared to have caused a significant increase in gastrointestinal illness, although the total number of such illnesses was very small (1657). Stevenson points out that these two cases do not constitute conclusive evidence of correlation between illness and bathing-water quality, because the numbers of individuals and days involved were so few.

A subsequent study was conducted by USPHS personnel on Long Island Sound to determine the relationship between illness and bodily exposure to contaminated salt water (2149). This investigation gave no evidence that variation in water quality of the sort encountered is capable of producing marked differences in the amount of illness experienced by swimmers. The data from this study were of sufficient internal consistency to indicate that significant effects would have shown up had they existed. Similar results from Poland were reported by Buczowska (2464).

In 1939 and again in 1955, the Joint Committee on Bathing Places of the Conference of State Sanitary Engineers and the Engineering and Sanitation Section of the American Public Health Association surveyed the state health departments to determine the incidence of disease attributable to swimming pools and bathing places. In 1939, there were several vague reports of sleeping sickness, sinusitis, intestinal upsets, eye inflammation, swimmer's itch, and impetigo believed to be associated with water contacts. In New Jersey, four cases of typhoid fever in 1923 and two cases in 1934 were believed to be due to bathing in grossly polluted streams. In Indiana, 144 cases of dysentery were believed to have been caused by bathing in water polluted by septic tank effluents. In

1955, the information submitted from 45 states and one territory revealed that there had been no authenticated cases of illness attributable to swimming pools and bathing places. "All in all, the 1939 and 1955 reports reveal surprisingly little reliable data to indict bathing places in the spread of disease. Whether or not intensive epidemiological investigations might produce additional information is a question" (2465).

Actually, an intensive epidemiological investigation was conducted by Moore, and his Committee on Bathing Beach Contamination, in England and Wales (2466, 2467, 2468, 2469, 2470, 2471). Extensive bacteriological and epidemiological studies were made over a period of five years in relation to more than 40 popular bathing beaches, the waters of the great majority of which were subject to contamination with sewage. The median presumptive coliform counts varied from 40 to 25,000 per ml, and as many as 40 percent of the samples contained over 10,000 coliforms per 100 ml. In addition to coliform bacteria, determinations were made for members of the salmonella group, of which 33 different species were isolated.

The general conclusions of the committee were that bathing in sewage-polluted sea water carries only a negligible risk to health and where the risk is present it is probably associated with chance contact with intact aggregates of infected fecal material. In the entire study there were four cases of paratyphoid fever that could possibly have been attributed to bathing in infected sea water. In each case, however, the bathing area was grossly contaminated with visible fecal material. The committee indicated that unless the water is so fouled as to render the bathing beach esthetically revolting, it would seem that public-health requirements are reasonably well met by the present British policy of improving grossly insanitary beaches and preventing as far as possible the pollution of the waters with undisintegrated fecal matter.

In contrast with the thorough epidemiological work of Brown and his committee, the literature contains several reports of enteric disease reputedly caused by bathing in polluted waters (2472, 2473, 2474, 2475). None of these reports, however, are supported by reputable epidemiological evidence. Indeed, Brown himself gives a thorough review (2467) of all historical information relating illness to bathing.

As a result of studies such as those described in this section on the rationale of bathing-water standards, it has been recommended that some of the strict bacterial

requirements for such waters might be relaxed (1522, 1655, 1658, 1659, 1660).

OTHER INFECTIONS FROM BATHING WATERS

There have been several reports of skin eruptions, respiratory infections, and outbreaks of other non-enteric diseases traced to water contacts. No attempt is made to cover all of these illnesses in detail, but mention of a few cases should suffice to indicate that these hazards exist. For more detail, see Chapter VII.

Abrasions of the skin that occur while swimming may become infected and produce granulomatous lesions. In Colorado at a warm mineral pool, 262 cases were found to be due to the tuberculosis-type organism Mycobacterium balnei (2476, 2477, 2478). Earlier in Sweden, about 80 cases of a similar lesion were traced to swimming pools (2479, 2480). Greenberg and Kupka (2481, 2482) have reviewed the literature relative to transmission of mycobacteria, lupus-like organisms, and other tubercular bacteria through swimming pools and contaminated waste water.

Schistosome dermatitis, or "swimmer's itch," has affected bathers in rivers, ponds, and lakes that support snails. The causative agents are the cercariae, the free-swimming larval stage of certain parasitic worms of the family Schistosomatidea. The snails serve as an intermediate host. While not related to man-made pollution, cercarial dermatitis is definitely attributable to bathing in water of less-than-desirable quality (2465, 2483, 2484).

Outbreaks of leptospirosis have occurred in the United States and most other parts of the world as a result of swimming in ponds, slow-moving streams, and even swimming pools contaminated by domestic or wild animals. This disease, like schistosome dermatitis, is due to natural sources of contamination and not to man's activities (2485, 2486, 2487, 2488, 2489, 2490, 2491).

Cases of primary tuberculosis in children have been attributed to immersion and near drowning in sewage-contaminated water (2492, 2493). A Russian source claims that tularemia may be caused by bathing in, as well as drinking, infected water (2494). Some aquatic plants, such as smartweed (Polygonum hydropiperoides) and a marine alga (Lyngbya majuscula), have been reported as causative agents of dermatitis on bathers (2287, 2495).

Although the viruses of poliomyelitis have been isolated frequently from sewage and contaminated water, there is no evidence that this disease has ever been transmitted through bathing waters (2465, 2468, 2470, 2496, 2497, 2498). Kelly and Sanderson (2499) isolated ECHO-type enteroviruses from unchlorinated wading pools in Albany, N. Y., but failed to detect viral agents in chlorinated swimming pools.

BOATING AND ESTHETIC ENJOYMENT

It is difficult to draw a sharp line dividing waters that are used for boating and esthetic enjoyment from those that are used for swimming, bathing, and water-contact sports, and from those that are used for fishing and wildlife. These three beneficial uses are normally compatible and frequently concurrent. In general, however,

the water-quality criteria for boating and esthetic enjoyment are not as rigid or restrictive as those for actual water contact by humans, fish, or wild animals. Of the three conditions listed for swimming, for example, only the first applies to boating and esthetic enjoyment.

Conditions of water quality that affect boating and esthetic enjoyment are visible floating, suspended, or settled solids arising from the disposal of sewage or garbage; sludge banks; slime infestation; heavy growths of attached plants or animals; blooms or high concentrations of plankton; discoloration or excessive turbidity from sewage, industrial wastes, or even natural sources; the evolution of dissolved gases, especially hydrogen sulfide; visible oil or grease, including emulsions; excessive acidity or alkalinity that leads to corrosion or delignification of boats and docks; surfactants that foam when the water is agitated or aerated; and excessive water temperatures that cause high rates of evaporation and cloudiness over the water.

Biological growths that are often attributable to certain industrial wastes sometimes produce infestations of slimes (2500, 2501, 2502) which interfere with boating and esthetic enjoyment. Sphaerotilis natans is especially troublesome in streams below industries that discharge wastes with a high earbon-nitrogen ratio (see Chapter VII).

Excessive inorganic nutrients (nitrates, phosphates, carbonates, silicates) hasten the eutrophication of lakes and also fertilize flowing streams with the resultant production of heavy plankton blooms (2012, 2166, 2262, 2288, 2503). In addition, attached water plants such as water hyacinth, watermilfoil, and water chestnut may clog water channels and interfere with various recreational uses of water (589, 858, 889, 891, 893, 2495, 2503, 2505). Amphipods and polychaetes, some of which utilize the organic detritus from sewage and industrial wastes, foul harbor structures and form thick masses on bottoms of ships (2506). For further details about corollary biological pollutants, see Chapter VII.

Several state and interstate agencies have promulgated bacterial standards for recreational waters that are not used for swimming and bathing. Such standards are similar to those for water contact except that they permit monthly average MPN values as high as 5000 coliforms per 100 ml during the recreational season. There does not appear to be any epidemiological evidence to support these standards. Apparently they have been adopted arbitrarily on the basis of common decency and economic attainment.

Surfactants are esthetically objectionable when they contribute to foam. Water containing alkyl benzene sulfonates (ABS) in excess of 1.0 mg/l is likely to foam when it passes over dams or riffles in a stream; indeed, the threshold for foaming in tap water may be as low as 0.5 mg/l (2063). For further detail, see Chapter X. Hexadecanol, on the other hand, apparently causes no interference with the normal recreational uses of lakes to which it has been applied for suppression of evaporation.

Boats themselves may be a source of esthetic degradation of recreational waters. Weekend surveys of a small boat harbor at Eaton's Neck near New York, free from any sources of pollution other than from boats, disclosed significant coliform concentrations in the water; but the most disturbing fact was the repeated observance of refuse, fecal matter, and toilet paper of boat origin (2507).

Considerable attention has been devoted in the past decade to the recreational use of domestic water supply reservoirs (2508, 2509, 2510, 2511, 2512). The American Water Works Association has issued a statement of policy (2513) that the recreational use of "equalizing" and "terminal" reservoirs, and the adjacent marginal lands, is inimical to the basic function of furnishing a safe and potable water supply and should be prohibited. Limited recreational use of "upstream" reservoirs is considered permissible under appropriate sanitary regulations except for those upstream reservoirs from which the water is delivered directly to the consumers with disinfection only. The California State Department of Public Health has published a comprehensive survey of the hazards associated with the recreational use of domestic water supply reservoirs (2514).

WATER POWER AND NAVIGATION

The pollutants in water that interfere with its beneficial use for water power and navigation are: (a) substances such as acid, alkali, and excessive salinity that accelerate corrosion, cavitation, or delignification, (b) debris, silt, and other suspended solids that block channels and intake devices or settle in reservoirs to reduce their useful storage, (c) organic matter that generates putrescible odors and corrosive hydrogen sulfide gas in deep reservoirs, (d) algae, fungi, worms, barnacles, and other corollary pollutants that clog passageways, cling to vessels, or accelerate corrosion, (e) marine borers that destroy wharves and docks, and (f) floating oil that poses a potential fire hazard.

Limiting and/or threshold concentrations for each of these categories of pollutants are seldom, if ever, found in the literature. Substances that accelerate corrosion include dissolved oxygen, hydrogen ions, sulfides, chlorides, free earbon dioxide, high temperatures, and certain types of bacteria and algae. To minimize corrosion by natural waters it is desirable to keep the concentration of each of these factors as low as possible, but no definitive limits can be set. As for silt, debris, and other suspended solids, it is desirable to keep all such material out of natural surface waters, but such a goal is impossible of attainment when natural sources contribute the bulk of such pollution. The formation of putrescible odors and hydrogen sulfide can be minimized by the maintenance of aerobic conditions (346, 1756) BOD, Dissolved Oxygen, Hydrogen Sulfide, and Oil in Chapter VI; and also Impoundments and Low-Flow Augmentation in Chapter II).

Much of the control over navigable waters in the U.S.A. resides with the Secretary of the Army, acting through the Corps of Engineers, in the enforcement of the River and Harbor Act of 1899. Section 13 of that Act specifies that: "It shall not be lawful to throw, discharge, or deposit, or cause, suffer, or procure to be thrown, discharged or deposited, either from or out of any ship, barge, or other floating craft of any kind, or from the shore, wharf, manufacturing establishment, or mill of any kind, any refuse matter of any kind or de-

scription whatsoever other than that flowing from streets and sewers and passing therefrom in a liquid state, into any navigable water of the United States, or into any tributary of any navigable water from which the same shall float or be washed into such navigable water; and it shall not be lawful to deposit, or cause, suffer, or procure to be deposited material of any kind in any place on the bank of any navigable water, or on the bank of any tributary of any navigable water, where the same shall be liable to be washed into such navigable water, either by ordinary or high tides, or by storms or floods, or otherwise, where navigation shall or may be impeded or obstructed: Provided, . . . that the Secretary of War, whenever in the judgment of the Chief of Engineers anchorage and navigation will not be injured thereby, may permit the deposit of any material above mentioned in navigable waters, within the limits to be defined and under conditions to be prescribed by him, provided application is made to him prior to depositing such material . . . " (emphasis added).

The original purpose of this act was to prevent shoaling and other interference to navigation caused by solids. In 1936, however, the Appellate Court sustained a decision that oil interfered with navigation by causing a hazard. As a consequence, this law can be used to prevent the discharge of oily substances from vessels in navigable waters or their tributaries and to compel treatment of wastes from refineries and other establishments.

The Secretary of the Army is charged also with the enforcement of Section 3 of the Oil Pollution Act of 7 June 1924 which reads in part, that: "Except in cases of emergency imperiling life or property, or unavoidable accident, collision, or stranding . . . it shall be unlawful for any person to discharge, or suffer, or permit the discharge of oil by any method, means, or manner into or upon the coastal navigable waters of the United States from any vessel using oil as fuel for the generation of propulsion power, or any vessel carrying or having oil thereon in excess of that necessary for its lubricating requirements and such as may be required under the laws of the United States and the rules and regulations prescribed thereunder. The Secretary is authorized and empowered to prescribe regulations permitting the discharge of oil from vessels in such quantities, under such conditions, and at such times and places as in his opinion will not be deleterious to health or sea food, or a menace to navigation or dangerous to persons or property engaged in commerce on such waters, and for the loading, handling, and unloading of oil."

This act is explicit in its application to vessels which may discharge oil to the coastal navigable waters and all inland waters navigable in fact in which the tide ebbs and flows. The 1899 Act is much broader in its scope, for it includes "any tributary of any navigable water," a phrase that embraces almost every stream in the United States.

The control over wastes "flowing from streets and sewers and passing therefrom in a liquid state" is excluded from Section 13 of the River and Harbor Act of 1899. Such control is exercised by the several states and by the U.S. Public Health Service, as described in Chapter III.

CHAPTER VI

POTENTIAL POLLUTANTS

Any substance that may enter or be contained in ground or surface waters is deemed for the purposes of this report to be a "potential" pollutant-potential in the sense that, if concentrated sufficiently, it can adversely and unreasonably affect such waters for one or more beneficial uses; and yet, if diluted adequately, it will be harmless to all beneficial uses. In view of this definition, every known substance is a potential pollutant and should be included in this investigation of waterquality criteria. Such was the intent of the first two editions of this compendium and such should be the ul-

timate goal of future revisions thereof.

In the three literature surveys that led to this edition, however, there were practical limits to the extent and scope of the work. The tremendous number of readily available references and the time required to abstract, catalogue, and evaluate them resulted in the fact that only the more-common and most-publicized pollutants are included. For the less-common minerals and compounds, few or no references were uncovered, although it is possible that significant literature exists and could be revealed in a specialized search. Indeed, this second edition includes hundreds of potential pollutants that were not mentioned in the first edition. Where no data were found, the substance has been omitted from this chapter. Later revisions of the report, however, may show the substance in question to be of significance to water-pollution-control agencies. It is hoped that the data contained herein will be of considerable value to the WPC boards in their case-by-case studies and that the framework here established can be used for subsequent revisions and expansions of this report.

The potential pollutants in this chapter are listed alphabetically by their correct or most-common names, with physical, inorganic, organic, and biological substances blended into the alphabetical listing. For chemical substances, the correct name was taken from the latest Merck Index (364) or the 43rd Edition of the Handbook of Chemistry and Physics (911), but where other names are in common use an attempt has been made to cross-reference. For example, CH₃SH is listed as Methanethiol but cross-referenced as Methyl Mer-

This second edition differs from the first and the Addendum in that biological pollutants, radioactive substances, pesticides, and surface-active agents are covered in separate chapters (VII to X inclusive). Nevertheless, this chapter remains the key one for the compendium because every potential pollutant listed in the following chapters is cross-indexed herein. When in doubt as to where to find an exotic compound that may be a pesticide and also a surface-active agent, for example, the reader is advised to check first the alphabetical listing in Chapter VI.

Where literature relating to a potential pollutant is extensive and where more than one beneficial use is involved, a standard outline has been followed. This outline gives a general statement describing principal characteristics, common uses, and likely sources of the pollutant; followed by cross-references to related substances, bibliographical reference numbers; and finally a description of the effects upon certain beneficial uses. Where the literature is sparse or where it refers almost exclusively to one beneficial use, the outline has been

discarded in favor of conventional paragraphs.

Many of the abstracted references deal with the effects upon beneficial uses of mixed wastes, involving many substances of unknown concentration, e.g., sulfite waste liquors, for which the overall strength is expressed as mg/l of total solids or BOD, or possibly in terms of the specific gravity or Baumé scale. Such wastes are treated as collective terms and listed directly as pollutants; hence the report contains such terms as "dairy wastes," "gas-plant wastes," and "metal-plating wastes." This listing of certain collective terms to the exclusion of others should not be construed as an attempt to single out a few industrial wastes for special mention; rather, it is a natural outgrowth of the cataloguing of wastes in terms of their constituent pollutants. Any industrial waste that is not listed, per se, was omitted because the polluting substances could be isolated and listed separately.

Cross referencing has been applied in many instances throughout this chapter, but as such it is far from being complete. The reader is assumed to understand the subject sufficiently well to use his own ideas of cross-referencing. When investigating the subject of "acetates," for example, the reader should check also on lead acetate, sodium acetate, zinc acetate, and similar listings.

In the literature used for this survey, the concentrations of substances are expressed in many ways, e.g., as parts per million, milligrams per liter, milliequivalents per liter, molar solutions or decimals thereof, normal solutions, or as volume dilutions of liquids and gases. Such variety in expressing concentrations is confusing to the reader and for that reason an attempt has been made in this report to convert all results to milligrams per liter. Some of these conversions are only approximate, for the original data may have been incomplete, e.g., in converting dilutions by volume the temperatures must be known in order to evaluate specific gravity precisely. In other instances, especially for mixed wastes of unknown constituents, conversion has been impossible and the original data have been presented without change. In a similar way, an attempt has been made to express all temperatures in degrees centigrade.

Just as a dictionary or an encyclopedia must abbreviate many facts and omit others, so has this chapter of the report been condensed to give only the most salient information relating to each potential pollutant. In a thorough case-by-case study, a water-pollution-control engineer will find the material as abstracted herein to be

inadequate and he may wish to investigate the extensive bibliography. To supplement this report, the WPC boards should have in their libraries a standard chemical handbook such as the latest edition of "The Handbook of Chemistry and Physics" (911) or "The Merck Index" (364), "Standard Methods For the Examination of Water and Wastewater" (469), the A.W.W.A.'s "Water Quality and Treatment" (152), a textbook of the chemical process industries such as that by Shreve (189), a book on water biology such as "The Microscopy of Drinking Water" (16), references dealing with insecticides such as those by Frear (2997) and by Rudd and Genelly (3005), and complete files of A.C.S., A.W.W.A. and W.P.C.F. journals, to mention only a few. It is recommended furthermore, that each board subscribe to "Water Pollution Abstracts," published monthly by the Water Pollution Research Board of Great Britain, which contains the finest and most complete abstracts of water-pollution literature on a worldwide basis.

The remainder of this chapter contains the alphabetical listing of potential pollutants.

ABIETIC ACID

 $C_{19}H_{29}COOH$

A widely available organic acid, prepared by the isomerization of resinous substances, this yellow amorphous powder is employed in the manufacture of esters for use in lacquers and varnishes, and in the production of metal resinates, soaps, plastics, and paper sizes. Sodium abietate from Kraft mill wastes is reported by Van Horn et al. (190, 344) to have a minimum lethal concentration of 3.0 mg/l for shiners in 120 hours at 18°C. Kawabe and Tomiyama (3240) found that pitch abietic acid was the most toxic of the ether-soluble components of the caustic soda digestion liquor at a pulp mill when tested against Scenedesmus obliquus and Carassius auratus.

ABS

(see Chapter X)

ACETALDEHYDE

CH₃CHO

This flammable liquid with a pungent odor is miscible with water. It is used extensively in the manufacture of plastics, dyes, synthetic rubber, and other chemical products. The oral LD_{50} for rats has been reported as 1.93 grams/kg of body weight.

According to Garrett and Daugherty (1441, 2959, 2960) the 24-hour TL_m for the marine pin perch (Lagodon rhomeboides) was 70 mg/l and the maximum concentration at which no deaths occurred was 60 mg/l. Toward the bluegill sunfish (Lepomis machrochirus) in soft water at 18-20°C, the 96-hour TL_m was 53 mg/l (2936). In similar water, a 50 percent reduction in growth of the diatom, Navicula seminulum, occurred when the concentration of acetaldehyde reached 249 mg/l (2936). To suppress oxygen utilization by synthetic sewage, a concentration of 230 mg/l was required (2923).

ACETAMIDE

CH₃CONH₂

Highly soluble in water, this crystalline compound is used in the plastics industry and in chemical manufac-

turing. The oral LD₅₀ for rats is reported as 30 grams/kg of body weight (364). Wallen et al. (2940) tested its toxicity toward the mosquito-fish (Gambusia affinis) in highly turbid water at 21-24°C. They found the 24-and 48-hour TL_m concentrations to be 26,300 mg/l while the 96-hour was 13,300 mg/l. Turbidity was not significantly clarified by this compound.

ACETATES

(see also Acetic Acid, Amyl Acetate, Butyl Acetate, Mercuro-Organic Compounds, Lead, Sodium, Zinc, and the other cations that form acetates)

Acetates are the salts or esters of acetic acid. They occur in numerous chemical industries and in the manufacture of synthetic textiles. Acetates appear to be much less toxic than undissociated acetic acid. Lockhart (3241) reports the taste threshold of the acetate ion to be 360 mg/l when sodium acetate is used and 1020 mg/l when potassium acetate is used.

In Lake Erie water after 48 hours exposure at 25°C, the threshold concentration of sodium acetate for Daphnia magna appears to be about 5,200 mg/l (352). Another value as high as 5,800 mg/l has been reported (353). This salt is probably toxic only when in concentration sufficient to exert an unfavorable osmotic pressure (352). The threshold of toxicity of sodium acetate at 15-18°C for Polycelis nigra (a flatworm) occurs at 8,850 mg/l (354). Phenyl mercury acetate and pyridyl mercuric acetate, however, appear to be much more toxic to aquatic organisms (see Mercuro-Organic Compounds).

Von Oettinger (3242) has compiled the following toxicological data for several acetates when the compounds were fed orally to animals:

Compound Ethyl acetate Isopropyl acetate Allyl acetate Butyl acetate Butyl acetate	Animal rats rats rats rats rats mice	LD₅ in grams/kg of body weight 5.62 6.75 0.13 4.13
Octyl acetate Benzyl acetate Benzyl acetate Heptyl acetate	rats rats rabbits rats	7.06 3.09 3.69 2.64 8.35

ACETIC ACID

CH₃COOH

(see also Acetates, Acidity, Acids-Organic)

In the pure state, acetic acid is a colorless, pungent, biting liquid, highly miscible with water. It occurs in beet-sugar, winery, vinegar, soured-fruit, wood-distillation, textile, or chemical wastes.

The oral $\rm LD_{50}$ for rats has been reported as 3.31 grams/kg of body weight and for mice 4.96 grams/kg (3242, 3243). Rats fed 100 to 5000 mg/l of acetic acid in their drinking water for 9 weeks showed a decrease in appetite and growth (2980).

Fish can stand 5000 mg/l of acetic acid for a short exposure; indeed this compound is sometimes used in the treatment of diseased fish (359). For longer exposures, however, much lower concentrations are lethal. Acetic acid can be toxic to fish without lowering the pH value to 5.0, for toxicity appears to be attributable primarily to the undissociated acid in solution; hence pH is not a reliable index of acetic-acid pollution (361).

Hardness appears to be antagonistic to the toxicity of acetic acid.

Lethal concentrations have been reported as 50 mg/l in 24 hours for brook trout and 114 mg/l in 24 hours for minnows (359). For creek chub at 15-21°C in well-aerated water, the lethal concentration ranged from 100 to 200 mg/l (1442). Some goldfish have been killed at concentrations as low as 100 mg/l during prolonged exposure (313), but the 24-hour MLD has been given as 286 mg/l (359) and as 423 mg/l (2920). For the bluegill sunfish, the 96-hour TL_m in soft water at 18-20°C was reported to be 75 mg/l (2936). Toward fingerling channel catfish at 25°C the 72-hour TL_m was approximately 270 mg/l, all fish were killed at 629 mg/l, and none at 15.8 mg/l (2979, 2981). In turbid water, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m concentrations toward the mosquito-fish (Gambusia affinis) all to be 251 mg/l.

For lower organisms, Palmer and Maloney (2041) reported that 2.0 mg/l of acetic acid had no effect on six species of algae (two blue-green, two green, and two diatoms). In a 5-day exposure in soft water at 20°C, 74 mg/l of acetic acid caused a 50-percent reduction in the growth of Navicula seminulum, a diatom (2936). The threshold concentration for immobilization of Daphnia magna in Lake Erie water after prolonged exposure at 25°C was 150 mg/l (358), but a threshold value as low as 80 mg/l has been reported (353). Ellis (313) indicates that the lethal concentration of acetic acid in hard water was 125 mg/l, with killing times of 24 to 72 hours.

ACETONE CH₃COCH₃

A volatile, inflammable, fragrant, colorless liquid that is miscible with water, acetone is used as a solvent for many organic compounds and in the manufacture of numerous substances. It may occur in wastes from many chemical industries, gas plants, coal-tar processes, paint manufacturing, or from the fermentation process by which it is produced. The oral LD_{50} for rats has been reported as 9.75 grams/kg of body weight (3244).

In stabilized tap water with adequate oxygen saturation, an acetone concentration of 792 mg/l had no effect on minnows after 24 hours (362), but in tap water sunfish were killed by concentrations of 14,250 mg/l (313, 363). Wallen et al. (2940) exposed mosquito-fish (Gambusia affinis) to acetone in highly turbid water at 23-27°C, for which the 48-and 96-hour TL_m values were both 13,000 mg/l.

The threshold concentration for immobilization of Daphnia magna in Lake Erie water with prolonged exposure at 25°C was 9,280 mg/l according to Anderson (358). The threshold concentrations for immobilization of several aquatic invertebrates in Lake Erie water at 20-25°C were reported (2955) as follows:

Organism	$Threshold \ Concentration \ in \ mg/l$
Daphnia magna, young Daphnia magna, adult Leptodora kindtii Cyclops vernalis Diaptomus oregonensis Miscellaneous fish	8,300 12,900 5,300 13,600 6,500 14,250

ACETONITRILE

CH₃CN

(see also Cyanides, Hydrogen Cyanide)

Sometimes known as methyl cyanide, acetonitrile is a colorless liquid used as a solvent for many organic compounds. It is miscible with water, but it does not appear to disocciate appreciably into methyl and cyanide ions. Consequently, it does not lead to the appreciable formation of HCN in water. For this reason, it is not expected that acetonitrile will be highly toxic.

In stabilized tap water kept saturated with oxygen, 17.1 mg/l of acetonitrile had no affect on minnows during a 24-hour exposure (362). Henderson et al. (2958) conducted bioassays using fathead minnows, bluegills, and guppies in hard and soft water saturated with oxygen at 25°C. The median toxic limits for commercial acetonitrile are shown below:

	m of	$TLm \ in \ mg/l$		
Kind of Fish Fathead minnow Fathead minnow Bluegill sunfish Guppy	Type of Water hard soft soft	24-hour 1150 1050 1850 1650	48-hour 1050 1000 1850 1650	96-hour 1000 1000 1850 1650

Adult bluegills exposed up to four weeks in water containing 100 mg/l of acetonitrile did not pick up any organoleptic properties that were apparent to a taste panel (2958).

ACETYLENE

HC = CH

This colorless flammable gas is used for welding and as a raw material for a great variety of organic syntheses. It is soluble in water at 18°C to the extent of 1,000 cc per liter (approximately 1,000 mg/l) and in such a saturated solution, sunfish were not killed by exposure for one hour (363). In stabilized tap water saturated with oxygen, Schaut (362) found that 17.1 mg/l of acetylene had no effect on minnows after one-hour exposure. Thus, minnows and sunfish appear to be able to withstand short-time exposures to this gas.

For longer exposures, however, it was found that brook trout fingerlings died in 33 hours or less in well-oxygenated water at 10° to 14°C containing 200 mg/l of acetylene, and goldfish died in 24 to 48 hours in water containing 400 mg/l (247). The State of Washington Department of Fisheries (2091) found that the critical level for fingerling chinook salmon in brackish water during a 3-day exposure was less than 3500 cc of acetylene per liter and for young rainbow trout in fresh water between 3000 and 5000 cc per liter.

ACIDITY

1. General. Strictly speaking, acidity cannot be a direct or specific pollutant, for it is merely a measure of the effects of a combination of substances and conditions in water. It may be defined as the power of a water to neutralize hydroxyl ions and it is expressed in terms of the calcium carbonate equivalent of the hydroxyl ions neutralized. Acidity is usually caused by the presence of free carbon dioxide, mineral acids such as sulfuric, weakly dissociated acids such as phosphoric that affect the buffering action, and salts of strong acids and weak bases. It is determined by titrating with 0.02N sodium

hydroxide to the methyl-orange end-point. If the initial pH value of a sample of water is less than about 4.1 or 4.2, the amount of 0.02N sodium hydroxide required to reach the methyl-orange end-point (at about pH 4.3) is a measure of the "mineral-acid acidity" and the amount required to reach the phenolphthalein end-point is a measure of the "total acidity" (469). Acidity should not be confused with pH value, for one water with a pH of 6.0 may have a low total acidity whereas another highly buffered water with a pH of 7.0 may have a high total acidity.

Acidity in surface or ground waters may be attributable to natural causes, such as humic acids extracted from swamps or peat beds, or to industrial wastes such as pickling liquors, effluent from the manufacture of explosives, acid-mine drainage, or sulfite waste liquors.

2. Cross References. Alkalinity, pH, and specific mineral and organic acids.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The U.S. Public Health Service Drinking Water Standards of 1962 (2036) do not specify limiting values for acidity. To the practical waterworks engineer, however, excessive acidity is frequently detrimental in that it must be neutralized to mitigate corrosion.

There has been a tendency to regard acid-mine streams as bacteriologically safe because of their extreme acidity. Joseph and Shay (1443), however, found *E. coli* in all of the acid-mine stream samples that they tested, and reported that although *E. coli* counts are rapidly reduced when polluted water is discharged into acid streams, a small number of viable bacteria persists even at a pH as low as 2.0.

Excessive acidity of the water promotes the solution of zine from galvanized pipes and other equipment, possibly to a degree harmful to the subsequent uses of the water (1444).

b. Industrial Water Supplies. Limits for acidity in industrial waters are seldom encountered inasmuch as such restrictions are generally expressed in terms of pH values (see pH and Chapter V).

c. Irrigation Water. Excessive acidification of soils containing nickel may render the nickel soluble, causing severe injury or death of plants (1445). In acid nutrient solutions, beryllium is highly toxic to plants (1446). Ligon and Pierre (1447) found that increasing the acidity of culture solutions from a pH of 6 to a pH of 4.5 resulted in a drop in yield of corn of about 50 percent. In general, however, moderate acidity in irrigation water is beneficial to alkali soils, for it helps to neutralize carbonates and prevent the precipitation of calcium (see Chapter V-Irrigation).

d. Fish and Other Aquatic Life. The pH values of ocean waters generally lie between 8.1 and 8.3; consequently acidity is not a factor to be considered in marine waters (346). In fresh waters, on the other hand, the pH values and acidities of natural streams vary widely, depending upon the soil and vegetation of the watershed. Brook trout were found to live comfortably in different streams with pH values ranging from 4.1 to 9.5, but in all cases the streams were substantially unpolluted and acidity, if any, was due to organic acids of natural origin (346).

Mineral-acid pollution, however, can be quite detrimental to fish at pH values considerably higher than those which fish can tolerate in unpolluted waters containing only acids of natural origin. Ellis (313) has investigated the toxicity of certain mineral and organic acids toward goldfish, and a summary of his results is shown in Table 6-1.

TABLE 6-1
TOXICITY OF ACIDS TO GOLDFISH

		(Afte	r Ellis) (313)	
		A mount added	Resulting	•
Acid		$in \ mg/l$	pH value	Period of survival
Sulfur		134*	4.3*	6.2 to 96 hours
Sulfur		134	4.5	Over 4 days
	chloric		4.0	4.5 to 6.5 hours
Hydro	chloric	159	4.5	Over 4 days
Nitric		750	3.4	0.5 to 0.8 hours
Nitrie		200	4.9	Over 4 days
Acetic		100	6.8	48 hours to over 4 days
Acetic		10	7.3	Over 4 days
Lactic		654	4.0	6 to 43 hours
Lactic		430	4.6	Over 4 days
Oxalic		1,000	2.6	0.4 to 0.5 hours
Oxalic		200	5.3	Over 4 days
Citric		894 ·	4.0	4 to 48 hours
Citric		625	4.5	Over 4 days
# To cofe	Lata	0 -47		

* In soft water. All other results were obtained in hard water.

From these and other data, Ellis concluded that any acid in a concentration sufficient to give a pH value less than 4.0 would be toxic to goldfish, but above pH 4.0 the toxicity depends on the specific action of the particular acid. Lactic acid, for example, was non-toxic in four days at pH 4.6 whereas acetic acid was toxic at pH 6.8.

Table 6-1 shows the amount of acid added and the resulting pH, but not the resulting acidity, which is a function of the buffering effect of the water. Thus, when 134 mg/l of sulfuric acid were added to soft water, the resulting pH value was 4.3 and survival was limited; but in hard water the same amount of acid gave a pH of 4.5 and extended survival. Synergism and antagonism of other substances affect markedly the toxic action of acidity; or, more likely, the toxic action of many substances is altered by the acidity of the water.

Stiemke and Eckenfelder (270) tested the reaction of bluegill fingerlings to solutions of various acids in distilled water. Acid was added at periodic intervals of time until all fish were killed. The results of their investigations are summarized in the table below.

	No. of		st Fish ied At		st Fish ied At
Acid Hydrochloric	Fish Tested	pH	A cidity mg/l	pH	Acidity mg/l
Nitrie Sulfurie	6 9	3.30 3.30 3.45	25 25 20	3.00 3.15 3.00	50 36 52
Phosphoric Acetic Propionic	3 9	3.11 3.75	78 85	$\frac{3.11}{3.65}$	78 140
Lactic Hydrochloric and sulfuric	6 3 3	3.94 3.50 3.45	55 37 31	3.84 3.41 3.05	90 50
Sulfuric and acetic Hydrochloric and acetic	- 3 3	3.45 3.50	57 62	3.20 3.47	54 80 78

In contrast to the foregoing results, Leitch (1015) reported that more than 4.0 mg/l of mineral acids will kill trout. Parsons (2797) surveyed a stream polluted by acid drainage from strip mines. In sections of the

stream where the pH dropped to 4.0 and the total acidity was 100 mg/l, no fish life and very few plankton existed.

e. Shellfish Culture. Loosanoff and Tommers reported that increased acidity, occurring either naturally as a result of the influx of acid swamp waters or as a result of industrial pollution, reduced the rate of pumping among oysters, thus interfering with their feeding activities. At a pH of 7.75 the oysters appeared to pump normally; at pH 6.5 the pumping rate was significantly lower; and at pH of 4.14 the pumping rate was only 10 percent of normal (1448).

ACIDS, ORGANIC, GENERAL

(see also pH, Acidity, and the specific acids)

Hammerton (360) reported that lactic, acetic, oleic, stearic, and palmitic acids were all destructive to portland cement, but that oxalic acid was not. Anderson (358) claims that in Lake Erie water at 25°C all of the organic acids tested, with the exception of benzoic and tannic acid, were non-toxic to Daphnia magna until they reduced the pH value to 6.0 or less.

ACRIDINE

C₆H₄CHN C₆H₄

Related to pyridine and quinoline, and like them a weak organic base, acridine is a solid substance that is only slightly soluble in boiling water. It may occur in wastes from coal-tar and gas plants, and possibly in dye wastes. It has been reported to kill perch in a concentration of 0.7 mg/l (365) and Daphnia in a concentration of 5.0 mg/l (313). Yearing trout lost equilibrium in 60 minutes at a concentration of 1.5 mg/l at 12°C (3245). A concentration of 5 mg/l was lethal to rainbow trout in two hours and to the bluegill sunfish in 13 hours. The sea lamprey withstood this concentration for 13 hours but with obvious distress (2976).

ACROLEIN

(see Chapter IX)

ACRYLONITRILE

CH₂CHCN

(see also Cyanides, Hydrogen Cyanide)

A flammable liquid used in the manufacture of plastics and synthetic rubber, and as a pesticide fumigant for stored grain (364), acrylonitrile is moderately soluble in water (3246). It does not appear to dissociate appreciably in water and consequently it does not form measurable HCN, the toxic cyanide principle. For this reason, it is not anticipated that acrylonitrile will be highly toxic to aquatic life (2958). Bandt (3247), however, states that acrylonitrile breaks down in water to yield HCN.

Daugherty and Garrett (1441) indicate that concentrations of 20 mg/l in sea water are deleterious for marine fish such as pin perch. According to Renn (2968) the tolerance level for mixed fresh-water fish is between 10 and 18 mg/l as N(38 to 68 mg/l as acrylonitrile). Bandt (3247) reports that the lower tolerance limit for fish is about 20 to 25 mg/l whereas all fish are killed within 24 hours by 100 mg/l. Garrett (2959, 2960) found the 24-hour TL_m for pin perch to be 24.5 mg/l. A concentration of 30 mg/l gave 100 percent mortality.

Henderson et al. (2958) conducted bioassays using three species of fish in both hard and soft water saturated with oxygen at 25°C. Their results as shown below are expressed as median toxic limits based on commercial acrylonitrile.

Wind of	Tupe of		TL_m in mg/l	!
Kind of Fish Fathead minnow Fathead minnow Bluegills Guppy	Water hard soft soft soft	24-hour 32.7 34.3 25.5 44.6	48-hour 16.7 21.5 14.3 33.5	96-hour 14.3 18.1 11.8 33.5

Adult bluegills exposed up to four weeks in water containing 5 mg/l of acrylonitrile did not pick up any organoleptic properties that were apparent to a taste panel (2958).

Cherry et al. (3246) studied the effect of acrylonitrile on the mixed biota in stream purification. They found that concentrations of 10 to 25 mg/l did not interfere with mixed cultures but at 50 mg/l the growth was predominantly fungal.

ACTINOMYCETES

(see Chapter VII)

ADIPONITRILE

NC(CH₂)₄CN

(see also Cyanides, Hydrogen Cyanide)

Henderson et al. (2958) conducted bioassays using three species of fish in both hard and soft water saturated with oxygen at 25°C. For commercial adiponitrile they found the following median toxic limits:

Kind of	Type of	TL_m in mg/l		
Fish Fathead minnows Fathead minnows Bluegill sunfish Guppy	Water	24-hour	48-hour	96-hour
	hard	835	835	820
	soft	1350	1300	1250
	soft	1250	815	720
	soft	1200	830	775

This compound does not appear to dissociate appreciably in water and consequently not much HCN can be formed to become toxic. Adult bluegills exposed up to four weeks in water containing 100 mg/l of adiponitrile did not pick up any organoleptic properties that were apparent to a taste panel (2958).

AEROSOL O. T.

(see Chapter X)

ALBUMIN

Egg albumin is a complex protein, soluble in water and dilute salt solutions, with a molecular weight of approximately 43,000. In stabilized tap water, Schaut (362) found that a concentration of 17.1 mg/l of albumin was not harmful to minnows during 24 hours of exposure, but the dissolved-oxygen content was lowered 28 percent, indicating that biochemical decomposition occurred.

ALBUMINOID AMMONIA or ALBUMINOID NITROGEN

(see also Ammonia and other nitrogen compounds)

Albuminoid nitrogen is defined in the 10th Edition of Standard Methods for the Examination of Water and Sewage (469) as "the nitrogen equivalent of ammonia formed or liberated from nitrogenous matter by the action of alkaline permanganate in water after expulsion of ammonia nitrogen by distillation." Its significance is difficult to determine or to define, for it merely represents a portion of the organic nitrogen that is readily released by a chemical reaction. Formerly determined and reported in most analyses of polluted waters, albuminoid ammonia (or albuminoid nitrogen if the results are reported as N rather than NH₃) is seldom used in modern analytical work in the U. S., and consequently most of the references thereto are in out-dated or foreign publications.

ALCOHOLS, GENERAL

(see also Allyl Alcohol, Amyl Alcohol, Benzyl Alcohol, Butyl Alcohol, Ethyl Alcohol, Cetyl Alcohol, Methyl Alcohol, Octyl Alcohols, Phytosterol, Propyl Alcohol, and other specific alcohols)

Under this heading are abstracted articles covering several alcohols for comparative purposes. Most of the criteria relating to specific alcohols are listed under the designated compound.

According to Welch and Slocum (3248) the acute oral toxicity of primary alcohols toward rats is as follows: methyl, 9.1 mg/kg of body weight; ethyl, 7.4 mg/kg; propyl, 3.3 mg/kg; butyl, 2.75 mg/kg; amyl, 3.3 mg/kg; hexyl, 4.1 mg/kg; and heptyl, 6.6 mg/kg.

Toxicity tests with creek chub, a fish considered to be average in tolerance, at 15 to 21° C in well-aerated water, revealed the "critical ranges" shown in the following table. Critical range is defined as the range in concentration below which all four test fish lived for 24 hours and above which all died (1442).

Alcohol	Critical Range in mg/l
n-propyl alcohol	350-500
n-amyl alcohol	350-500
mixed primary isoamyl alcohols	400-600
isopropyl alcohol	900-1100
n-butyl alcohol	1000-1400
tertiary amyl alcohol	1300-2000
tertiary butyl alcohol	3000-6000
ethyl alcohol	7000-9000
methyl alcohol	8000-17000

Hodgson (2956) determined the concentrations of primary alcohols required to stimulate the movement of the water beetle (*Laccophilus*), with the following results:

Alcohol	Critical Range in mg/l
methyl	115,000
ethyl	198,000
n-propyl	192,000
n-butyl	3,410
n-pentyl	644
n-hexyl	112

ALCOHOL SULFATES

(see Chapter X)

ALDEHYDES

(see Acetaldehyde, Benzaldehyde, Formaldehyde, Furfural, and Vanillin)

ALDRIN

(see Chapter IX)

ALGICIDES

(see specific compound in Chapter IX)

ALIPHATIC AROMATIC SULFONATES

ALIPHATIC SULFONATES

(see Chapter X)

ALKALINITY

1. General. Like acidity, alkalinity is not a specific polluting substance, but rather a combined effect of several substances and conditions. It is a measure of the power of a solution to neutralize hydrogen ions and it is expressed in terms of an equivalent amount of calcium carbonate. Alkalinity is caused by the presence of carbonates, bicarbonates, hydroxides, and to a lesser extent by borates, silicates, phosphates, and organic substances. It is determined by titrating with 0.02N sulfuric acid to the phenolphthalein and methyl-orange endpoints, the former measuring the so-called caustic alkalinity and the latter the total alkalinity. Like acidity, alkalinity is related to pH but high alkalinities should not be confused with high pH values. Thus, a relatively pure water with a pH value of 7.0 will have a low total alkalinity whereas a buffered water at pH 6.0 will have a high total alkalinity. For a more thorough discussion of alkalinity and an evaluation of the hydroxyl, carbonate, and bicarbonate components thereof, see Standard Methods For the Analysis of Water and Wastewater

Some natural waters, especially those in the southwestern U. S., are highly alkaline while others, such as those in western Washington or the New England states, are low in alkalinity. The alkalinities of streams are frequently increased by the addition of municipal sewage and many industrial wastes, too numerous to list herein.

2. Cross References. Acidity, pH, Hardness, Dissolved Solids, Carbonates, Bicarbonates, Hydroxides, and other specific substances that may affect akalinity.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. In itself, alkalinity is not considered to be detrimental to humans but it is generally associated with high pH values, hardness, and excessive dissolved solids, all of which may be deleterious.

b. Industrial Water Supplies. Alkalinity is detrimental in many industrial processes, especially those involving the production of food and beverages. It is particularly frowned upon in the production of carbonated and acid-fruit beverages because it neutralizes the natural taste-producing substances and makes the beverage more susceptible to bacterial action (179). The ranges of recommended threshold values of total alkalinities in industrial water supplies are presented in Table 6-2.

In contrast, alkalinity is desirable in many industrial waters, especially if it serves to inhibit corrosion by creating a favorable calcium-carbonate balance. In oilfield work, Nelson (349) recommends that the alkalinity

of unaerated water should be at least 20 mg/l.

c. Irrigation Water. Excessive alkalinity in irrigation water is detrimental in that it adds to the total salinity and is frequently accompanied by high pH values. In conventional chemical analyses of irrigation waters, however, alkalinity is frequently not listed (see Chapter V).

d. Stock and Wildlife Watering. High alkalinities in water are reported to have been detrimental to stock. When the caustic alkalinity reaches 50 mg/l, trouble with diarrhea in chickens begins (1019), and at a total alkalinity of 170 mg/l animals were reported to develop

diarrhea (1020).

e. Fish and Other Aquatic Life. Doudoroff and Katz (361) cite references indicating that none of the strong alkalies, such as calcium, potassium, and sodium hydroxide, has been shown clearly to be lethal to fully developed fish in natural waters when its concentration is insufficient to raise the pH well above 9.0. Interference with normal development and other damage to fish life sometimes may occur, however, at lower pH values. When caused almost entirely by bicarbonates, alkalinity does not seem to have any harmful effect upon plankton and other aquatic life (1021).

TABLE 6-2

RANGES OF RECOMMENDED THRESHOLD VALUES OF TOTAL ALKALINITIES IN INDUSTRIAL PROCESS WATERS

Industry and Process	Recommended Threshold Values in mg/l	Reference
Brewing		450 450
Light beer	75-80	152, 173
Dark beer	80-150	152, 173
Carbonated beverages	; 30-85	173
Carbonated beverages	50_	152, 180
Carbonated beverages	51.3	1016
Carbonated beverages	60-100	1017
Carbonated beverages	85	185
Carbonated beverages	3 100	184, 188
Carbonated beverages	125	179
Carbonated beverages	3 128.5	186
Carbonated beverages	s 170	185
Food products	30-250	173
Fruit juice	100	164
Laundrying (diapers	s) 60	993
Pulp and paper maki	ng	044
Groundwood pulp	150	244
Kraft paper, bleac	hed 75	351
Kraft paper, unble	eached 150	351
Fine papers	45-75	551, 350
Soda and sulfate I	oulp 75	245
Rayon manufacture	50	152
Rayon manufacture	75	550, 405
Tanning	128.2	1018
Tanning	135	152

Stiemke and Eckenfelder (270) found that the average lethal doses of various alkaline solutions toward bluegill fingerlings were as follows:

Sustance	Alkalinity as Calcium Carbonate in mg/l	pH
Sodium hydroxide	70	10.55
Ammonium hydroxide	31	9.60
Sodium carbonate	120	
Potassium iodide and sodi hydroxide	om 57	

According to Warrick et al. (599) high alkalinity is antagonistic toward the toxicity of copper sulfate to fish. The relative toxicity of 25 mg/l of copper sulfate to brown trout fry varied inversely with the alkalinity,

with all fish dying in 2.5 hours when the alkalinity was only 6.0 mg/l whereas some fish survived after 12.5 hours when the alkalinity was 248 mg/l.

It is generally recognized that the best waters for the support of diversified aquatic life are those with pH values between 7 and 8, having a total alkalinity of 100 to 120 mg/l or more (3249, 3250). This alkalinity serves as a buffer to help prevent any sudden change in pH value, which might cause death to fish or other aquatic life. In Michigan, the addition of lime to Stoner Lake increased the alkalinity from 6 to 15 mg/l, improved the biological productivity, and even caused some extensive phytoplankton blooms.

ALKENYL DIMETHYL ETHYL AMMONIUM BROMIDE

ALKYL ARYL COMPOUNDS

ALKYL BENZENE SULFONATE

ALKYL DIMETHYL COMPOUNDS

ALKYL SULFATE

ALKYL SULFONATE

(See Chapter X)

ALLYL ALCOHOL

CH₂=CHCH₂OH

A colorless liquid with a pungent mustard-like odor, allyl alcohol is miscible with water. It is used in war gases, resins, and plasticizers. It is very irritating to mucous membranes and skin (364). The oral LD₅₀ is reported as 40 mg/kg of body weight for dogs (364) and 100 mg/kg for rats (3251). When fed in the drinking water of rats, retardation of weight gain began at 250 mg/l, but other effects were minor even at 1000 mg/l (3252). According to Woelke (2989), allyl alcohol is lethal toward bivalve larvae at 2.5 mg/l. Hubault (3253) reported the threshold of harmfulness of allyl alcohol toward rudd to be 10 mg/l.

ALUM

(see Aluminum Sulfate, Aluminum Ammonium Sulfate, and other aluminum compounds that are sometimes called alum)

ALUMINA

(see Aluminum Oxide)

ALUMINUM

Al

1. General. One of the most abundant elements on the face of the earth, aluminum occurs in many rocks and ores but never as a pure metal in nature. Although the metal itself is insoluble, many of its salts are readily soluble. Other aluminum salts, however, are quite insoluble and consequently aluminum is not likely to occur for long in surface waters because it precipitates and settles or is absorbed as aluminum hydroxide, aluminum carbonate, etc. In streams the presence of aluminum ions may result from industrial wastes or more likely from wash water from water-treatment plants. This section of the report deals with references to aluminum ions in water, where no mention is made of the salts from which

the pollution was derived. For the salts, see subsequent pages and cross references.

- 2. Cross References. Aluminum Ammonium Sulfate, Aluminum Chloride, Aluminum Nitrate, Aluminum Oxide, Aluminum Potassium Sulfate, Aluminum Sulfate.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. As one of the most abundant elements, aluminum is a constituent of all soils, plants, and animal tissues. It occurs in fruits and vegetables in concentrations up to 3.7 mg/kg and in some cereals up to 15 mg/kg. The total aluminum in the normal diet has been estimated at 10 to 100 mg per day (2121). Very little of the ingested aluminum is absorbed in the alimentary canal and consequently it is almost entirely evacuated in the feces. The total aluminum content of an adult human body is only about 50 to 150 mg (2121). Aluminum in public supplies is not considered a public-health problem, at least when it is present as a result of treatment processes. No evidence has ever been found to prove that the use of aluminum in water supplies, cooking utensils, or baking powders is harmful to human beings (32, 36, 152, 155, 353, 633). Evidence has been uncovered to indicate that salts of aluminum in food lower the toxicity of calcium fluoride occuring in combination with natural phosphates (1022,
- b. Industrial Water Supplies. Aluminum compounds in water in concentrations as low as 0.05 mg/l may cause trouble in industries such as laundries and mineral water plants (36). Aluminum in the concentrations commonly found in water has no effect on the brewing of beer (175). For rayon manufacturing and processing, the recommended maximum permissible concentration is 0.25 mg/l (405, 550).
- c. Irrigation Water. Aluminum is generally a minor constituent of irrigation waters, and is of little importance to irrigation (268); however, aluminum in high concentrations in reclaimed effluents could be toxic to crops (269). Scofield has found that aluminum, like calcium, reduces the injurious effect of sodium in soil, and when present in soil or irrigation water may be beneficial (348).

The following concentrations of aluminum have been reported to be harmful to various plants grown in solution cultures:

Concentration of Aluminum, in mg/l 1.0	Plants Corn, barley and sorghum		Reference 1447
1.0-4.56	Corn	in this order Reduced yields Abnormal growth Depressed growth Depressed growth Depressed growth	1447
1.0-100	Flax		1458
2.0	Barley		1447
7 or less	Sorghum		1447
14	Corn		1447

On the other hand, McLean and Gilbert as reported by Ligon and Pierre (1447) found that 3.4-13.6 mg/l of Al*** stimulated the growth of rye and oats; and 13.6 mg/l reduced yields of corn by only 4-7 percent. Aluminum in small amounts was reported to reduce the symptoms of manganese poisoning in flax grown in solution culture (1458).

Ligon and Pierre (1447) suggested that some of the conflicting results of independent studies might be attributable to differences in the pH values of the culture

solutions used. In their experiments, the pH was maintained at 4.5 to keep aluminum in solution; at this pH, without aluminum, the yield of corn was 50 percent lower than that of corn grown at pH 6.0. At pH 4.5, aluminum at a concentration of 1.0 mg/l further reduced the yields by about 25 percent; at concentrations of 2.28 and 4.56 mg/l, aluminum further reduced the yields by 39 and 59 percent respectively.

- d. Stock and Wildlife Watering. An average daily dose of 2 mg aluminum has not harmed rats (353). According to Maynard (995), aluminum has not been proved to be essential for animals. Much higher levels of aluminum than those found in food or water have been fed continuously to rats, dogs, pigs, and man without observable harm. However, in excessive amounts, there is the risk that aluminum will interfere with phosphorus metabolism, causing secondary symptoms of phosphorus deficiency.
- e. Fish and Other Aquatic Life. The following concentrations of aluminum have been reported lethal to aquatic animals in the time specified:

Aluminum, mg/	Compound Used	Time of Exposure	$Type \ of \ Fish$	Reference
0.10 0.27 0.3 0.5 2.7 5.0 17.8	Al(NOs)s AlCls Al(NOs)s AlCls AlCls AlCls AlCls (in sea water)	1 week 50 hours 1 day 3.6 hours 5 minutes short	sticklebacks sticklebacks eels sticklebacks fish eels trout redfish	2941 1460 1459 1460 1023 1459 604 1461

The following concentrations of aluminum have not harmed fish in the period specified:

Concentration in mg/1 0.25	Type of water	Time of Exposure	Type of Fish	Reference
0.25	acid		fish	1023
1.0		50 hours	young eels	1459
8.9	seawater	5 minutes	trout	604
0.0	sca water		fish & oysters	1461

f. Water for Bathing. Alum in swimming pools in a concentration equivalent to 0.1 mg/l aluminum may cause irritation of human eyes; and 0.5 mg/l is acutely irritating (1024).

ALUMINUM AMMONIUM SULFATE

 $AlNH_4(SO_4)_2 \cdot 12H_2O$

Occurring generally as the colorless crystalline compound with 12 molecules of water, aluminum ammonium sulfate is highly soluble in water and may be found in wastes from dye works and cloth-printing industries.

The threshold concentration of this compound for immobilization of Daphnia magna in Lake Erie water was found to be 190 mg/l (358). According to Ellis (313) trout succumbed to 523 mg/l of aluminum ammonium sulfate in tap water within 10 hours. The highest concentration of this salt tolerated by young eels for more than 25 hours was reported (1459) to be about 12 mg/l.

ALUMINUM CHLORIDE AlCl₃ and AlCl₃·6H₂O

This salt of aluminum, highly soluble in water, is used in dyeing fabrics, manufacturing parchment paper, refining operations, and disinfection.

When aluminum chloride was dissolved in tap water at pH 7.2-7.4, concentrations of aluminum in excess of 0.5 mg/l were fatal to various fishes. Young eels died

within 3.6 hours in a solution of aluminum chloride containing 2.7 mg/l of aluminum but they tolerated 0.27 mg/l for 50 hours (1459). Wallen et al. (2940) studied the effect of aluminum chloride on the mosquito-fish (Gambusia affinis) in highly turbid water at 20-21°C. They found a 96-hour TL_m value of 133 mg/l. This dosage reduced the turbidity from 230 mg/l to less than 25 mg/l.

The following concentrations of aluminum chloride have been reported to be lethal to various test fish in sea water:

Concentration of AlCls in mg/l 88 88 132	Type of Water sea water sea water sea water	Test Organism redfish other fish all fish tested all fish tested	Effect killed quickly killed more slowly most killed in a few hours, all in a few days all killed in a few hours	Reference 1461 1461 1461 1461
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The foregoing information shows a wide variation in the toxic level of AlCl₃ toward fish. In a similar manner there is no consistent pattern of toxicity toward lower forms of aquatic life. Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158) studied the threshold effects of aluminum chloride on various organisms during an exposure of 4 days at 23-27°C. They found that Daphnia withstood a concentration of 1000 mg/l as aluminum whereas Scenedesmus exhibited toxic effects at 1.5-2.0 mg/l of aluminum. In contrast, the threshold concentration of aluminum ehloride (AlCl₃) for immobilization of Daphnia magna in Lake Erie waters at 25°C was found to be less than 6.7 mg/l, for a 64-hour period (598).

Oysters do not appear to be sensitive to the action of AlCl₃ in seawater (2977).

ALUMINUM NITRATE

Al(NO₃)₃ and Al(NO₃)₃·9H₂O

This highly soluble salt of aluminum is used in the manufacture of the incandescent filaments, as a mordant in printing fabrics, and in the tanning and finishing of leather.

Aluminum nitrate has been found to be toxic to Polycelis nigra (a flatworm) in concentrations equivalent to 110 mg/l of aluminum (608). The threshold concentration of aluminum nitrate for death of stickleback in tap water is reported to be 0.55 mg/l (598). Using aluminum nitrate in very soft water, Jones found the lethal concentrations limit of aluminum for stickleback to be 0.07 mg/l. In different concentrations of aluminum from this compound, the average survival times of this fish were one day at 0.3 mg/l and one week at 0.1 mg/l (1459, 1460, 2920, 2941).

ALUMINUM OXIDE

 Al_2O_3

This white amorphous powder, also known as alumina or aluminum trioxide, readily absorbs water from the air, but is insoluble in water. It is used as an abrasive, for paint filler, and in paper mills.

Alumina as a colloidal residue has been blamed for an increase in cancer incidence, but residual salts of alumina appear to be without harmful effects (1025).

The following concentrations of aluminum oxide have been suggested (152, 162) as limits permissible in water for use in boilers:

For rayon (viscose) pulp production, the concentration of alumina should not exceed 8.0 mg/l (152).

The constant intake of water containing almost 3 grains per imperial gallon (about 42.9 mg/l) of aluminum oxide was believed to be the cause of death of a number of cattle (1026).

ALUMINUM POTASSIUM SULFATE AlK(SO₄)₂

Readily soluble in water, aluminum potassium sulfate may be found in wastes from dye works, tanneries and leather works, canneries, paper mills, and explosives works. The salt generally occurs as $AlK(SO_4)2 \cdot 12H_2O$ or as $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$.

The threshold concentration of anhydrous aluminum potassium sulfate for immobilization of Daphnia magna in Lake Erie water was found to be 206 mg/l (358). The following concentrations of AlK(SO₄)₂ have been reported to have killed fish within the period of time specified:

Concentration in mg/l 10 100 250 544 544 1000	Type of Water hard hard tap tap	Time of Exposure 4 days 12-96 hours 6 hours 15 hours 1-10 hours	Type of Fish goldfish minnows salmon trout goldfish	Reference 353 598, 2920 313 313 313 313
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In contrast to the foregoing tabulation, Ellis (313) reports that goldfish withstood 100 mg/l of AlK(SO₄)₂ in hard water for 100 hours without detriment. The maximum concentration of aluminum potassium sulfate tolerated by young eels for more than 25 hours was reported to be about 13 mg/l (1459).

ALUMINUM SULFATE

(ALUM) $Al_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 18H_2O_4$

- 1. General. Aluminum sulfate is used in water treatment as a coagulant for colloidal and suspended solids, including turbidity and organisms, with doses of from 5 to 70 mg/l generally being used (587). Aluminum sulfate has been found partially effective for inactivating viruses of infectious hepatitis (885) and polio (724), for removal of cysts of amoeba (743), and for removal of color (837), but it appears to have no effect on odors in water (1028). It has been reported that a study made in 1907 of the effects of various metallic sulfates on fish, germinated seeds of peas, wheat, and rape, yeasts, and various soluble enzymes indicated that aluminum sulfate was poisonous (921).
- 2. Cross References. Aluminum, Aluminum Ammonium Sulfate, Aluminum Potassium Sulfate.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The USPHS Drinking Water Standards of 1962 (2036) do not prescribe limits for alum in water. Solutions of 1 to 5 mg/l aluminum sulfate did not increase the solubility of lead sulfate or carbonate beyond their solubility in distilled water. However, where lead service pipes are used, high con-

centrations of aluminum sulfate may cause an increase in the lead content of the water (1029).

- (b) Industrial Water Supplies. Aluminum sulfate is undesirable in water for use in the paper and textile industries (257). Excessive quantities of alum in water used for paper have a deleterious effect on the strength of the paper product (1030). For use in dyeing rayon, a residual content of alum of less than 0.4 mg/l is desirable (852).
- c. Irrigation. As aluminum sulfate, 10 mg/l of aluminum caused no apparent injury to oat plants but 25 mg/l or more significantly reduced growth (1462).
- d. Fish and Other Aquatic Life. In fresh water, 7 mg/l of aluminum sulfate has been reported to be fatal to Fundulus within 5 days and 14 mg/l within 36 hours (1459). Schaut (362) reported that 17.1 mg/l of Al₂(SO₄)₃·18H₂O was harmless to minnows in stabilized tap water during one hour of exposure. Sanborn (1030) found that 100 mg/l of Al₂(SO₄)₃·18H₂O did not affect goldfish, sunfish, and bass during seven days of exposure but that 250 mg/l killed them in 8 to 24 hours. Wallen et al. (2940) studied the effect of aluminum sulfate on the mosquito-fish (Gambusia affinis) in turbid water at 19-22° C. They found the 96-hour TL_m to be 235 mg/l, at which concentration the turbidity was reduced from 180 mg/l to less than 25 mg/l, owing to the coagulating action of the alum.

The threshold concentration of aluminum sulfate for immobilization of *Daphnia magna* in Lake Erie water was found to be 106 mg/l (358).

AMINES AND AMINO COMPOUNDS

(See also Aniline, Benzene Derivatives, Benzylamine, Diethanolamine, Diethylamine, Dimethylamine, Ethylamine, Hydroxylamine, Methylamine, Rosin Amines (in Chapter IX), Triethylamine, Trimethylamine, and Urea).

Compounds derived from ammonia by the replacement of hydrogen by one or more univalent hydrocarbon radicals are known as amines; for example, methylamine is $(CH_3)_2NH$, and trimethylamine is $(CH_3)_2N$. Several of the references uncovered in this survey refer to specific amines. In such cases, these compounds are generally listed separately in this volume. Other references cover multiple amines in such a manner that they can best be shown as a group under this section.

Gillette, Miller, and Redman (1442) ran toxicity tests with creek chub, a fish considered to be average in tolerance, at 15-21°C in well-aerated water. Toxicity was expressed in terms of a "critical range," defined as the range of concentration in mg/l below which all four fish lived for 24 hours and above which all died. For the amines and related compounds, the critical ranges were reported to be as follows:

Substance	Critical Range, in mg
Diamylamine	. 5-20
Bis-benzylethylenediaminediacetate	_ 5-20
Monomethylamine	. 10-30
Di-sec-butylamine	15-40
Tri-n-butylamine	20-40
Di-isobutylamine	20-40
Mono-sec-butylamine	
Mono-isobutylamine	20-60

Substance	Critical Range, in mg/l
Di-n-propylamine	90.60
Di-n-butylamine	20.60
Nonic 218 (trade name)	60.00
Dimethylamine	90 50
monosculiamins	90 E0
Ethylenediamine	20.60
Monoamylamine	20 50
1. 3-dibutylthionres	20.100
Mono-n-butylamine	90 ላለ
Tri-n-propylamine	50-70
Di-iso-propylamine	- 30-70
Mono-n-propylamine	40-60
Monoethylethanolamine	40-60
Monoisopropylamine	40-70
Triethylamine	40-80
Diethylamine	50-80
Diethylethanolamine	70-100
1, 3-diethylthiourea	80-120
Ethyldiethanolamine	100-300
Diethylnitrosoamine	160-200
Buramine (trade name)	
Endothal (trade name)	1000-1500
Diethyleminehydreckleride	1600-3200
Diethylaminohydrochloride	4000-6000
Ethylenethiourea	6000-8000
1, 3-dimethylurea	
Urea	16,000-30,000

According to Smith et al. (2978) the oral DL_{50} for rats and the 95-percent confidence limits for several amino compounds are as follows:

Compound	LD_{so} in gm/kg of body weight	95 percent confidence limits
Ethylamine	0.40	0.29-0.56
Disopropylamine	0.77	0.61-0.94
Dibutylamine	0.55	0.48 - 0.62
Hexylamine	0.67	0.62 - 0.74
2-Ethylbutylamine	0.39	0.34-0.45

4-AMINO-M-TOLUENE SULFONIC ACID

 $C_7H_6NH_2SO_3H$

Wallen et al. (2940) studied the effect of this compound on the mosquito-fish (Gambusia affinis) in highly turbid water at 22-24°C. They found the 24-, 48-, and 96-hour TL_m concentrations to be 425, 410, and 375 mg/l respectively. The turbidity was reduced from 650 mg/l to 220 mg/l and the maximum dosage lowered the pH to only 6.3.

AMINOTRIAZOLE

(see Chapter IX)

AMMATE (AMMONIUM SULFAMATE)

(see Chapter IX)

AMMONIA

NH₃

1. General. In the pure form, ammonia is a colorless gas with a very pungent odor, made synthetically from atmospheric nitrogen and hydrogen, or obtained during the manufacture of coal gas. In surface or ground waters, however, it generally results from the decomposition of nitrogenous organic matter, being one of the constituents of the complex nitrogen cycle. It may also result from the discharge of industrial wastes from chemical or gas plants, from ice plants, or from scouring and cleaning operations where "ammonia water" is used. Rivers known to be unpolluted have very low ammonia concentrations, generally less than 0.2 mg/l as N (2972).

Being soluble in water to the extent of 100,000 mg/l at 20°C, ammonia gas reacts with water, liberating much heat, to form ammonium hydroxide. This, in turn, dissociates readily into ammonium and hydroxyl ions, thereby tending to raise the pH value of the solution. The combined reversible equations are as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Inasmuch as the dissociation constant for ammonium hydroxide is 1.8×10^{-5} at 25° C (911), the ratio of ammonium ions to ammonium hydroxide molecules is a function of pH as follows:

$$\frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} = \frac{1.8 \times 10^{-5}}{[\text{OH}^-]}$$

At pH 6, this ratio is 1800 to 1, at pH 7 it is 180 to 1, and at pH 8 it is 18 to 1. For common ranges of pH, therefore, it is evidence that most of the ammonia in water exists in the form of ammonium ions. Furthermore, all of the common ammonium salts are also readily soluble in water, yielding NH₄⁺ and an anion. In the case of the chloride, nitrate, and sulfate, the solution of ammonium salt results in a decrease in pH since part of the ammonium ions combine with hydroxyl ions in the water.

Despite the fact that the ammonium ion predominates, except at high pH values, the data in much of the literature are in terms of ammonia (NH₃). In recent work, however, the term "ammonia nitrogen" (expressed as N) is gaining prominence. The test for ammonia nitrogen, as outlined in Standard Methods for the Analysis of Water and Sewage (469), measures all of the nitrogen in the form of NH₃, NH₄OH, and NH₄*.

The results given below pertain only to literature dealing with the terms ammonia or ammonium ion. Where concentrations are expressed in terms of the hydroxide or as salts of ammonia, the data are listed separately under the respective heading.

- 2. Cross References. Albuminoid Ammonia, Ammonium Hydroxide, Various Ammonium Salts, Chapter IX (Pesticides) and Chapter X (Surface-Active Agents)
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. No limits on ammonia are set by the USPHS Drinking Water Standards of 1962 (2036) or the WHO International Standards (2328); but the WHO European Drinking Water Standards (2329) set a recommended limit of 0.5 mg/l as NH₄⁺. According to Laufer (170) a generally accepted limit for free ammonia for sanitary purity of water supplies is between 0.05 and 0.10 mg/l. Although free ammonia is often of vegetable origin and without hygienic significance, its concentration in water in excess of 0.10 mg/l renders the water suspect of recent pollution (855).

In discussing the use of tinned vs. untinned copper tubing for distribution of domestic water, Royden et al. (1042) feel that untinned copper should not be used if the ammonia content of the water exceeds 5.0 mg/l.

Although the ingestion of "aqua ammonia" or "ammonia water" containing 28 to 29 percent ammonia in water has been reported to be fatal (364) there appears to be no physiological harm in concentrations of am-

monia that might occur in natural or polluted waters. In fact, ammonia is used in waterworks to form chloramines for sterilization and residual action in water.

The odor threshold for ammonia has been reported as 0.037 mg/l (1756), but for the brewing of coffee the taste threshold is 34 mg/l (2059).

- b. Industrial Water Supplies. The slight concentrations of ammonia in natural waters appear to be of no industrial significance, although Hammerton (360) reports that ammonium salts are destructive to concrete made from portland cement. For steeping of barley in malting processes, the concentration of ammonium salts should be low (240).
- c. Irrigation Waters. Ammonia is one of the minor constituents of irrigation water, usually occurring in low concentrations, and of little importance to irrigation practice (268). Because it changes rapidly to nitrites and nitrates, ammonia is actually a fertilizer for most crops. Indeed, ammonium salts constitute a major source of nitrogen fertilization.
- d. Stock and Wildlife. It has been reported (353) that the ingestion of 50 to 80 ml of 0.5 percent ammonia by rabbits at intervals of one to two days for periods up to 17 months caused chronic acidosis and tissue changes. On the other hand, 23,850 mg/kg of ammonia (fed as ammonium persulfate) in the diet of dogs had no apparent effect in 16 months.
- e. Fish and Other Aquatic Life. According to many references, (1043, 1464, 3057, 3332, 3333) the toxicity of ammonia and ammonium salts to aquatic animals is directly related to the amount of undissociated ammonium hydroxide in the solution, which in turn is a function of pH as explained under "General" above. Thus, a high concentration of ammonium ions in water at a low pH may not be toxic, but if the pH is raised toxicity will probably increase (361). Ellis found that the toxicity of a given concentration of ammonium compounds toward fish increased by 200 percent or more between pH 7.4 and 8.0.

The presence of carbon dioxide, up to concentrations in the range of 15 to 60 mg/l, appears to reduce the toxicity of ammonia presumably by lowering the pH value (139, 140, 142, 143, 3321). Inasmuch as CO₂ is excreted by the fish, the pH value at the gill surface will be lower than in the bulk of the solution, thereby reducing the proportion of un-ionized ammonia at the gill (3321).

The toxicity of ammonia to fish is increased markedly at low tensions of dissolved oxygen (144, 2096, 2518, 2640, 2952, 3334). A concentration of non-ionized ammonia equivalent to 0.2 mg/l of nitrogen decreased the survival time of trout at a level of dissolved oxygen that otherwise had no lethal effect (2096). The concentration of excreted carbon dioxide at the gill surface varies with the oxygen content of the water; hence as the oxygen tension is reduced, the concentration of excreted CO₂ is also reduced and the pH value of the water in contact with the gill surface rises, leading to an increased toxicity of an ammonia solution. This mechanism explains the increased toxicity of ammonia at low oxygen tensions (3321).

The following concentrations of ammonia have been reported to be toxic or lethal to fish in the time specified:

				- Troomer
	Concentration NHs in mg/l		Type of Fish	Reference
	0.3-0.4		trout fry	1465
	0.3 - 1.0	===	fish	
	0.6*	100-200 minutes	rainbow trout	1044
	0.7	390 minutes	rainbow trout	88
	1.0-2.0		fish	2970
	1.2	193 minutes	Squalius cephalus	1465
	2.0	TOO IMMUTED	fish	2970
	2.0-2.5	1-4 days	goldfish	1045
	2.5			313
		1-4 days	goldfish	1466
	2.0-7	.7.7.	fish	1460, 1466
	2.9	13 hours	Cichla ocellaris	145
	3.1 (soft water	Γ,		
	30°C)	96-hour TLm	bluegill sunfish	2936
	3.4 (soft water			2000
	20°C)	96-hour TLm	bluegill sunfish	2936
	5.0		rainbow trout	2977
	5-7 (distilled			4911
	water, 20°C)	6 hours	minnows	90.49
	6-7 (hard	· 110 21 2	2222110778	2942
	water, 20°C)	6 hours	minnows	20.40
	7-8	1 hour	sunfish	2942
1	3	1 Hou	fish	363
	7.1	1 hour	minnows	346
Ť				362
		15-16 minutes	eel, roach, trout	1467
4	3.7 (hard			
	water, 30°C)	96-nour TLm	bluegill sunfish	2936
Z	4.4 (hard			
_	water, 20°C)	96-hour TLm	bluegill sunfish	2936
	5.7	less than 4 minutes	trout	146
				-+-

*un-ionized ammonia

Brockway (1044) states that an ammonia concentration of 1.0 mg/l decreases the ability of the hemoglobin to combine with oxygen and hence the fish may suffocate. A concentration as low as 0.3 mg/l causes a noticeable drop in the oxygen content of the blood of fishes. In the foregoing table, the work of Ellis (313) is most widely quoted and concentrations of 2.5 mg/l have been considered harmful in the pH range from 7.4 to 8.5. Ellis reports, however, that concentrations of 1.5 mg/l are not harmful to most varieties of fish and Schaut (362) claims that minnows were not harmed by a one-hour exposure to 4.3 mg/l. Solutions containing mixtures of ammonium and cyanide ions are more toxic to fish than solutions containing either ion alone (1468).

With respect to other aquatic life, the following results were reported by the Academy of Natural Sciences of Philadelphia (2936):

Organism	Time of Exposure	Tupe of Water	Tempera- ture °C	Concentration of NH: as N in mg/l producing noted effect
Physa hetero-	95-hour	soft	20	90 (a.)
stropha (snail)		hard	20	133.9 (a)
		soft	30	94.5 (a.)
		hard	30	133.9 (a)
Navicula	5-day	soft	22	420 (b)
seminulum		hard	22	420 (b)
(diatom)		soft	28	320 (b)
		hard	28	420 (b)
		soft	30	410 (b)
		harđ	30	350 (b)

(a) 96-hour TLm (b) 50-percent reduction in division (growth)

Algae, which thrive on high nitrate concentrations, appear to be harmed or inhibited when the nitrogen is in the form of ammonia. Gusseva (584) reported that 0.4 to 0.5 mg/l of ammonia nitrogen caused a complete disappearance of Aphanizomenon. The lethal concentration of ammonia for Daphnia has been reported at 8 mg/l (2977). Stammer (147) reports the following toxicity threshold values for indicator organisms of a saprophytic system, in terms of free ammonia:—Organisms of the oligosaprobic and β -mesasaprobic zones, 0.08 to 0.4 mg/l; those of the α -mesasaprobic zones 0.3 to 4.3 mg/l; and those of the polysaprobic zone 3.2 to 220 mg/l.

AMMONIA LIQUOR FROM COKE-GAS PLANTS

- 1. General. The concentrations of eight constituents of ammonia waste liquors have been reported (1466) as follows: phenols—10 mg/l; higher tar acids—10 mg/l; ammonia as ammonium hydroxide—10 mg/l; ammonium salts—500 mg/l; thiocyanate—200 mg/l; cyanide—10 mg/l; pyridine—400 mg/l; and naphthalene—5 mg/l.
- 2 Cross References. Ammonia, Ammonia Salts, Cyanides, Naphthalene Organic Acids, Phenols, Pyridine, and related compounds.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. In the extracts from ammonia waste liquors, the following threshold odors were determined (1469):

Phenolic wastes	10 mg/1
Acidic wastes	100 7
Neutral wastes	10. 0
Basic wastes	$3.0 \mathrm{mg/I}$

- b. Irrigation Waters. Ammonia gas liquors containing 1.5-2.0 percent nitrogen may be used as nitrogenous fertilizer, especially in combination with other balanced fertilizers. The small concentrations of phenol and thiocyanate may cause temporary damage to crops, but their disinfecting action may possibly have a beneficial effect on plant diseases. The waste liquors should be applied in early spring or after grasses have been cut (148, 1470, 1471).
- c. Fish and Other Aquatic Life. Ammonia liquors contain free ammonia, sulfide, and cyanide, all of which are relatively high in toxicity to aquatic life. They also contain phenol, which has a medium toxicity, and substances with relatively low toxicity such as thiosulfate and the higher tar acids (1466).

Schaut (362) studied the affect of ammoniacal liquor from a coke-gas plant on minnows in stabilized tap water. At a dilution of 1:2400, the minnows were not affected after one hour of exposure, but at a dilution of 1:240 the reaction of fish was similar to that of 0.5 mg/l of sodium cyanide, i.e., it excited the fish, caused them to stop eating, and killed 25 percent in a 24-hour period.

The waste liquor, as tested, contained 1100 mg/l of phenol, 60 mg/l of cyanide as HCN, and 600 mg/l of HCNS as well as ammonia. At a dilution of 1:500,000 it gave a faint medicinal taste and at a dilution of 1:240, a faint yellow color.

AMMONIUM ACETATE

CH3COONH4

(see also Ammonia, Acetates)

Used in textile dyeing, for preserving meat, and as a mild diuretic for animals, this compound is highly soluble in water. According to Wallen et al. (2940), the 24-hour, 48-hour, and 96-hour TL_m values for mosquito-fish (Gambusia affinis) in turbid water at pH 7.6-8.4 were all 238 mg/l. This concentration reduced the turbidity from 1400 mg/l to less than 25 mg/l.

AMMONIUM ALUM

(see Aluminum Ammonium Sulfate)

AMMONIUM ARSENATE

(NH₄)₂HAsO₄

(see also Ammonia, Arsenic)

This highly soluble salt was found to have no effect upon the sea lamprey, rainbow trout, or bluegill sunfish when exposed for 24 hours at a concentration of 5 mg/l in Lake Huron water at pH 7.5-8.2 (2976).

AMMONIUM CARBONATE

 $(NH)_2CO_3$

(see also Ammonia)

This colorless crystalline or amorphous substance is used in baking powders, for wool scouring, in tanning and textile mills, and in many manufacturing processes. It has been reported in gas-manufacturing wastes (363) and ice-plant effluents (808).

Being highly soluble in water, this salt dissociates into ammonium ions that may combine with hydroxyl ions to form NH₄OH. It has the added detrimental effect that the carbonate ion offsets the tendency of the ammonium ion to lower the pH (see Ammonia). The carbonate has a buffering action that influences toxicity of the ammonium ion. For example, 240 mg/l of ammonium carbonate in distilled water killed goldfish in about 3.5 hours whereas 5350 mg/l of ammonium chloride did not kill in 12 hours (1043). The following information on the toxicity of ammonium carbonate toward fish has been noted:

Concentration (NH4):CO: in m	of na/l Remarks F	eference
•	Lethal toward fish	808
5.5-7.0	Tolerated by goldfish for over 100 hours	313
10	Threshold effect toward fish	1466
	Threshold effect toward usu	313
48	Killed goldfish in 6 days in hard water	
100	Killed goldfish in 4-10 hrs. in hard water	
155-197	Fatal to shiners and carp in a few hours	
238	96-hour TLm for mosquito-fish in turbid	2940
600-800	Killed orange-spotted sunfish in one hour	363

AMMONIUM CHLORIDE

NH₄Cl

(see Ammonia)

This highly soluble colorless salt is used extensively in industry for dyeing, tanning, washing, and other operations. One source of ammonium chloride in streams is the weathering of granite or other rock; hence the presence of ammonium ion in water is not necessarily an indication of human pollution (1472).

The toxicity of this compound, like that of other ammonium salts, depends on the resulting pH of the water. Unlike the carbonate, however, this salt in high concentrations tends to lower the pH value, thereby counteracting the toxicity of ammonium hydroxide. In distilled water, 5,350 mg/l of ammonium chloride did not kill goldfish in 12 hours but a solution of 2,695 mg/l in distilled water became toxic when sodium hydroxide or other alkalies were added, the increase in toxicity being proportional to the increase in hydroxyl ions (1043). In other experiments tabulated below, ammonium chloride was less toxic in distilled water (where the pH was lowered) than in tap water or hard water that provided buffering action to maintain a high pH.

The effect of ammonium chloride toward fish has been reported as follows:

Concentra of NH ₄ Cl in mg/l 6 38	Time of Exposure 96-hour TLm 7.5 hours	sunfish	standard dilution water not lethal limiting concentration	Reference 2935 2907 346 313
180 268 300	6-days 6 hours	shiners and carp	no effect in tap water killed in hard water minimum lethal dose in hard water toxic threshold	313 2943, 2944 1046
314 490 535 535 700-800 1570 4000-4500	96-hour TLm 4.75 hours 18 days 1 hour 6 hours	mosquito fish bluegills bluegills sunfish rainbow	turbid water killed in tap water	2940 313 313 363 2920 2943, 2944

According to Anderson (598) the threshold concentration for immobilization of Daphnia magna in Lake Erie water at 25° C. was found to be 91 mg/l in 64 hours. Ellis (313) found that 535 mg/l killed Daphnia magna in six hours. Fairchild (2946) studied the effects of varying oxygen tensions on Daphnia exposed to ammonium chloride for 100 hours at 23° C., with the following results:

Dissolved oxygen, mg/l	Threshold toxicity value, mg/l
6.4 3.14	247 174
1.48	100

For Lake Erie water at 20-25° C., threshold concentrations of ammonium chloride were reported (2955) as follows:

Threshold concentration (mg/l)

I In C	STOCKE CONTRACTOR
Organism	for immobiliza
Danhnia magna, young	92 3.1
Leptodora kindtii	86
Mesocylops leukarti Diaptomus oregonensis	19
Diapiomus oregonensis	

Hodgson (2956) found that the median concentration of ammonium chloride required to stimulate the movement of a water beetle (Laccophilus maculosis) was 2460 mg/l.

AMMONIUM CHROMATE

 $(NH_4)_2CrO_4$

According to Wallen et al. (2940) the 96-hour TL_m of this highly soluble salt toward the mosquito-fish (Gambusia affinis) in highly turbid water was 240 mg/l. The addition of this concentration did not materially lower the turbidity.

AMMONIUM DICHROMATE (NH₄)₂Cr₂O₇

This highly soluble salt is used in lithography, photoengraving, in special mordants, pyrotechnics, and porcelain finishes (364). According to Wallen et al. (2940), the 96-hour TL_m toward the mosquito-fish (Gambusia affinis) in turbid water was 136 mg/l. This concentration did not lower the turbidity appreciably.

AMMONIUM FERROCYANIDE (NH₄)₄Fe(CN)₆

(see also Ammonia, Iron Salts, and Cyanides)

According to Shelford (363) orange-spotted sunfish were killed in one hour by 150 to 200 mg/l of this freely

soluble compound which the author states is a constituent of some gas-manufacturing wastes.

AMMONIUM FLUORIDE

NH₄F

This highly soluble compound is used in textile dyeing and printing, for preserving wood, for etching glass, and as a mothproofing agent (364). According to Simonin (3271) 200 mg/l will kill the fish, *Tinca vulgaris*, in less than 48 hours. For the related compound, ammonium fluosilicate, the lethal dose was found to be only 50 mg/l, and for ammonium bifluoride it was 100 mg/l.

AMMONIUM HYDROXIDE

NH₄0H

(see Ammonia)

This substance is dealt with separately from ammonia and the ammonium salts only because some the references report data in terms of ammonium hydroxide. Whenever ammonia gas or ammonium salts are dissolved in water, or when ammonium ion is formed in the decomposition of organic matter, the undissociated compound NH₄OH results. The proportion of ammonium ion and undissociated base is a functions of pH, as explained under Ammonia and the toxicity of the resulting solution depends primarily on the concentration of NH₄OH, i.e., the undissociated compound is the toxic principle.

In as much as toxicity varies considerably with pH and hence is a function of the buffering action of the water used, it is difficult to compare the results of many investigators. Toxic concentrations of ammonium hydroxide toward fish have been reported as follows:

Concentr	ation of _Time o			
NH_iOH_i	n mg/l Exposu		-	
4~5	bir - wposa		Remarks	Reference
6.25	24 hours	goldfish	lethaI	2920
10	74 HOULS	brook trout	lethal	313, 359
		suckers, shiners,	. lethal	808
10	24 hours	carp, trout		
13	24 hours		not lethal, 15-	21°C 1442
	- Prinouts		lethal	313, 359
15	48-hour TLm	carp bluegill sunfish		
		bruegin suniisn	Philadelphia t	
17.5	48-hour TLm	fathead	water, 20°C	2093
	_	minnows		
18.5	48-hour TLm	bluegill sunfish	Dharadalas	3335
		Ball Bullish	Philadelphia to	ap
			water, reoxyge	
20	15 minutes	suckers, shiners.	lethal	2093
30		carp	icular.	313
30 30	24 hours	small fish	lethal	313, 359
30	24 hours	creek chub	lethal, 15-21°C	1442
37	001	perch	lethal	2920
01	96-hour TLm	mosquito-fish	turbid water	2940
_				2010

In contrast, it has been reported (359) that a concentration of 9.4 mg/l has not harmed suckers, shiners, and carp in 24 hours of exposure.

According to Anderson (358) the threshold concentration of ammonium hydroxide for the immobilization of *Daphnia magna* in Lake Erie water at 25°C was found to be less than 8.75 mg/l.

AMMONIUM MOLYBDATE (NH₄)₆Mo₇O₂₄·H₂O

(see Ammonia, Molybdenum)

This highly soluble salt is used for decorating ceramics and in photography. Bringmann and Kuhn (2158) tested ammonium molybdate in River Havel water from which the test organisms had been recovered. They found no adverse response by Daphnia held for 48 hours at 23°C nor by E. coli incubated at 27°C even at 1000 mg/l of molybdenum. For Scenedesmus held for 4 days at 24°C,

however, the median toxic threshold effect occurred at 54 mg/l of molydenum.

AMMONIUM NITRATE

 NH_4NO_3

(see Ammonia)

This soluble odorless compound is used as a fertilizer, in pyrotechnics, for explosives and matches, and in chemical industries. Ellis (313) quotes references to the effect that a concentration of ammonium nitrate of 800 mg/l in tap water killed bluegills in 3.9 hours but in distilled water not until 16 days. Goldfish were killed in distilled water by 4.545 mg/l in 90 hours. This salt dissolves readily and dissociates into its ions but since the ammonium ion combines with the hydroxyl ion of the water, the pH is lowered markedly in unbuffered water. Since it is the undissociated NH₄OH that is the toxic principle, it is easy to understand why a solution in tap water is more toxic than in distilled water.

AMMONIUM PERSULFATE

 $(NH_4)_2S_2O_8$

(see also Ammonia)

Highly soluble in water, this compound is used in dyeing, electroplating, photography, and many other applications (364). Using water of the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158) found that the median threshold effect of this compound toward Daphnia held for 48 hours at 23°C occurred at 120 mg/l, measured as persulfate. Toward Scenedesmus during a 4-day exposure at 24°C, the median threshold effect occurred at 33 mg/l of S₂O₈, but toward E. coli at 27°C, there was no measurable effect at 1000 mg/l of persulfate.

AMMONIUM PICRATE

 $C_6H_2ONH_4(NO_2)_3$

(see Ammonia, Picric Acid, Explosives)

This substance is used in the manufacture of explosives and fireworks. Being freely soluble in water, it may occur in waters from munitions works. According to Ruchhoft and Norris (655) 0.5 mg/l of ammonium picrate in drinking water can be detected by taste and 1.0 mg/l is objectionable.

AMMONIUM SULFAMATE (AMMATE)

(see Chapter IX)

AMMONIUM SULFATE

 $(NH_4)_2SO_4$

(see Ammonia)

Used widely as a fertilizer and in many industrial processes, this crystalline salt dissolves readily in water with a resulting decrease in pH; hence its toxic effect upon fish is analogous to that of ammonium nitrate and ammonium chloride but less severe than that of ammonium carbonate which has a buffering action.

Ellis (313) quotes a reference to the effect that 66 mg/l in tap water killed bluegills in 3.5 hours, but in distilled water the same concentration required 17 days to kill the bluegills (Note: this is the pH effect on ammonium hydroxide concentration. See Ammonia). In his own experiment Ellis found that 264 mg/l in hard water killed goldfish in six days or less. According to Shelford (363) orange-spotted sunfish were killed in one hour by 420 to 500 mg/l.

LeClerc and Devlaminck (2944) report the minimum lethal concentration in 6 hours toward minnows in hard water at 18°C to be 400-500 mg/l; but in distilled water at 16°C, the minnows did not succumb until the concentration reached 4000-5000 mg/l. Wallen et al. (2940) found the 96-hour TLm for mosquito-fish (Gambusia affinis) in turbid water at 20-21°C to be 1290 mg/l. The ammonium sulfate reduced the turbidity from 240 mg/l to less than 25 mg/l.

Fairchild (2946) studied the effects of varying oxygen tension on the toxicity of ammonium sulfate toward Daphnia exposed for 100 hours at a temperature of 23° C. Results showed a toxicity threshold of 288 mg/l when the dissolved oxygen was 6.6 mg/l; but the toxicity level of the ammonium sulfate dropped to 116 mg/l when the dissolved oxygen was only 1.52 mg/l. Threshold concentrations for other organisms were reported (2955) as

shown below:

Organism

Concentration in mg/l for Threshold Immobilization

Daphnia magna, young Daphnia magna, adult Diaptomus oregonensis 106 152

AMMONIUM SULFIDE

 $(NH_4)_2S$

(see also Ammonia, Sulfides)

According to Ellis (313), 100 mg/l of ammonium sulfide in hard water killed goldfish in 72 hours, but with only 10 mg/l the fish survived more than 100 hours of exposure. He reports that this substance may occur in chemical, beet-sugar, or gas-plant wastes. Wallen et al. (2940) found the 96-hour TLm toward the mosquito-fish in turbid water at 21°C to be 248 mg/l. The addition of this compound had very little effect upon the turbidity.

The solution of this colorless crystalline substance in water results in a dissociation into ammonium ions and sulfide ions. The former react in part when the hydroxyl ions to form NH4OH while the latter react with hydrogen ions to form HS- and H2S, depending on the pH of the solution. Thus, toxicity is controlled by the resulting combinations in the water, rather than by the added salt itself.

AMMONIUM SULFITE

 $(NH_4)_2SO_3 \cdot H_2O$

This highly soluble compound is used as a reducing agent in photographic work. Wallen et al. (2940) tested its toxicity toward the mosquito-fish in highly turbid water at 20-21°C. They found the 24-hour, 48-hour, and 96-hour TLm values to be 240 mg/l. The addition of this compound lowered the turbidity from 220 to less than 25 mg/l.

AMMONIUM THIOCYANATE

NH₄SCN

(see also Ammonia, Cyanides)

This highly soluble substance is used in textile processes, pyrotechnics, and in chemical process industries (364). It may also occur in gas-plant wastes (313, 363).

According to Shelford (363), orange-spotted sunfish were killed in one hour by 280 to 300 mg/l, and Demyamenko (431) reports that a concentration of 200 mg/l is deadly to fish. In highly turbid water at 16 to 23°C, Wallen et al. (2940) found the 96-hour TLm toward the mosquito-fish (Gambusia affinis) to be 114 mg/l, although the 24-hour TLm was as high as 910 mg/l. The addition of this salt did not lower the turbidity. The lethal limit for 24 hours exposure has been reported (2977) at 1600 mg/l for goldfish and tench.

Larvae of chironomus are killed by 50 mg/l of this salt, but Carinogammarus and Asellus aquaticus withstand 100 mg/l without noticeable harm (2977). The concentration of NH4SCN required to lower the BOD of sewage is in excess of 5000 mg/l (2923).

AMMUNITION PLANT WASTES

(see Explosives, Trinitrotoluene)

AMYGDALIN

C20H27NO11

(see also Hydrocyanic acid)

This substance, a cyanogetic glucoside, is widely distributed in nature, being found in bitter almonds, leaves of cherry laurel, peach, cherry, apricot, quince, plum kernels, other hard-nut fruits, cotoneaster, and many other plants. The enzyme emulsin hydrolyzes amygdalin to glucose, benzaldehyde, and hydrocyanic acid. According to Schaut (362), about 7 mg/l of amygdalin is toxic to young carp and minnows.

Chlorination of water containing amygdalin may produce a very toxic median when chlorine and the hydrolysis product HCN are brought together. Apparently chlorine does not destroy amygdalin or the enzyme, but it may retard enzymatic action.

AMYL ACETATE

CH₃COOC₅H₁₁

Isoamyl acetate, a colorless neutral liquid with a pearlike odor, is soluble in 400 parts of water. It is used extensively in organic chemical industries, varnishes, lacquers, and dyeing (364). The threshold odor is reported at a concentration of only 0.0006 mg/l (1756).

Toxicity tests with creek chub, a fish considered to be average in tolerance, at 15-21°C in well-aerated water indicated that all four test fish lived for 24 hours at concentrations of 50 mg/l or less, and all died at concentrations exceeding 120 mg/l (1442). Using highly turbid water with mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values all to be 65 mg/l.

For Daphnia exposed for two days at 23°C, the median threshold of harmful effect occurred at 120 mg/l of amyl acetate; for Scenedesmus at 180 mg/l during 4 days exposure at 24°C; but for Escherichia coli, 1000 mg/l at 27°C had no apparent effect (2977).

AMYL ALCOHOL

 $C_5H_{11}OH$

Normal amyl alcohol is a liquid used in organic syntheses and as a solvent for resins, varnishes, lacquers, fats, and oils. It is slightly soluble in water and occurs in chemical wastes and some distilling wastes. The oral toxicity toward rats has been reported (3248) as 3.3 mg/kg of body weight.

The toxicity of n-amyl alcohol toward fish has been reported as high as 1000 mg/l (2920) and as low as 1.0 mg/l (313). Ellis (313) found that concentrations of iso-amyl alcohol of 100 mg/l in hard water killed goldfish in 82 hours, but as little as 1.0 mg/l killed in 161 hours. For the gudgeon, a small European fresh-water fish, the lethal range of n- amyl alcohol has been reported (2977) as 350 to 500 mg/l; but for tertiary amyl alcohol, the lethal range is 1300 to 1500 mg/l.

In Lake Erie water, according to Anderson (358) the threshold concentration of n-amyl alcohol for immobilization of Daphnia magna at 25°C after prolonged exposure was 881 mg/l. Bringmann and Kuhn (2158) reported the threshold toxic effect on Daphnia as 440 mg/l, during two days exposure at 23°C, the threshold effect occurred at 280 mg/l, but for Escherichia coli at 27°C, 1000 mg/l showed no effect.

AMYLENE

(see Pentene)

ANILINE

 $C_6H_5NH_2$

(see also Dyes)

Known also as phenylamine, this highly soluble colorless oily liquid occurs in dye, varnish, rubber, chemical, and gas-plant wastes. The oral LD₅₀ in dogs is reported as 500 mg/kg of body weight (364). In humans, acute doses of aniline may cause cyanosis, headache, or mental confusion, while chronic doses may produce anemia, anorexia, loss of weight, cretaneous lesions, and bladder trouble. The maximum allowable concentration in water has been given as 5.0 mg/l, and serious poisoning may result from the ingestion of 0.25 ml of the pure liquid (364).

Toward fish, a wide range of toxic levels has been reported. Burgess (2962) eites 100 mg/l for trout, 200 mg/l for minnows, and 1000 mg/l for goldfish. In a concentration of 1020 to 1120 mg/l, aniline killed orange-spotted sunfish in one hour (363), but at a concentration as low as 250 mg/l it was reported to be deadly to fish in an unspecified time (431).

For lower organisms, the threshold concentration for immobilization of *Daphnia magna* during prolonged exposure in Lake Erie water at 25°C was 279 mg/l (358). In contrast, Bringmann and Kuhn (2158) claim that the median threshold effect toward *Daphnia* occurred at 0.4 mg/l during a 2-day exposure at 23°C. For *Scenedesmus* at 24°C for 4 days, the threshold effect occurred at 10 mg/l, while for *E. coli* at 27°C no effect was apparent at concentrations up to 1000 mg/l.

ANILENE HYDROCHLORIDE

(see Benzene derivatives)

ANILENE SULFATE

 $(C_6H_5NH_2)_2 \cdot H_2SO_4$

(see also Dyes)

This crystalline powder is highly soluble in water. It may occur in wastes from textile and chemical industries. According to Bringmann and Kuhn (2158) the threshold of toxicity toward *Daphnia* occurred at 0.6 mg/l during a 2-day exposure at 23°C. For *Scenedesmus* held 4 days at 24°C, the threshold concentration was 32 mg/l, but for *E. coli* at 27°C, no effect was observed at concentrations up to 1000 mg/l.

ANIMAL AND VEGETABLE OILS

(see also Oil-petroleum)

Large quantities of grease and fat are found in wastes from packing plants, slaughter houses, rendering plants, refineries, cotton seed processing plants, textile mills, milk-processing plants, and chemical works (917). Free oil was the most harmful constituent of the wastes from a quinine-manufacturing plant in India (758).

In many wastes containing oils, such as maize and soya-bean oil, tastes are imparted to fish flesh, owing to the unsaturated fatty acids (616). According to Eldridge and Purdy (983) soluble oils used in machining operations coat stream surfaces, prevent aeration, and create a nuisance. Such wastes have B.O.D. values ranging from 1300 to 12,000 mg/l. The Michigan Stream Control Commission considers 15 mg/l of such oil to be an upper limit.

Schaut (362) reports that saponified grease liquors from an animal oil plant, diluted 1:240 with stabilized tap water, gave a fragrant odor and a noticeable turbidity. Minnows in this dilution showed no distress in five days of exposure. Waste liquor from the sulfonation of animal oils, at 1:240 dilution, gave high turbidity and surface oil spots, with a strong oily odor, and minnows placed in such a dilution would not eat. They recovered their appetities in fresh water. At a dilution of 1:2400, no deleterious effect was observed during a one-hour exposure.

ANTHRACENE

 $C_{14}H_{10}$

Used as an important source of dyestuffs, this solid hydrocarbon is insoluble in water although it can be dissolved in alcohol and other organic solvents. Even if it should be discharged in industrial wastes, it may be expected to precipitate from solution. In Lake Huron water during a 24-hour exposure at 12°C, a concentration of 5.0 mg/l had no effect on rainbow trout, the bluegill sunfish, or the sea lamprey (2976).

ANTIBIOTICS

(see Chapter IX)

ANTIMONY

Sb

(see also Antimony Potassium Tartrate, Antimony Trichloride, Antimony Triffuoride, Antimony Trioxide) This silvery-white metal, also known as stibium, is seldom found pure in nature. It occurs chiefly as the sulfide (stibnite) or as the oxides, cervantite (Sb2O4). and valentinite (Sb₂O₃). The metal is used for alloys and other metallurgical purposes. The salts, primarily sulfides and oxides, are employed in the rubber, textile, fireworks, paint, ceramic, and glass industries (2121). The trichloride is a dye and it may occur in textile wastes. Antimony forms salts with a +3 and +5 valence. The trichloride, sulfate, potassium tartrate, and pentachloride are soluble in water but the antimony tends to be precipitated as Sb₂O₃ or Sb₂O₅. The sulfides are also insoluble. Consequently, any dissolved antimony that might be discharged to natural waters would soon precipitate and be removed by sedimentation and/or adsorption.

There is no evidence that antimony is an essential element in human nutrition, but it has been found to be toxic. Indeed, it has been used since ancient times as an emetic. Doses as low as 100 mg have been fatal. The symptoms are similar to those of arsenical poisoning. Since 1949, antimony potassium tartrate has been given intravenously for the treatment of schistosomiasis. On the other hand, it has been known to produce severe electrocardiographic abnormalties, skin eruptions, and

even pneumonia (2121).

The compounds of antimony are toxic, and are classed as acutely moderate or chronically severe. According to this categorizing, moderate toxicity includes injury to internal organs, and severe toxicity includes seriously debilitating effects or death (2325). It has been reported that 97.2 mg of antimony has caused the death of an adult, and 48.6 mg the death of a child. Antimony metal, up to 100 mg/day per 100 gm body weight fed to rats, allowed normal growth but resulted in a consistent injury to the heart. Antimony added to the food of rabbits caused a progressive increase in both the hemoglobin and in the total red cells, and when fed to cats was accompanied by a decrease in white cells (2121).

It has been reported (3344) that antimony can be concentrated by certain forms of marine life to over 300 times its concentration in the surrounding waters.

ANTIMONY POTASSIUM TARTRATE

 $K(SbO)C_4H_4O_6\cdot\frac{1}{2}H_2O$

Known as "tartar emetic", this soluble salt of antimony is used as a mordant in the textile and leather industry (364), and for ant baits or thrip control. The death of man may result from ingestion of 150 mg of tartar emetic by mouth. Daily doses of 20 mg of tartar emetic have limited the growth of rats. A single dose of 115 mg tartar emetic per kg of body weight has been fatal to rabbits within 26 to 72 hours; and 120 to 125 mg per kg has been fatal within 24 to 36 hours (353). The minimum lethal oral dose for rats is reported at 300 mg/kg. Rats fed up to 100 mg/kg daily for 12 months reportedly grew normally, but heart injury resulted (2121). Horses can take 5.8 grams, and cattle 3.8 grams three times daily without apparent harm (353).

Tartar emetic has been employed in medical use, particularly for the treatment of certain tropical parasitic diseases, but is no longer recommended because of the frequency and severity of toxic reactions, less toxic antimony compounds being available (364). It is also used in veterinary medicine. Effects on the heart have been frequently noted as a toxic manifestation of tartar emetic, the mortality from cardiac arrhythmia being reported as 50 percent between the years 1952 and 1954. Seven out of 12 patients manifested considerable electrocardiographic abnormalities while undergoing tartar emetic therapy. A more recent survey of eleven patients led to the conclusion that the cardiac disturbance is a combined effect of functional disorder of the autonomic system caused by an inhibitory effect of antimony on the cerebral cortex and hyperexcitability of the myocardium induced by antimony (2121).

The 96-hour TLm of fathead minnows has been estimated at 20 mg/l in soft water and 12 mg/l in hard water, as antimony (2125, 2154). Tartar emetic is re-

ported to begin hindrance of protozoan food intake at 15 mg/l, of cellular division in green algae at 3.5 mg/l, and of movement of Daphnia at 9 mg/l (3343). A concentration of 5 mg/l had no effect on sea lampreys in Lake Huron water during a 24-hour exposure (2976).

Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158) studied the threshold effects of antimony ammonium tartrate on various organisms. For Daphnia exposed for 48 hours at 23°C, the median threshold effect occurred at 9 mg/l of antimony; for Scenedesmus at 24°C for 4 days, the median toxic threshold was 3.5 mg/l as antimony; and for Escherichia coli at 27°C, it was 33 mg/l as antimony.

ANTIMONY TRICHLORIDE

SbCl₃

This liquid substance is used in an acid solution as a mordant for patent leather and in dyeing (364). It has been encountered in poisoning cases. Anderson (598) has reported a threshold immobolization concentration for Daphnia magna in Lake Erie water at 25°C of 37 mg/l. The 96-hour TL_m for the fathead minnow has been estimated at 9 mg/l in soft water and 17 mg/l in hard water, both as antimony, based on exploratory tests only (2154). In Lake Huron water at pH 7.5-8.2, saturated with dissolved oxygen, and at 13°C, rainbow trout, bluegill sunfish, and the sea lamprey were not affected during a 24-hour exposure to 5 mg/l of SbCl3 or SbCl5 (2976).

ANTIMONY TRIFLUORIDE

This soluble trivalent salt of antimony is soluble in water. It is used for dyeing in the textile industry and also for the manufacture of pottery and porcelains (364). At a concentration of 200 mg/l it killed fish (Tinca vulgaris) in less than 24 hours. Given orally to adult guinea pigs, 100 mg/kg of SbF₃ was fatal (3271).

ANTIMONY TRIOXIDE

This oxide of antimony, used as a paint pigment and a mordant, is insoluble in water and consequently not likely to be found for long in polluted streams. The oral $\overline{\mathrm{LD}_{50}}$ in rats is greater than 20 gm/kg (364). In chronic studies, dosages up to 4 mg daily have been well tolerated by rats (2121). When it was administered in food at a 2 percent level, reduced growth rates were observed in rats and rabbits (149). Single doses of 2 to 3 grams of antimony trioxide, antimony pentoxide (Sb₂O₅), and sodium metantimonate (2NaSbO₃·7H₂O), cause no indication of poisoning in rats. Daily doses of 250 to 500 mg of antimony trioxide, antimony pentoxide, and sodium metantimonate had no effect on the growth of rats. Daily doses of 150 mg/kg of antimony trioxide have been apparently harmless to rabbits over a 4-week period (353). The 96-hour TL_m toward the fathead minnow in hard or soft water, based on exploratory tests only, was found to be over 80 mg/l, as antimony (2154).

ARAMITE

(see Chapter IX)

ARESKAP

ARESKET 300

ARESKLENE 400

(see Chapter X)

AROMATIC SOLVENTS

(see Chapter IX)

ARQUAD C

ARQUAD D

(see Chapter X)

ARSENIC

As

1. General. Found to a small extent in nature in the elemental form arsenic occurs mostly as the arsenides of true metals or as pyrites. It is generally recovered as a by-product from the processing of other ores, e.g., copper, lead, zinc, tin. Upon smelting of these ores, arsenic is oxidized and liberated in the flue dust, chiefly as arsenic trioxide. It also forms a tetraoxide and pentoxide. Hence, arsenic may have valences of +3, +4, and +5.

Arsenic is used in metallurgy to increase hardening and heat resistance, in glassware and ceramics, in tanneries, in dye manufacture, and in chemical industries. Its major use, however, has been for pesticides (insects, weeds, fungi) and as a wood preservative. It is also used in the manufacture of arsenical organic compounds for therapy (364, 2121). Elemental arsenic is insoluble in water but many of the arsenates are highly soluble. Indeed, arsenic compounds occur naturally in some waters of the western U.S.

The following material has been derived from the general literature on arsenic. In addition, however, the reader should consult the information given under specific arsenic compounds.

- 2. Cross References. Ammonium Arsenate, Arsenic Triexide, Lead Arsenate, Sodium Arsenate, Sodium Arsenite, Selenium, Chapter VIII, Chapter IX.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Although arsenic compounds are constantly taken into the body as a constituent of food, there is no evidence that arsenic is an essential element in human nutrition (2121). Normal human blood contains 0.2 to 1.0 mg/l of arsenic. It is found naturally in many foods such as vegetables and fruit, and shellfish may contain over 100 mg/kg. It also occurs as a residue on sprayed fruits and vegetables, for which the U. S. Food and Drug Administration has set a limit of 3.5 mg/kg. The Food Standards Committee for England and Wales put into effect on August 1959 a new regulation for arsenic limiting ready-to-drink beverages to 0.1 mg/l and food to 1.0 mg/kg (150).

Arsenic is notorious for its toxicity to humans. Ingestion of as little as 100 mg usually results in severe poisoning and as little as 130 mg has proved fatal (2121). One reference (3336) reports a lethal dose at 325 mg of sodium arsenite or 187 mg of As. Furthermore, arsenic accumulates in the body, so that small doses may become fatal in time. A single dose may require ten days for complete disappearance and this slow excretion is the

basis for the cumulative toxic effect. Chronic arsenosis is of slow onset, and may not become apparent for 2 to 6 years. Small eruptions occur on the hands and on the soles of the feet, sometimes developing into arsenical cancers. Liver and heart ailments may also supervene (155, 996). In water taken over a long period of time the following concentrations of arsenic have been reported as poisonous to human beings:—0.21 mg/l (997), 0.3-1.0 mg/l (155), and 0.4-10.0 mg/l (996, 997). On the other hand, the following concentrations have been reported to be safe in drinking water:—0.05 mg/l (152, 353, 897), 0.10 mg/l (32, 155, 460, 1000, 1001), 0.15 mg/l (353, 579, 997), 0.15-0.25 mg/l (1000), 0.2 (152, 633), and 1.0 mg/l temporarily for several months in a part of Los Angeles (152).

Arsenic has been suspected as a causal factor for Haff's disease among human beings, but no proof has been found that there is any relationship between them (998, 999). Arsenical pollution of wells is reported to have caused deaths of humans in South Africa; in one case the water contained 12 mg/l of arsenic (1048).

Several incidents have demonstrated that arsenic in water may be carcinogenic. There have been several instances where cancers of the skin, and possibly the liver, have been attributed to arsenic in the domestic water supply (3337, 3338, 3339).

In 1942 for the first time, the USPHS Drinking Water Standards prescribed a maximum permissible concentration of 0.05 mg/l for arsenic and this mandatory limit is still in effect (2036). In 1962, however, a recommended limit of 0.01 mg/l was added to the mandatory limit of 0.05 mg/l. The WHO International (2328) and European (2329) Drinking Water Standards prescribe a maximum allowable concentration of 0.2 mg/l for arsenic.

b. Irrigation. Arsenic is a normal constituent of most soils, with concentrations ranging up to 500 mg/kg. Although very low concentrations of arsenates actually stimulate plant growth, the presence of excessive soluble arsenic in irrigation waters will reduce the yield of crops, the main effect appearing to be the destruction of chlorophyll in the foliage. Plants grown in water containing one mg/l of arsenic trioxides showed a blackening of the vascular bundles in the leaves. Beans and cucumbers are very sensitive, while turnips, cereals, and grasses are relatively resistant. Old orchard soils in Washington that contained 4 to 12 mg/kg of arsenic trioxide in the top soil were found to have become unproductive.

The root growth of lemon plants grown in solution cultures was stimulated by 1 mg/l of arsenic dosed as either an arsenate or an arsenite; however, 5 mg/l of arsenate arsenic and 10 mg/l of arsenite arsenic were definitely toxic to root growth and top growth (3340). Hewitt (1473) found that 23 mg/l of arsenate was slightly injurious to sugar beets in sand culture.

c. Stock and Wildlife Watering. In New Zealand, sickness and death among cattle have been caused by arsenic of natural origin in water supplies (1002, 1049). The lethal dose of arsenic for animals is believed to be about 20 mg per animal pound (1003). Fowl and pigs have died after eating one feed of contaminated pig meal containing 6.5 mg of arsenic per ounce (1004).

On the other hand, selenium poisoning among cattle, dogs and chickens has been treated by feeding arsenic in concentrations of 12 to 15 mg/l in water (1005); and 5 mg/l arsenic (as Na₂HAsO₄) in drinking water has counteracted selenium poisoning among pigs, dogs, and rats (921).

In a brief outline of the toxic effects of some common poisons, Wadsworth (3108) gives the following toxic doses for arsenic:

Animal	Toxic dose, in gram		
43. 7	0.05- 0.10		
The same	0.10- 0.20		
SwineSheep, goats, horses			
Sheep, goats, norses	15-30		
COW8			

For rats and mice, 96-hour $\rm LD_{50}$ doses of arsenic trioxide varied from 15.1 to 214 mg/kg based on oral administration (3341). Another reference (2999) reported the $\rm LD_{50}$ for female rats was 298 mg/kg based on calcium arsenate, or 112 mg/kg as arsenic. The minimum lethal dose of arsenic trioxide for various laboratory animals ranged from 5 to 100 mg per kg of body weight, solutions being more lethal than powders (364). Doses of 324 mg have killed experimental chickens in 24 hours (1004).

d. Fish and Other Aquatic Life. (see also Arsenic Trioxide, Sodium Arsenate, Sodium Arsenite). The folfollowing concentrations of arsenic have been reported as toxic to fish:

7.6 10 days 11.6 36 hours 15 — 17.8 16 hours	crabs bass minnows crappies and bluegills minnows minnows minnows	2977 311 617 900 2962 617 2962
---	---	--

In contrast, the following concentrations have been reported as tolerable within the period specified:

Concentration of Arsenic, mg/l 0.7-1.1 0.76 1.1-1.6 1.5-5.3 2.2 2.2 3.1 5.3 6.0 7.6	Exposure 48 days 11 days 1-7 days 1-7 days 13 days 13 days 90 days 24-148 hours 232 hours 30 days	Type of Fish pike perch fish bleak fish carp eels crabs fish bass trout minnows	Reference 2977 677 2977 353 2977 2977 2977 2977 313, 778, 1009 900 1012 353
13.0	1 hour	minnows	353

With respect to lower forms of aquatic life, arsenic concentrations of 3-14 mg/l have not harmed mayfly nymphs and 10-20 mg/l has been harmless toward dragon and damsel flies (574). Concentrations of 2-4 mg/l of arsenic are reported not to interfere with the self-purification of streams (579). Bacteria grow even in the presence of 10,000 mg/l of potassium arsenate and algae are not killed at 1000 mg/l of arsenate (2977). The fermentation and propagation of yeast are stopped at 300 mg/l of arsenate (2977).

Arsenic-76 occurs in the effluent from nuclear reactors (3342) and may be concentrated to a limited ex-

tent in the aquatic food chain. For more detail, see Chapter VIII.

The Mersey and Severn River Boards in England have adopted working standards limiting the total concentration in effluents of all heavy metals, including arsenic, to 1.0 mg/l (1756, 2950).

4. Summary. On the basis of the foregoing information, the following limits for arsenic are indicated for these beneficial uses:

90	D 0110	~ ~=	
	Domestic water supplies	0.05	mg/i
a.	Irrigation	10	mg/l
b.	Irrigation	1.0	
_	Charle and wildlife watering	1.0	щь/ •
c.	Stock and withing the series	10	mg/l
d.	Fish and other aquatic life	1.0	

ARSENIC TRIOXIDE

 As_2O_3

(see also Arsenic, Lead Arsenate, Sodium Arsenate, Sodium Arsenite)

This compound is the most common oxide of arsenic and owing to the method of recovery of arsenic from ores of other metals, arsenic trioxide serves as the primary material for other arsenic compounds. It is also called "white arsenic" and arsenous acid. It is the primary ingredient of arsenical pesticides. It is sparingly and slowly soluble in cold water.

The following concentrations of arsenic trioxide have been harmful to fish or other aquatic life.

Concentration of Arsenic Trioxide in mg/l 1.96 2 to 3 2.5 2.5 to 4 5.3 10 10	Time of Exposure, days	Type of Organism Chironomus fish food organisms fish food organisms fish food organisms pink salmon fish bass bass, bluegills, crappies	Reference 574, 1008 1007 311 313 2091 1011 311 3005
16 40	3 to 16	mussels flatworms	353, 313

Surber and Meehan (1008) carried out a comprehensive study of the toxicity of arsenic trioxide to many different fish food organisms. Their results indicated that important fish food organisms can tolerate 2.0 mg/l of arsenic trioxide. For detailed information on the percentage survival of various forms, see the original paper.

The following concentrations of arsenic trioxide have not been harmful to some aquatic organisms in the time specified:

1			
Concentration Arsenic Trioxi in mg/l		e Organism	Reference 677
1.0		fish _	574
7.0		chironomus larvae	353, 1008
1.9 2 2 2 2-6		food organisms	393, 1000
z		food organisms	313
2		bass, bluegills,	3005
2-6		pass, pinegins,	
·		crappies	35 3
2-7	1-7 days	fish	574
9 1 4		mayfly nymphs	574
3-14 5 5		some zooplankton	0.1
2 ·	24 hours	trout, bluegills,	2976
- 5	24 Hours	sea lamprey	
		fish	353
5		IISH	2988
5 5-10	15-30 minutes	coho salmon	1009, 778, 313
7	24-148 hours	fish _	313
9		mussels	1012
7 8 10	1 month	trout	574
10 00	_ 111011-	insect larvae	353
10-20	1 hour	minnows	จูออ
17.1	THOM	initiate	

ATA

(see Chapter IX)

ATABRINE

(see Quinacrine Hydrochloride)

BARIUM

Ra

1. General. This yellowish-white alkaline-earth metal is rapidly decomposed by water to form barium ions. It is found in nature as barytes, BaSO₄, witherite, BaCO₃, and other ores. Many of its salts are soluble, but the carbonate and sulfate are highly insoluble (911); consequently it is to be expected that any barium ions discharged to natural waters will be quickly precipitated and removed by adsorption or sedimentation. Barium ions are not normally present in natural surface or ground waters in measurable concentration although they have been detected in a few springs and in effluents from areas where barytes or witherite are mined (2972). For sea water, the concentration of barium has been reported (3345) as 0.0062 mg/l.

Barium and its salts are used in the metallurgical industry for special alloys, in the paint industry, as a constituent of cements designed to withstand salt water, in the ceramic and glass industries, and in several other applications (2121)

2. Cross References. Barium salts, Chapter VIII.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Neither the WHO International nor WHO European Drinking Water Standards (2328, 2329) prescribes a recommended or maximum allowable limit for barium; and until 1962 there was no limit in the USPHS Drinking Water Standards. At that time, however, a mandatory limit of 1.0 mg/l was established, presumably because of possible toxic effects of barium on the heart, blood vessels, and nerves (2062).

The fatal oral dose of barium for man is reported to be 550 to 600 mg, although a case is recorded where a man ingested about 7 grams of BaCl₂ and recovered eventually (2121). Barium salts are considered to be muscle stimulants, especially for the heart muscle. By constricting blood vessels, barium may cause an increase in blood pressure. On the other hand, there is no evidence that barium accumulates in the bone, muscle, kidney, or other tissue. It is excreted more rapidly than calcium. Hence there is no danger of a cumulative effect (2121).

Stokinger and Woodward (2325) have calculated a safe concentration of barium in drinking water on the basis of the threshold limiting values in industrial atmospheres, an estimate of the amount absorbed into the blood stream, and daily consumption of two liters of water. On this basis a limiting concentration of 2.0 mg/l was computed; but to provide a safety factor and to allow for possible accumulation in the body, a limit of 1.0 mg/l was recommended.

b. Irrigation. Barium is present in trace amounts in most soils and up to 1.0 percent in some. It is apparently not utilized by most plants except possibly in trace quantities, and indeed it is considered to be poisonous to most plants. An exception is the Brazil nut which may contain over 1000 mg/kg (2121).

c. Fish and Other Aquatic Life. The lethal concentration limit of barium for stickleback (Gasterosteus aculeatus) has been given as 400 mg/l (353, 2941). The

lethal concentration limit is defined as the concentration to which the substance must be reduced before definite toxic effect disappears (2941). Barium is concentrated by goldfish from solution by a factor of approximately 150 (2435). The Mersey and Severn River Boards in England have established effluent standards that restrict barium alone or in combination with all heavy metals to a total concentration of 1.0 mg/l (2950). For further details relative to the toxicity of barium toward aquatic life, see Barium Acetate, Barium Carbonate, Barium Chloride, Barium Fluoride, and Barium Nitrate.

4. Summary. On the basis of quite limited information, the following tentative limits for barium are suggested:

a. Domestic water supplies_______ 1.0 mg/l b. Fish and other aquatic life______ 5.0 mg/l

BARIUM ACETATE

 $\mathrm{Ba}(\mathrm{C_2H_3O_2})_2\!\cdot\!\mathrm{H_2O}$

(see also Barium)

Highly soluble in water, this salt is used as a mordant in dyeing. The oral LD_{50} in rabbits is reported as 236 mg/kg of body weight (364). In Lake Huron water at 12°C, 5 mg/l of barium acetate had no effect on rainbow trout, bluegill sunfish, or the sea lamprey during a 24-hour exposure (2976).

BARIUM CARBONATE

BaCO₃

(see also Barium)

Occurring in nature as the mineral witherite, this compound is soluble in water only to the extent of 22 mg/l at 18° C (911). The oral LD₅₀ for rats is reported as 800 mg/kg of body weight (364). Wallen et al. (2940) tested its toxicity toward the mosquito-fish (Gambusia affinis) in highly turbid water at 17-20°C. They reported the 96-hour TL_m as greater than 10,000 mg/l but it is not evident that more than 22 mg/l went into solution.

BARIUM CHLORIDE

 $BaCl_2 \cdot 2H_2O$

(see also Barium)

This readily soluble salt is used as a mordant for acid dyes, for weighting and dyeing fabrics, in paint manufacture, and in tanning operations. The oral LD_{50} for dogs is 90 mg/kg of body weight (364).

Toward fish, the following effects have been reported:

Concen-					
tration					
of BaCl		Type of			
in mg/l	Exposure	Fish	Remarks		Refer- ence
50	72 hours	young silver salmon	harmed nervous	system	2091
158	72 hours	young silver salmon	killed 90 percent	:	2091
282	23 hours	young silver salmon	total kill		2091
520	over 50 hours	young eels	tolerated at 20°C	•	1459
1640	96 hours		TLm in turbid wa at 20°C		2940
2083	36 hours	young eels	TLm at 20°C		1459
2480	9 hours	minnows	lethal at 15°C		1459
3200	48 hours	mosquito-fish	TLm in turbid wa at 20°C	ter	2940
3260	24 hours	Orizias	lethal concentrat	ion	1459
4400	24 hours	mosquito-fish	TLm in turbid wa at 20°C		2940
5000	12-17 hours	goldfish	lethal in dist. was	ter	312
8-10,000			lethal at 20.5°C	353, 364,	

For fish-food organisms, Anderson (598) reports the threshold concentration for immobilization of Daphnia magna in Lake Erie water at 25°C to be 29 mg/l in 64 hours. Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158) found the toxic threshold for Daphnia at 23°C to be 170 mg/l as barium or 200 mg/l as BaCl₂ during a 48-hour exposure. For Scenedesmus the toxic threshold at 24°C was 34 mg/l as barium or 40 mg/l as BaCl₂ during a 96-hour exposure; while E. coli were not affected by 1000 mg/l as barium at 27°C.

The following threshold concentrations for aquatic invertebrates in Lake Erie water at 20-25°C were reported (2955):

Organism
Daphnia magna
Leptodora kindtii
Cyclops vernalis
Other fish

Threshold Concentration For Immobilization, mg/l 29

12 123 5000

According to Bijan and Deschiens (3346) barium chloride was lethal to aquatic life as follows:

Type of Organism	Scientific Name	Lethal Concentration in mg/l
Snail	Bulinus contortus	14.3
Snail	Planorbis glabratus	11.1
Goldfish	Carassius auratus	200
Aquatic plant	Elodea canadensis	10.0

BARIUM FLUORIDE

BaF₂

(see also Barium)

This highly soluble salt is used in heat treating metals, in embalming, and as an opacifier for vitreous enamels. The oral LD₅₀ for guinea pigs is 350 mg/kg of body weight (364). The lethal dose in 48 hours toward the tench, *Tinca vulgaris*, is reported (3271) to be 10,000 mg/l.

BARIUM NITRATE

 $Ba(NO_3)_2$

(see also Barium)

Readily soluble in water, this compound is used in the vacuum-tube industry, for green signal flares, and for pyrotechnics (364).

The lethal concentration of barium nitrate toward stickleback at 15-18°C has been reported as 400 mg/l as barium, or 760 mg/l as barium nitrate (598, 1460, 2920). The average survival times for higher concentrations were one week at 500 mg/l, four days at 1000 mg/l, two days at 2500 mg/l, and only one day at 3000 mg/l, all as barium (1460). Mathews et al. (3347) found that the maximum concentration of barium nitrate that did not affect fish was 25 mg/l. In Lake Huron water at 12°C, 5.0 mg/l had no effect on rainbow trout, bluegill sunfish, or the sea lamprey during a 24-hour exposure (2976). According to Bijan and Deschiens (3346), two species of snails (Bulinus contortus and Planorbis glabratus) were killed by 20 mg/l of barium nitrate, goldfish by 200 mg/l, and the aquatic plant, Elodea canadensis, by 10 mg/l.

BARIUM SULFIDE

BaS

(see also Barium)

This slightly soluble gray powder is used as a depilatory, in luminous paints, and for vulcanizing rubber (364). A concentration of 5.0 mg/l in Lake Huron water

at 12°C had no effect on rainbow trout, bluegill sunfish, or the sea lamprey during a 24-hour exposure (2976).

BARON

(see Chapter IX)

BEET SUGAR WASTES

(see also Saponin, B.O.D.)

The introduction of beet-sugar wastes suddenly into a stream has caused mass killing of fish, the inhibiting of diatom growth, the stimulation of sewage fungus, and the destruction of normal benthal organisms (457). The lethal effect is attributed to a combination of the deoxygenating effect of the B.O.D. and the toxicity of the beet saponins (458). Cole reported that a 2-percent solution of Steffen's waste was fatal for fish (311).

BENOCLOR

(see Chapter IX)

BENZALDEHYDE

C₆H₅CHO

(see also Amygdalin)

This aromatic liquid aldehyde, highly soluble in water, is used extensively in the chemical industry in the synthesis of compounds containing aromatic groups. It is also employed as a perfume and flavoring material under the name of oil of bitter almonds.

Ruchhoft (459) reports that in chlorinated water the lowest concentration of p-hydroxybenzaldehyde (HOC₆H₄CHO) that usually caused a taste in water is 0.002 mg/l. According to Klein (1756), a concentration of 0.003 mg/l of benzaldehyde causes a faint odor in water.

In stabilized tap water saturated with oxygen, Schaut (362) found that 17.1 mg/l of 85 percent benzaldehyde caused minnows to stop eating, but they did not die.

BENZENE C₆H₆

(see also Benzene Derivatives, Cyclohexane)

Benzene, the simplest of the aromatic compounds, is used extensively as a commercial solvent and for the synthesis of other organic substances. It occurs in wastes from chemical plants, dyeing and other textile operations, and many other industrial processes. At normal temperatures, it is a volatile, flammable, colorless liquid with an ethereal odor. It is soluble in water to the extent of 820 mg/l at 22°C. The oral LD₅₀ for rats is reported as 5600 and 5700 mg/kg of body weight (364, 3348).

According to Avramenko (3349) the benzene content of drinking water should be kept below 4.5 mg/l to avoid taste, but Kirkor (460) claims that the minimum detectable concentration of benzene in water is 0.5 mg/l. Chlorination and the presence of other substances, however, may alter this figure.

Toward fish, the toxicity of benzene has been reported as low as 5 mg/l and as high as 395 mg/l. According to LeClerc (2942), the minimum lethal dose of benzene toward minnows during a 6-hour exposure was 5 to 7 mg/l in distilled water at 18°C and 6 to 7 mg/l in hard water at 16°C. Using the bluegill sunfish in Philadelphia tap water at 20°C, Turnbull et al. (2093) found the 24- and

48-hour TL_m values both to be 20 mg/l. At 60 mg/l all fish died within two hours. At 34 mg/l all died within 24 hours. The lethal concentration for rainbow trout has also been reported as 10 to 20 mg/l and the toxicity threshold as 5 mg/l (2977). Several other investigators (461, 462, 463, 2961) reported that concentrations of benzene as low as 20 mg/l killed fresh-water fish in one hour or longer. According to Shelford (363) the lethal concentration for sunfish is 35-37 mg/l. Using highly turbid water at 20-22°C and the mosquito-fish (Gambusia affinis), Wallen et al. (2940) found the 24- and 48-hour TL_m to be 395 mg/l and the 96-hour TL_m to be 386 mg/l. The addition of benzene did not help to clarify the turbid water.

Photosynthetic activity of the giant kelp (Macrocystis pyrifera) was not affected by exposure to 10 mg/l of benzene over a period of 96 hours (2108).

BENZENE DERIVATIVES

(see also Benzene, Cyclohexane, Phenol, Halogenated Hydrocarbons, Halogenated Phenols, and their cross-references; also Chapter IX)

Sollman (1474) tested the toxicity of phenols, quinones, and other benzene derivatives to goldfish in glass aquaria containing two liters of tap water at room temperature to which the goldfish had been adjusted. The chemical under investigation was added and symptoms or fatality were observed during one to three days. Death after 48 hours was so exceptional that this time was selected for fatality calculation. The "approximate fatal concentration" was taken as the geometric mean between the largest concentration survived for 48 hours and the smallest concentration that was fatal in this time for practically all fish. The results of these tests are represented below.

- cochica bolo ;;			
	Approximate Fatal		
Substance	Concentration, in mg/l		
Hydroquinone	0.287	27	
p-methylaminophenol (metol, elon)		4	
2, 2, 4-trimethyl (a-phenyl-isopropyl)		-	
1, 2, dihydroquinoline	1.8	4.	
p-aminophenol	2.0	4	
2-mercaptobenzothiazol (captax)	_ 2	4	
hydroquinone monobenzyl ether (algerite	•	_	
alba)	2.5	5	
n-phenyl-β-naphthylamine (algerite power	ler) 4.4	6	
aniline bydrochloride	5.5	3	
p-isopropoxy diphenylamine (iso)	5.7	3	
p-phenylenediamine	5.74	6	
pyrocatechol	14	3	
pyrogallol	18	5	
p-hydroxyphenylglycine	20	2	
phenoi	28.9	8	
4-chloro-2, 5-dihydroxy diphenyl sulfone	35	4	
4, 5-dimethyl-2-mercaptothiazole	56	3	
resorcinol	57.4	3	
p-octyl diphenylamine		4	
2, 4-diaminophenol hydrochloride (amido	ol) 80	3	
hydroquinone monomethyl ether	200	4	
phloroglucinol		4	
= -			

BENZENE HEXACHLORIDE

(see Chapter IX)

BENZOIC ACID

 C_6H_5COOH

1. General. Benzoic acid is a white crystalline solid which occurs naturally in resin, gum benzoin, and to a

limited extent in cranberries. It may occur in wastes from chemical or gas plants, food-processing plants, or textile processes.

2. Cross References. See Sodium Benzoate, Phenol, Salicylic Acid.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Ruchhoft (459) quotes references to the effect that, in chlorinated water, the lowest concentrations of the following substances producing tastes are:

Substance	Concentration in mg/l
m-hydroxybenzoic acid	1.0
p-hydroxybenzoic acid	0.01
o-hydroxylbenzyl alcohol	less than 0.001

b. Fish and Other Aquatic Life. Ellis (313) states that 200 mg/l of benzoic acid is lethal to goldfish in 7 to 96 hours and Shelford (363) shows that concentrations of 550 to 570 mg/l killed orange-spotted sunfish in one hour. Wallen et al. (2940) tested the effect of benzoic acid on the mosquito-fish (Gambusia affinis) in highly turbid water at 19-21°C. They found the 24-, 48-, and 96-hour TL_m values to be 240, 225, and 180 mg/l respectively. The benzoic acid precipitated the turbidity. The threshold concentration for immobilization of Daphnia magna during prolonged exposure with Lake Erie water at 25°C was 146 mg/l (348).

According to Doudoroff and Katz (361) benzoic acid can be toxic to fish without lowering the pH value to 5.0. Toxicity is attributed to the undissociated acid in solution; hence pH is not a reliable index of dangerous pollution.

The introduction of the COOOH group into the phenol molecule to form HOC₆H₄COOH in either the meta or para position decreases the toxicity to goldfish but in the ortho position, toxicity is increased. Gersdorff (464) reports that relative toxicities, i.e. minimal products of concentration and survival time, were as follows at 27° C:

Substance	Relative Toxicity
p-hydroxybenzoic acid	0.22
m-bydroxybenzoic acid	0.35
phenol	1.00
benzoic acid	1.6
o-hydroxybenzoic acid	2.5

BENZONITRILE

C₆H₅CN

This flammable liquid with the odor of almond is slightly soluble in cold water. At a concentration of 5 mg/l it caused no effect upon rainbow trout, bluegill sunfish, or sea lamprey exposed for 24 hours in Lake Huron water at 12°C (2976). Henderson et al. (2958) found the TL_m concentrations at 25°C toward three species of fish to be as follows:

		Type of		TL_m in mg/l	
Fish		Water	24-hour	48-hour	96-hour
Fathead	minnow	Hard	116	78	78
	minnow	Soft	240	180	135
Bluegill	sunfish	Soft	78	78	78
Gupples		Soft	400	400	400

Adult bluegills exposed for four weeks in water containing 35 mg/l of benzonitrile did not pick up any organoleptic properties that were apparent to a taste panel but there was a sweetish solvent odor in the test aquaria (2958).

BENZOPYRENE

(see Chapter X)

BENZYL ALCOHOL

 $C_6H_5CH_2OH$

Known also as phenylmethanol, this liquid with a faint aromatic odor is highly soluble in water. It is used in perfumery, in flavoring, as an insect repellant and as an organic solvent (364). According to Bringmann and Kuhn (2158) the median threshold effect of benzyl alcohol toward Daphnia held at 23°C for two days occurred at 360 mg/l; toward Scenedesmus during a 4-day exposure at 24°C the threshold was 640 mg/l; and toward E. coli at 27°C no effect was evident for concentrations up to 1000 mg/l.

BENZYL BROMIDE

 $C_6H_5CH_2Br$

(see also Benzyl Chloride)

This compound of bromine with toluene is a lachrymatory liquid that is insoluble in, but slowly decomposed by, water (364, 3292). Studying the relation of chemical structure to the irritant responses in marine fish, Hiatt et al. (3350) found that 0.05 mg/l of benzyl bromide produced no irritant response but 0.1 mg/l caused violent irritant activity.

BENZYL CHLORIDE

 $C_6H_5CH_2Cl$

(see also Benzyl Bromide)

This refractive liquid with an unpleasant irritating odor is produced by chlorinating toluene (364). It is insoluble in water (3292). Hiatt et al. (3350) found that 1.0 mg/l of benzyl chloride produced no irritant response in marine fish but 10 mg/l caused a slight irritant activity.

BENZYLAMINE

 $C_6H_5CH_2NH_2$

This liquid is miscible with water, producing a strong alkaline reaction, apparently from dissociation and the formation of ammonium ions. It is used industrially for organic synthesis (364). Bringmann and Kuhn (2158) found that the toxic threshold for Scenedesmus occurred at 6 mg/l during a 4-day exposure at 24°C. For Daphnia the threshold was 60 mg/l during 2 days at 23°C, but E. coli at 27°C showed no adverse response at concentrations up to 1000 mg/l.

BERYLLIUM

Be

- 1. General. A relatively rare element, found chiefly in the mineral beryl, this substance is not likely to occur in natural waters. Although the chloride and nitrate are very soluble in water and the sulfate moderately so, the carbonate and hydroxide are almost insoluble in cold water (364). Beryllium is used primarily in metallurgy to produce special alloys, in the manufacture of X-ray diffraction tubes and electrodes for neon signs, and in nuclear reactors (2121).
 - 2. Cross References. Cadmium, Zinc.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Pomelee, in a comprehensive review article, reported that as late as 1953 there was no indication that beryllium in any form is harmful

when taken internally through the digestive tract (1478). On the other hand, beryllium has been incriminated in pulmonary ailments of workers exposed to beryllium dusts (2121).

Following the development about 1947 of spectrochemical techniques for detecting beryllium in air, there has been a substantial increase in the number of cases of beryllium poisoning reported in the literature. These cases have occurred as an occupational disease among individuals exposed in industry. The toxicity of beryllium to animals has been demonstrated in the laboratory, and it has been determined that poisoning among human beings has been caused by exposures to beryllium in the atmosphere at concentrations of less than 1 to 100 micrograms per cubic meter of air. The symptoms of berylliosis include skin and lung diseases of variable severity. The reactions of individuals to a given exposure level are said to vary widely, but apparently all persons will show a reaction if time and level of exposure are great enough (1477).

Absorption of beryllium from the alimentary tract is slight (about 0.006 percent of that ingested) and excre-

tion is fairly rapid (2121).

b. Irrigation Waters. In nutrient solution, at acid pH values, beryllium is highly toxic to plants. At pH values above 11.2, however, beryllium appears to be beneficial to plants with magnesium deficiency (1446). Solutions containing 15 to 120 mg/l of beryllium delayed germination and retarded the growth of cress and mustard seeds in solution culture (1479).

- c. Stock and Wildlife Watering. Rats were healthy after 2 years on a diet that included about 6.0 mg of beryllium sulfate per day, i.e., 3.6 mg of beryllium per day, or 18 mg of beryllium per kg of body weight per day. If it is assumed that this dosage is applicable to cows, then a cow could drink 250 gallons per day of water containing 6000 mg/l of beryllium without ill effects. Two dogs showed no ill effects after 19 months of daily ingestion of 10 mg of beryllium sulfate daily per kg of body weight. Of three dogs fed one gram of beryllium sulfate daily per kg of body weight, two showed no ill effects after 9 and 19 months; but one lost weight during a 9-month period and was killed for examination. No evidence of tissue damage was found (1478).
- d. Fish and Other Aquatic Life. Pomelee (1478) described a series of experiments to determine the effect of beryllium on fish and snails. In all of these experiments beryllium sulfate was complexed with sodium tartrate to keep beryllium in solution at pH 7-9. Beryllium in concentrations up to 28.5 mg/l was not toxic to goldfish, minnows, or snails; this concentration was reached after a period of three weeks during which beryllium sulfate and sodium tartrate were added daily to the aquaria.

When lagoon wastes from a beryllium plant were added to the aquarium water at the rate of 100-300 mg/l daily, no symptoms of injury to the fish could be detected at the end of 15 days, when the aquarium liquid contained less than 3 mg/l of Be, less than 1.0 mg/l of Fe, and less than 2100 mg/l of sulfate at pH 8.0. For five more days, 1000 ml of lagoon waste was added daily, but on the sixth day the fish became sluggish. Goldfish, transferred to fresh water at that time, recovered; minnows and snails left in the waste solution died after 4

days. A 5-percent waste solution was not toxic to fish, but a 10-percent solution was toxic. It has been suggested that the toxicity might be attributable to the high salt concentration of the lagoon water rather than to the presence of berryllium (1478).

Tarzwell and Henderson (2125, 2154) tested the toxicity of three beryllium salts toward fathead minnows and bluegills in hard and soft waters with the following 96-hour TL_m results in terms of beryllium:

•	Conc	centration of B	eryllium in n	na/I
	Fathead 1	Ainnows .		egills
Compound	Soft	Hard	Soft	Hard
Beryllium chloride Beryllium sulfate	0.15 0.2	15 1 !	1.3^{-}	1 2
Beryllium nitrate	0.15	20		

These results demonstrate that beryllium is considerably more toxic in soft water than in hard water. According to Hodgson (2956) a barium nitrate concentration of 30,000 mg/l is required to evoke a stimulatory reaction in the water beetle, *Laccophilus*.

e. Swimming and Other Recreational Uses. No information is available concerning the specific effect of beryllium in swimming waters. However, Pomelee has stated that water-soluble beryllium salts can cause ulcers if they enter a break in the skin (1478).

BHC

(see Chapter IX)

BICARBONATES

HCO₃

(see also Alkalinity, pH, Carbonates, Hydroxides, Chapter V-Irrigation)

The concentration of bicarbonates in natural and polluted waters is a function not only of the bicarbonates added thereto but also of the temperature, pH, and concentration of other dissolved solids. A full discussion of carbonate equilibria is beyond the scope of this report and the reader is referred to the work of Langelier (692). For this study of water-quality criteria, however, it is important to note that bicarbonates tend to reach an equilibrium with carbonates in accordance with the reactions:

$$H^{+} + CO_{3}^{--} \rightleftharpoons HCO_{3}^{--}$$

$$\frac{[H^{+}][CO_{3}^{--}]}{[HCO_{3}^{-}]} = K$$

where K is reported (911) to be 4.4×10^{-11} at 25°C. Thus, at pH 7 the ratio of bicarbonate ions to carbonate ions will be 2270 to 1, but at pH 10 it will be only 2.27 to 1 and at pH 11, the ratio will be 1 to 4.4. The concentration of bicarbonates therefore, depends on the pH value and the concentration of carbonates.

At medium and low pH values, a second equilibrium reaction occurs, for bicarbonates tend to unite with hydrogen ions to form $\rm H_2CO_3$ which, in turn, releases free $\rm CO_2$, thus

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

The equilibrium equation for this reaction is

$$\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} = K_1$$

where K_1 is reported (911) to be 3.5×10^{-7} at 18° C. Thus at pH 8 the ratio of carbonic acid to bicarbonate ions is only 0.0286, but at pH 7 it is 0.286 and at pH 6 it is 2.86.

Bicarbonates may reach water from many natural sources, including absorption of CO₂ from the air and the decomposition of organic matter, or they may be discharged by innumerable industrial processes, for bicarbonates are among the most commonly used salts.

Other than the fact that excessive bicarbonates add to the salinity and total solids content of water, and through the complex operations of the carbonate equilibria tend to form carbonates and scale at high temperatures, bicarbonates in water are seldom considered to be detrimental. Hibbard (250) recommends the following concentrations of bicarbonates:

Concentration				
$oldsymbol{Use}$	mg/l	Remarks		
Domestic water supplies		•		
Drinking	150	desirable or permissible		
Cooking	150	desirable or permissible		
Washing	60	desirable or permissible		
Laundering	none ·	desirable or permissible		
Industrial water supplies		-		
Textile	200	undesirable or objectionable		
Sugar	100	undesirable or objectionable		
Pottery	200	desirable or permissible		
Steam Boilers	100	undesirable or objectionable		

In concentrations of 257 mg/l or less, sodium bicarbonate caused a white shell in ice manufacturing (229). For limitations in boiler feed water, see Chapter V. High bicarbonate contents are reported to affect the stability of vitamins in the manufacture of preserves and to cause swelling of skins in tanneries (2368).

In a general discussion of alkali waters in Montana, Cobleigh (1059) points out that carbonates and bicarbonates in drinking waters react with gastric acids sometimes to the benefit of the drinker. He refers to a modified list of USGS data which gives 700 mg/l as the concentration of bicarbonates unhealthful to most people. Lockhart et al. (3241) report the taste threshold in distilled water of the bicarbonate ion (added as NaHCO₃) to be 770 mg/l.

The 10-year weighted average analyses of Colorado River water, according to Kelley (1060), show 172 mg/l of bicarbonate. It did not appear to Kelley that the use of this water for irrigation would seriously affect the underground supply, growth of citrus trees, or condition of the soil in southern California. Harley and Lindner (1061), on the other hand, found that irrigation waters in north central Washington containing 200 mg/l and more of bicarbonates caused a marked decline in the vigor of apple and pear trees after a number of years.

Chapter V of this report includes a discussion of "residual sodium carbonate", defined as carbonates plus bicarbonates minus the sum of calcium and magnesium, all in milliequivalents per liter. Where the residual sodium carbonate is high, i.e., over 2.5 milliequivalents per liter, calcium and magnesium ions tend to be precipitated as carbonates, leaving a high ratio of sodium to calcium ions. In irrigation water, bicarbonates in themselves do not cause difficulty, but by aiding in the precipitation of calcium carbonate they adversely affect the sodium ratio.

In U. S. waters that support a good fish fauna, 5 percent of such waters have less than 40 mg/l of bicarbonate, 50 percent have less than 90 mg/l, and 95 percent have less than 180 mg/l (310).

BIOCHEMICAL OXYGEN DEMAND

(see also Dissolved Oxygen, Oxygen Consumed)

As in tests for alkalinity, acidity, color, turbidity, and specific conductance the determination of biochemical oxygen demand (B.O.D.) does not reveal the concentration of a specific substance. Instead it measures the effect of a combination of substances and conditions. The rate at which B.O.D. is exerted generally follows the unimolecular pattern as shown by equations in Chapter II.

As a parameter of the detrimental effects of organic matter upon a surface water, the 5-day B.O.D. value alone means very little. In itself, B.O.D. is not a pollutant and exercises no direct harm. Only by depressing the dissolved-oxygen content to levels that are inimical to fish life and other beneficial uses does B.O.D. exert an indirect effect. Where reaeration, dilution, and/or photosynthetic action offset or minimize this depletion, B.O.D. does not interfere with the reasonable uses of the water.

B.O.D. is important only insofar as it produces septicity or decreased dissolved oxygen, or subsequent growth of saprophytic bacteria which increase the turbidity or other undesirable characteristics of the streams. In a slow, sluggish stream, a 5-day B.O.D. of 5 mg/l might be sufficient to produce deoxygenation resulting in anaerobic conditions, whereas a swift mountain stream can easily handle 50 mg/l of 5-day B.O.D. without appreciable depletion of dissolved oxygen. Each stream must be considered in its own right, and until the reaeration characteristic of the stream is known the limiting values of B.O.D. cannot be set.

Many state and interstate agencies include B.O.D. limitations in stream standards while others specify that effluents shall not exceed a given concentration of B.O.D. or that B.O.D. reduction by treatment shall reach or exceed a stated efficiency. For details of these state and interstate standards, see Chapter III of this report and the appendices thereto.

BLAST

(see Chapter X)

B.O.D.

(see Biochemical Oxygen Demand)

BORANES

(see Boron)

BORAX

(see Sodium Borate)

BORIC ACID

(see Boron)

BORON

1. General. Never found in nature in its elemental form, boron occurs as sodium borate (borax) or as calcium borate (colemanite) in mineral deposits and natural

waters of southern California and in Italy. Elemental boron is used in nuclear installations as a shielding material (neutron absorber). It is also used in metallurgy to harden other metals (364, 2121).

Boric acid and boron salts are used extensively in industry for weatherproofing wood, fireproofing fabrics, manufacturing glass and porcelain, production of leather and carpets, cosmetics, photography, artificial gems, and many other purposes. Boric acid is used as a bactericide and fungicide. Finally, boron in the form of boron hydrides or borates is used in high-energy fuels (354, 2121).

Boron may be substituted for carbon in many organic compounds, e.g., boron trichloride, boron tribromide. It may also be synthesized directly with hydrogen to form boranes, such or diborane, B_2H_6 , a gas with a nauseating odor; pentaborane, B_5H_9 , a volatile liquid with a sweetish odor; and a decaborane, $B_{10}H_{14}$, a crystalline solid with a bitter-chocolate odor. The boranes are used as rocket fuels and may be encountered in other situations where high-energy fuels are desired.

2. Cross References. Sodium Borate, Sodium Perborate, Chapter V—Irrigation Waters.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Although boron is essential in the nutrition of higher plants, there is no evidence that it performs any vital function in human or animal nutrition (2121). It is present in the ordinary human diet to the extent of 10 to 20 mg/day, with fruits and vegetables as the largest contributors. In food or in water it is rapidly and completely absorbed by the human system, but it is also promptly excreted in urine (2121).

The ingestion of excessive doses of borates may cause nausea, cramps, convulsions, coma, and other symptoms of distress. The fatal dose for adults has been reported as 5 to 20 grams (364) and as 20 to 45 grams (2121). Normal adults were fed 3 grams of boric acid daily for 11 to 16 days without apparent toxic effects (3265).

Boron in drinking water is not generally regarded as a hazard to human beings (633). Goudey and others have reported that boron concentrations up to 30 mg/l are not harmful in drinking water. Above this concentration, it may interfere with digestion because of its preservative action on foods (353, 1055, 1056). Quantities up to 0.5 grams per day of either borax or boric acid have no immediate effect of any kind on healthy individuals (997). Hoskins, however, has recommended a boron limit of 20 mg/l in drinking water (1057).

b. Irrigation. The problem of boron in irrigation water is covered extensively in Chapter V under "Irrigation." Boron is an essential element in the nutrition of higher plants, yet concentrations of boron in irrigation waters in excess of 0.5 mg/l may be deleterious for eertain crops. Crops such as asparagus, date palms, sugar beets, alfalfa, onions, turnips, cabbages, lettuce, and carrots can tolerate boron concentrations of 2.0 to 4.0 mg/l. Crops such as potatoes, tomatoes, peas, wheat, corn, oats, and lima beans can grow well at 1.0 to 2.0 mg/l of boron. Among the sensitive crops are pecans, artichokes, plums, pears, apples, cherries, grapes, peaches, oranges, avocados, grapefruits, and lemons, which can tolerate no more than 0.5 to 1.0 mg/l of boron (2391).

6-

Plant roots take up small quantities of dissolved boron from the soil solution Boron adsorbed on the soil is not utilized by plants (3352). The absorbed boron is moved to the leaves, where the water is lost by transpiration. Boron remains in the leaf and tends to accumulate in the tip and margin. As the process continues, the boron concentration becomes sufficiently high to be toxic to the leaf tissue. This type of injury is found only on mature leaves, thus differing from boron-deficiency symptoms

that appear only on the new growth (3266).

c. Stock and Wildlife Watering. The lethal dose of boric acid for animals varies from 1.2 to 3.45 grams per kg of body weight, according to the species (2121). Concentrations of 2500 mg/l of boric acid in drinking water have been detrimental to animals only insofar as growth was inhibited (2121). A dairy cow received 16 to 20 grams of borax daily over a 40-day period without ill effects, but the concentration of boron in the milk rose from 0.7 to 3.0 mg/l. The synthetic boranes are far more toxic to animals than natural boron compounds, for example the LD_{50} for decaborane administered orally to rats was reported as 64.3 mg/kg (3267, 3268).

d. Fish and Other Aquatic Life. LeClerc and Devlaminck (2942, 2943, 2944) reported the minimum lethal dose for minnows exposed to boric acid for six hours at 20°C to be 18,000 to 19,000 mg/l in distilled water and 19,000 to 19,500 mg/l in hard water. Wallen et al. (2940) tested the effect of boric acid and sodium borate in highly turbid water on the mosquito-fish (Gambusia affinis), with the following results:

_		•	Conce	entration in	mg/l
Chemical Boric acid Sodium borate	emperatur	e	24-hour	48-hour	96-hour
	Range	pH Range	TLm	TLm	TLm
	20-23°C	5.4-7.3	18,000	10,500	5,600
	22-26°C	8.6-9.1	12,000	8,200	3,600

Wurtz (1054) has reported the results of a study of the effects of boric acid on one rainbow trout and one rudd. A solution of 2,000 mg/l of boric acid was harmless to both fish; 5,000 mg/l caused only a slight darkening of the skin of the trout. The trout became immobile and lost its balance in a few minutes in concentrations up to 80,000 mg/l but recovered rapidly when it was transferred to fresh water, even after immersion in the boric-acid solution for 30 minutes. The rudd appeared unharmed by concentrations up to 80,000 mg/l for short periods; however, it died after 18 hours in a 6,250 mg/l solution of boric acid. A roach in 6,250 mg/l solution also died, after 46 hours.

Boric acid can be toxic to fresh water fish without lowering the pH to 5.0. Thus, pH is not a reliable index of dangerous pollution by boric acid (361).

Turnbull et al. (2093) found the 24-hour TL_{m} of boron trifluoride toward the bluegill sunfish in Philadelphia tap water at 20 °C to be $15{,}00\overline{0}$ mg/l.

To produce a 50-percent inhibition of the 5-day oxygen utilization of synthetic sewage, Herman (2923) found that over 1000 mg/l of boric acid was required.

BREWERY WASTES

(see also B.O.D., Sugars, Detergents, Soaps)

For a thorough discussion of the nature of brewery wastes, the reader is referred to a standard text on chemical processes and industrial wastes (189, 346). The principal deleterious effect of such wastes is their high B.O.D. It has been reported (465) that yeast wort is harmless to fish in a dilution of 1:40.

BROMINE

 Br_2

A dark reddish-brown fuming liquid, elemental bromine is relatively soluble in water. It is used for medicinal compounds, dyestuffs, and antiknock compounds for gasoline motors. It has also been used for sterilization of swimming-pool water. Sources of molecular bromine in water are chemical industries and salt-works effluents. Bromine, like other halogens, is antiseptic and disinfectant; hence it may possibly interfere with bacterial and other natural purification processes.

A concentration of 10 mg/l of bromine in soft water has killed Daphnia magna (313). Jones (2920) reported that 20 mg/l of bromine killed goldfish at 18-23°C. Hiatt (3350) indicated that 1.0 mg/l of bromine showed no irritant response from marine fish, but 10 mg/l caused violent irritant activity.

BSM - 11, BUFFEN 30, BUTROL

(see Chapter IX)

BUTADIENE

CH₂=CHCH=CH₂

A colorless gas, 1, 3-butadiene is insoluble in water. It is used as a polymer component in the synthesis of rubber. According to Garrett (2959), the 24-hour TLm for the marine pinperch (Lagodon rhomebodies) is 71.5 mg/l. No deaths occurred at 50 mg/l.

BUTANONE

(see Methyl Ethyl Ketone)

BUTYL ACETATE

CH₈COOC₄H₉

Normal butyl acetate is a liquid highly soluble in water. It is used in the manufacture of plastics, lacquer, artificial leather, and photographic films (364). The oral LD₅₀ for rats has been reported as 4.13 grams/kg of body weight and for mice 7.06 grams/kg (3242).

Bringmann and Kuhn (2158) found that the median threshold effect of n-butyl acetate toward Daphnia during a two-day exposure at 23°C occurred at a concentration of 44 mg/l. For Scenedesmus at 24°C for 4 days, the median effect occurred at 320 mg/l; but for E. coli at 27°C, no effect was apparent at concentrations less than 1000 mg/l.

BUTYL ALCOHOL

 C_4H_9OH

Normal butyl alcohol, a colorless liquid, is used extensively in industry, being prepared from cornstarch or from acetylene. It may occur in many types of wastes, including those from the paint, varnish, and chemical industries. The oral LD50 of n-butyl alcohol for rats has been reported as 4.36 mg/kg of body weight (364) and as 2.75 mg/kg (3248). According to Ettinger et al. (2172, 3269) the median response to the odor threshold of n-butyl alcohol occurred at a concentration of about 0.2 mg/l.

Toward fish, the deleterious concentrations reported in the literature vary widely. Ellis (313) quotes several references to the effect that butyl alcohol in a concentration of 20 mg/l killed goldfish in hard water in 15 to 96 hours; 29 mg/l killed minnows and goldfish; and 250 mg/l killed goldfish in 7 to 20 hours. A concentration of 400 mg/l is reported to have killed fish in 51 minutes. For gudgeon, a European fresh-water fish, the lethal range for n-butyl alcohol is 1000 to 1400 mg/l; but for tertiary butyl alcohol it is 3000 to 6000 mg/l (2977).

The concentration of n-butyl alcohol required to stimulate the movement of 50 percent of a group of water beetles (*Laccophilus*) was reported as 3410 mg/l (2956).

BUTYRIC ACID

 $\mathrm{CH_3CH_2CH_2COOH}$

This oily liquid with an unpleasant rancid odor is miscible with water. It is used to decalcify hides, for varnishes, and in the manufacture of esters used in artificial flavoring (364). According to Smyth et al. (2978) the oral LD₅₀ for rats is 8.79 gm/kg of body weight, while von Oettingen (3270) reports a minimum lethal dose for animals of 3.6 to 3.7 gm/kg.

For trout, the lethal concentration has been given as 400 mg/l whereas the threshold for harmful effect is about 100 mg/l (2977). Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158) found the median threshold effect of butyric acid toward Daphnia occurred at 60 mg/l after two days of exposure at 23°C; and toward Scenedesmus at 200 mg/l after 4 days exposure at 24°C.

CADMIUM

Cđ

1. General. In the elemental form, cadmium is insoluble in water. It occurs in nature largely as the sulfide salt, greenockite or cadmium blend, often as an impurity in zinc-lead ores. Cadmium is used in metallurgy to alloy with copper, lead, silver, aluminum, and nickel. It is also used in electroplating, ceramics, pigmentation, photography, and nuclear reactors. Cadmium salts are sometimes employed as insecticides and antihelminthics (364, 2121, 2129).

Although the chloride, nitrate, and sulfate of cadmium are highly soluble in water, the carbonate and hydroxide are insoluble; hence, at high pH values, cadmium will be precipitated. Cadmium salts may be found in wastes from electroplating plants, pigment works, textile printing, lead mines, and chemical industries. Welsch and Lieber (2130) reported ground-water contamination by cadmium to the extent of 3.2 mg/l on Long Island, N. Y., as a result of wastes from electroplating industries. High concentrations of cadmium have been reported in Missouri mine waters and one spring there had 1000 mg/l of cadmium (2132).

This section deals with literature in which cadmium or cadmium ion, per se, have been reported. Where cadmium salts are referred to, they are covered under the appropriate heading.

- 2. Cross References. Cadmium Salts.
- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Cadmium poisoning of humans has resulted from the consumption of foods or liquids prepared and left in cadmium-plated containers

(2121, 2129). As a result, several health departments have forbidden the use of cadmium-plated food containers and pipes. Cadmium-contaminated ice cubes in cold drinks have caused acute gastritis symptoms within one hour (921). Consumption of cadmium salts causes cramps, nausea, vomiting, and diarrhea. Oral ingestion of cadmium has been reported as the cause of a number of human deaths (2129). A single dose of about 8.9 grams of cadmium chloride caused the death of a boy within 1.5 hours (353).

Cadmium tends to concentrate in the liver, kidneys, pancreas, and thyroid of humans and animals (2134). Once it enters the body, it is likely to remain. Normally, many plant and animal tissues contain about 1 mg of cadmium per kg of tissue (2121) but there is no evidence that cadmium is biologically essential or beneficial. The daily intake of cadmium in man can vary from 4 to 60 micrograms, depending on the foods chosen. The major sources appear to be seafoods and grains (2137).

Human beings have been sickened by 13 to 15 mg/kg of cadmium in popsicles, 67 mg/l in punch, 300 mg/l in a cold drink, and 530 mg/kg in gelatin (353). As little as 14.5 mg of cadmium taken orally has caused nausea and vomiting; yet in another instance, as much as 330 mg has not caused permanent injury (353, 1062). Four members of a family whose drinking water contained 0.047 mg/l of cadmium had no history of adverse effects (2132). For further evidence of the action of cadmium on mammals, see Stock and Wildlife Watering below.

Prior to 1950, the USSR established the maximum permissible concentration of cadmium in domestic supplies at 0.1 mg/l (460). The 1962 Drinking Water Standards of the USPHS (2036) set a mandatory limit of 0.01 mg/l for cadmium and the WHO European Standards (2329) prescribe a tolerance limit of 0.05 mg/l. No limit is set in the WHO International Standards (2328).

- b. Irrigation. A cadmium concentration of 28 mg/l in a nutrient solution was reported to be injurious to sugar beets grown in sand culture (1473).
- c. Stock and Wildlife Watering (see also Cadmium Chloride). The fatal dose of cadmium for dogs has been reported to be 0.15 to 0.3 grams per kilogram of body weight; it has also been reported at 0.3 to 0.6 grams. The fatal dose of cadmium for rabbits appears to be 0.3 to 0.5 grams (353). Ingestion of cadmium in drinking water or food caused a decrease in the hemoglobin content of the blood of rats (1063). Cadmium at a concentration of 5 mg/l in the drinking water increased the mortality among rats on a diet containing 11 mg/l of selenium (1481).

Byerrum and his colleagues (2138, 2142, 2145, 2146, 2147, 2150) conducted extensive tests on rats and dogs fed cadmium, in the form of cadmium chloride, in dosages ranging from 0.1 to 10.0 mg/l of cadmium in drinking water for one year. There were no differences between the treated animals and the controls in water consumption, food intake, or body weight, nor were any pathological changes in blood or other tissues noted. The cadmium content of livers, and kidneys increased in direct proportion to the cadmium intake. Calculated as micrograms of cadmium per gram of tissue, kidneys retained two to three times the amount of cadmium retained by the liver. Some rats, fed 50 mg/l of cadmium

for three months, showed a reduction in growth rate, water consumption, and blood hemoglobin. Moreover, teeth were bleached.

The emetic property of cadmium was found to occur among dogs at cadmium concentrations as low as 5.0 mg/l during warm weather when large volumes of water were consumed. Dogs received up to 10 mg/l of cadmium for four years without pathological changes.

Byerrum (2138) concluded that, owing to the accumulation and retention of cadmium in the liver and kidney, a limit should be placed on this substance in drinking water. He suggested that the limit should not be above 0.1 mg/l and preferably lower.

d. Fish and Other Aquatic Life. Most of the quantitative data on toxicity of cadmium toward fish and other aquatic organisms are given under the specific cadmium salt. Expressed as cadmium, these data indicate that the lethal concentration for fish varies from about 0.01 to about 10 mg/l depending on the test animal, the type of water, temperature, and time of exposure. Schweiger (2151) found that 0.03 mg/l of cadmium was not harmful to one- and two-year-old tench, carp, rainbow trout and char, nor to the crustacea, worms, and insect larvae on which they fed. Concentrations of 0.05 to 0.10 mg/l of cadmium in distilled water produced distress syndromes in the water snail, Australorbis glabratus (2733).

Cadmium acts synergistically with other substances to increase toxicity. Cadmium concentrations of 0.03 mg/l in combination with 0.15 mg/l of zinc from galvanized screens caused mortality of salmon fry (2153). Cadmium can form a complex with cyanide in plating baths, but in dilute solutions the complex is almost completely dissociated and highly toxic. Synergism of the toxic cadmium and cyanide ions liberated in the dissociation is indicated (2157).

CADMIUM CHLORIDE

 $CdCl_2 \cdot 2\frac{1}{2}H_2O$

- 1. General. This soluble salt of cadmium occurs generally in the crystalline form with 2½ molecules of water. It is used in dyeing and printing of calico, and in photography (364).
- 2. Cross References. Cadmium and other cadmium salts.
 - 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. After their teeth had become calcified, the use by rats of drinking water containing 40 mg/l of cadmium chloride was followed by an increase in the incidence of caries (1064). In the form of cadmium chloride, 50 mg/l of cadmium in the food or water caused a decrease in blood hemoglobin and in the pigmentation of the tooth enamel of rats (921). A concentration of 16 mg/l of cadmium chloride in the diet of rats caused bleaching of the teeth; 31 mg/l affected the rate of growth; and 250 mg/l was fatal *(353).

For rabbits, 0.15 to 0.3 grams cadmium chloride per kilogram body weight has been lethal (353). For cats, 125 mg/l of cadmium chloride in the diet has been fatal, but 62.5 mg/l had no effect on growth, and a daily dose of 0.56 mg had no cumulative effect (353).

b. Fish and Aquatic Life. The threshold concentration of cadmium chloride for immobilization of Daphnia magna in Lake Erie water at 25°C was found to be less than 0.0026 mg/l (353, 598). In water of the River Havel, the threshold concentrations for detrimental effects of cadmium added as cadmium chloride have been reported (2158) for three organisms as follows:

Test Organism	Threshold Concentration of Cd in mg/l	
Daphnia magna	0.1	
Scenedesmus	0.1	
Escherichia coli	0.15	

Goldfish in distilled water have been killed by a concentration of cadmium chloride of 0.0165 mg/l in 8.5 to 18 hours (313). The highest concentration of cadmium chloride tolerated by young eels for more than 50 hours was about 0.18 mg/l, and at a concentration of 1.83 mg/l the average survival time was only 18.4 hours at 21°C (1459). The lethal concentration of cadmium chloride for three mature small fresh-water fish (Orizias), exposed for 24 hours to the test solution, was reported to be about 45 mg/l (1459). In exploratory tests, Tarzwell and Henderson (2125, 2154) found the 96-hour TL_m of CdCl₂·2½H₂O toward fathead minnows to be 0.9 mg/l in soft water and 5.0 mg/l in hard water. The wide range of toxicities between distilled water and hard water suggests a definite antagonistic action of calcium, magnesium, and perhaps other salts toward cadmium toxicity.

CADMIUM NITRATE

 $Cd(NO_3)_2 \cdot 4H_2O$

The toxicity threshold of cadmium for the flatworm Polycelis nigra has been reported to be 2.7 mg/l (608). For sticklebacks the toxic threshold concentration of cadmium nitrate has been reported to be 0.42 mg/l in tap water (598). Jones found the lethal concentration limit of cadmium to sticklebacks at 15-18°C to be 0.2 mg/l as cadmium when cadmium nitrate was used as the test compound (1460, 2920). The fish survived 0.3 mg/l (as cadmium) for one week, 0.7 mg/l for four days, 3.0 mg/l for two days, and 7 mg/l for only one day. In fresh water, 6 mg/l of cadmium nitrate has been fatal to the fish Fundulus within 36 hours (1459). Toward the guppy, the LD₅₀ concentration of cadmium nitrate was found to be 0.056 mg/l, as cadmium (2921).

CADMIUM SULFATE

 $CdSO_4 \cdot 2\frac{2}{3}H_2O$

This highly soluble salt of cadmium may be found in wastes from lead mines and chemical industries. The sulfates of cadmium and zinc have an additive toxic effect upon fish; sulfates of cadmium and copper are synergistic in their effect (353) (see also Chapter V).

The following concentrations of cadmium sulfate have killed minnows in distilled water (991).

Concentration	Time of Exposure
in mg/l	in minutes
1,042	180
5,200	102
10,400	

A 50-percent reduction in the 5-day biochemical oxidation of sewage treated with cadmium sulfate was caused by 55 mg/l of cadmium (2922) and by 142 mg/l of cadmium (2923).

Ca

1. General. Elemental calcium does not occur in nature because it oxidizes readily in air and reacts with water to release hydrogen gas. Calcium salts and calcium ions, however, are among the most commonly encountered substances in water. They may result from the leaching of soil and other natural sources or they may be contained in sewage and many types of industrial wastes.

Under this heading are grouped the references that pertain to calcium or calcium ions. Where the literature deals with calcium salts, the references are grouped under the specified salt. The effects of calcium are also to be noted under the heading of "Hardness".

- 2. Cross References. Hardness; Calcium salts, Chapter V, and Chapter VII (Insects).
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The human body requires approximately 0.7 to 2.0 grams of calcium per day as a food element (36, 152), an amount considerably in excess of the calcium concentration of normally consumed quantities of even hard water. According to many people, calcium deficiency is the most common nutritional lack in the U.S. (3362). It is assumed that in the adult, the calcium requirement in the diet should equal the calcium excretion, which is about 10 mg per kg per day (3362). Some investigators believe that calcium in water can be used by the body as a supplement to the calcium in the diet (1065); however, the nutritional value of calcium in water has not yet been established and is still questionable (623, 653). Concentrations up to 1800 mg/l of calcium in drinking water have been reported to be harmless (353). The calcium concentration of vegetables cooked in water of high calcium content has been found to be higher than that of vegetables cooked in low-calcium water (921, 1066, 1067).

Excessive calcium and magnesium in drinking water have been implicated as factors predisposing to the formation of concretions in the body, such as kidney or bladder stones (3365). On the other hand, there is also evidence of adverse physiological effects from an insufficiency of calcium in water. Urovsk disease, a severe type of rickets, occurs in regions where the concentration of calcium in drinking water is low (3366, 3367). Morris et al. (3368, 3369) report an inverse correlation between the calcium content of waters and cardiovascular disease, i.e., high calcium is associated with a low ncidence of heart attacks, but Schroder and Duran (3370) failed to find a similar relationship in Japan. While several effects of calcium in drinking water and ohysiological reactions have been suspected, no definite ausal relationship has been proved as yet. So far as can De determined at the present time, calcium limits are lesirable for domestic supplies not because of a hazard o health, but because calcium may be disadvantageous for other household uses, such as washing, bathing, and aundering, and because it tends to cause incrustations in cooking utensils and water heaters.

Hibbard (250) has recommended the following limitng concentrations of calcium in waters for domestic use:

Drinking	and cooking	30 mg/l	
Washing		10 mg/I	
Laundry		0 mg/I	

The Spanish Royal Decree of 1920 fixed the limit of calcium in potable waters at 150 mg/l, as CaO (631, 997). Baylis (499) has recommended the following limiting calcium concentrations for the several classes of water: Class A, the ideal, 50 mg/l, Class B, minimum aim, 75 mg/l, Class C to D, permissible with restrictions, 100-150 mg/l.

The USPHS Drinking Water Standards (2036) of 1962 and the WHO European Standards (2329) of 1961 do not contain any limits for calcium; but the WHO International Standards (2328) of 1958 indicate that 75 mg/l is a permissible limit and 200 mg/l an excessive

limit in drinking water.

b. Industrial Water Supplies. (see also Hardness). Calcium in the water used for preparing developer solutions for photography may cause the precipitation of calcium sulfite, resulting in spots on the films unless the precipitate is allowed to settle out of solution (242). Calcium in brewery water causes the precipitation of calcium phosphate (166). Nordell (2338) points out that high calcium can cause undesirable effects by (a) forming scale, (b) reacting with alkaline solutions to form precipitates and curds, especially in washing operations using soap, (c) interfering with the preparation of emulsions, where the calcium tends to break the emulsions, (d) interfering with the processing of other colloids, (e) causing difficulties in electroplating rinsing operations, and (f) upsetting certain fermentation processes.

On the other hand, calcium is beneficial in water as one of the factors that tend to inhibit corrosion of cast

iron and steel (3363, 3364).

The following concentrations of calcium have been recommended as limits for various industrial uses:

Thresho	ld Concentration	
Use	in mg/l	Reference
Brewing, light beer	100-200	152
Brewing, dark beer	200-500	152
Soda and sulfate pulping	20	245
Sugar mfg.		250
Textile mfg.	10	250

- c. Irrigation Water. Calcium in irrigation water has been covered in detail in Chapter V. Calcium is essential for normal plant growth and for the maintenance of good tilth in the soil, and is desirable in water for irrigation (268, 278, 635, 3371, 3372).
- d. Stock and Wildlife Watering. Stander (3373) has suggested an interim threshold limit of 1,000 mg/l of calcium in water used by livestock. For more details, see Hardness.
- e. Fish and Other Aquatic Life. Calcium in water reduces the toxicity of many chemical compounds to fish and other aquatic fauna; for example, mature fish have been killed by 0.1 mg/l of lead in water containing only one mg/l of calcium, but have not been harmed by this amount of lead in water containing 50 mg/l of calcium. A concentration of 50 mg/l of calcium has cancelled the toxic effect upon some fish of 2 mg/l of zinc; 0.7 mg/l of lead; and 10 mg/l of lead (573). Aluminum has been found to be toxic to river crabs in water containing little calcium (575).

The data of various independent investigators indicated that calcium chloride and nitrate, when added to distilled or soft waters, could be toxic to fish at concentrations between 300 and 1000 mg/l as calcium. Other available data concerning lethality of higher concentrations of calcium salts, generally calcium chloride, in various waters indicate that fish have survived from one to three days at concentrations of 2500 to 4000 mg/l of calcium (1459).

According to a reference cited by Hart et al. (310), of the U.S. waters supporting a good mixed fish fauna, ordinarily about 5 percent have less than 15 mg/l of calcium; 50 percent have less than 28 mg/l; and 95 per-

cent have less than 52 mg/l.

Marine fish have been shown to concentrate Ca-45 from sea water at a factor of 10 or 20 to 1 (3374, 3375). Furthermore, marine fish discriminate against strontium in favor of calcium (3374). Daphnia and Cyclops also concentrate Ca-45 from fresh water, but when transferred to non-radioactive solutions, they quickly excrete the Ca-45. See also Chapter VIII.

For a flatworm, *Polycelis nigra*, the threshold of toxieity of calcium has been reported as 2600 mg/l when calcium is present as calcium chloride; and 1200 mg/l when calcium is present as calcium nitrate (608).

The lethal threshold concentration of calcium for stickleback is reported to be 800 mg/l (353, 2941).

f. Shellfish Culture. Thinness of shells of fresh-water mussels is associated with a deficiency of calcium in the water (331).

CALCIUM CARBONATE

CaCO₃

(see also Calcium, Carbonates)

Commonly found in nature in the form of limestone or calcite, this salt is difficultly soluble, having a solubility product of 0.87×10^{-8} at $25^{\circ}\mathrm{C}$ (911). Its concentration in natural or treated waters is intimately linked with the complex carbonate equilibria (see Carbonates). In addition to its natural sources, calcium carbonate in molecular or dissociated form may be contained in innumerable industrial wastes. The references described below pertain only to calcium carbonate molecules and not to the effects of calcium or carbonate ions, which are reported elsewhere.

The taste threshold of calcium carbonate has been reported as 50 to 200 mg/l (621). Water to be used in making ice should be treated if the total concentration of calcium and magnesium carbonates is more than 70 mg/l (168). Calcium carbonate in water appears to be necessary to permit complete utilization of food by aquatic animals (1068). For the effects of adding lime on the productivity of lakes, see Calcium Hydroxide.

Wallen et al. (2940) studied the effect of adding calcium carbonate to highly turbid waters containing the mosquito-fish (Gambusia affinis) at 19-21°C. They found that the 96-hour TL_m was greater than 56,000 mg/l of calcium carbonate. At this dosage, the turbidity was reduced from an initial value of 260 mg/l to 35 mg/l.

CALCIUM CHLORIDE

 $CaCl_2$

1. General. This salt of calcium is highly soluble in water. Calcium chloride is used in brewing and in manufacturing mineral waters. It is found in wastes from bromine and salt works, oil wells, and surface run-off from roads treated against dust. Calcium chloride in

natural waters is invariably associated with larger quantities of other calcium and magnesium salts, which together may render the water too highly mineralized for drinking and domestic purposes, but do not alone render water hazardous to people.

- 2. Cross References. Dissolved Solids, Specific Conductance, Distilled Water.
 - 3. Effects on Beneficial Uses.
- a. Domestic Water Supplies. The taste threshhold of calcium chloride in drinking water is said to be 150 to 350 mg/l (621). According to Lockhart et al. (3241) the taste threshhold of calcium ion is 125 mg/l and of the chloride ion 222 mg/l; hence the chloride ion controls and CaCl₂ can be tasted at 347 mg/l. In order to prevent unpleasant salty tastes and disturbances of appetite, it has been recommended that water should not contain more than 500 mg/l of calcium chloride (284). On the other hand, it has also been stated that small quantities of calcium and magnesium chloride, even concentrations of 40 to 50 mg/l, are objectionable in domestic water supplies because of taste and hardness (32).

b. Industrial Uses. The following are reported maximum concentrations of calcium chloride permissible in brewing waters:

	Concentration	
$oldsymbol{U}$ se	$in \ mg/l$	Reference
Brewing, light and dark	200	173
Brewing	100	170
Brewing, pale ales, I	30	170
pale ales, II	35-55	170
mild ales	55-110	170
stout	110-165	170

- c. Irrigation Use. In high concentrations, calcium chloride in nutrient solutions will reduce plant growth. Gauch and Wadleigh (3376, 3377) showed that an increase of one atmosphere in the total osmotic concentration as the result of adding CaCl₂ (about 1775 mg/l) to the nutrient solution reduced the dry weight of red kidney bean plants by 15.5 percent while 3550 mg/l caused a 26 percent reduction. On the other hand, the guayule plant was shown to be very tolerant of CaCl2, making satisfactory growth in the presence of 3 atmospheres of osmotic pressure from added CaCl₂ (about 5390 mg/l) (3378). One atmosphere (1775 mg/l) of added CaCl₂ reduced the dry weight of rice straw, rich grains, and rice roots at maturity (3379). Two atmospheres of added CaCl₂ injured four varieties of table grapes grown in sand culture (3380). It should be recognized that the foregoing concentrations of one and two atmospheres are far higher than any likely to be found in irrigation waters.
- d. Stock and Wildlife Watering. The following concentrations of calcium chloride have produced the noted effects on animals:

Concentration of CaCls in mg/l	Animal	Effect	Reference
8,325	rats	decreased water consumption	2398
10,000	rats	interfered with production of normal litters	287, 640
10,000-15,000	cows	moderate effect on nerves and appetite	2980
10,000-25,000	rats	interfered with reproduction	2980
15,000	rats	decreased growth rate	287, 640
15,000-20,000	chickens	interfered with growth	2980
20,000	rats	interfered with lactation	287, 640
20,000-25,000	sheep	tolerated for six weeks	2980
25,000	rats	caused death	287, 640

In Lake Erie water at 20-25°C, threshold concentrations of CaCl₂ for immobilization of aquatic organisms were reported (2955) as follows:

Organism	Threshold Concentration in mg/l
Daphnia magna, young	920
Cyclops uernalis	1730
Mesocyclops leukarti Whitefish fry	1440 22080
Pickerel fry	12060

The following concentrations of calcium chloride have been reported to have killed or injured fish:

Concentra- tion in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
555	tap	1 week	rock bass	313
2,775	distilled	2-4 days	minnows	313, 598
5,000		142 hours	shiners	645
7.752	distilled	22-27 hours	goldfish	313, 2920
8.400	synthetic	24-hour TLm	bluegills	1459
9.500	standard	96-hour TLm	bluegill sunfish	2933, 2934, 2935
10,000		3 hours	tench	645
10,000			fish	1070
10,000			sunfish	1070
10,000		27.6 hours	shiners	645
10,000		48.8 hours	bream	645
10,650		96-hour TL-	bluegill suufish	3381, 2936
11,100		50 hours	young eels	1459
12,060				
(threshold)			pickerel	353
12,500			fish	598, 4 31
13,400	turbid	96-hour TLm	mosquito-fish	2940
13,900		24 hours	Orizias	1459
22,080				
(threshold)			whitefish	353

A concentration of 277 mg/l of calcium chloride in distilled water was not harmful to minnows over a period of five to seven weeks (313). A gradually increasing concentration of calcium chloride up to 9500 to 13,500 mg/l has resulted in the death of fish within 12 days (644).

CALCIUM FLUORIDE

CaF₂

(see also Calcium, Fluorides)

Known also as fluorspar, this mineral occurs widely throughout the world. It is soluble to the extent of about 15 mg/l at 18°C (364). Fluorspar is the primary source of fluorine and its compounds. It is also used as a flux in steel manufacture, and it finds many uses in glass, ceramics, and chemical industries. According to Simonin (3271) the oral LD₅₀ for guinea pigs is more than 5.0 grams/kg of body weight. The lethal dose required to kill the fish, *Tinca vulgaris*, is reported by Simonin (3271) to be 30,000 mg/l, which is far greater than the solubility.

CALCIUM HYDROXIDE

Ca(OH)2

- 1. General. Known also as calcium hydrate and slaked lime, calcium hydroxide is moderately soluble in water, to the extent of about 1700 mg/l at 15°C (364). Calcium hydroxide may be found in wastes from tanneries, canneries, leather and leatherette works, chemical and paint plants, glue factories, and other industrial processes.
- 2. Cross References. Calcium, Hydroxides, Carbonates.
 - 3. Effects on Beneficial Uses.
- a. Domestic Water Supplies. The solvent action of 0 to 25 mg/l of calcium hydroxide was fairly constant, but 1000 mg/l dissolved considerable quantities of lead salts from pipes. In concentrations normally found in

water supplies, however, calcium hydroxide would probably not increase plumbosolvency (1029).

b. Stock and Wildlife Watering. A concentration of 1800 mg/l of calcium hydroxide produced no ill effects through several generations of rats (284, 287).

c. Fish and Other Aquatic Life. The following concentrations of calcium hydroxide have been reported as toxic to fish in the time specified.

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
18		fish	808
92	26 minutes	trout	2977
<100 (pH 11.1)	20 minutes	goldfish	2920
100	3-5 hours	goldfish, bass, sun	t -
100	5 6 225 22	fish	1030
100	3-7 days	bass	1030
(unadjusted pH	3)		
100-200		carp	1071
198	10 minutes	trout	2977
200	30-80 minutes		1030
(unadjusted pH	1)		
500	20-53 minutes	goldfish	1030
(unadjusted pE	I)		
700	26 minutes	trout	313

Goldfish, bass, and sunfish have survived 50 mg/l for seven or more days (1030).

Using highly turbid water at $21-23^{\circ}$ C and the mosquito-fish (Gambusia affinis) as the test organism Wallen et al., (2940) found the 24-hour, 48-hour, and 96-hour TL_m values to be 240, 220, and 160 mg/l of calcium hydroxide respectively. At these dosages, initial turbidities of 800 mg/l were reduced to 200 mg/l or lower.

The application of lime to soft-water lakes has increased their productivity, presumably by raising the alkalinity and providing larger reservoirs of immediately available carbon dioxide in the form of bicarbonates (2173, 2174). A high content of lime in an impounding reservoir in Germany encouraged the development of hornweed (Ceratophyllum demersum) which tended to block waterworks intake screens (3382).

CALCIUM HYPOCHLORITE

Ca(OCl)₂

(see also Calcium, Chlorine)

Calcium hypochlorite is discharged occasionally in trade wastes. It has been reported that concentrations of calcium hypochlorite from 0.5 to 10 mg/l have killed trout and other fish (359).

CALCIUM MOLYBDATE

CaMoO₄

(see Molybdenum)

CALCIUM NITRATE

 $Ca(NO_3)_2$

(see also Calcium, Nitrates)

Calcium nitrate is very soluble in water and may be found in some chemical wastes. It is used in manufacturing matches, explosives, fireworks, etc.

A concentration of 3,280 mg/l in tap water is reported as the toxicity threshhold for stickleback (598). In distilled water 6,061 mg/l has killed goldfish in 43 to 48 hours (313). For stickleback in soft water, the lethal concentration limit for calcium nitrate was found to be 800 mg/l as calcium. The average survival time was

one week at a concentration of 1000 mg/l (as calcium), four days at 1500 mg/l, two days at 3000 mg/l, and only one day at 4500 mg/l (1460). In contrast, Traina (3381) found the 96-hour TL_m for the bluegill sunfish

at 20°C to be 10,000 mg/l of calcium nitrate.

CALCIUM SILICOFLUORIDE

CaSiF₆·2H₂O

This anhydrous salt is almost insoluble in cold water. Its oral LD₅₀ for guinea pigs is reported (364, 3271) as 250 mg/kg of body weight, while for the fish, Tinca vulgaris, the lethal dose is given as 50 mg/l (3271).

CALCIUM SULFATE

CaSO₄

- 1. General. Known also as gypsum or plaster of Paris, calcium sulfate is soluble to the extent of about 2,500 mg/l in cold water (364). It is used in paint manufacture and in paper mills, among other industrial processes.
- 2. Cross References. Calcium, Sulfate, and Chapter V-Irrigation.
 - 3. Effects on Beneficial Uses.
- a. Domestic Water Supplies. High calcium sulfate concentrations in water are disadvantageous for most household uses, but for drinking purposes, 300 mg/l or more is not harmful (1072). The taste threshold of calcium sulfate has been reported to be 250 to 900 mg/l (621). Calcium sulfate significantly increases plumbosolvency; raising the calcium sulfate concentration from 25 to 250 mg/l increased by 10 percent the amount of lead dissolved from lead pipes (1073).
- b. Industrial Water Supplies. Calcium sulfate in small amounts is beneficial in mash water for pale beer (171, 174, 175, 1074). The permissible amount of gypsum varies, according to different authorities, from 300 to 1750 mg/l (1074).

The following maximum concentrations of calcium sulfate have been recommended for brewing:

Type of beer	Concentration in mg/l	Reference
Light brews	100-200	173, 152
Dark brews	200-250	173
Dark brews	200-500	152, 170
Pale ales, I	200-340	170
Pale ales, II	340-540	170
Mild ales	70-200	170

In general, calcium sulfate is beneficial in the brewing industry, for it helps to maintain the acidity of the wort and therefore causes more complete coagulation of albuminous matter. It also reduces the solubility of the bitter substances of the hop (2344).

- c. Irrigation. Gypsum in irrigation waters improves or restores the permeability and tilth of soil with an unfavorable sodium ratio (271, 283). See also Chapter V—Irrigation.
- d. Stock and Wildlife Watering. A saturated solution of calcium sulfate, used as the sole source of drinking water for rats, permitted satisfactory growth (287). A concentration of 2,400 mg/l of calcium sulfate permitted normal growth and reproduction among rats (284).
- e. Fish and Other Aquatic Life. Trama (3381) reported that a saturated solution of calcium sulfate at 20°C did not produce significant mortalities among bluegills; but a later report from the same organization (2936) indicated that this concentration was the 96-hour TL_m at 18-20°C in soft water for the bluegill sunfish. It was also reported (2936) that 3200 mg/l caused a 50percent reduction in the rate of growth of the diatom,

Navicula seminulum. Using highly turbid water at 21-25°C and the mosquitofish (Gambusia affinis) as the test animal, Wallen et al. (2940) indicated that the 96-hour TL_m was greater than 56,000 mg/l, a concentration much larger than the solubility.

f. Shellfish Culture. Calcium sulfate in sea water in concentrations up to 633 mg/l was found to be toxic to

Japanese oysters (811).

CAMPHOR

 $C_{10}H_{16}O$

This ketonic derivative of a saturated dicyclic hydrocarbon is a gumlike crystalline compound that is obtained by steam distillation of wood, twigs, and leaves of the camphor tree. It is used in medicine as a diaphoretic, stimulant, and sedative, in the manufacture of celluloid, and in pyrotechnics. Kirkor (460) reports that the minimum detectable concentration of camphor that can be tasted in water is 1.9 mg/l. In Lake Huron water at 12°C, the sea lamprey was not effected by 5.0 mg/l of camphor during a 24-hour exposure (2976).

CAPTAN 50-W

(see Chapter IX)

CARBOHYDRATES

(see Sugars)

CARBOLIC ACID

(see Phenol)

CARBON

(see also Carbon Dioxide, Carbonates, Bicarbonates, Chapter VIII)

Elemental carbon occurs in three forms: (a) as diamends, (b) as graphite, and (c) as coal, lampblack, or other amorphous substances. Animal and wood charcoals are used chiefly as "activated carbons" for clarifying, deodorizing, decolorizing, and filtering; while gas black and lamp black are used as pigment for rubber tires, for printing and drawing inks, for electrical and insulating apparatus, and for phonograph records (364). Granular or powdered carbon may be present in rinse waters, floor drainage, or other wastes from many of these processes.

A study of carbon-plant wastes at St. Marys, Penna. (7) showed that their B.O.D. was negligible, that they were practically saturated with oxygen, that the pH values were near normal, and that alkalinities were not excessive. The only pollutant in these wastes appeared to be the high suspended solids content arising from the powdered carbon. Such wastes, however, imparted a black discoloration to the stream, added turbidity, and precipitated films of carbon on rocks and stream beds, thereby interfering with normal aquatic life.

Activated carbon apparently has the power to inactivate the virus of infectious hepatitis (885) and it has been used to control algae in reservoirs, at dosages of 0.26 lb per 1,000 sq ft of surface. Both of these effects upon biological life are probably attributable to surfaceaction phenomena rather than to toxicity.

The radioisotope, C-14, has gained prominence owing to its long half-life and its production in the testing of atomic weapons. See Chapter VIII for information on concentration factors.

Organic carbon, the carbon oxidized by dichromate or another strong oxidizing agent, is frequently determined in polluted waters and benthic deposits. As in the case of B.O.D., this test measures one significant criterion of the strength of a waste, but it is not per se a potential pollutant.

CARBONATES

CO₃--

- The concentration of carbonates in nat-1. General. ural and polluted waters is a function not only of the substances added thereto but also of the temperature, pH, cations, and other dissolved salts. A full discussion of carbonate equilibria is beyond the scope of this report and the reader is referred to the work of Langelier (692). For a review of the relationship between carbonates, bicarbonates, and pH, see Bicarbonates in Chapter VI. Inasmuch as many of the carbonates are quite insoluble in water, generally more so than the chlorides, nitrates, or sulfates, there is a tendency for certain carbonate salts to be removed from polluted waters by precipitation and adsorption. For these reasons, carbonates are less widely present than chlorides and sulfates in western irrigation waters (275).
- 2. Cross References. Alkalinity, pH, Bicarbonate, Hydroxides, Chapter V-Irrigation.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The USPHS Drinking Water Standards of 1962 (2036) place no restrictions on carbonates in natural waters, nor in chemically treated waters as was done in the 1946 standards. Hibbard (250) recommends that the concentration of carbonate ion in drinking and cooking water be kept below 20 mg/l (33.3 mg/l as alkalinity). In his discussion of alkali waters in Montana, Cobleigh (670) points out that carbonates and bicarbonates in drinking waters react with gastric juices sometimes to the consumer's benefit. He presents a modified list of USGS data that gives 350 mg/l of carbonates as the concentration unhealthful to most people. According to Lockhart (3241) the taste threshold of carbonate in distilled water, when added as sodium carbonate, is 44 mg/l.
- b. Industrial Water Supplies. Excessive carbonates interfere with acid and carbonated beverages (see Alkalinity), with brewing, with ice making, and with boiler water (see Chapter V). For boiler feed water, the permissible carbonate concentration is a function of pressure in the boiler, as follows (152):

Pressures, psi	Carbonate Concentration in mg/l
0-150	200
150-250	100
250-400	40
Over 400	20

For brewing, carbonate concentrations should not exceed 50 to 60 mg/l (see Chapter V).

c. Fish and Other Aquatic Life. For the effects of ammonia, potassium, and sodium carbonates on fish and Daphnia, see the appropriate cation in this chapter. Hedgepeth (1085) claims that the presence of free car-

bonates may be responsible for the absence of *Diaptomus franciscanus*, a crustacean, from certain ponds near San Francisco. In general, it may be expected that carbonates, in themselves, are not detrimental to fish life but their buffering action and effect upon pH may contribute to the toxicity of high pH value.

CARBON CHLOROFORM EXTRACT

The 1962 USPHS Drinking Water Standards (2036) set a recommended limit of 0.2 mg/l on carbon chloroform extract based on analytical techniques developed at the Robert A. Taft Sanitary Engineering Center (3004, 3353, 3354, 3355, 3356). In this procedure, a sample of water varying from 100 to 75,000 gallons, depending on the source of the sample and the anticipated amount of extractable material, is filtered through 1200 to 1500 grams of granular activated carbon at a filter rate of 2 to 10 gpm per square foot. The carbon is then air-dried and extracted with chloroform. This solvent does not recover all of the adsorbed material nor are all organic substances adsorbed, but the materials recovered by this technique are representative of the taste- and odor-producing components of waste water.

CCE concentrations of Ohio River water have been reported to range from 0.1 to 0.36 mg/l, and the raw water at Nitro, West Virginia had CCE values of 0.17 to 3.05 mg/l (3357). In contrast, only 0.024 mg/l of CCE material could be recovered from the Columbia River (3102). Gasoline can cause taste and odor if the hydrocarbons are present in amounts of a few micrograms per liter (3102). Water from clean sources rarely exceeds 0.05 mg/l of CCE substances while water that exceeds 0.20 mg/l usually is of poor quality from a taste and odor standpoint (3358). Middleton and Lichtenberg (3356) report that CCE concentrations of 0.1 mg/l or less occurred in the following percentages of samples from five major rivers:

Ohio River	50 percent
Mississippi River	72 percent
Missouri River	90 percent
Colorado River	92 percent
Columbia River	96 percent

According to Derby et al. (2062) analysis of available data indicates that water supplies containing over 0.2 mg/l of CCE represent an exceptional and unwarranted exposure of the water consumer to ill-defined chemicals.

CARBON DIOXIDE

 CO_2

1. General. A colorless, odorless, non-combustible gas, constituting about 0.04 percent of normal air (330), carbon dioxide is highly soluble in water. At one atmosphere of partial pressure, pure water will absorb 1688 mg/l of CO₂, (911) but at 0.0004 atmospheres the dissolved CO₂ will be only about 0.7 mg/l. The source of free carbon dioxide in water is seldom that from the air phase, however, for CO₂ is a product of aerobic or anaerobic decomposition of organic matter and it is intimately bound in the complex carbonate equilibria (see Bicarbonates and Carbonates).

Dissolved carbon dioxide reacts with water to form carbonic acid,

 $CO_2 + H_2O \rightleftharpoons H_2CO_3$ which, in turn, dissociates thusly

$$\mathrm{H_{2}CO_{3}} \rightleftharpoons \mathrm{H^{+}} + \mathrm{HCO_{3}^{-}}$$

such that

$$\frac{[H^{+}][HCO_{3}^{-}]}{[H_{2}CO_{3}]} = 3.5 \times 10^{-7} \text{ at } 18^{\circ}\text{C}$$

Thus, at pH 8 the ratio of carbonic acid to bicarbonate ions is only .0286 but at pH 7 it is 0.86 and at pH 6 it is 2.86. Below pH 4.3, almost all of the bicarbonate is converted to carbonic acid.

The tests for carbon dioxide as described in Standard Methods for the Examination of Water and Wastewater (469) do not distinguish between dissolved CO₂ and carbonic acid, and the direct test or the computation of "free CO₂" indicates the sum of these two forms. In this report, therefore, references to carbon dioxide should be understood to embrace carbonic acid as well.

- 2. Cross References. Alkalinity, Acidity, Bicarbonates, Carbonates, and pH.
 - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Free carbon dioxide in domestic water is of significance only in connection with corrosion and aggressiveness of water, for it appears to have no direct physiological effect (155, 1080). In fact, soft drinks and beer are highly charged with CO₂. Such carbonated water showed no bactericidal action against *E. coli* and *E. typhosa* after an exposure of 40 minutes (1081), and a concentration of less than 100 mg/l produces no taste in water (855). Poultry fed for 30 days with highly carbonated water showed no ill effect (2980). High concentrations in domestic water systems are detrimental, however, in that they accelerate the corrosion of iron and steel, and they promote the solution of lead (155, 855, 1082).

b. Industrial Water Supplies. Restrictions on the content of free CO₂ do not appear directly in many standards of industrial waters (see Chapter V), but requirements of pH, acidity, and alkalinity indirectly restrict the carbon-dioxide content. The T.A.P.P.I. specifications for chemical composition of process waters for the manufacture of various types of paper state that free CO₂ should not exceed 10 mg/l. According to Ruppert (3769) beer prepared with water containing free CO₂ shows an undesirable bitterness.

According to Schmassmann (856), free carbon dioxide is the constituent of natural waters that is most likely to damage calcareous building materials such as cement. The presence of free CO₂ in water increases the solvent action on calcium carbonate in cement and concrete (196), this action being proportional to the concentration of carbon dioxide. Dr. Ruth Terzaghi (197) reports that free carbon dioxide in concentrations exceeding 20 mg/l will attack concrete sufficiently rapidly to require protective action (see Chapter V-Concrete Mixing and Concrete Corrosion). Molinari (2356) confirms this observation for subsurface waters that contained up to 41.2 mg/l of free CO₂.

c. Fish and Other Aquatic Life. The concentrations of dissolved CO₂ and carbonic acid in water have a marked effect on fish. In their migration, fish tend to respond to slight gradients in carbon-dioxide tension (1083) and to avoid concentrations of 1.0 to 6.0 mg/l (367). According to Wells (1075) it is doubtful if any freshwater fishes can continue to live throughout the year in water with an average CO₂ content as high as 12 mg/l, and concentrations of 20 mg/l will quickly prove fatal to the more-sensitive species. The lethal limit for trout has been reported as 45 mg/l and for tench as 200 mg/l (2977). According to Surber (3359), concentrations of CO₂ between 55 and 78.5 mg/l interfered with the hatching of trout eggs; but Alderdice and Wickett (3360) report that mortality to chum salmon eggs is independent of CO₂ below 125 mg/l.

Lagler (308) indicates that free carbon dioxide in excess of 20 mg/l may be harmful to fish in normal fresh water, but when the dissolved-oxygen content drops to 3 to 5 mg/l, lower CO₂ concentrations may be detrimental. This observation has been supported by the Water Pollution Research Board of England (2907, 3321) and the National Council for Stream Improvement (2500).

The presence of carbon dioxide may, at times, have a beneficial effect insofar as fish are concerned. It has been shown by several investigators (139, 140, 143, 2518, 3057) that CO₂ lowers the pH and consequently the unionized ammonia in certain waters. Herbert (143) reported that 30 mg/l of CO₂ reduced the toxicity of ammonia to trout by lowering the pH value. On the other hand, lowering of the pH value would increase the toxicity of cyanides. The sensitivity of fish to carbon dioxide appears to decrease directly with an increase in temperature (1084).

In U.S. waters that support good fish fauna, ordinarily 5 percent have less than 0.1 mg/l, 50 percent have less than 1.5 mg/l and 95 percent have less than 5.0 mg/l of free carbon dioxide (310). According to Doudoroff and Katz (361), concentrations of 100 to 200 mg/l of CO₂ can be rapidly lethal to more-sensitive fish in presence of adequate dissolved oxygen, and 50 to 100 mg/l or even lower may be lethal after prolonged exposure or with less oxygen. Some delicate marine species, such as herring, are even more sensitive than freshwater forms. Carbonic acid can be toxic even at pH values which are not in themselves harmful; hence pH is not a reliable index of dangerous CO₂ pollution (361).

CARBON DISULFIDE

CS₂

In its commercial form, this colorless, clear, foul-smelling, flammable liquid is miscible with water to the extent of one ml in 530 ml (364). It is used extensively in industry as a solvent for fats, oils, waxes, and resins, for varnishes and lacquers, and for disinfection. It has been reported in gas manufacturing wastes and chemical plant effluents (313, 362). In public waters in the U.S.S.R. the maximum permissible concentration of carbon disulfide is 1.0 mg/l, according to Kirkor (460).

Shelford (363) states that concentrations of 100 to 127 mg/l in tap water killed orange-spotted sunfish in

one hour. Ellis (313) quotes a reference to the effect that a brief 7-minute exposure to 5,000 mg/l caused trout to die two days later. The threshold of toxicity for perch and bleak is reported (2977) at 35 mg/l.

CARBONIC ACID

(see Carbon Dioxide)

CARBON MONOXIDE

co

This colorless, odorless, highly poisonous gas is soluble in water to the extent of 28.4 mg/l under a total pressure of one atmosphere. It may occur in wastes from quenching operations, gas manufacturing, or plants where exhaust gases are scrubbed with water (313, 363).

Experiments on various species of fish have revealed the following lethal characteristics of carbon monoxide

in water:

Lethal Concentration in mg/l	Time of Exposure in Minutes	Type of Fish	Reference
1.2		Varied fish Minnows and sunfish	2920 _ 1075
1.5 47.5	60 to 370 45 to 330	Minnows and sunfish	1075
75	60	Orange-spotted sunfish	363 1075
146 1,160	10 to 240 60	Straw-colored minnows	313
1,160	115	Blunt-nosed minnows	313
1,160 1,160	800 340	Green sunfish Orange-spotted sunfish	
11,314	595	Black bullhead	313

Doudoroff and Katz (361) state that toxic concentrations of carbon monoxide vary, with levels as low as 0.1 to 1.0 mg/l. They maintain that the presence of more than a trace of this gas should be considered as a hazard to fish life.

CARBON TETRACHLORIDE

 CCL_4

This colorless nonflammable liquid with a strong odor is soluble in water to the extent of 800 mg/l at 20°C. It is used extensively in industry as an organic solvent, as a fire extinguisher, for dry cleaning of clothing, and as an antihelminthic in human and veterinary medicine. Death has occurred from ingestion of 5 ml (about 8 grams), inhalation of its fumes has caused numerous respiratory symptoms and even death, and dermatitis results from repeated skin contacts (364, 3292). According to Wadsworth (2971), the toxic oral dose for sheep is 1.0 ml and for cows 5.0 ml. The Soviet Union has established the maximum permissible concentration of CCl₄ in surface waters at 5.0 mg/l, based on its organoleptic properties (3107).

CCE

(see Carbon Chloroform Extract)

CEMETERIES

According to van Haaren (1482) analyses of the surface and ground waters of a number of cemeteries have shown severe pollution. Ten years are required for the decomposition of a corpse.

CERIUM

Ce

(See also Chapter VIII—Radioactivity)

Metallic cerium does not occur free in nature, the principal source of this element being monazite sand (a phos-

phate). Cerium salts are used in textile dyeing and printing, in glass manufacture, as an abrasive, in the manufacture of arc lamps and neon tubes, and medicinally as antiemetics. There is conflicting opinion about the possible deleterious effects of cerium salts, but there is no evidence of severe toxicity (364, 2121).

Cerium forms salts with valences of +3 and +4. Among the ceric salts (+4), the ammonium nitrate, ammonium sulfate, and sulfate are highly soluble in water, but the oxide and fluoride are insoluble. Most of the cerous salts (+3) are soluble, except for the carbonate and fluoride. It is probable, therefore, that ceric or cerous salts discharged in industrial wastes will remain in solution except at high pH values until they are oxidized and precipitated as CeO₂.

The lethal limit of cerous chloride to small mature fresh-water fish (Orizias) during a 24-hour exposure was reported (1459) to be 190 mg/l. Using water of the River Havel, from which the test organisms were taken. Bringmann and Kuhn (2158) found that the toxic threshold of cerous chloride toward Scenedesmus at 24° C during a 4-day exposure was only 0.15-0.20 mg/l as cerium; and for Escherichia coli the threshold was at 0.75-1.5 mg/l as cerium. Yet, for Daphnia at 23°C and a 48-hour exposure, a concentration of 1000 mg/l of cerium showed no deleterious effect. In similar tests with cerous sulfate, Scenedesmus exhibited threshold effects at 0.14 mg/l of cerium whereas Daphnia was unaffected at 1000 mg/l of cerium. The lethal dose of cerous fluoride required in 48 hours for the fish, Tinca vulgaris was reported as 30,000 mg/l (3271).

Cerium is accumulated from the water environment by many forms of aquatic life. Morgan (2800) found concentration factors for cerium-141 of 15,170 for Ochromonas, 5100 for Platymonas, 7400 for Chlamydomonas (all flagellates), 28,500 for the diatom Nitzschia, and 280-1740 for marine bacteria. It has been reported (3272, 3273) that particulate cerium became associated with Nitzschia cells at a faster rate than ionic cerium. For further information about concentration factors, see Chapter VIII—Radioactivity.

CESIUM

 $\mathbf{C}\mathbf{s}$

(see also Chapter VIII)

This silvery-white ductile metal reacts violently with air or water; consequently it is not found pure in nature. It is obtained from the ore pollucite (cesium aluminum sodium silicate). Cesium forms salts similar to those of sodium or potassium but they have found little use in industry except in the manufacture of photoelectric cells (364, 2121).

Until it occurred as an important constituent of radioactive fall-out, as Cs-137, cesium was virtually ignored as an element. Relatively little is known about its properties or toxicities. It appears to behave very much like potassium in human and animal metabolism, and consequently has a low level of toxicity.

There is considerable literature dealing with the accumulation of Cs-137 and Cs-134 from the water environment into aquatic organisms. A few of these concentration factors are presented in the following table:

	Concentration		
Organism	Factor	Reference	
Bacteria	15-116	3386	
Algae (9 species)	52-1530	3388	
Algae	28-2180	3385	
Algae	34.200	3385	
Aquatic organisms, mixed	50-10.000	3387	
Carp	3000	3387	
Sunfish	9500	3387	
Oysters (soft tissue)	50	3375	

Pendleton (3387) claims that the principal route through which Cs-137 in hazardous amounts could reach man is by way of the aquatic food chain. The presence of potassium in water has a slight depressing effect on the concentration of cesium by water (3388).

Cesium-137 is absorbed readily by rocks and soils; hence it is not likely to travel far through ground water (1976).

CETYL ALCOHOL

 $\mathrm{CH_{3}(CH_{2})_{14}CH_{2}OH}$

(see also Protozoa and Insects, in Chapter VII)

Known also as hexadecanol, this white crystalline substance has long been used as an emollient in cosmetics, as an emulsifier, and in the manufacture of sulfated alcohol for textile soaps (364). It is insoluble in water. Indeed, tests with a sensitivity of 0.005 mg/l could not detect it in solution (3274). Recently, cetyl alcohol and related compounds have been used experimentally to form a monomolecular film on water which tends to minimize evaporation. Reports indicate that evaporation may be decreased by 9 to 65 percent, depending on temperature, winds, wave action, and the extent and thickness of the film (3275, 3276, 3277). Scores of articles have appeared since 1954 describing this procedure and its effects on evaporation. Only those publications that deal directly with the effect of cetyl alcohol on beneficial uses of water are relevant to this report.

In general, there appear to be four properties of water that may be altered by the application of cetyl alcohol to lakes, viz temperature, surface tension, bacterial densities, and dissolved oxygen. In the field tests reported through 1961, there appeared to be no change in dissolved solids (3278), no mortality or modification of the fish population or upon the ability of anglers to catch fish (2291), no deleterious effect on plankton or benthic organisms (2291), and no evidence of increased taste and odor (3275).

By reducing evaporation and the natural cooling action attendant thereto, a monomolecular film tends to increase the temperature of the lake waters, especially near the surface. In comparison with controls, temperature rises of 1° to 3°C have been reported (2293, 2684, 3279, 3280). The surface tension of lakes treated with cetyl alcohol drops from about 72 dynes per cm to as low as 30 dynes per cm (2293, 2294). Large water striders were observed to fall through the altered water films and drown (2293). There is also some evidence that the lower surface tension may interfere with the emergence of midge flies (2683, 2684, 3278), a factor that might influence the fish population in the long term.

Bacterial densities in lakes treated with cetyl alcohol have been observed to increase markedly (2290, 2292, 2293, 2294, 3281, 3282) owing to the bacterial decomposition of this compound. No detrimental effect of this in-

crease has been reported. The monomolecular film may reduce the transfer of gases into or out of the waters of a lake (3283) but any change in dissolved oxygen appears to be limited to about 2 percent of saturation (2291).

Berger (3274) reported tests in which fathead minnows were exposed for 5 days to emulsified cetyl alcohol in concentrations of 1, 10, 100, and 500 mg/l. All fish survived but at 500 mg/l there was sufficient depletion of oxygen that fish were distressed. This substance caused no mortality among fish in aquaria maintained on a diet containing 50 percent hexadecanol for periods up to 91 days. Trout planted in a treated pond showed the same growth at the end of one year as those planted in an untreated pond (3278).

CETYL AMMONIUM COMPOUNDS

CETYL PYRIDINIUM CHLORIDE

(see Chapter X)

CHEMICAL WARFARE AGENTS

(see also Hydrogen Cyanide, Explosives, Chapter VIII, Chapter IX)

Acts of sabotage or war might be aimed at impairing the potability or other usefulness of water supplies. Various chemical poisons have been known for a long time, but many have only limited practical value because very large quantities are needed to contaminate an entire water supply to a harmful degree; for example, about 600 lbs of chemical per million gallons of water would be needed to produce a lethal concentration HCN (1483).

More recently, however, various chemical poisons have been produced which are lethal to man at dosages of less than one mg per kilogram of body weight. Among these agents are mustard gases, fluoroacetate compounds, and various organic phosphates (nerve gases) that may cause death in only a few seconds. These poisons make more practical the possibility of contaminating an entire water supply, but still 50 to 500 lbs of chemical per million gallons of water would be needed (1483).

Greenberg (1484) has pointed out that contamination of large supplies of water, such as city reservoirs, with war gases is not very likely inasmuch as enormous amounts would be required to render the water unsafe to drink. The most effective war gases are the blister gases and nerve gases about which few published data are available. It has been estimated that in order to contaminate a 189 million gallon reservoir, 79,000 lbs of mustard gas or 36,000 lbs of lewisite would be required (1484).

There are numerous agents of chemical warfare that may pollute natural waters as a result of enemy action or accidental discharges from manufacturing plants. Normally, however, such agents would not enter into the deliberations and case-by-case studies of water-pollution control boards. For a thorough review of the polluting potential of numerous chemical-warfare agents, reference is made to the work of Sanchis (466).

CHENOPODIUM OIL

Oil of chenopodium is derived from the goosefoot plant. Schaut (362) found that 5 to 10 mg/l of this oil

killed minnows in 24 to 48 hours. A concentration of 17.1 mg/l gave a strong, pleasant odor in tap water but this concentration affected minnows in four hours and killed all in 24 hours.

CHLORAMINES

NH₂Cl, NHCl₂ and NCl₃

1. General. Chloramines are formed when water containing ammonia, ammonium hydroxide, or ammonium ions is chlorinated, thus

$$NH_4^+ + HOCl \rightleftharpoons H^+ + H_2O + NH_2Cl$$
 (monochloramine)
 $NH_2Cl + HOCl \rightleftharpoons H_2O + NHCl_2$ (dichloramine)
 $NHCl_2 + HOCl \rightleftharpoons H_2O + NCl_3$ (trichloramine)

The proportion of mono-, di-, and trichloramine in any solution is a function of temperature, pH, and the concentrations of ammonium ions and hypochlorous acid (1087). Trichloramines will not be formed except at low pH values. At the normal range of pH (6.0 to 8.0) mono-chloramine and dichloramine apparently react to produce nitrogen gas thus: $NH_2Cl + NHCl_2 \rightarrow N_2 + 3H^+ + 3Cl^-$

Not only do mono- and di-chloramines exist in treated water supplies where they are used to provide disinfection without chlorinous tastes, but they also occur in chlorinated effluents from municipal sewage works and in wastes from many industrial processes that employ chlorine for disinfection and bleaching. Hence, chloramines are likely to occur in polluted waters.

- 2. Cross References. Ammonia, Chlorine, Chloramine-T.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. A discussion of the use and merits of chloramines as compared with free chlorine as disinfectants for treated waters is beyond the scope of this report, and the reader is referred to the work of Moore (1087) and others at Harvard University and to that of Butterfield and Wattie (490, 494).

Where chlorination of water results in the formation of taste-bearing chloro-organic compounds, the use of ammonia to form chloramines appears to result in a taste reduction (956, 1028, 1086)

b. Fish and Other Aquatic Life. According to Westfall (311, 673), chloramine is more toxic than free chlorine to warm-water fish; with 0.4 mg/l killing adult fish and 0.06 mg/l being lethal to trout fry. Ellis (313) reports that 0.4 mg/l killed sunfish and bullheads, 0.76 mg/l, hardy minnows; and 1.2 mg/l, large carp. According to Merkens (717) 0.08 mg/l of residual chlorine, mostly in the form of chloramine, killed about half of a batch of rainbow trout in 7 days at saturated dissolved oxygen.

The Department of Fisheries of the State of Washington conducted extensive experiments on the effects of chlorine and chloramines on chinook, pink skeeria, and silver salmon in fresh and saline waters (2091). The critical level for a 72-hour exposure of these three species was less than 0.1 mg/l of chlorine. Chloramines were not formed in salt water by the concentrations and ratios

of chlorine and ammonia (1:3) used in these experiments; but in aerated fresh water, chloramines were found to be more toxic than chlorine, and dichloramine was more deadly than monochloramine under the conditions of the experiment. In contrast, the Water Pollution Research Board of England (1816) found monochloramine slightly less toxic than free chlorine toward rainbow trout at pH 7.0.

Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158) found that the threshold concentration of chloramines for *Daphnia* exposed for 48 hours at 23°C was 4 mg/l, and for *Scenedesmus* during a 96-hour exposure at 24°C it was 10 mg/l.

CHLORAMINE-T

CH₃C₆H₄SO₂N NaCl

(see also Chloramines, Chlorine)

This soluble compound releases HOCl when dissolved in water and hence it is used as a bactericidal agent. Ellis (313) quotes a reference to the effect that 5 mg/l of chloramine-T in Nile River water killed *Daphnia* and *Cyclops*.

CHLORATES

(see Potassium Chlorate and Sodium Chlorate)

Chlordane

(see Chapter IX)

CHLORIDES

Cl-

1. General. Chlorides are found in practically all natural waters. They may be of natural mineral origin, or derived (a) from sea-water contamination of underground supplies, (b) from salts spread on fields for agricultural purposes, (c) from human or animal sewage, or (d) from industrial effluents, such as those from paper works, galvanizing plants, water softening plants, oil wells, and petroleum refineries.

The Ohio River Valley Water Sanitation Commission has set chloride standards for river water (3389, 3390). On the main stem of the Ohio River, it is recommended that the chloride concentration never exceed a monthly average of 125 mg/l at the most probable minimum monthly average 10-year flow, and that the maximum concentration at any time never exceed 250 mg/l. The primary concern is economic damage rather than public health. For public supplies, the water is classified as "acceptable" if the chloride concentration is less than 125 mg/l, "doubtful" if between 125 and 250 mg/l, and "unsatisfactory" above 250 mg/l. For industrial needs, the corresponding limits are less than 50, 50-175, and over 175 mg/l respectively.

- 2. Cross References. Tastes, Chloride Salts under the appropriate cation, Dissolved Solids.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Chlorides in drinking water are generally not harmful to human beings until high concentrations are reached, although chlorides may be injurious to some people suffering from diseases of

heart or kidneys. Restrictions on chloride concentrations in drinking water are generally based on palatability requirements rather than on health.

Chlorides in water may impart a salty taste at concentrations as low as 100 mg/l (152, 1080), although in some waters 700 mg/l may not be noticeable (152) (see also Tastes). According to the Kettering Laboratory (3389, 3391, 3392), the most taste-sensitive people can detect chloride from calcium salts at 96 mg/l and from sodium salts at 121 mg/l (based on work by Whipple in 1907). For average individuals, the taste threshold is about 400 mg/l. Lockhart et al. (3241) reported the taste thresholds of NaCl KCl, and CaCl₂ to be 345, 650, and 347 mg/l, corresponding to chloride concentrations of 210, 310, and 222 mg/l respectively. The fact that a taste is detectable, however, does not mean that it is objectionable; indeed, many people prefer water that is partly mineralized to the flat taste of distilled water.

The tolerance of chlorides by human beings varies with climate and exertion, and chlorides lost through perspiration may be replaced by chlorides in either the diet or drinking water. From hot dry areas have come reports that chloride concentrations up to almost 900 mg/l have not been harmful (1073), and Rudolfs maintains that even 1000 mg/l is harmless (855). According to a Kettering Laboratory survey (3392), laxative effects of chloride are generally apparent only when an individual has been accustomed to a lower concentration of the salt. Within a few days, an individual adjusts physiologically to a higher level of salt intake. In general, it is the cation (calcium, magnesium, sodium, or potassium) associated with the chloride that produces a harmful effect. It has been reported in Russia (3393, 3394) that under conditions of artifically induced thirst, test subjects drank 40-60 percent less water containing 1000 mg/l of chloride than they did of tap water.

Chloride limits, both those in use as standards and those recommended for use as possible standards, vary over a wide range. It is believed that the source of the chlorides may be a more important factor for drinking water than their quantity and that any sudden increase in the chloride content of a supply should be suspected as a possible indication of pollution and should be investigated further.

The USPHS Drinking Water Standards of 1962 (2036) recommend that chlorides do not exceed 250 mg/l. In other agencies or other countries, the criteria for chlorides have been given at values ranging from 5 mg/l to 600 mg/l (250, 499, 627, 630, 631, 632, 929, 944, 992, 1088, 1457). The WHO International Standards of 1958 set a permissible limit of 200 mg/l and an excessive limit of 600 mg/l (2328). For the WHO European Drinking Water Standards (2329), the recommended limit is 350 mg/l and no tolerance limit is specified.

b. Industrial Water Supplies. In Chapter V it is to be noted that several industrial processes have recommended threshold concentrations for chloride ions or chloride compounds. Some of these values are tabulated below, but for more complete information, see Chapter V. Recommended Threshold Concentration, in mg/l

Industry	Chlorides	CaCl	MoCl:	NaCl
Brewing	_ 60-100	100-200		275-500
Carbonated beverages	_ 250			
Dairy industry Food canning and freezing _	_ 30			
Food equipment washing	250			1000-1500
Paper making:				
Groundwood pulp Soda pulp	_ 75 _ 75			
Kraft pulp	_ 200			
Steel manufacture	175			
Sugar making	_ 20			
Textile processes	_ 100			

Chlorides appear to exert a significant effect on the rate of corrosion of steel and aluminum. The Bethlehem Steel Corporation reported that there was evidence of corrosion attack on rolled surfaces when the chloride content of quenching waters reached 185 mg/l. Many producers of rolled stainless steel consider 50 mg/l the chloride limit for roller cooling waters. Corrosion of all metals used in the water-handling system has been re-

ported at 45-50 mg/l of chlorides (3389).

Research by several independent investigators (2361, 3305, 3395, 3396) has shown that chloride ions have an immediate effect on corrosion of steel at concentrations as low as 3.0 mg/l, and for stainless steel at 10 mg/l. Indeed, in the stainless steel portion of a power reactor, chloride concentrations over 0.5 mg/l were found to accelerate stress corrosion (3395). For aluminum, one reference (3397) indicates that 5.0 mg/l of chloride caused some pitting and increased the corrosion rate slightly; but another article (3305) reports that there was no substantial increase in the corrosion rate of aluminum in aerated distilled water at 26°C at chloride concentrations as high as 300 mg/l.

c. Irrigation Use. Chlorides are considered to be among the most troublesome anions in irrigation water. They are generally more toxic than sulfates to most plants, including lemons, alfalfa, fruit trees, and potatoes; but sulfates are more toxic than chlorides to sugar beets (273).

The following concentrations of chloride can be harmful to plants (see also Chapter V—Irrigation):

	•	8-1-0-	,
Concentra in mg/		Concentration in meg./liter	Reference
100-150		3-4	1089
200		6	1090, 275
177-355		5-10	271
225			3398
250			618
350			219, 921
1260		35.5	1091
1500			9 21

The following concentrations of chloride have been reported as not harmful: less than 71 mg/l (264); less than 177 mg/l (271); 62 mg/l (1060).

- d. Stock and Wildlife Watering. Chloride concentrations in excess of 4000 mg/l have been reported to cause injury to livestock (932). Chloride concentrations of 1500 mg/l are reported to be safe for cattle, sheep, swine, and chickens (3391). A limiting concentration of 3000 mg/l has been proposed in South Africa (3373). For further details of the effect of dissolved solids on livestock, see Chapter V.
- e. Fish and Aquatic Life. Hart et al. (310) cite data indicating that among U.S. waters supporting a good fish fauna, ordinarily the concentration of chlorides is below

3 mg/l in 5 percent; below 9 mg/l in 50 percent and below 170 mg/l in 95 percent of such waters. The following concentrations of chloride have been reported to be harmful to fish:

Concentration	Type of	
in mg/l	Fish	Reference
400	trout	932
2000		1092
4000	bass, pike, perch	932
4500-6000		1489
8100-10,500	small bluegills	2692

On the other hand, 2000 mg/l of chloride has been reported as not harmful for some fish (1092). Chlorinity is closely related to the total salinity and its effects on osmosis; hence it is evident that fresh-water fish cannot tolerate excessive changes in salinity but similarly, most salt-water fish are vulnerable to waters of low salinity.

The Aquatic Life Advisory Commission of ORSANCO concluded that it is impossible to generalize on the effects of chloride concentrations on aquatic life, for each mixture of chlorides with other salts must be evaluated separately (3390).

4. Summary. On the basis of the foregoing information, it appears that the following concentrations of chloride will not be normally deleterious to the specified beneficial uses:

a.	Domestic v	water suj	pply _	 250	mg/l
b.	Industrial	water st	upply	 50	mg/l
c.	Irrigation			 100	mg/l
đ.	Stock and	wildlife		 1500	mg/l

CHLORINATED BENZENES

(see Chapter IX)

CHLORINATED CAMPHENE

(see Chapter IX, Toxaphene)

CHLORINATED HYDROCARBONS

CHLORINE

1. General. Not to be confused with chlorides, which are present in almost all natural waters, chlorine is not a normal constituent of such waters. It is the elemental form of a greenish-yellow gas that dissolves readily in water. At 20°C, one volume of water will dissolve 2.3 volumes of chlorine gas, or about 7,000 mg/l (364). When it dissolves in water, chlorine hydrolyzes immediately and completely, according to the reaction:

$$Cl_2 + H_2O \rightarrow HOCl + H + Cl$$

At concentrations of total chlorine below 1,000 mg/l, no measurable quantity of chlorine gas exists in solution as Cl₂, all chlorine being present as HOCl or its dissociated ions. The HOCl is a weak acid and dissociates according to the equation.

$$HOCl \rightleftharpoons H^+ + OCl^-$$

where the dissociation constant is given as 3.3×10^{-8} at 20°C. Thus it can be seen that the ratio between HOCl and OCl is a function of pH, with the percentage of HOCl being 96 percent at pH 6, 75 percent at pH 7, 22 percent at pH 8, and only about 3 percent at pH 9. This relationship of HOCl and pH is particularly significant

inasmuch as the undissociated form appears to be the primary toxic principle and the bactericidal agent in the use of chlorine for disinfection (1087).

Free available chlorine, i.e. HOCl and OCl-, and combined available chlorine, i.e. the chloramines, may appear briefly in surface or ground waters as a result of discharges from municipal sewage-treatment works or industrial processes. In the chlorination of sewage and treatment-plant effluents before discharge to a water course it is customary to add chlorine in an amount equivalent to only a fraction of the chlorine demand, and hence free available chlorine is seldom found in such effluents. Combinations of chlorine with ammonia, organic matter, and cyanides may be present, however, and may prove to be detrimental to fish life and other beneficial uses. Industrial processes most likely to contain free or combined chlorine are those employing bleaching operations, e.g., textile mills and paper pulping operations, or those using chlorine for the control of organisms in cooling waters (346).

- 2. Cross References. Calcium Hypochlorite, Chloramines, Cyanides, Chlorides, Halogenated Hydrocarbons, Halogenated Phenols, Insecticides, and other chlorinated compounds.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Chlorine is used extensively in the U.S. and elsewhere as a bactericidal agent in municipal water works. Extensive literature pertaining to the effectiveness of chlorination against viruses, viable bacteria, spores, amoeba, cysts, ova, and other forms of biota is available, but it is not within the province of this report to deal with methods of treatment or the quality of treated water. It is relevant to note, however, instances where free chlorine, per se, might be regarded as a pollutant in raw water sources.

In normal concentrations, chlorine does not render water abnormally corrosive to zine (977) nor does it increase the solubility of lead salts (1029). In pure water, residual chlorine concentrations as high as 2.0 mg/l have not been found to cause objectionable tastes and odors (1086) but where certain organic substances, such as phenols, are present, very small concentrations of chlorine can produce undesirable tastes and odors. Rohlich and Sarles (759) quote references to the effect that chlorine in dosages up to 0.1 mg/l did not produce odor with phenol when the latter was present up to 0.05 mg/l, and that the critical range for chlorophenol tastes was for chlorine dosages from 0.175 to 0.4 mg/l with phenol from 0.002 to 0.17 mg/l. According to Campbell (2059) the taste threshold of chlorine in redistilled water was 5.2 mg/l.

It is generally agreed that the small amounts of chlorine present in chlorinated water are dissipated by reaction with saliva and gastric juices as soon as the water is swallowed (152). Muegge (1467) and Hudson (3303) report that 50 to 90 mg/l of chlorine in drinking water have been used by humans without adverse effect, but Muegge (1467) also cites an instance where 90 mg/l produced strong physiological reactions. According to Watson and Kibler (1096), and another reference (1098), chlorinated drinking water may cause asthma, colitis, and eczema. When patients drink distilled water instead of

chlorinated water, their condition improved, but when they returned to chlorinated water the symptoms reappeared.

- b. Industrial Water Supplies. Many industrial waters are chlorinated to control bacteria and other slime-producing organisms (222, 436, 1099, 1100), but in the food-processing industries, chlorine may cause tastes in the canned or frozen products (225) or may be detrimental in corroding cans (223). Traces of chlorine in water used for metal-plating baths will affect the smoothness or brightness of the deposits (214). For the manufacture of fine papers, T.A.P.P.I. recommends that the residual chlorine not exceed 2.0 mg/l (350), but in earlier work under T.A.P.P.I. sponsorship Fleming et al., (552) set the limit at 0.3 mg/l for high-grade paper and 0.8 mg/l for lower-grade products.
- c. Irrigation. No injury to land plants occurs when irrigation water contains 50 mg/l or less residual chlorine (152, 1089); concentrations of 100 to 150 mg/l injured or retarded some plants and did not affect others; 200 to 300 mg/l injured tops of plants but did not harm roots; and 500 to 1000 mg/l retarded growth of seedlings and killed tops and roots of plants. Roots from tomato cuttings in chlorinated water were not affected by 5.0 mg/l but were retarded in growth at 10 mg/l. Cut flowers were not affected by concentrations up to 10 mg/l but aquatic plants were harmed by concentrations of 3.0 mg/l or more (1089).
- d. Stock and Wildlife Watering. According to Blabaum and Nichols (1468), white mice can grow from weanlings to adulthood and thrive on water containing 200 mg/l of free available chlorine. Weight gain and growth of mice using 100 and 200 mg/l of free available chlorine were equal to those of controls.
- e. Fish and Other Aquatic Life. Free available chlorine in water may be toxic to fish and other aquatic life at low concentrations, and combinations of chlorine with cyanides, phenols, and other substances may be even more detrimental (see cross references). It is known that the toxicity of chlorine to bacteria is due primarily to undissociated HOCl and consequently lethality increases with decreasing pH values. It is probable that the toxicity to fish is also affected by pH value but so far as it is known this question has not been explored thoroughly (346). The following concentrations of free chlorine have been reported to be toxic or harmful to fish:

Concentration in mg/l	Time of Exposure	Type of Fish	Remarks	Doforman
٠.	Burposure			Reference
0.03		rainbow trout	killed	2920, 2962
0.05	23 days	young salmon	critical level	2091
0.08	7 days	rainbow trout	half killed	717, 1816
0.11 to 0.13	days	fish	harmful	603
0.15 to 0.2	12 to 16 days	carp	25% killed	346, 776
0.2 to 0.3		fish	harmful	1101
0.25	5 hours	fingerlings	killed	361
0.3	2 hours	trout	killed	361. 311
0.3 to 1.0		fish	killed	1102, 311
0.8	47 minutes	small trout	killed	346
0.8	4 hours	golden shiners	killed	3361
1.0	1 hour	trout	killed	361
1.0	4 days	many types	killed	346, 776
1.0	=	goldfish	killed	361
1.0		trout and gold-	Killed	901
1.0		fish	killed	1010
0.0				1012
2.0		goldfish	killed	2920, 2962
2.0 to 4.0	57.	fish	30% killed	912
3.0	24 hours	green sunfish	28% killed	3361

In contrast, fish have been reported to have survived the following concentrations of free chlorine:

Concentra- tion in mg/l	Time of Exposure	Type of Fish	Remarks	Reference
0.1	2.5 hours	small trout	not harmed	346
0.1		fish	not harmed	1101
0.25	42 hours	goldfish	no effect	361
0.3	2 hours	minnows	no effect	362
0.5		trout and goldfish	survived	1012
1.0		minnows	survived	1103
1.0		goldfish	recommended	
		*	threshold	1103.633
1.0	100 hours	eels	not effected	776
1.0		carp	not harmful	361
1.0	48 hours	fish	max, conc. sur-	
			vived	1058
2.0	48 hours	green sunfish	no mortality	3361
3.8	48 hours	tadpoles	no mortality	3361
5.0		goldfish	survived	384

The wide discrepancy in the foregoing tabulations is evidence of the fact that pH, temperature, dissolved oxygen, and the synergism and antagonism of other pollutants markedly affect the toxicity of free chlorine toward fish. The Water Pollution Research Board of England (1816) found that the toxicity of chlorine in ammoniated water at pH 7.0 was proportional to the titrable chlorine residual and not to the chlorine added. Rainbow trout was the test fish. It was also determined that free chlorine was slightly more toxic than monochloramine.

According to Hiatt et al. (3350), marine fish exhibit a slight irritant activity at 1.0 mg/l of chlorine and violent irritant activity at 10.0 mg/l.

The tolerances of other aquatic organisms toward free chlorine appear to vary widely. Most algae have been controlled by 0.25 to 3.0 mg/l (587, 1490, 2255) and 5 to 10 mg/l killed Synura (587). For Chironomus (blood worms) dosages as high as 15 to 50 mg/l may be required (1490). Minute crustacea, rotifers, and diatoms were killed by 1.0 mg/l but worms, molluscs, mites, and larvae were not affected (1102). In soft water, 0.5 mg/l killed Daphnia in 72 hours (313), 1.0 mg/l is reported to "control" Daphnia (385) and in Nile River water, Daphnia and Cyclops were killed by 2.0 mg/l (313). Larvae of Chironomus were killed by 2.6 mg/l in 1.5 hours (100 percent); by 1.3 mg/l in 3.2 hours (100 percent); and 85 percent by 0.65 mg/l in 24 hours (568). Fresh-water mussels, snails, and sponges in cooling systems were killed, but not dislodged, by 2.5 mg/l.

In sea-water conduits, exposure for 8 hours per day to sea water containing 10 mg/l chlorine did not kill all adult mussels and anemones. Most barnacles were killed by exposure of 4 hours per day to this concentration; and tunicates and bryozoa were all killed by exposure for one hour. With continuous chlorination to a residual of 2.5 mg/l, all organisms were killed in 5 to 8 days, but with 1.0 mg/l a few barnacles and all anemones were alive after 15 days (976).

Chang et al. (2812) found that free-living nematodes ingest pathogenic bacteria and viruses, and that these pathogens can remain viable within the nematodes for 24 to 48 hours. Furthermore, the nematodes are highly resistant to free chlorine in water, not being affected by 3.0 mg/l in 120 minutes or by 15 to 45 mg/l in a one-minute exposure at 25°C. Even with an initial chlorine concentration of 95-100 mg/l, 50-60 percent of the nematodes survived a 5-minute contact and 10-20 percent survived a 15-minute contact.

According to Clendenning and North (2106, 2865), the photosynthetic capacity of bottom fronds of the giant kelp, *Macrocystis pyrifera*, was not affected in 5 days

exposure to 1.0 mg/l of chlorine in sea water; but at 5 to 10 mg/l there was a 10-15 percent reduction in photosynthesis after two days and 50-70 percent reduction after 5 to 7 days.

The Mersey River Board in England (2950) has proposed that the free chlorine residual of wastes discharged to the River Alt and the River Bollin should not exceed 1.0 mg/l.

- f. Shellfish Culture. Clams and oysters will withstand short exposures to free chlorine, and such treatment has been used in purification of shellfish. In Massachusetts, clams are conditioned for 24 hours in sea water containing a residual of 0.3 to 0.5 mg/l. In England, shellfish are exposed briefly to water containing 5.0 mg/l of free chlorine, then placed in chlorine-free water (1100). The USPHS Manual of Recommended Practice For Sanitary Control of the Shellfish Industry (527) requires that water used to condition shellfish carry a residual of not less than 0.05 mg/l at all times. Experimental evidence indicates that most oysters are sensitive to initial chlorine concentrations varying from 0.01 to 0.05 mg/l, i.e., their pumping activity is reduced, and effective pumping cannot be maintained at chlorine concentrations over 1.0 mg/l (1104).
- g. Bathing Waters. Free residual chlorine in natural waters should not be considered detrimental to bathing inasmuch as this bactericidal agent is used in swimming pools and many state health departments require residual chlorine concentrations in such pools. Mood et al. (1105) report that a slight increase in eye irritation is obtained by increasing the chlorine residual from 0.05 to 0.50 mg/l, but within the pH range of 7.0 to 8.0, the pH has a greater effect upon eye irritation than does the chlorine residual in concentrations between 0.05 and 0.50 mg/l.

CHLOROAURIC ACID

AuCl₃·HCl·4H₂O

This acid gold trichloride, a yellowish crystalline solid very soluble in water, is used in photography, gold plating, and the manufacture of ruby glass (364). The lethal concentration of AuCl₃·HCl for three mature small fresh-water fish (*Orizias*) exposed for 24 hours to only 20 ml of test solution, was reported to be about 14 mg/l (1459). With this same substance, Jones (1460) found the lethal limit to be 0.4 mg/l, as gold, for stickleback. The average survival times at other concentrations were as follows: one week at 0.6 mg/l, and only 4 days at 1.0 mg/l as gold.

CHLOROBEN

(see Chapter IX, Chlorinated Benzenes)

CHLOROFORM

CHCl3

This colorless, volatile, but non-inflammable heavy liquid of ethereal odor and sweetish taste is used as an anesthetic, counterirritant, solvent, cleansing agent, and antiseptic. Stickleback will avoid solutions of 100 to 200 mg/l of chloroform in tap water and at 500 mg/l they become anesthetized (467). At this latter concentration, the respiration of the fish decreased rapidly in 10 minutes and stopped in 20 minutes. At a concentration as low as 10 mg/l, fish struggled for 20 to 30 minutes then

sank to the bottom. When placed in fresh water for 90 minutes, however, they revived (468).

CHLOROMETHANE

(see Methyl Chloride)

CHLOROPHENOLS

(see Chapter IX)

CHLOROPHENYL DIMETHYL UREA (CMU)

(see Chapter IX)

CHLORPLATINIC ACID

H₂PtCl₆·6H₂O

A brownish-yellow crystalline solid, easily soluble in water, this acid salt is used in platinum plating, photography, indelible ink, mirrors, and as a catalyzer (364). To three mature small fresh-water fish (*Orizias*), exposed for 24 hours to only 20 ml of test solution, the lethal concentration of H₂PtCl₆ was reported to be about 33 mg/l (1459).

CHLORTHION

(see Chapter IX)

CHROMATES

(see Chromium)

CHROMIC ACID

(see Chromium)

CHROMIUM

1. General. This section deals with chromium ions in their various forms, i.e. as chromous ion (Cr++), as chromic ion (Cr+++), as chromite ion (CrO₃---) or (CrO₂-), as chromate ion (CrO₄--), and as dichromate ion (Cr2O7-). In the chromic or chromite condition the chromium is trivalent, while in the chromate and dichromate form it is hexavalent. All chromous compounds. tend strongly to be oxidized to the chromic condition. Hexavalent chromium can be reduced to the trivalent form by heat, by organic matter, or by reducing agents. Confusion in terminology frequently arises from the fact that chromium trioxide, a hexavalent form, is also called "chromic acid" or "chromic acid anhydride", thereby confusing it with the trivalent chromic ion. In the following abstract of literature, care has been taken to avoid this confusion of terms.

Of the trivalent chromic salts, the chloride, nitrate and sulfate are readily soluble in water, but the hydroxide and carbonate are quite insoluble. Of the hexavalent chromate salts, only sodium, potassium, and ammonium chromates are soluble. The corresponding dichromates are also quite soluble.

Hexavalent chromium salts are used extensively in metal pickling and plating operations, in anodizing aluminum, in the leather industry as a tanning agent, in the manufacture of paints, dyes, explosives, ceramics, paper, and many other substances. Trivalent chromium salts, on the other hand, are used much less extensively, being employed as mordants in textile dyeing, in the ceramic and glass industry, and in photography (364,

1106, 2121). Chromium compounds may be present in wastes from many of the foregoing industries or they may be discharged in chromium-treated cooling waters (152). Rather extensive literature is available to describe the effects of chromium as a corrosion inhibitor in cooling systems and further numerous references deal with the effect of hexavalent and trivalent chromium upon biological sewage treatment processes and sludge digestion (346), but such literature is not within the province of this survey.

- 2. Cross References. Chapter VIII (Radioactivity)
- 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The USPHS Drinking Water Standards of 1962, as well as those of 1946, set a mandatory limit of 0.05 mg/l for hexavalent chromium, but none for the trivalent form (2036). The WHO International (2328) and WHO European (2329) Drinking Water Standards also prescribe a limit of 0.05 mg/l for hexavalent chromium. The 1942 standards in the U.S. were even more severe in permitting no hexavalent chromium whatsoever, but this restriction was relaxed in 1946 to allow certain ground-water supplies that were slightly affected by chromates to qualify (1106). Also, at that time, a concentration of 0.05 mg/l was the lowest amount that was analytically determinable.

There is no evidence that chromium salts are essential or beneficial to human nutrition. When administered orally, chromium salts are not retained in the body but are rapidly and completely eliminated (2121). Although the salts of trivalent chromium are not considered to be physiologically harmful (997), there is evidence that large doses of chromates leads to corrosive effects in the intestinal tract and to nephritis (2129). The toxic dose for man is reported by Rothstein (2129) to be about 0.5 grams of potassium bichromate.

On the basis of physiological effects, it is difficult to understand why the USPHS and WHO have placed such a low limit on hexavalent chromium and why they made this limit mandatory. On Long Island, according to Davids, and Lieber (1106), a family used water for over three years from a well that was polluted with hexavalent-chromium wastes, with no apparent ill effects. When first discovered, hexavalent chromium was present in a concentration in 1.0 mg/l, and in May 1951 the water contained 25.0 mg/l. One physical exam of the entire family (man, wife, and two children) revealed no abnormalities and the family has refused to abandon the supply, or to submit to further examinations. The persistence of this family may eventually prove to be a valuable source of information concerning the physiological effects of hexavalent chromium in drinking water (1106).

Pomeroy (2924) used as his only fluid for drinking for 15 days water to which potassium dichromate had been added at a concentration of 10 mg/l as chromium. During that time he ingested 235 mg of chromium. Three periods of nausea were noted. The experiment was continued for two more weeks at concentrations of 2.5 to 5.0 mg/l. At a concentration of 5 mg/l, mild nausea resulted from drinking freely on an empty stomach, but under similar conditions, concentrations of 2.5 and 3.5 mg/l

failed to produce any symptoms. On the basis of the animal experiments described below (under Stock and Wildlife Feeding), it would appear that man could drink water containing 5.0 mg/l of hexavalent chromium without deleterious physiological effects.

Chromium is not commonly encountered in natural foods, although traces enter cooked food from stainless-steel utensils. The amount of chromium so ingested is not known to have any physiological effects.

Chromium salts impart color to water, but this effect is not discernible below about 1.5 mg/l. Similarly, the taste threshold for the most sensitive person is about 1.5 mg/l.

b. Irrigation. Chromium is present in trace amounts in soils and in plants, but there is no evidence that chromium is essential or beneficial for plant nutrition (2121). Sedova (2925) reported that concentrations of trivalent or hexavalent chromium in excess of 1.0 mg per kg of soil inhibited nitrification. On the other hand, the addition of 5 mg of chromium per kg of soil resulted in a slight increase of the nitrogen content of peas (2926). Chromium is picked up by plants from the soil, for vegetables grown on soil irrigated with wastewaters containing chromium had 3 to 10 times more chromium than those grown on similar soils devoid of chromium (2925).

According to Klintworth (1493) chromium is toxic to plants at all concentrations. In sand culture, concentrations of 3.4 to 17.3 mg/l of trivalent chromium in nutrient solutions were slightly toxic to various crops. The chromate ion was slightly more toxic than the chromic ion at equivalent concentrations (1473). Added as potassium dichromate, 5 mg/l of chromium in a nutrient solution caused slight chlorosis among oat plants, 10 mg/l caused marked chlorosis, and 15 to 50 mg/l markedly reduced the growth of the plants. A concentration of only 2 mg/l intensified the injury caused by nickel (1462).

e. Stock and Wildlife Watering. It has been reported (353) that one gram of trivalent chromium per day, as CrPO₄, over a period of 17 weeks did not cause illness, loss of weight, or tissue damage to cats. For hexavalent chromium salts, according to Gross and Heller (1108) the maximum non-toxic level in drinking water for white rats is 500 mg/l. Also, drinking water containing 500 mg/l of potassium chromate does not affect utilization of food by rabbits, but 10,000 mg/l of zinc chromate markedly interfered with digestion. A concentration of 5 mg/l of chromium (valence not specified) in the drinking water caused an increase in mortality among rats on a diet containing 11 mg/l of selenium (1481). As much as 100 mg/kg of chromium, fed as Na₂CrO₄, had no effect on the growth, feed conversion, or mortality of chicks (2927).

Byerrum and his colleagues (2138, 2145, 2147, 2150, 2928, 2929) conducted extensive experiments with rats and dogs to determine the long-term effects of trivalent and hexavalent chromium in drinking water. Controls received distilled water while other rats received chromium from K₂CrO₄ at dosages up to 11 mg/l of chromium for a year. Other tests were run with 25 mg/l of chromium from potassium chromate and 25 mg/l from chromic chloride. No significant differences in weight,

food intake, water consumption, or blood analyses were observed between the experimental groups and the controls. At chromium concentrations of 5 mg/l and lower, little chromium was found in any tissue, indicating that it was not being retained in the body. At 7.7 mg/l and higher, however, all tissues, especially the spleen showed an appreciable increase. The group receiving 25 mg/l of hexavalent chromium had an average tissue chromium content about eight times that of the group that was given trivalent chromium. Even at 25 mg/l, however, there was no significant difference in weight gain or food consumption. Over a 4-year period with dogs, no pathological changes were noted, even up to 11 mg/l of chromium.

d. Fish and Other Aquatic Life. The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but lower forms of aquatic life are extremely sensitive, as the following information reveals. There appears to be no evidence to lead to a conclusion that hexavalent chromium is more toxic toward fish than the trivalent form. Toward fish, the toxicities of hexavalent chromium compounds have been reported as follows:

Conce	ent ra :
41	

tion of				
	n Co <u>mpou</u> nd	OT	Remarks	Reference
mg/l	Used	Type of Fish	Remains	-
5		fish	toxic	1109
5.2	K2Cr2O7	brown trout	toxic	346
7.1	K2Cr2O7	carp	not harmed	2930
9	CrO ₄	fish	toxic limit	353
10	Na ₂ Cr ₂ O ₇		only slightly haz-	* ***
		•	ardous	1492
10		silver salmon	fresh water, toxic	2931
17.8		silver salmon	sea water, toxic	2931
20	K2Cr2O7 and			0100
	K2CrO4	rainbow trout		17, 1110, 2190
35.3	K2Cr2O7	goldfish	not harmed	313
45	K2Cr2O7	bluegills	tolerated in hard	
			water for 20 day	s 1459
50	K2Cr2O7	trout	killed within 33 hrs	. 1459
50		bluegills	toxic limit for 30-	
			day exposure	1111
52	K2Cr2O7	young eels	tolerated for 50 hrs	
$\overline{52}$	CrO ₃	goldfish	toxic in 30 minutes	313
52	CrOs	goldfish	survived 4 days	313
68	K ₂ Cr ₂ O ₇	bluegills	tolerated in hard	
			water for 5 days	1459
70		bluegills	toxic limit for one	****
			week's exposure	1111
75	K2Cr2O7	bluegills	died within 4 days	1459
83	K ₂ Cr ₂ O ₇	bluegills	tolerated for 10	4.150
			days	1459
100	K ₂ CrO ₄	trout	24-hour TLm	2932
100	K2Cr2O7	trout	fatal after 6 hrs.	1459
103	K2Cr2O7	bluegills	96-hour TLm 29	33, 2934, 2935
104	CrOs	goldfish	toxic in 6 to 84 hrs.	353, 2190
110	K2Cr2O7	su nfish	96-hour TLm	2937, 2938
113	K2Cr2O7	sunfish	96-hour TLm	2936
130	K2Cr2O7	young eels	tolerated over 50	
		-	hours	1459
135	K2CT2O7	sunfish	96-hour TLm (hard	i
			water)	2936
145	Na ₂ Cr ₂ O ₇	bluegills	24-hour TLm	1317
		bluegills	toxic limit	353
148	Na ₂ Cr ₂ O ₇		96-hour TLm	2937, 2938
170	K ₂ CrO ₄	sunfish		313
177	$K_2Cr_2O_7$	goldfish	toxic in 3 days	
180-362		several species	stoxic	1459
196		large-mouth		
		bass	TLm	2939
200	K2Cr2O7	mummichogs	tolerated in sea	
200	11201201		wtr. for over a w	k. 1459
919	Na ₂ Cr ₂ O ₇	bluegills	48-hour TLm	2093
213			24-hour TLm	1317
300	Na ₂ CrO ₄	bluegills	killed in 5-12 hrs.	1459
520	K2CrO4	young eels	Killed in 9-12 nrs.	1403

In highly turbid water, Wallen et al. (2940) found the 96-hour TL_m values for several chromate and dichromate compounds toward the mosquito-fish (*Gambusia affinis*) to be as follows:

			$96-hour\ TL_m\ in\ mg/l$	
Compound	Temperature	pH	For	As
	Range	Range	Compound	Chromium
Ammonium chromate	19-23°C	7.5-7.8	240	82
Ammonium dichromate	18-20	5.7-7.4	136	56
Potassium chromate	17-21	7.6-8.1	400	104
Potassium dichromate	21-23	5.4-6.7	280	99
Sodium chromate	20-22	7.7-8.6	420	135
Sodium dichromate	24-27	6.0-7.9	264	92

For trivalent chromium, toxicities and survival times for fish have been reported as follows:

Concentre tion of Chromiun mg/l	ı- n, Compound Used	Type of Fish	Remarks	Reference
1.2	Cr2(SO4)3	Sticklebacks	Lethal limit	1460, 2941
1.3	Cr2(SO4)8	Sticklebacks	Survived only 1 wk.	1460
2.0	Cr2(SO4)3	Sticklebacks	Survived only 2 days	1460
2.4	Cr2 (SO4)3	Sticklebacks	Lethal limit	598
5.0	Cr2(SO4)8	Sticklebacks	Survived only 1 day	1460
5.2	KCr (SO ₄)2	Young eels	Survived an average of 18.7 hours	1459
40	Cr2(SO4)8	Minnows	Survived in distilled water only 6 hours	1459, 2942, 2943, 2944

From the foregoing tables, it appears that trivalent chromium might be more toxic than the hexavalent form despite apparent beliefs to the contrary. On the other side of the ledger, Olson (2945) reports that young chinook salmon were exposed for 12 weeks to either 0.2 mg/l of hexavalent or trivalent chromium. The hexavalent form showed reduced growth and increased mortality whereas the trivalent form had no observable effect.

Towards other organisms, toxicities of hexavalent chromium have been reported as follows:

Concentration of Chromium, mg/l	Compound used	Type of organism	Remarks	Refer- ence
0.016 0.05 <<0.10* <<0.10* 0.21 0.25 0.51 0.7 0.7 0.7 1.4 17.3 25.0 40.6	NagCrgO7 NagCrgO7 NagCrgO7 NagCrgO7 KgCrgO7 KgCrgO7 NagCrGO KgCrgO7 KgCrgO7	Daphnia magna Daphnia magna Daphnia magna Daphnia magna Protozoan (Micro- regma) Diatom (Navicula) Diatom (Navicula) Daphnia magna Daphnia Scenedesmus E. coli Gammarus pulez Snail Midge fly larvae Snail	toxic threshold isilled in 6 days toxic threshold toxic threshold toxic threshold toxic threshold threshold effect softwater TL _m , 22°C. hardwater TL _m , 22°C. toxic threshold threshold effect threshold effect threshold effect total mortality softwater TL _m , 20°C. not toxic hardwater TL _m , 20°C.	2158 2947

^{*&}lt;<signifies "very much less than"

For trivalent chromium, Anderson (598) reports that the toxic threshold for Daphnia magna in Lake Erie water at 25°C is very much less than 1.2 mg/l (3.6 mg/l of CrCl₃). Bringmann and Kuhn (3343) indicate that the thresholds of toxicity occurred at 5 mg/l for Scenedesmus, 37 mg/l for Microegma, and 42 mg/l for Daphnia. With a flatworm, Polycelis nigra, Jones (608) found the toxic threshold in 48 hours of exposure to be 75 mg/l of chromium. Thus, toward Daphnia magna, hexavalent chromium appears to be more toxic than the trivalent form; but toward Polycelis nigra the opposite is true.

The toxicity of sodium chromate toward Daphnia magna increases as the dissolved oxygen tension of the water is lowered (2946).

Algae concentrate radioactive chromium by factors of 100 to 500 or more (2442). For further details of concentration factors, see Chapter VIII. Radioactivity.

According to Ingols and Kirkpatrick (1491) the toxicity of chromium toward bacteria is controlled by (a) the valence of the chromium, (b) the type of organism, (c) the amount of organic matter present, and (d) the presence or absence of dissolved oxygen. The chromate is much more toxic under anaerobic conditions than the chromic ion whereas, in general, the chromic ion is more toxic under aerobic conditions than the chromate ion. It must be recognized, of course, that the chromate ion is reduced to the chromic form at low concentrations under aerobic conditions.

Trivalent chromium has been reported to lower the 5-day BOD by 50 percent as a concentration of 62.5 mg/l (2922) and at 117 mg/l (2923). Hexavalent chromium at 100 mg/l lowered the 5-day BOD by 50 percent (2922). Trivalent chromium is somewhat more toxic to microorganisms than the hexavalent form in the range of 1 to 10 mg/l (2948), probably because the trivalent salts are sufficiently acid to depress the pH somewhat (2949).

Clendenning and North (2106, 2107, 2865, 2866) tested the effect of hexavalent chromium, supplied as $K_2Cr_2O_7$, on the rate of photosynthesis of the giant kelp, *Macrocystis pyrifera*. At 1.0 mg/l of chromium, photosynthesis was not diminished by two days contact, was reduced 10-20 percent after 5 days, and 20-30 percent after 7-9 days. The concentration of chromium required to cause a 50 percent inactivation of photosynthesis in 4 days was estimated at 5.0 mg/l.

The Severn and Mersey River Boards in England have adopted working standards that limit the total concentration of all heavy metal, including chromium, to 1.0 mg/l (1756, 2950).

4. Summary. On the basis of the foregoing information, it appears that the following concentrations of chromium, trivalent or hexavalent, will not interfere with the specified beneficial uses:

a. Domestic water supply	0.05	mg/l
b. Stock and wildlife watering	5.0	mg/i
c. Fish life		mg/l

CITRIC ACID

C₃H₄OH (COOH)₃

(see also Sodium Citrate)

One of the acids most widely distributed in nature, occurring particularly in citrus fruits, citric acid is a colorless, crystalline substance which is highly soluble in water. It is used extensively in the beverage and food industries and in pharmaceutical preparations. The acid may be obtained by extraction from citrus juices, precipitation as calcium salt, and freeing by dilute sulfuric acid; but it is also produced commercially by controlled fermentation of sucrose (189).

Ellis (313) found that, in hard water, 625 mg/l of citric acid was not lethal to goldfish in 100 hours but 894 mg/l killed them in 4 to 28 hours at 18-23°C. In soft water, on the other hand, 120 mg/l killed Daphnia magna in 24 to 72 hours. Anderson (358) showed that the threshold concentration for immobilization of Daphnia magna after prolonged exposure, using Lake Erie water at 25°C, was 153 mg/l. The difference between the foregoing values for Daphnia is probably attributable to hardness and other constituents in the Lake Erie water.

There appears to be an antagonistic effect of calcium and magnesium on the toxicity of citric acid, inasmuch as the weak acid is only slightly dissociated in water and inasmuch as calcium precipitates the dissociated citrate ion. Doudoroff and Katz (361) report that citric acid can be directly lethal to fully developed fish only when it lowers the pH value to 5.0 or lower; hence toxicity varies with the buffering of the water.

CMU (MONURON)

(see Chapter IX)

COAL-TAR PRODUCTS

(see Tar, Oil, Hydrocarbons, Phenol, Naphthalene)

COAL-TAR PRODUCTS PLANT WASTES

(see also Naphthalene, Phenanthrene, Pyridine, Xylene, Quinoline, Thiophene, Acridine, Cresylic Acid, Cresols, Phenols)

Containing a mixture of many substances, this waste gave a slight medicinal taste when chlorinated, at a dilution of 1:25,000. Without chlorination, a dilution of 1:2400 gave a slight odor of naphthalene. According to Schaut (362) minnows in a 1:2400 dilution tended to regurgitate their food but otherwise they were normal.

COBALT

1. General. Cobalt and its salts are used for making alloys, in nuclear technology, as pigment in the china and glass industry, and as binders in the tungsten-carbide tool industry. Cobalt salts may be divalent or trivalent. Solutions containing cobaltous ions (Co++) are relatively stable but cobaltic ions (Co+++) are powerful oxidizing agents and consequently they are unstable in natural waters.

The following material refers only to the literature related to the cobalt ion, per se, without reference to the accompanying anions. For cobalt salts, see the cross references.

- 2. Cross References. Cobalt Chloride, Cobalt Nitrate, Cobalt Sulfate, Chapter VIII.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. It has been reported (353, 2121) that cobalt has a relatively low toxicity to man, and that traces of cobalt are essential to nutrition. The ingestion of soluble salts in sufficient concentration, however, produces nausea and vomiting by local irritation (364). A maximum safe concentration of cobalt in drinking water cannot be established or estimated on the basis of present knowledge (3284). The ingestion of 0.1 to 0.25 mg per day does not appear to have any adverse effect whereas single daily doses of 25 mg per day over a period of a week or longer affect the hemoglobin content of blood (3284). No literature relative to taste or color thresholds was uncovered.

The existence of 0.09 mg/l of copper, 0.08 mg/l of cobalt, and 0.03 mg/l of nickel in a public water supply containing 80 to 90 mg/l of total solids, 4.4 mg/l of chlorides and with a pH value of 3.8 to 4.5 caused pitting of aluminum teakettles; but without the trace elements no pitting occurred (561).

b. Irrigation. In concentrations of 0.1 and 0.27 mg/l cobalt in culture solutions caused specific symptoms of injury to tomato plants. Cobalt sulfate in concentrations of 2.0 mg/l of cobalt stunted the growth of plants and caused withering (2977). A concentration of 10.7 mg/l caused severe injury and subsequent death of the plants. The presence of manganese in the culture solutions reduced somewhat the symptoms of cobalt injury (1499). It has not yet been proved that cobalt is essential for all green plants (1498).

A concentration of one mg/l of cobalt was toxic to flax grown in water culture, but the symptoms were reduced somewhat in the presence of small amounts of molybdenum (1458). Concentrations of 5.9, 14.7, and 29.5 mg/l of cobalt were very toxic to sugar beets, tomatoes, and other crops in sand culture (1473).

c. Stock and Wildlife Watering. Animals vary in their ability to tolerate cobalt. Indeed, trace amounts of cobalt appear to be essential in the diet. The minimum daily requirement of cobalt for growing lambs is reported to be 0.1 mg (1497) and for sheep it is probably 0.07 to 0.08 mg (1498). Forage containing 0.1 mg/kg of cobalt will supply the needs of cattle and sheep (3285).

The daily addition of 500 mg of cobalt, as chloride, sulfate, or carbonate, to the diet of calves for 30 days caused loss of appetite and weight. A loss of appetite among lactating cows has followed single doses of from 1 to 5 grams of cobalt sulfate. Two young bulls have tolerated daily doses of 10 grams for 90 and 127 days (1494). Cobalt in excess of 0.9 mg per kg of body weight produced toxic effects in dairy calves (1495), yet the lethal dose of cobalt in a dog is reported (353) to be more than 30 mg per kg of body weight. Toxic symptoms were observed among young rats receiving more than 0.6 mg of cobalt per day. A daily dose of 2 mg caused death in two weeks. In drinking water for rats, 100 mg/l caused tissue damage (353), a concentration of 200 mg/kg in the daily diet was toxic to rats, and 500 mg/kg caused death in 3 to 5 weeks (1495). Levels of dietary cobalt in excess of 5 mg/kg caused linear depression of chick growth and levels in excess of 50 mg/kg resulted in chick mortality (3286). In the drinking water, a concentration of 5 mg/l of cobalt caused increased mortality among rats fed a ration containing 11 mg/l of selenium (1481). The daily intake of a small amount of cobalt is reported to produce a striking polycythemia in a number of different species of animals (1496). There appears to be a relationship between the beneficial and detrimental effects of cobalt in the diet and the content of choline and vitamin V_{12} (3287).

d. Fish and Other Aquatic Life. (see cross references). Trace amounts of cobaltous ion appear to stimulate the growth of some organisms. A definite growth response in the protozoan ciliate, Tetrahymena, was produced by 0.5 micrograms per liter of cobalt, while the optimum total growth and rate of growth occurred at 8 micrograms per liter (3288). The addition of 1 to 5 mg/l of cobalt, as cobalt chloride or cobalt sulfate, to a medium used in the propagation of actinomycetes gave conspicuous growth (3289). Cobalt concentrations of 1.0 mg/l were not harmful to one-year-old tench, carp, rainbow trout, and char; or to crustacea,

worms, and insect larvae forming the food of these fish (2151).

At higher concentrations, however, cobalt ions have demonstrated pronounced toxic effects. Jones (2941) found that the lethal concentration for sticklebacks, Gasterosteus aculeatus, was 10 mg/l of cobalt ion. The concentration of cobalt required to cause a 50 percent decrease in oxygen utilization of sewage or synthetic media was found to be 25 mg/l and 29 mg/l by independent investigators (2922, 2923). Other toxic concentrations are reported under the specific cobalt salts, i.e., cobalt chloride, cobalt nitrate, and cobalt sulfate.

Organisms tend to concentrate cobalt from the surrounding medium. According to Morgan (2800), cobalt-60 is concentrated 1070 to 1500 times by the flagellate Ochromonas and 271 times by the diatom Navicula.

COBALT CHLORIDE

CoCl₂

(see also Cobalt)

Cobalt chloride, or cobaltous chloride, is a highly soluble salt that is used for sympathetic ink, barometers, hydrometers, galvanoplating, ceramics, and as a feed supplement in salt licks (364).

Ellis (313) found that concentrations of 1,000 mg/l in hard water killed goldfish in 30 to 32 hours, but a concentration only 10 mg/l in soft water was fatal to some goldfish in 168 hours. In tap water, the lethal limit for stickleback has been given as 22 mg/l (598). The threshold concentration for immobilization of Daphnia magna in Lake Erie water at 25°C according to Anderson (598) was found to be less than 3.1 mg/l in 64 hours, and has been reported to be about 2.8 mg/l (353).

The lethal concentration of cobalt chloride for fish has been reported at 16 mg/l for fundulus within 5 days; at 4050 mg/l in 24 hours for fish; and at 5200 mg/l for three mature small fresh-water fish (Orizias) exposed for 24 hours to only 20 ml of the test solution. A concentration of 200 mg/l had no effect on mummichogs in sea water (1459).

Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of cobalt added as cobalt chloride (CoCl₂·6H₂O) on various species. For Daphnia, the median threshold effect occurred at 5 mg/l of cobalt, for E. coli at 2.5 mg/l, for Scenedesmus at 1.0 mg/l, and for a protozoan (Microregma) at 0.5 mg/l.

COBALT NITRATE

 $Co(NO_3)_2$

This soluble salt is used in the manufacture of cobalt pigments and sympathetic ink, also in decorating porcelain (364). According to Jones (608) the threshold concentration for toxicity to *Polycelis nigra*, a flatworm, in 48 hours was 83 mg/l of cobalt.

The lethal concentration limit for cobalt nitrate toward sticklebacks was reported to be 10 mg/l as cobalt. In different concentrations of cobalt, the average survival times of the fish were as follows: one week at 15 mg/l, 4 days at 20 mg/l, two days at 50 mg/l, and one day at 150 mg/l as cobalt (1460). Another investigator (2920, 2941) reported the lethal concentration of this salt toward sticklebacks at 15 mg/l as cobalt.

COBALT SULFATE

CoSO₄

This red crystalline substance, readily soluble in water, is used in decorating and plating with cobalt and for supplying cobalt deficiencies in cattle and sheep. Too much cobalt sulfate, however, may be deleterious. Two ewe lambs became anemic after receiving cobalt sulfate in a dose of 5 mg as cobalt daily for 10 months. Cattle, however, have tolerated 50 mg of cobalt daily without polycythemic symptoms (1497). Blood changes occurred in calves when cobalt sulfate was consumed at a daily rate of about 50 mg per 100 lbs. of body weight. At higher dosages, appetite, growth and coordination were also affected (1500). A loss of appetite among lactating cows has followed single doses of from one to five grams of cobalt sulfate. Two young bulls have tolerated daily doses of 10 grams for 90 and 127 days (1494).

Applied as cobalt sulfate, 10 to 15 mg/l of cobalt was only slightly injurious to oat plants. More than 15 mg/l was severely toxic and caused a marked reduction in growth. In a nutrient solution, the addition of 2 mg/l of cobalt, added as sulfate, intensified the toxic effect of 2.5 mg/l of nickel (1462).

COLOR

1. General. Color in water may be of natural mineral or vegetable origin, caused by metallic substances, such as iron and manganese compounds, humus material, peat, tannins, algae, weeds, and protozoa. Waters may also be colored by inorganic or organic soluble wastes from many industries including nailworks, mining, refining, explosives, pulp and paper, chemicals, and others. Returned irrigation water also contributes to color.

In water-works practice, the true color of water is considered to be only that attributable to substances in solution after the suspensoids have been removed by centrifuging, because an accurate determination of color in water containing suspended matter is not possible. The term "apparent color" is used for color that includes an effect from suspended matters. However, the color of water with low turbidity is substantially the same as that of clear water. (Filtration has a decolorizing effect and should not be used to remove suspended matter). The unit of color considered as a standard is the color produced by the platinum-cobalt method of measuring, with the unit being one mg/l of platinum in water. Results are conventionally expressed as units of color, and not mg/l. The method is described in Standard Methods for the Examination of Water and Wastewater (469). In field work, the color of water may be compared with that of glass discs calibrated to correspond with colors on the platinum scale. Nemerow et al. (3399, 3400) have attempted to improve the quantitation of color in streams by the development of a "Stream Colorimeter."

- Cross References. See Chapter III for standards of state and interstate agencies, also Chapter V.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The 1962 USPHS Drinking Water Standards (2036) limit the color of acceptable water to 15 units. The 1958 International Standards for Drinking Water (2328) indicate that 5 units of color are "permissive" but 50 units are "excessive."

For high quality domestic water, Lubratovich and Ruble (1746) recommend that color be limited to 5 units, while Bean (1745) would place the limit at 3 units of color. The stream standards promulgated by various state and interstate agencies (see Chapter III) limit the color in the raw water to be used as sources of drinking water to values ranging from none to 100 units. Some standards specify that color in the raw water shall not be in sufficient amount or of such character as to make the stream unsuitable as a source of water supply for drinking, culinary, or food-processing purposes, after reasonable treatment. In domestic water, color is undesirable from esthetic considerations and also because it may dull clothes, or stain food and fixtures.

b. Industrial Water Supplies. Color is undesirable in water for laundries (240, 339, 499, 505, 542, 546, 547, 548); ice-making (534); dairy products (549); bottled beverages (180, 181, 186); photography (242); textiles (212, 256, 257, 258, 405, 550); pulp and paper (212, 244, 245, 350, 351, 551, 2372, 2373); for nitrocellulose production (2405) and other uses. For color limits per-

missible in industrial processes, see Table 6-3.

c. Fish and Other Aquatic Life. A reddish-brown or yellow discoloration has been observed in sea waters where catastrophic mass deaths of fish and shellfish have been associated with the appearance of multitudes of certain poisonous plankton organisms, either algae or protozoa (red tide) (420, 539, 545). Eutrophication of lakes, with concomitant production of algae, generally leads to increased color (2012, 2503, 3351).

TABLE 6-3

COLOR LIMITS PERMISSIBLE IN WATER FOR INDUSTRIAL USE

INDUSTRIAL USE					
Use	Units of color	Reference			
Baking	. 10	159			
Boiler feed water	2-80, according				
	to pressure	159			
Bottled beverages	5-10	186			
Brewing	0-10	159			
Dairy Industry	. 0	2344			
Food Equipment Washing		(see Chapter V)			
Food Processing		159			
Food Products	10	173			
Nitrocellulose Production	1	2405			
Pulp and paper		_100			
Alkaline pulps	5	245, 2372			
High-grade paper Special papers (tissue,	5	552, 551, 350			
filter, etc.)	5	950			
Bleached kraft papers	25	350 251 9270			
Unbleached kraft papers	100	351, 2372 351, 2372			
Groundwood papers	30	351, 2372			
Tanning	10-100	159			
Textiles		200			
Cotton	50	256			
Rayon	5	550, 405			
General	0-70	(see Chapter V)			

CONDUCTANCE

(see Specific Electrical Conductance)

CONIINE

 $C_8H_{17}N$

This colorless, oily, liquid alkaloid with a peculiar mousy odor is very poisonous to humans, causing paralysis of the motor endings of the nerves. It is obtained from the poison hemlock, especially the seeds, and in olden days was used for suicide. In humans, a dose of 30 to 60 mg will cause weakness, drowsiness, and labored respiration and a dose of 120 mg is reported to be fatal (364). At a concentration of 17.1 mg/l in stabilized tap water, however, it showed no effect upon minnows during five days of contact (362).

COPPER Cu

1. General. The effects of copper in water have been reported in terms of copper or of copper salts. This section summarizes literature on the effects of copper in solution without regard to the anion involved. The effects of specific copper salts are described under separate headings. Metallic copper is insoluble in water, but many copper salts are highly soluble as cupric or cuprous ions. References in this section to copper refer to the copper ions.

Copper salts occur in natural surface waters only in trace amounts, up to about 0.05 mg/l, so that their presence is generally the result of pollution, attributable to the corrosive action of the water on copper and brass tubing, to industrial effluents, or frequently to the use of copper compounds for the control of undesirable plankton organisms. Under special conditions, copper has been found in ground water in concentrations up to 12 mg/l. Metallic copper is used in many alloys, for cooking utensils, extensively in the electrical industry, and for pipes, roofing, and many purposes where its conductivity or corrosion resistance are important. Copper salts are used in textile processes, pigmentation, tanning, photography, engraving, electroplating, insecticides, fungicides, and many other industrial processes (364, 2121, 3293).

The chloride, nitrate, and sulfate of divalent copper are highly soluble in water, but the carbonate, hydroxide, oxide, and sulfide are not. Indeed, cupric ions introduced into natural waters at pH 7 or above will quickly precipitate as the hydroxide or as basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, to be removed by adsorption and/or sedimentation. As a result, copper ions are not likely to be found in natural surface waters or ground water

Because copper in concentrations high enough to be dangerous to human beings renders water disagreeable to taste, it is believed that copper is probably not a hazard in domestic supplies. However, copper in water may be disadvantageous or detrimental for certain industrial uses; and although, in trace amounts, copper may be beneficial or even essential for the growth of living organisms, in excessive quantities it has been found toxic to a wide variety of aquatic forms, from bacteria to fish (152, 553).

- 2. Cross References. Copper Chloride, Copper Sulfate, other copper salts, Chapter VIII—Radioactivity and Chapter IX—Pesticides (Paris Green, Omazene).
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Copper is found in traces in all plant and animal life, and it is believed to be essential for nutrition. The physiological function of copper appears to be involved in the metabolism of iron, for the utilization of iron by the blood-forming organs

does not occur properly in the absence of copper (2121, 3293). The copper requirement is reported to be about 2 mg per day for children and about 3 mg per day for adults (152, 553). Common foodstuffs contain up to 10 mg/kg of copper and a few foods such as liver, yeast, and oysters exceed 20-50 mg/kg (3294). The daily intake of copper is generally about 2 to 5 mg/day, but for some people a deficiency exists.

Copper is not considered to be a cumulative systemic poison, like lead or mercury. Most of the copper ingested is excreted by the body and very little is retained. Doses of 60 to 100 mg taken by mouth cause symptoms of gastroenteritis, with nausea and intestinal irritation, but doses of 10 to 30 mg have not caused poisoning even when continued for many days. It is believed that a normal daily diet may provide as much as 20 mg, and that a man weighing 60 kilograms can take one gram of copper per day safely. Many authorities believe that only doses over 100 mg are likely to be injurious (152, 553, 2129). An outbreak of 18 cases of gastroenteritis occurred in a Liverpool, England factory canteen owing to the contamination of tea by copper from a corroded drinking fountain. Analysis showed the copper in this water to be 44 mg/l. Although exhibiting acute copper intoxication, all workers recovered (3295). Although copper has been suspected as a cause of haemachromatosis, a rare liver disease among middleaged men (554), chronic copper poisoning among human beings has never been proved, even among people in copper industries who have absorbed enough copper for their skin and hair to be colored green (36, 152, 553, 2121). There is no evidence that poisoning has ever occurred as a result of consumption of copper in water.

The limiting factor in domestic water supplies is taste. Threshold concentrations for taste have been generally reported in the range of 1.0-2.0 mg/l of copper, while as much as 5-7.5 mg/l makes the water completely undrinkable (152, 553, 555, 556, 3296, 3297, 3298, 3299, 3300). Using cupric chloride in distilled water and in hard spring water (to which carbon-dioxide was added to prevent precipitation of basic copper carbonate), Cohen et al. (3301) found the reactions of a taste panel. The median response for threshold taste was at 6.6 mg/l for distilled water and 12.7 mg/l of copper ion for spring water. Five percent of the panel, however, detected copper in distilled water at 2.6 mg/l and in hard spring water at 5.0 mg/l. It has also been reported (3299) that 1.0 mg/l of copper reacts with soap to produce insoluble green curds, and similar small concentrations cause bluegreen stain on porcelain fixtures.

The limit for copper set by the USPHS Drinking Water Standards (2036) has varied markedly during the history of these standards. In 1925 the limit was set at 0.2 mg/l and it was mandatory. In 1942 the limit was raised to 3.0 mg/l and it was a recommended standard but no longer mandatory. In the most recent (1962) standards, the recommended limit was lowered to 1.0 mg/l. This reduction was made primarily because of the taste problem (2062).

The WHO International Drinking Water Standards (2328) set a "permissible" limit of 1.0 mg/l and an "excessive" limit of 1.5 mg/l of copper, but no maximum allowable (mandatory) limit is established. The WHO

European Standards (2329) have a recommended limit of 3.0 mg/l of copper after 16 hours of contact with new pipe in the distribution or plumbing system; but water entering a distribution system should have less than 0.05 mg/l of copper.

b. Industrial Water Supplies. In food-preserving industries, copper causes undesirable color reactions, forming tannates and sulfides. In the milk industry, metals such as copper are catalysts for the oxidation of fatty matter and for the hydrolysis of milk constituents, i.e. they cause fatty, oily, and fishy tastes in the products (223, 2344). Traces of copper in metal-plating baths affect the smoothness and brightness of the metallic deposits (214). No domestic water supply was found containing enough copper to affect photography (560), but 100 mg/l of copper sulfate added to water used for the preparation of developing solutions for photographic work has caused fogging (242). Aluminum utensils have been damaged by water containing a mixture of salts, including copper compounds (561, 562, 3302). There is evidence that dissolved copper can deposit on other metals, especially aluminum and the zinc coating of galvanized steel, thereby markedly accelerating their corrosion (3303, 3304, 3305). Copper is especially undesirable in the woolen industry for it is absorbed readily on wool, e.g. for 5 mg/l of copper in the water solution, the concentration on the treated fabric will be about 70 mg/kg. In the bleaching of wool, copper catalyzes the reaction with hydrogen peroxide, the bleaching agent, to the extent that holes are formed in the material (3306). Reclaimed rubber processed with river water containing 10-25 mg/l of copper deteriorated more rapidly than rubber processed with water containing no copper (1523).

The British Ministry of Agriculture, Fisheries, and Food has established limits for copper in foods and beverages (3294). For ready-to-drink beverages, the limit is 2 mg/l, but for eider and concentrated soft drinks it is 7 mg/l, and for soft-drink concentrates, 20 mg/l. For most foods, the limit is 20 mg/kg, but for yeast and yeast products, 60 mg/kg, and for solid pectin, 300 mg/kg.

c. Irrigation. Minute quantities of copper are beneficial or essential for plant growth (553, 558, 563, 564, 2926, 3307). However, 0.17 to 0.20 mg/l concentrations have been toxic to sugar beets and barley grown in nutrient solution (565). A concentration of 0.02 mg/l was adequate to supply the copper requirement of tomatoes grown in nutrient solution, but 2.0 mg/l was toxic (564). Copper in nutrient solution at a concentration of 0.1 mg/l was toxic to orange and mandarin seedlings (1524) and prevented the growth of water hyacinths (1525). A concentration of 0.5 mg/l or higher was very toxic to flax in water culture (1458). In sand culture, nutrient solutions containing 6.4 to 31.8 mg/l of copper were injurious to sugar beets, tomatoes, and potatoes, but not to oats and kale (1473). Solutions containing 425 mg/l of copper delayed germination and retarded the later growth of cress and mustard seeds in solution culture, while only 106 mg/l retarded growth (1479). In the presence of 0.01 mg/l of molybdenum, concentrations of copper in excess of 0.01 mg/l had a marked effect in decreasing the length of the main stem of tomato roots,

and indeed concentrations of copper as low as 0.00001 mg/l had a measurable effect (3308).

In a nutrient solution, one mg/l of copper sulfate stopped the root growth of peas and barley (1479). A concentration of 2 mg/l (as copper) occasionally, but not always, caused slight chlorosis in oats, but no other injury; 10 mg/l caused severe chlorosis; and 20 mg/l stunted growth (1462). A copper sulfate concentration of 1000 mg/l, as copper, partly destroyed the germinating powers of various seeds (1479).

Tobia and Hanna (3309) investigated the chemical fate of copper salts in the soil, especially with respect to organic matter and carbonate content of the soil. They found that when copper sulfate was added to irrigation water at a concentration of 20 mg/l, it reached an equilibrium in the soil at 1.0 mg/l after 6 hours at 20°C. Copper retention in the soil appeared to be correlated more with organic matter and soil alkalinity than with the clay content of the soil, and organic matter appears to be more effective than carbonates in retaining copper.

d. Stock and Wildlife Watering. Small amounts of copper are beneficial for hemoglobin count and growth in rats (353, 553). Copper is beneficial for the growth of suckling pigs and has been used, as copper sulfate, to cure anemia among pigs (553). Copper deficiency in animals is associated with a severe anemia similar to that caused by an iron deficiency. It is generally understood that copper is an active agent in the synthesis of hemoglobin (2121). Traces of copper in the diet of cattle and sheep are necessary to prevent scouring and wasting diseases (566, 1049). The effects of copper and molybdenum are related, and the two elements are reciprocally antagonistic (566, 1049, 1498, 1527).

Daily copper doses of 2 to 4 mg have been harmless to the growth of rats; doses of 6 to 9 mg per day have been harmful; doses amounting to more than one mg per kg of body weight for 5 days are injurious to growth (353).

Hale (553) has reported that one gram daily of soluble copper salts is safe for dogs, but more can be fatal; and that all test sheep died when given 18 to 182.5 grams of copper in quantities as high as 2 grams daily, although two survived for 53 and 128 days respectively. Cartwright (567) has reported that among cattle toxicity develops on one gram of copper sulfate per pound of live weight per day; the symptoms of poisoning include loss of appetite, copper accumulation in the liver, jaundice and yellow discoloration of the entire animal. Added to the daily ration of sheep at a rate of 25 mg per day, copper has been reported as toxic (1526). The minimum toxic level of copper in the diet of chicks was found to be 500 mg/kg in the feed (3310, 3311).

Cunningham (566) has found that cattle can tolerate 5 grams of copper sulfate per day for at least 18 months without toxic effects; for British breeds of sheep, however, doses of 1.5 to 2.0 grams daily are fatal within 30 days; and a dose of 2.5 grams is said to be near the toxic level for small ewes. Cartwright (567) reports that among cattle, copper toxicity develops on a daily dose of one gram of copper sulfate per pound of live weight.

Chronic poisoning of sheep has been caused by 1.5 grams of copper sulfate daily for 30 to 80 days. One sheep was poisoned in 6 months by a daily dose of 0.5

grams but another sheep was not poisoned by one gram per day over a 4-year period (353).

As a therapeutic dose 60 mg of copper sulfate daily has been administered to anemic pigs (553). A dog could take 4 grams daily with only slight effect.

The only reference found concerning the effect of copper sulfate in water states that 2500 mg/l of $CuSO_4$ · $5H_2O$ in water was harmful to turkeys when such water was the only drinking water available; 630 mg/l or more sometimes caused the turkeys to stop drinking the water entirely (597).

e. Fish and Other Aquatic Life. (see also Copper Chloride, Copper Nitrate, and Copper Sulfate). toxicity of copper to aquatic organisms varies significantly not only with the species, but also with the physical and chemical characteristics of the water, such as its temperature, hardness, turbidity, and carbon dioxide content (2407, 3312). In hard water, the toxicity of copper salts is reduced by the precipitation of copper carbonate or other insoluble compounds (553, 3312). Ellis (1076) has found that the toxicity of copper to fish varies greatly depending on the presence of magnesium salts and phosphates. In the control of Chironomus larvae, copper and chlorine together act synergistically to increase the toxicity of each acting alone (568). The sulfates of copper and zinc, and of copper and cadmium are synergistic in their toxic effect on fish (353, 1528, 2973). Synergism also exists between copper and mercury (3313), and between copper and pentochlorophenate (3314). On the other hand, sodium nitrite (311) and sodium nitrate (353) have been reported to decrease the toxicity of copper sulfate to fish, and copper has shown evidence of decreasing the toxicity of cyanide (2965).

Copper concentrations varying from 0.1 to 1.0 mg/l have been found by various investigators to be not toxic for most fish (353, 572, 1467, 1468, 1528, 1529, 3315). On the other hand, concentrations of 0.015 to 3.0 mg/l have been reported as toxic, particularly in soft water, to many kinds of fish, crustacea, mollusks, insects, phytoplankton, and zooplankton (74, 353, 572, 573, 574, 575, 1529, 2093, 2154, 2263, 2271, 2409, 2495, 2921, 2931, 2936, 2941, 2962, 3312, 3316, 3317, 3318, 3319, 3320).

Doudoroff (1528) found that, although fish could survive for 8 hours at 8 mg/l of zinc alone and 0.2 mg/l of copper alone, most fish died within 8 hours when exposed to a mixed solution containing only 1.0 mg/l of zinc and 0.025 mg/l of copper. The Water Pollution Research Board of England conducted similar experiments with rainbow trout in soft and hard waters. The results showed synergism at the higher concentrations in soft water, although the threshold concentration for the mixture of copper and zinc was about the same that would be expected on the assumption that there was no synergism (88). In hard water, no synergism between copper and zinc was evident (74). These English investigators also demonstrated that the toxic threshold concentrations of copper for rainbow trout were diminished as the dissolved-oxygen tension was lowered (74, 3321, 3322).

Barnacles and related marine fouling organisms were killed in 2 hours by 10 to 30 mg/l of copper (569); in 2 to 10 days, by 0.22 to 1.0 mg/l (570). The growth of attached young barnacles was inhibited by 0.2 to 0.3

mg/l (571). Mytilus edulis, a mussel, was killed in 12 hours by 0.55 mg/l (570). About 0.1 mg/l of copper in distilled water produced distress in the snail (Australorbus glabratus) within a few hours (2733, 2734). Lobsters died within one day after being transferred to wooden tanks lined with copper, although 80 percent had lived for two months in aluminum, stainless steel, or iron tanks (1530).

In contrast, Surber (2688) found that the larvae of the midge, *Cricotopus bicincus*, matured in Michigan rivers at a copper concentration of 2.2 mg/l, although most other common benthic invertebrates were absent from this environment.

Copper is concentrated by plankton from the surrounding waters by factors of 1000 to 5000 or more (2436, 3375, 3386). For further detail on concentration factors, see Chapter VIII, Radioactivity.

Copper concentrations as low as 0.1 to 0.5 mg/l have been reported toxic to bacteria and other microorganisms (353, 574, 576, 577, 3324). Copper concentrations as low as 0.01 to 0.5 mg/l have interfered with B.O.D. determinations (576, 578, 2949, 3323), and also the self-purification processes of streams. However, Rudolfs cites a report that 0.4 mg/l did not interfere with self-purification (579). Also, the concentration of copper required to cause a 50-percent reduction in 5-day B.O.D. has been reported at 8.4 mg/l (2923) and 35 mg/l (2922).

The Severn and Mersey River Boards in England have established working standards that limit effluents to a total concentration of heavy metals, including copper, not to exceed 1.0 mg/l (1756, 2950).

Copper has been used extensively, as copper sulfate, for the control of algae (see Copper Sulfate and also Chapter IX, Pesticides). Ingols (3325) maintains that copper chelated by citrate or lignin is just as effective in controlling algae as the free copper ion, but the chelated copper is not toxic toward fish.

Clendenning and North (2106, 2107, 2865, 2866) evaluated the effect of copper (from the chloride and sulfate salts) upon the rate of photosynthesis of the giant kelp, *Macrocystis pyrifera*. With 0.1 mg/l of copper, net photosynthesis was inhibited 50 percent in 2 to 5 days and 70 percent in 7-9 days. Visible injury appeared within 10 days. Copper was slightly less toxic than mercury, but more so than nickel, chromium, lead, or zinc.

- f. Shellfish Culture. For setting, oyster larvae require a copper concentration about 0.05 to 0.06 mg/l (328), but concentrations above 0.1 to 0.5 mg/l were found to be toxic to some oysters (329). The 96-hour TL_m concentration of copper for oysters was estimated at 1.9 mg/l (3326). Oysters cultured in sea water containing 0.13-0.5 mg/l of copper deposited the metal in their bodies and became unfit as a food substance (3326).
- 4. Summary. On the basis of the foregoing information, the following threshold concentrations of copper are indicated for specic beneficial uses:

2.	Domestic supply	1.0	mg/l
Ъ.	Irrigation	0.1	mg/l
c.	Fish and aquatic	life:	
	Fresh water	0.02	mg/l
	Sea water	0.05	mg/l

COPPER ACETOARSENITE (PARIS GREEN)

(see Chapter IX)

COPPER CHLORIDE

CuCl₂·2H₂O

(see also Copper and other copper salts)

Used in the electroplating of aluminum, the manufacture of indelible inks, and as a mordant in dyeing and printing fabries, cupric chloride is highly soluble in water, Cuprous chloride, on the other hand, is almost insoluble in water.

The rapid death of goldfish in dilute solutions of copper chloride (0.009 mg/l as copper) has been reported (1459). The highest concentration of CuCl₂ tolerated by young eels for more than 50 hours was 0.13 mg/l (1459). The lethal concentration of copper chloride for three mature small fresh-water fish (*Orizias*), exposed for 24 hours to only 20 ml of test solution, was reported to be 3.3 mg/l (1459). Ellis quotes references to the effect that concentrations of copper chloride of 0.0188 mg/l in distilled water killed goldfish in 3½ to 7 hours; 672 mg/l in distilled water killed minnows in 82 minutes (313).

The 96-hour TL_m of copper chloride toward the bluegill sunfish in soft water at 18-20°C was reported as 1.25 mg/l measured as copper (2936). In Lake Huron water, 5.0 mg/l of copper chloride caused death to the rainbow trout in 10 hours and to the sea lamprey in 12 hours; however, this same concentration had no effect on the bluegill sunfish in 24 hours (2976).

The threshold concentration for immobilization of Daphnia magna by cupric chloride added to Lake Erie water was found by Anderson to be 0.027 mg/l (598) or 0.096 mg/l (358). According to another source (353), the threshold has also been reported to be 0.08 mg/l. For cupric ammonium chloride, threshold concentration toward Daphnia was 0.039 mg/l (598). In a similar manner, threshold concentrations of other aquatic animals in Lake Erie water in the 20-25°C range were found to be as follows (2955):

Organism	Threshold Concentration in mg/l For Immobilization		
Cyclops vernaus	0.027		
Mesocyclops leuckarti			

COPPER NITRATE

 $Cu(NO_3)_2 \cdot 3H_2O$

Highly soluble in water, this copper salt is used in pyrotechnics, textile dyeing and printing, photography, insecticides, and the electroplating industry (364).

Using copper nitrate, Jones found the lethal concentration limit at 15-18°C for sticklebacks to be 0.015 mg/l as copper. At higher concentrations, survival times were as follows: four days at 0.06 mg/l and one day at 0.3 mg/l as copper (1460). The Washington Department of Fisheries (2931) reports the minimum lethal concentration of copper nitrate to be 0.18 mg/l (as copper) in fresh water and 0.56 mg/l (as copper) in sea water. In tests with young pink salmon, the same agency (2091) reported that loss of equilibrium and initial mortalities occurred in less than 66 hours at 0.178 mg/l. There was some indication that the long-term dangerous concentration or lethal threshold was about 0.10 mg/l. In Lake

Huron water, 5 mg/l of copper nitrate caused death or obvious distress to rainbow trout in 11 hours and to the sea lamprey in 13 hours. There was no effect toward bluegills in 24 hours.

Ellis (313) quotes a reference to the effect that 0.0188 mg/l of cupric nitrate in tap water killed many tadpoles and interfered with the development of the survivors.

COPPER OXIDES

CuO and Cu₂O

(see also Copper and other copper salts)

Copper oxide is only slightly soluble in water and is not stored to any appreciable extent in the human body (580). Up to 0.6 grams of copper oxide daily have been ingested by several investigators over long periods without harmful effects (558).

Wallen et al. (2940) tested cupric oxide (CuO) in highly turbid water at 19-20°C to determine the effect upon the mosquito-fish, Gambusia affinis. The 96-hour TL_m was found to be greater than 56,000 mg/l and the turbidity was changed only from 330 to 165 mg/l.

COPPER POTASSIUM CYANIDE

(see Potassium Cupric Cyanide)

COPPER SULFATE

CuSO₄ and CuSO₄·5H₂O

1. General. This most common salt of copper, highly soluble in water, is used extensively in industry for tanning, dyeing, electroplating, process engraving, pigment manufacture, and scores of other processes. It is also used in human medicine as a fungicide, bactericide, astringent, and irritant; and also in veterinary medicine as an emetic, as an antihelminthic, and for the treatment of anemia (364).

One of the most important sources of copper pollution in water is the use of copper sulfate for the control of undesirable plankton growth in reservoirs and streams.

Because of variable toxicity of copper to living organisms (see also copper) the killing concentrations of copper sulfate reported by independent workers vary over a wide range. For example, concentrations from 0.01 to 20 mg/l of copper sulfate have been used to control different aquatic fauna, from insect larvae to snails. Concentrations from 0.05 to 10.0 mg/l have been effective against different kinds of algae, protozoa, and weeds. Owing to its extensive use as an algicide, copper sulfate might well be listed as a pesticide in Chapter IX; however, its many other uses justify its inclusion as part of this chapter.

- 2. Cross References. Copper, other copper salts.
- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. See Copper.
- b. Industrial Water Supplies. See Copper.
- c. Irrigation. See Copper.
- d. Stock and Wildlife Watering. See Copper.
- e. Fish and Aquatic Life. The toxicity of copper sulfate to fish varies with the species and exposure period, and the physical and chemical characteristics of the water (see Copper). Goldfish have been reported to have been killed by as little as 0.002 mg/l (573), and yet they have survived concentrations of one mg/l in hard water for at least the three-day period of study (598). Ander-

son (598) gives 0.016 mg/l as the toxic threshold of copper sulfate for stickleback in tap water. Hale (385) and Hopkins (384) have found 0.14 to 2.0 mg/l to be limiting safe concentrations for many different kinds of fish. Briefly summarizing the data from numerous papers, concentrations from 0.002 mg/l to 200 mg/l or more have been reported lethal to various fish in different waters (74, 313, 353, 359, 363, 415, 573, 586, 598, 599, 600, 601, 602, 603, 604, 605, 606, 1459, 1531, 2091, 2093, 2154, 2314, 2920, 2921, 2936, 2987, 3050, 3327).

On the other hand, concentrations from 0.14 mg/l to 900 mg/l have been reported non-toxic for fish of various species in different kinds of water (313, 359, 415, 572,

592, 602, 605, 607, 2988, 3315).

The highest concentrations of copper sulfate tolerated by specific fish have been reported (384, 385, 1531, 1532, 1533, 2255, 2263) as follows:

	Concentration		Concentration
Fish	in mg/l	Fish	in mg/l
Trout	0.14	Goldfish	0.5_
Carp	0.33	Perch	0.67
Suckers	0.33		d bluegills 0.8
Catfish	0.40	Sunfish	1.35
Pickerel	0.40	Black bass	2.00

Wallen et al. (2940) studied the toxicity of pure chemicals to the mosquito-fish (Gambusia affinis) in highly turbid waters. At temperatures of 24-27°C, the 96-hour TL_m for copper sulfate was 75 mg/l. Furthermore high concentrations of this chemical lowered the turbidity from 750 mg/l to less than 25 mg/l.

Fish have been more resistant to copper sulfate in hard, alkaline waters than in soft, acid waters (553, 599, 600, 601, 602, 1011, 2936). Indeed, toward rainbow trout at 17-18°C, copper sulfate was found to be about ten times more toxic in soft water (12 mg/l as CaCO₃) (74). The sulfates of copper and zinc and those of copper and cadmium are synergistic in their toxic effect upon fish (353). On the other hand, sodium nitrite has an antagonistic effect on the toxicity of copper sulfate to goldfish; 5000 mg/l of sodium nitrite has decreased the toxic effect of 10 mg/l of copper sulfate, and the addition of 50 mg/l of sodium chloride has still further reduced it (311). Sodium nitrate has also been reported to have antagonistic action against copper sulfate (353).

Turnbull et al. (2093) studied the toxic effect of copper sulfate toward bluegill sunfish at 20°C using a synthetic test water containing 172 mg/l of dissolved solids, 101.2 mg/l of hardness (as CaCO₃), 72.0 mg/l of alkalinity (as CaCO₃), and pH 8.3. Similar tests were conducted in waters approximately twice and half as mineralized as the standard water. They found the 48-hour TL_m to be 7.0 mg/l of copper sulfate with the standard test water, only 3.0 mg/l in the half-strength water, but 44 mg/l in the double-strength water.

Among other aquatic fauna, Chironomus larvae have not been harmed by copper sulfate in concentrations of 5.0 mg/l (568) and 100 mg/l (440, 1079); Polycelis nigra has been killed in 48 hours in lake water by 0.47 mg/l (353, 608); Daphnia magna has been killed by 0.096 mg/l (353); 0.01 to 0.02 mg/l (573, 598), and 0.08 mg/l (358); and planarian worms have been killed by 1.0 mg/l (573). The addition of 1.0 mg/l of copper sulfate to a culture medium completely inhibited the growth of Sphaerotilus (2836).

Using water from the River Havel, from which the test organisms had been recovered, Bringmann and Kuhn (2158, 3343) found that the threshold dosages of copper sulfate that produced a noticeable effect were 0.15 mg/l (as copper) for Scenedesmus, 0.10 mg/l (as copper) for Daphnia, 0.08 mg/l (as copper) for Escherichia coli, and 0.05 mg/l (as copper) for Microregma.

Larvae of the gnat, Simulium dentalosum was unaffected by 10.0 mg/l of copper sulfate (3316). Also 0.065 mg/l (as copper) had no effect on the fertilization and cleavage of the eggs of the sea urchin, but noticeable abnormalities occurred at 0.16 mg/l (as copper) (3328).

Klock and Pearson (2314) found the first apparent significant response to copper sulfate occurred at 0.02 mg/l for the isopod, Neosphaeroma oregonensis, and at 0.32 mg/l for the mussel, Mytilis edulis, and the polychaete, Mercierella enigmatica.

According to Hale (553), concentrations of copper sulfate ranging from 0.5 to 20.0 mg/l have killed typhoid and cholera bacteria both in solution and in laboratory cultures. Concentrations of 1250 to 2500 mg/l of CuSO₄·5H₂O had a sterilizing effect on microorganisms in drinking water (597). Oxygen utilization in a 5-day BOD test was decreased 50 percent by 31 mg/l of copper sulfate (2923).

The concentration of copper sulfate required to control plankton in water-supply reservoirs varies from as little as 0.05 or 0.10 mg/l for some organisms to as much as 12 mg/l for very resistant species (2861). Most algae and protozoa succumb to dosages of 1.0 mg/l or less (1490). Duckweed and pondweed were controlled by 0.6 to 1.0 mg/l of CuSO₄·5H₂O, but a few cattails and tules survived this residual concentration (1531). To kill snails in swampy areas and streams, 2.0 mg/l of copper sulfate has been recommended (2739). The following rates of application of copper sulfate have been recommended (3329) to control specific types of algae in farm ponds:

Navicula 0.07 mg/1
Oscillatoria 0.1-0.4 mg/l
Scenedesmus 5.0-10.0 mg/l
Spirogyra 0.05-0.3 mg/l
Ulothrix 0.2 mg/l
Volvox 0.25 mg/l

The amount of copper sulfate required to control algae varies with the temperature, increasing about 2.5 percent for each degree below 15°C (2253). Tests were conducted with 30 different cultures of algae to determine the concentration of CuSO₄·5H₂O required for control. None of the species was controlled by 0.25 mg/l of the salt, 13 percent mere controlled by 0.50 mg/l, 37 percent by 1.00 mg/l, and 53 percent by 2.0 mg/l (2987).

The constant application of copper sulfate to lakes and ponds may result in the accumulation of copper in bottom muds and subsequent changes in the bottom populations. In a group of Wisconsin lakes, however, when the maximum concentration of copper in muds was 438 mg/kg no differences in the density of benthal populations could be attributed to copper (1534).

In alkaline waters, copper sulfate was ineffective in killing weeds even at a high concentration of 10 mg/l, owing to the precipitation of copper by hydroxide and carbonate ions (2876).

COPPERAS

(see Ferrous Sulfate)

CO-RAL

(see Chapter IX)

COTTONSEED OIL MONOGLYCERIDE

(see Chapter X)

CREATINE

 $C_4H_2N_3O_2$

A white, crystalline, nitrogenous substance, creatine is found in the muscles, brains and blood of vertebrates. In decomposing, it exerts a BOD, but otherwise appears to have no detrimental effect. Schaut (362) found that 17.1 mg/l of creatine in stabilized tap water was not harmful to minnows during a 24-hour exposure, but the dissolved oxygen was lowered 6 percent.

CREATININE

 $C_4H_7N_3O$

(see also Creatine)

Creatinine is easily formed from creatine in aqueous solution in the presence of mineral acid, and as such might be considered as a decomposition product. Creatinine is normally excreted in urine at a daily rate of 25 mg per kg of body weight and it also occurs widely distributed in plants. Like creatine, it appears to be inimical only by its BOD. Schaut (362) reports that 17.1 mg/l of creatinine in stabilized tap water was not harmful to minnows during a 24-hour exposure, but the dissolved oxygen was lowered 32 percent.

CREOSOTING-PLANT WASTES

(see also Phenols, Cresols, Tar)

Wastes from crossoting plants contain mixtures of phenols, cresols, and other organic substances. The toxicity of the mixed wastes depends primarily on phenolic groups and it varies sharply with temperature and the content of dissolved oxygen. According to Ellis (611) as little as 6.0 mg/l of some components can kill fish in less than 10 hours. Smaller concentrations have cumulative effects on the taste of fish, being stored in the fatty tissues and giving a carbolic taste. Such wastes may accumulate also on stream beds and interfere with natural flora and fauna.

CRESOLS

CH₃C₆H₄OH

- 1. General. Cresols are colorless oily liquids or crystalline solids obtained from the distillation and chemical treatment of coal tar or wood tar. There are three isomers, all highly soluble in water. A crystalline solid or liquid (m.p. 30° C), o-cresol is used as a solvent or disinfectant. The oral LD₅₀ in rats is given as 1,350 mg/kg of body weight. A liquid above 12°C, m-cresol is used in photographic developers and explosives, as well as in disinfecting and fumigating compounds. Its oral LD₅₀ in rats is 2020 mg/kg of body weight. A solid below 36°C, p-cresol has an oral LD₅₀ in rats of 1800 mg/kg of body weight.
- 2. Cross References. Cresylic Acid, Phenol, Toluene, Xylenol.
 - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The 1962 USPHS Drinking Water Standards (2036) limit the recommended concentration of "phenols" to 0.001 mg/l. Presumably the cresols are included in this category. The limit has been set on the basis of taste and odor, especially in chlorinated waters (for more details, see Phenol). Ruchhoft (459) quotes references to the effect that, in chlorinated waters, the following concentrations of cresols represent the taste threshold:

Compound	Lowest Concentration, mg/l, Causing Taste in Chlorinated Water
o-cresol	0.0001
m-cresol	0 0020
p-cresol	0.0010
o-cresol carbonate	0.0050

According to Cass and Lange (3401), the following thresholds of chlorinated cresols in water have been reported:

•	Taste Threshold, my/l in Chlorinated Water			
Compound o-cresol m-cresol tricresol (a mixture of	pH 4 0.00002 0.002	pH 7.4 0.0005 0.005	pH not given	
o-, m-, p-)			0.0002	

Nesmeyanova (3402) gives the taste threshold for cresols in chlorinated water as 0.0002 to 0.001 mg/l.

In odor-free water without chlorine, Hoak (2982, 3403) found the threshold odor concentrations to be as follows:

	Odor Thresi	Odor Threshold in mg/l		
Compound	at 30°C	at 60°C		
o-cresol	0.071	0.025		
m-cresol	0.333	0.100		
p-cresol	0.0455	0.200		

b. Fish and Other Aquatic Life. The reported effects of o-, m-, and p-cresol on fish are shown in the following tabulations:

Type of Fish	Effect	Referenc
2801		•
salmonide embryos minnows perch fingerling catfish tench, bleak perch minnows	lower toxic limit, 15°C. 96-hour TLm, 21°C. 24-hour TLm, approx. immobilized in 10 min., 15 immobilized in 54 min., 15 48-hour TLm, approx. killed in one hour killed, 17°C. 72-hour TLm, 21°C.	1535 3405 2981 3404 °C 3405 °C 3405 3335 3404 363 2920
roach	killed in 5 hours, 21°C	910
0.7	minutes, 9.0°C	- 910
salmonide embryos perch perch minnows tench, bleak carp	24-hour TLm, approx. lower toxic limit, 15°C immobilized in 10 min., 15' immobilized in 38 min., 15' 24-hour TLm, approx. 24-hour TLm, approx.	3404 3405 C 3405 C 3405 C 3404
	•	
rainbow trout yearling trout pearch perch perch perch minnows ninnows arp	killed, 17°C toxic limit, 1 hour, 13°C lower toxic limit, 15°C killed 24-hour TLm, approx. immobilized in 10 min., 15° immobilized in 21 min., 15° killed, 17°C 24-hour TLm, approx. killed, 17°C 24-hour TLm, approx. killed in one hour	1535 2920 3245 3405 3404 C 3405 C 3405 - 2920 - 3403
	salmonide embryos minnows perch perch minnows perch minnows fingerling catfish tench, bleak perch minnows fingerling catfish roach roach roach roach salmonide embryos perch minnows tench, bleak carp ol salmonide embryos minnows rainbow trout yearling trout perch perch perch perch perch minnows	salmonide embryos salmonide embryos salmonide embryos salmonide embryos perch fingerling catfish tench, bleak perch minnows fathead minnows fingerling catfish roach sol salmonide embryos perch minnows perch minnows perch minnows perch minnows fathead minnows fingerling catfish roach sol salmonide embryos perch minnows fathead minnows perch minnows perch minnows fathead minnows filled in 3 hours, 21°C killed in 5 hours, 21°C killed in 5 hours, 9.5°C lower toxic limit, 15°C minnobilized in 10 min., 15° minnobilized in 10 min., 15° Lower toxic limit, 1 hour, 13°C lower toxic limit, 1 ho

CN-

Concentra- tion in mg/l	Type of Fish	Effect Re	ferenc
4. Isomer no	t given		
8-10	minnows	min. lethal dose, 6 hours, dist. water 20°C	2942
10.0-13.6	bluegill sunfish	96-hour TLm, 20°C	2935
10-15	fish	killed	935
10-20	goldfish	killed in 3-5 days, hard wirs.	313
21-14	minnows	min. lethal dose, 6 hours,	•
21-14	mmo wa	hard water, 20°C	2942
17-20	fish	killed	313
22	mosquito-fish	96-hour TLm, turbld water,	2940
26	brook trout	killed in 5.5 min., 22.5°C	3406

One observer, noting that 10 mg/l killed fish, also reported that 0.5 mg/l had no appreciable effect.

The toxicity of cresols to fish appears to vary with the dissolved-oxygen content of the water, with low oxygen being synergistic (1051). Thus, 6.2 mg/l of paracresol in tap water caused trout to float helplessly in 100 minutes when the dissolved oxygen was 10 mg/l; but when the dissolved oxygen was only 3.0 mg/l the trout succumbed in 13 minutes (313).

Southgate (610) studied the toxicity of mixtures of KCN and p-cresol to trout. These substances do not appear to be synergistic, but exert an independent action on fish. Furthermore, concentrations of p-cresol and phenol of equivalent toxicity are interchangeable and appear to exert their toxic action on trout in the same manner. Paracresol and 1, 2, 6-xylenol are only partly interchangeable. Sub-lethal concentrations of 1, 2, 6-xylenol increase the toxicity of p-cresol but sub-lethal concentrations of p-cresol do not appreciably affect the toxicity of xylenol.

Clendenning and North (2106, 2856, 2870) investigated the effects of cresols on the giant kelp, *Macrocystis pyrifera*. The concentration required to cause a 50-percent inactivation of photosynthesis in bottom kelp fronds during a four-day exposure was 5-10 mg/l. Para-cresol was slightly less toxic than o- or m-cresol.

Toward lower aquatic life, the following effects of cresols have been reported:

· · · · · · · · · · · · · · · · · · ·				
Concentration in mg/l	Isomer	Organism	Effect	Refer- ence
6	P	Scenedesmus	toxic threshold, 24°C.	2158
6 10		Crustacea	killed in two hours	609
10	p	Microregma	toxic threshold	3343
10		Gammaridae	not affected toxic threshold, 23°C toxic threshold, 23°C	609
12	. p	Davhnia	toxic threshold, 23°C.	2158
16	ō	Davhnia	toxic threshold, 23°C	2158
20	m	Містотедта	toxic threshold	3343
20-30		Culex larvae	reaction threshold	3404
25		Gammaridae	killed	609
28	m	Daphnia	toxic threshold, 23°Creaction threshold	2158
30-40		Daphnia pulex	reaction threshold	3404
40	. 0	Scenedesmus	toxic threshold, 24°Ctoxic threshold, 24°C.	. 2158
40	m	Scenedesmus	toxic threshold, 24°C	2158
50	0	Microregma	toxic threshold	3343
80-100		Sayomia plum.		
		larvae	reaction threshold	3404
90-100		Pyonocypris vidua	reaction threshold	3404
100120		Culex pupae	reaction threshold	3404
600	o	E. coli	toxic threshold, 27°C	
600	700	E. coli	toxic threshold, 27°C.	2158
940	0	bacteria.	inhibited oxygen utilization	2923
1000	p	E. coli	not affected, 27°C.	2158

CRESOTIC ACID

CH₃C₆H₃OH COOH

(see also Cresols)

Used in the manufacture of dyes, cresotic acids are white to slightly reddish crystals. Ruchhoft (459) quotes references to the effect that, in chlorinated water, the

lowest concentrations of cresotinic (cresotic) acids giving taste are:

Compoun	d	Concer	ntration
o-Cresotinic	acid	0.01	mg/l
m-Cresotinic	acid	1.0	mg/l
p-Cresotinic	acid	0.1	mg/l

CRESYLIC ACID

(see also Cresols, Xylenol, and Phenols)

This substance, which is a mixture of isomeric cresols and xylenols from coal tar, mine flotation wastes, and sheep and cattle dips, killed goldfish at a concentration of 0.1 mg/l in hard water in five days and at a concentration of 1.0 mg/l in 6 to 48 hours. In soft water, 0.1 mg/l killed Daphnia in 72 hours (313).

Chinook, silver, and pink salmon were exposed for three days in both sea water and fresh water to varying concentrations of refined and crude cresylic acid (2091). Concentrations of 3.12 to 6.98 mg/l gave 100 percent kills, and the critical levels were estimated to be as low as 1.65 mg/l. Using a commercial impure o-cresylic acid, Clemens and Sneed (2981) found its 96-hour TLm toward fingerling channel catfish to be 11.2 mg/l at 21°C. No fish were killed by 4.0 mg/l and all succumbed to 15.8 mg/l. Using refined cresylic acid, the Washington State Department of Fisheries (2091) found that concentrations of 3.12 to 6.60 mg/l killed most of the chinook and silver salmon exposed for three days in both fresh water and sea water. Critical levels were given as 1.65 to 3.40 mg/l. With crude cresylic acid, the lowest concentrations causing a significant kill varied from 3.27 to 8.69 mg/l and the critical levels were estimated at 3.27 to 6.1 mg/l.

Commercial preparations of cresylic acid in sulfonated oil have been used as insecticides and larvacides. Knowles, et al. (612) found that 25 gallons per acre of this preparation killed 29 percent of goldfish and 25 percent of minnows in 24 hours.

CUPRIC CHLORIDE

(see Copper Chloride)

CYANIDES

1. General. Under this heading are grouped all of the references that cite cyanides as toxic or deleterious compounds and give concentrations in terms of the cyanide ion (CN-) without specifying the salt. Cyanides occur in the effluents from gas works and coke ovens, from the scrubbing of gases at steel plants, from metal cleaning and electroplating processes, and from chemical industries.

Attention is invited particularly to the general discussion under "Hydrogen Cyanide" with reference to the fact that HCN is largely undissociated at pH values of 8 and less. Hence, when toxicities are expressed in terms of the cyanide ion it must be realized that most of the cyanide in water is in the form of HCN. It is apparent that HCN rather than the cyanide ion is the major toxic principle. It must also be recognized that toxicities may vary markedly with pH and that a given concentration that is innocuous at pH 8 may become detrimental if the pH is lowered to 6 or less. On the other hand, Southgate

(346) reported that within the range of 6.0 to 8.5, pH had no appreciable effect on the toxicity of cyanide. In natural streams, cyanides deteriorate or are decomposed by bacterial action, so that excessive concentrations may be expected to diminish with time. Renn (2968) found a 90-95 percent removal of cyanides in percolation of waste waters through soil columns. Removal was greater in soils rich with organic matter than in clean sand or sandy clay. According to Ware (3407) the biochemical degradation of cyanide is little affected by temperature in the range of 10° to 35°C, but at lower or higher temperatures, decomposition proceeds much more slowly.

- 2. Cross References. Ammonium Thiocyanate, Nitriles, Cyanogen Chloride, Hydrogen Cyanide, Potassium Cyanate, Potassium Cyanide, Potassium Ferricyanide, Potassium Thiocyanate, Sodium Cyanate, Sodium Ferricyanide, Sodium Thiocyanate.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The WHO International (2328) and WHO European (2329) Drinking Water Standards both set a maximum allowable limit of 0.01 mg/l for cyanides, as CN. For the first time in 1962, the U.S.P.H.S. Drinking Water Standards (2036) set a recommended limit of 0.01 mg/l and a mandatory limit of 0.2 mg/l.

According to Klein (1756) the odor threshold for hydrogen cyanide in water is 0.001 mg/l. The maximum safe total ingestion of cyanide by humans has been estimated at something less than 18 mg/day, part of which will come from the normal environment and industrial exposure (2963).

It has been postulated (731, 733, 1119) that there may be a relation between cyanide intake and the incidence of poliomyelitis and pellagra. In a report from the Kettering Laboratory of the College of Medicine, University of Cincinnati, April, 1952, Dr. J. S. Cass pointed out that symptoms of eyanide poisoning are quite different from those of poliomyelitis. According to Cass, the body normally takes in small amounts of substances which contain cyanides, e.g., members of the cabbage family. The CN ion, except for a small portion exhaled, is changed rapidly to the relatively non-toxic sulfur complex (SCN, thiocyanate) in the liver, and is eliminated irregularly and slowly in the urine. There is no evidence that CN ion is stored in the body. Small doses of CN, incapable in themselves of causing intoxication, can be disposed of indefinitely in the body, since the natural detoxifying mechanisms are practically inexhaustible, although slow.

- b. Stock and Wildlife Watering. See Hydrogen Cyanide and Sodium Cyanide.
- c. Fish and Other Aquatic Life. The toxicity of cyanides toward fish is affected by the pH, temperature, dissolved oxygen, and concentration of minerals. As noted above and also under Hydrogen Cyanide, HCN appears to be the major toxic principle rather than CN; hence the lower the pH the greater the proportion of undissociated HCN. The toxicity of cyanide is also increased at elevated temperatures, a rise of 10°C producing a two- to three-fold increase in the rate of lethal

action (3034, 3408). Low tensions of dissolved oxygen also increase the toxic action of cyanides (2109). Southgate (2411) reports the median period of survival of trout at 17°C in a solution containing 0.105 mg/l of CN to be about 8 hours at 95 percent oxygen saturation; about 5 hours at 73 percent, and only 10 minutes at 45 percent saturation. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic (2157).

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for the transferring of oxygen from the blood to the tissues (346). The toxicities of cyanides toward fish have been reported as shown below; (but see also HCN, KCN, and NaCN).

Cyanides in mg/l	Time of Exposure	Type of Fish	Remarks	Reference
0.05	120-136 hrs.	brook trout	all killed	1120
0.05 - 0.10	 .	fish	MLD	1121
0.05	5 days	trout	lethal	2977
0.07	74 hours	rainbow trout	overturned	1580, 1645
0.1	l day	fish	overturned	3409
0.1	37	fish	MLD	1122, 1123
0.1 - 0.2	1 to 2 days	rainbow trout	MLD	346
0.12 - 0.18	96-hour TLm	bluegill sunfish	hard and soft	4.10
0.100			water	2936
0.126	170 minutes	trout	overturned	353
0.15	4.8 to 64 min.	trout	overturned	659
0.176	77.	bluegill, sunfish	toxic limit	353
0.18	24-hour TLm		soft water	2093
0.2	11 min.	rainbow trout	MLD	3410
0.2	150 min.	fish	overturned	3409
0.2 0.33	57.1	fish	killed rapidly	1124
	2.5 hours	adult chub	killed	1465
0.42 0.50	11 min.	trout	overturned	353
1.0	141 min.	adult chub	MLD	2970
	20 min.	trout	ali killed	1120
10.0	1.5 hours	carp	MLD	936

The following concentrations of cyanides were survived by fish:

Cyanides in mg/l	Time of Exposure	Type of Fish	Remarks	Reference
0.02	27 days	trout	survived	1120
0.084		trout	not toxic	353
0.20		adult chub	survived	2970
$0.25 \\ 0.375$		bluegills	survived	353
0.315	55.1	bullheads	survived	353
0.5	96 hours	bluegills	survived	353
V.D	96 hours	bullheads	survived	353

In its Third Progress Report, the Aquatic Life Advisory Committee of the Ohio River Valley Water Sanitation Commission (2109) reviewed much of the research on cyanides and recommended that concentrations of free cyanide in excess of 0.025 mg/l be considered unsafe in the waters of the Ohio River.

Toward lower organisms, cyanide does not appear to be as toxic as toward fish. Surber (2688) reported that larvae of the midge, Cricotopus bicinctus, survived electroplating wastes that had cyanide concentrations up to 3.2 mg/l. For Daphnia magna the toxicity level for a 48-hour exposure was given at 3.4 mg/l (2977). The amoeba, Mayorella palestinensis, was killed at a cyanide concentration of 130 mg/l (2969), but a significant inhibition of photosynthesis by Chlorella did not occur until the cyanide concentration reached 7300 mg/l. The organisms that exert BOD were found to be inhibited at 1.0 mg/l (2962) and at 60 mg/l (3411) although the effect is more one of delay in exertion of BOD than total reduction.

CYANOBUTADIENE

According to Daugherty and Garrett (1441, 2959, 2960) 1-cyano-1, 3-butadiene exhibited the following effect upon the marine pinperch, Lagodon rhomeboides:

Maximum concentration at which no deaths occurred 50 mg/l Minimum concentration at which deaths occurred 60 mg/l 24-hour TL_m 71.5 mg/l

CYANOGEN CHLORIDE

CNCI

(see also Hydrogen Cyanide)

Cyanogen chloride is formed when sewage effluents containing gas liquor are chlorinated, by action of the chlorine on the hydrogen cyanide. Concentrations of cyanogen chloride ranging from 1.0 to 0.08 mg/l have killed fish (361, 1129, 1130).

CYCLIC QUATERNARY AMMONIUM COMPOUND

(see Chapter X)

CYCLOHEXANE AND CYCLOHEXENE

C₆H₁₂ and C₆H₁₀

(see also Benzene)

These cycloparaffins, found in petroleum, are used as solvents for lacquers and resins, or for paint remover. They are slightly more toxic to fish than is benzene. The oral LD_{50} for rats has been reported (2980) to be 29,820 mg/kg of body weight. According to Hubault (462), 10 mg/l of cyclohexene was toxic in four hours at 11.5°C and 10 mg/l of cyclohexene in 3.16 hours at 9°C. These compounds produce a state of torpor in the fish.

The toxicity of these hydrocarbons is diminished by the addition of a methyl group to form methylcyclohexane or methylcyclohexane. Hubault (462) reports that 50 mg/l of methylcyclohexane was toxic to freshwater fish in 3.67 hours at 10.5° C. This is five times the toxic concentration of straight cyclohexane. In Lake Huron water at 12° C, cyclohexene at a concentration of 5 mg/l has no effect on rainbow trout or the sea lamprey during a 24-hour exposure (2976). Using turbid water at $21-24^{\circ}$ C and mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values to be 15,500 mg/l.

CYCLOHEXANE CARBOXYLIC ACID

C₆H₁₃COOH

(also known as Naphthenic Acid)

This odorless solid, slightly soluble in water, is extracted from petroleum. It is used in insecticide formulations in paper mills, as a clarifier for mineral oil, and as a solubilizer for vulcanized rubber (364). It is reported to be fatal to European perch in concentrations of 4 to 16 mg/l (463, 614, 615). Crayfish were killed in 18 to 60 hours by exposure to 5 to 50 mg/l of this acid (614, 615), and minnows were killed in 72 hours by a concentration of 5.0 mg/l. At low concentrations it imparts a taste to the flesh of fish (616).

Cairns et al. (2936, 2954, 2957) found the following 96-hour TL_m values for the bluegill sunfish (Lepomis macrochirus), a pulmonate snail (Physa heterostropha),

and the diatom (Navicula seminulum) in hard and soft water:

		96-hour TLm in mg/l	
Organism	$Temperature {}^{\circ}C$	Soft Water	Hard Water
Fish	18-20	5.6	7.1
	30	5.6	7.0
Diatom	22	43.1	79.8
Dictor	28	41.8	56.0
	30	43.4	28.2
Snail	20	6.6 - 7.5	11.8
Dimin	30	18-19	11.7

As this table shows, the toxicity of naphthenic acid is not greatly affected by temperature or hardness. Periodic low oxygen tensions, however, lowered the TL_m values for the snail and fish to 2.0 mg/l at 20°C in soft water.

2. 4-I

(see Chapter IX)

DAIRY WASTES

(see also Lactic acid, Sugars, Soaps, Synthetic Detergents, BOD, and Chapter X)

Dairy wastes contain soaps and detergents, lactic acid, sugars, whey, and other substances that may exert a deleterious effect on a stream, either directly or indirectly. In some instances, fresh milk wastes have been beneficial by stimulating the production of fish-food organisms, especially Chironomus larvae (601). At a dilution of 1:240, dairy wastes had no effect on minnows (362), but at 1:15 dilution, other milk wastes were on the verge of distressing fish (601). At a dilution of 1:35, whey has been shown to be toxic to fish in a few hours. Cole (311) reports that dairy wastes contain soaps that are toxic to bass at concentrations of 600 mg/l. Lactic acid can be toxic to fish at 654 mg/l, or even less at low dissolved-oxygen contents.

DALAPON

(see Chapter IX)

DDD

(see Chapter IX)

DDT

(see Chapter X)

DECABORANE

(see Boron)

DECYL BENZENE SODIUM SULFONA

(see Chapter X)

DELRAD (RADA)

(see Chapter IX)

DERRIS ROOT

(see Chapter IX, Rotenone)

DETERGENTS

(see Chapter X)

DEXTROSE

C6H12O6

(see also Sugars)

This crystalline sugar, which occurs widely in plants and animals, does not exhibit any toxic action or dele-

terious effects other than osmotic pressure and B. O. D. In stabilized tap water kept saturated with oxygen, Schaut (362) showed that 17.1 mg/l of dextrose had no effect on minnows during 24 hours of observation.

DIAZINON

(see Chapter IX)

DIBORANE

(see Boron)

DIBUTYL PHENYL PHENOL SODIUM DISULFONATE

(see Chapter X)

DICAPTHON

(see Chapter IX)

DICHLONE

(see Chapter IX-Dichloronaphthoquinone)

DICHLOROBENZENE

 $C_6H_4Cl_2$

Metadichlorobenzene is a colorless liquid, insoluble in water, and seldom used commercially. Orthodichlorobenzene, also a liquid and insoluble in water, is used as a solvent for waxes, for preserving plants, and for destroying insects such as termites. Paradichlorobenzene, a white crystalline solid with a characteristic odor, is used largely for killing moths, their larvae, and other insects. It is soluble in water to the extent of 70 mg/l at 25°C. Demyanenko (313, 431) reports that a concentration of 50 mg/l of p-dichlorobenzene was lethal to fish.

DICHLORODIPHENYLTRICHLOROETHANE

(see Chapter IX-DDT)

DICHLOROETHANE

C₂H₄Cl₂

Known also as ethylene dichloride, this heavy liquid with a pleasant odor and sweet taste is highly soluble in water. It is used as an organic solvent in industry and in the manufacture of tobacco extract. The oral LD₅₀ for rats is given as 770 mg/kg of body weight (364). According to Garrett (2959) the TL_m for the marine pinperch was 250-275 mg/l for 1, 1-dichloroethane and 150-175 mg/l for 1, 2-dichloroethane.

DICHLORONAPHTHOQUINONE

(see Chapter IX)

DICHLOROPHENOL

(see Halogenated Phenols, also Chapter IX)

DICHLOROPHENOXY ACETIC ACID (2, 4-D)

(see Chapter IX)

DICHLOROPROPENE

 $C_3H_4Cl_2$

This liquid with a chloroform-like odor is used as a soil fumigant for the control of nematodes (364). The threshold of toxicity toward *Daphnia* and *Scenedesmus* has been reported as 40 mg/l. For the protozoan *Microregma* the toxic level is 100 mg/l (2977).

DICHROMATES

(see Chromium)

DIELDRIN

(see Chapter IX)

DIETHANOLAMINE

 $(C_2H_4OH)_2NH$

This deliquescent solid forms a viscous liquid that is miscible with water with an ammoniacal odor and a strong alkaline reaction, apparently from dissociation and the formation of ammonium ion. It is used in the petroleum and rubber industries, for the manufacture of surface-active agents, and for organic synthesis (364).

According to Gillette et al. (1442) the critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 80 to 120 mg/l, i.e., all fish survived 80 mg/l but all died at 120 mg/l. Hence, the 24-hour TL_m was approximately 100 mg/l. Turnbull et al. (2093) used bluegill sunfish (Lepomis macrochirus) in aerated water at 20°C and found the 24-hour TL_m to be 2100 mg/l and the 48-hour TL_m to be 1850 mg/l. In highly turbid water with the mosquito-fish (Gambusia affinis), Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values to be 1800, 1550, and 1400 mg/l respectively. High dosages of this compound raised the pH value to 10.4 but did not clarify the turbidity.

DIETHYLAMINE

 $(C_2H_5)_2NH$

This flammable liquid is miscible with water, producing a strong alkaline reaction, apparently from its dissociation and the formation of ammonium ions. It is used in the rubber and petroleum industry and for the manufacture of resins, dyes, and pharmaceuticals (364). The oral LD₅₀ for rats has been reported as 540 mg/kg of body weight (364).

Gillette et al. (1442) found that creek chub, a fish of average tolerance, in well-aerated water at 15-21°C withstood 70 mg/l of diethylamine for 24 hours, but all died at 100 mg/l. The approximate 24-hour TL_m was about 85 mg/l. Bringmann and Kuhn (2158, 3343) reported that the toxic threshold for Scenedesmus during 4 days of exposure at 24°C was only 4 mg/l, while for Daphnia during two days at 23°C the threshold concentration was 100 mg/l and for Microregma, 70 mg/l. There was no apparent effect on E. coli at concentrations up to 1000 mg/l.

DIETHYLENE GLYCOL

 $C_4H_{10}O_3$

This colorless liquid with a sweetish taste is miscible with water. It is used in antifreeze solutions, as a finishing agent for textiles, as a solvent for vat dyes, and in the composition of many products (364). In water of 1500 mg/l turbidity at 23-25°C, Wallen et al. (2940) found the 96-hour TL_m toward the mosquito-fish (Gambusia affinis) to be over 32,000 mg/l.

DIISOBUTYL CRESOXYMETHOXY ETHYLDIMETHYL BENZYL AMMONIUM CHLORIDE

DIISOBUTYL PHENOXYETHOXY ETHYLDIMETHYL BENZYL AMMONIUM CHLORIDE

(see Chapter X)

DILAN

(see Chapter IX)

DIMETHYLAMINE

 $(CH_3)_2NH$

A gas at ordinary temperatures, dimethylamine is highly soluble in water with a strong alkaline reaction, apparently from dissociation and the formation of ammonium ions. It is used industrially in tanning operations, in the manufacture of detergents, and in vulcanizing rubber. The threshold odor concentration has been reported (3412) as 0.6 ml/l.

According to Gillette et al. (1442) the critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 30 to 50 mg/l, i.e. all fish survived 30 mg/l but all died at 50 mg/l. Corti (146) tested rainbow trout (Salmo irideus) at a dimethylamine concentration of 205 mg/l. The resulting pH was 10.3 and the temperature was 13°C. The fish showed their first reaction in 33 to 40 seconds, turned over in 3 to 4 minutes, and made their last movement at 10 to 13 minutes.

DIMETHYLBENZYLAMMONIUM CHLORIDE

(see Chapter X)

DIMETHYLDIOXANE

 $C_6H_{12}O_2$

According to Klimkina (3413) this compound, used in organic synthesis, may be found in effluents. He recommends a maximum permissible concentration in water of 0.005 mg/l, based on toxic effects to aquatic life. The odor threshold is 2.5 mg/l, but a concentration of 30 mg/l does not inhibit oxygen consumption in biochemical degradation of wastes.

DINITROBENZENE

 $C_6H_4(NO_2)_2$

(see also Nitrobenzene, Trinitrobenzene)

The meta-, ortho-, and para-forms of this compound are crystalline solids that are moderately soluble in water. The oral $\rm LD_{50}$ for p-dinitrobenzene in cats is given as 29.4 mg/kg of body weight (364). According to LeClerc (2942), the minimum lethal dose of dinitrobenzene (isomer not specified) toward minnows during a 6-hour exposure at 23°C was 10-12 mg/l in distilled water and 8-10 mg/l in hard water. The lethal level for fish has also been given as 2.0 mg/l (2977).

DINITROCRESOLS

 $(NO_2)_2C_6H_2OHCH_3$

Sparingly soluble in water, 4,6-dinitro-o-cresol is used as a selective herbicide and insecticide. The oral LD₅₀ in rats is given as 30 mg/kg of body weight (364). According to LeClerc (2942) the lowest concentrations that eaused minnows to overturn within six hours were 1.5-2.0 mg/l in distilled water at 23°C and 3.0-4.0 mg/l in hard water at 18°C. Using River Havel water, Bringmann and Kuhn (2158, 3343) found that the beginning of toxic effects appeared at 8 mg/l for *Daphnia* at 23°C, 30 mg/l

for the protozoan Microregma, 36 mg/l for the alga Scenedesmus at 24°C, and 100 mg/l for E. coli at 27°C.

2,4-dinitro-6-methyl cresol (DNC) is used as a herbicide. At 1.0 mg/l, the sodium salt of DNC caused the death of fish and snails in aquaria (3009).

DINITROPHENOLS

 $(NO_2)_2C_6H_3OH$

(see also Phenol, Nitrophenol, Trinitrophenol)

The nitration of phenol with dilute nitric acid produces first the ortho or para nitrophenols, then 2,4-dinitrophenol, and finally 2,4,6-trinitrophenol, known as picric acid. These various substances may occur in chemical, dye, and ammunition-plant wastes. Grindley (617) reports that the threshold concentration of dinitrophenol, below which neutral solutions were not toxic to minnows, was 30 mg/l. In solutions of 200 mg/l in neutral water, minnows overturned in 22 minutes. LeClerc (2942) observed that the minimum concentration of m-dinitrophenol causing minnows to overturn within 6 hours at 22-23°C was 35-38 mg/l in hard water, but only 0.5-1.0 mg/l in distilled water.

In River Havel water, the thresholds of toxic effect of 2,4-dinitrophenol were found by Bringmann and Kuhn (2158) to be 6 mg/l for Daphnia at 23°C, 40 mg/l for Scenedesmus at 24°C, and over 100 mg/l for E. coli at 27°C. Hermann (2923) reported that 100 mg/l of this compound caused a 50-percent decrease in oxygen utilization in the BOD test. According to Batte et al. (2993), 10 mg/l caused complete mortality to Lymnaeid snails within 24 hours.

2,4-dinitro-6-sec-butylphenol (DNBP) and 2,4-dinitroo-cyclohexylphenol are used as pesticides, especially as herbicides. Small trout have died from concentrations of 100 mg/l of DNBP and from 12 mg/l of its sodium salt. DNCHP in concentrations of 1 to 10 mg/l killed all fish (3009).

DIOCTYL ESTER OF SODIUM SULFOSUCCINIC ACID

(see Chapter X)

DIPTEREX

(see Chapter IX)

DISODIUM HYDROGEN PHOSPHATE

(see Sodium Phosphates)

DISODIUM SALT OF DIBUTYL PHENYLPHENOL DISULFONATE

(see Chapter X)

DISSOLVED OXYGEN

1. General. Dissolved oxygen in natural-waters cannot rightfully be designated as a primary pollutant, but it does come under the category of a corollary pollutant because excessive dissolved oxygen arising from algal growths may adversely or unreasonably affect such waters for one or more beneficial uses. It is not with a surplus of dissolved oxygen, however, that the sanitary engineer is normally concerned, but rather with a deficiency or complete absence thereof. Inadequate dissolved oxygen in surface waters may contribute to an unfavor-

able environment for fish and other aquatic life, as explained below, and the absence of dissolved oxygen may give rise to odoriferous products of anaerobic decomposition.

The content of dissolved oxygen in water at equilibrium with a normal atmosphere is a function of the temperature and salinity of the water, the ability of water to hold oxygen decreasing with increases in temperature or dissolved solids. Tables of saturated dissolved-oxygen values are available in textbooks and handbooks (330, 911). Natural waters, however, are seldom at equilibrium and seldom exactly saturated with dissolved oxygen, for temperatures are changing and physical, chemical, bio-chemical, or biological activities are utilizing or liberating oxygen. For a formulation and discussion of deoxygenation and reaeration in surface water, see Chapter II.

- 2. Cross References. B.O.D., Algae, Ozone and Nascent Oxygen, Chapter II, and Chapter V.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The presence of dissolved oxygen in municipal water supplies is seldom considered to be deleterious, for it has no adverse physiological effect and actually increases the palatability of the water. It is detrimental, however, in the corrosion of metal pipes and efforts are sometimes made to eliminate or decrease the dissolved-oxygen content of water to inhibit corrosion (1149). Methods of treatment for corrosion control are not within the province of this report, and since dissolved oxygen is a natural constituent of surface waters, its planned suppression does not appear to be a function of water-pollution control.
- b. Industrial Water Supplies. For many industrial uses of water, zero dissolved oxygen would be desirable as a means of inhibiting corrosion (1149), especially in cooling waters. In practice, however, industries anticipate the use of normal surface waters containing dissolved oxygen, or ground waters that acquire dissolved oxygen in the process of handling. In packaged power reactors, the dissolved-oxygen content of water should not exceed 0.03 mg/l to prevent stress corrosion of stainless steel (3395). For boiler feed water, the limiting dissolved-oxygen concentrations have been given as 2.0 mg/l for boiler pressures of 0 to 150 psi; 0.2 mg/l for 150 to 250 psi; and 0.0 mg/l for 250 psi and up (152).
- c. Fish and Other Aquatic Life. There is a great deal of literature pertaining to the minimum dissolvedoxygen concentration necessary to sustain healthy aquatic life, especially fish, and the concentration below which fish will be killed by short-time exposures. To tabulate all of this literature would be meaningless, for much of it is repetitious and much of it cannot be correlated. No general statement can be made to give the minimum dissolved-oxygen concentration required to support fish life, owing to the fact that the oxygen requirements of fish vary with the species and age of the fish, with prior acclimatization, with temperature, with the concentration of other substances in the water. and with several other factors. A thorough summary of the effects of low concentrations of dissolved oxygen toward fish is given by Southgate (346), and by the Aquatic Life Advisory Committee of ORSANCO (2109,

2408, 2414). Much of the following material is condensed from those sources. For a further discussion of this subject, see also Chapter V—Propagation of Fish and Other Aquatic Life.

Temperature affects not only the amount of available dissolved oxygen in water but also the rate at which fish utilize such oxygen. At 6.2°C, goldfish consumed 16.1 ml per kg per hour; at 15°C, 50.1 ml per kg per hour; and at 20.8°C, 90.4 ml of oxygen per kg of fish flesh per hour. As a result of such oxygen requirements, the minimum concentration at which fish are asphyxiated will be higher at higher temperatures, e.g. for trout 1.16 mg/l at $10^{\circ}C$ and 2.14 mg/l at $18^{\circ}C$ for relatively short exposures. For longer exposures, the asphyxial points would probably be much higher; yet it has been shown that fish may, under natural conditions, become acclimatized to low oxygen concentrations. Within certain limits, fish can adjust their rate of respiration to compensate for changes in the concentration of dissolved oxygen. It is generally agreed, moreover, that those species which are sluggish in movement (e.g., carp, pike, eel) can withstand lower oxygen concentrations than fish (such as trout or salmon) which are more lively in habit.

At 13°C, according to Jones (1543), the stickleback has no immediate appreciation of water of low D.O. content and will swim into it with no hesitation. If the fish remain in water of low D.O., respiratory distress develops, accompanied by uneasiness and random movement. When the random movement carries the fish back into oxygenated water the fish recover quickly. Over a wide range of dissolved oxygen (from less than 3.0 mg/l up to 6.6 mg/l at 13°C this reaction takes 1-3 minutes. At 3°C, however, the reaction is very slow, taking 5-6 minutes even when water contains as little as 0.3 mg/l of dissolved oxygen. At 20°C and with D.O. values below 2 mg/l, response is very prompt with stress developing so quickly that fish will usually not swim into the poorly oxygenated water. Results with trout and minnows were similar (1543). Whitmore, Warren, and Doudoroff (3447) also reported on avoidance reactions of juvenile chinook salmon, coho salmon, largemouth bass, and bluegills.

The lethal effect of low concentrations of dissolved oxygen appears to be increased by the presence of toxic substances, such as excessive dissolved carbon dioxide, ammonia, cyanides, zinc, lead, copper, or cresols (144, 2109, 2957, 2964, 3321, 3324, 3228). With so many factors influencing the effect of oxygen deficiency, it is difficult to estimate the minimum safe concentration at which fish will be unharmed under natural conditions.

Extensive studies have been made by Moore (865) in which fish of several species were confined in boxes of wire netting and lowered to varying depths in lakes. The concentration of dissolved oxygen and the temperature were noted at each depth, and the reactions of the fish were observed. His results, summarized in Table 6-4, show that the median fish will die at concentrations of 3.1 mg/l in summer and 1.4 mg/l in winter, and will live at 4.2 mg/l in summer and 3.1 mg/l in winter.

In a somewhat similar study, the Water Pollution Research Board of England (2952) found the minimum 0.3 mg/l

1.4 mg/l

oxygen tensions at which various fish would survive for 84 hours at three temperatures to be as follows:

ингес вешре	LOUGHT OF T		
Minimum Di	ssolved Oxygen	Concentration	in mg/l at

M inimur	n Dissoive	W Oxfiden Conc.	100.000.00
Fish	10°C	16°C	20°C
Rainbow trout	1.89	3.00	2.64
Perch	1.00	1.34 0.71	$1.25 \\ 1.42$
Roach	0.65 0.48	1.73	3.74
Tench	0.35	0.54	
Dace		1.14 1.50	-
Bleak		1.00	.

TABLE 6-4

THRESHOLDS OF DISSOLVED OXYGEN FOR FISH

Species

Pike ____ Black bass_ Black crappie

Common sun-

Data After Moore (865) WINTER SHMMER Lowest observed Highest Highest Lamest observed concentration at which fish were killed in observed concentration observed observed concentration at which fish were killed in 48 hours at which fish survived for at which fish survived for 24 hours 48 hours 2.3 mg/l 2.3 mg/l 1.4 mg/l 3.1 mg/l 4.7 mg/l 6.0 mg/l 3.1 mg/l5.5 mg/l 4.2 mg/l 1.5 mg/l 0.8 mg/l 1.5 mg/l 0.8 mg/l $3.1 \, \text{mg/l}$ 1.4 mg/l $4.2 \, \text{mg/l}$ fish _____ 4.2 mg/l Yeliow perch 4.2 mg/l Sunfish ____ 3.3 mg/l Blk. bullhead 3.3 mg/l 4.7 mg/l3.5 mg/l3.1 mg/l 2.9 mg/l

 $3.1 \, \text{mg/l}$

Median values 4.2 mg/l Ellis (247, 313) indicated that under average stream conditions, 3.0 mg/l of dissolved oxygen, or less, should be regarded as hazardous or lethal, and that to maintain a varied fish fauna in good condition the dissolved-oxygen concentration should remain at 5.0 mg/l or higher. For trout in soft water, the lower limit has been set as high as 6.0 mg/l (1155). Quoting other authorities, Ellis (1156) reports that sustained dissolved-oxygen concentrations of 2.0 mg/l will kill all kinds of fish, 3.5 mg/l will be lethal to most species, and few fish will be found at under 4.5 mg/l. In contrast, salmon parr have been reported (1157) to live at least five days at 2.2 mg/l of dissolved oxygen, and in winter, fish have been reported (865) to tolerate 1.0 to 2.0 mg/l of dissolved oxygen for a short time. Numerous other references describe the effect of lowered oxygen tensions on various species of fish under many conditions of exposure (2409, 2952, 3321, 3414, 3415, 3416, 3417, 3418, 3419, 3420, 3421, 3422, 3423, 3424, 3425, 3426, 3427, 3428, 3429, 3430, 3431, 3432, 3433, 3434, 3435, 3436, 3437, 3438, 3439, 3440. 3441.)

3.1 mg/l

Several factors aside from the deoxygenating effects of pollutants influence the concentration of dissolved oxygen in surface waters. There is a diurnal variation owing to the photosynthetic action of algae during daylight hours and their respiration at night (2279, 2280, 2972). Indeed, heavy fish mortalities have arisen from the oxygen demand caused by the decomposition of algae (2283). There is also a variation of oxygen with the depth of water, especially in lakes and stagnant ponds. For this reason, fish may avoid the deeper, cooler waters and be forced to remain in shallow warm areas (3442). Dissolved-oxygen concentrations near the bottom muds of lakes and sluggish rivers may approach zero. Under such conditions, the hatching of fish eggs has been delayed, or the fish hatching from such eggs have been deformed (3443, 3444, 3445, 3446).

The Aquatic Life Advisory Committee of ORSANCO (2408) has recommended that the minimum permissible oxygen concentration for a well-rounded warm-water fish population be as follows: The dissolved-oxygen content of warm-water fish habitats shall be not less than 5 mg/l during at least 16 hours of any 24-hour period. It may be less than 5 mg/l for a period not to exceed 8 hours within any 24-hour period, but at no time shall the oxygen content be less than 3 mg/l. To sustain a coarse fish population, the dissolved-oxygen concentration may be less than 5 mg/l for a period of not more than 8 hours out of any 24-hour period, but at no time shall the concentration be lower than 2 mg/l.

Supersaturation with dissolved oxygen has also been reported as detrimental to fish. In ponds at 150 percent of saturation, the carp population seemed to have a higher percentage of disease than in ponds where the oxygen value was 100-125 percent of saturation (1544). There may also be a relationship between dropsy and gill damage by gas bubbles. In Westlake Park in Los Angeles fish died when oxygen reached 300 percent of saturation, the lethality being attributed to oxygen bubbles surrounding the gills (418). According to Cole (311) bass could tolerate 40.3 mg/l for only short periods, but Ellis (313) reports that a variety of hardy fish survived supersaturated solutions for at least 24 hours. Apparently fish require dissolved oxygen and not air bubbles (1158), the latter proving deleterious at times (see also Ozone and Nascent Oxygen).

Studies by Fairchild (2946) of the toxicity of nine inorganic salts to Daphnia magna indicated that a reduction in the level of dissolved oxygen below 4.5 mg/l reduced the resistance of this crustacean to the salts. In bottom deposits, the eggs of Ascaris developed to the larval stage in two months when the dissolved oxygen was 7 to 9 mg/l; but the eggs failed to reach the larval stage at 5.0 to 5.6 mg/l of dissolved oxygen (1727).

- d. Shellfish Culture. Oysters show considerable resistance to oxygen deficiencies, according to Mitchell (326). Only when exposed for more than a week to very low concentrations of dissolved oxygen were oysters killed, and hence a temporary decrease in available oxygen is not considered by Mitchell to be a significant factor in oyster culture. Clark (327) studied the effect of dissolved-oxygen content on oyster larvae. Although the normal concentration was 7.9 mg/l, larvae developed adequately at 2.4 mg/l.
- 4. Summary. On the basis of the available information described above, it is not feasible to attempt to suggest an optimum dissolved-oxygen content of water for domestic, industrial, stock and wildlife, or recreational uses. For fish and other aquatic life, the recommendations of the Aquatic Life Advisory Committee of ORSANCO (as quoted above) appear to be logical.

DISSOLVED SOLIDS

1. General. In natural waters the dissolved solids consist mainly of carbonates, bicarbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese and other substances. The mineral content of natural waters may be lowered artificially by dilution or raised by the addition of chemical wastes, dissolved salts, acids, alkalis, gas and oil-well brines, or drainage waters from irrigated land (313, 611, 618, 2032, 2180, 2340).

All salts in solution change the physical and chemical nature of the water and exert osmotic pressure. Some have physiological or toxic effects as well. Discussions of the effects upon the beneficial uses of water of "dissolved solids" under this heading are limited to the effects attributable only to total salt concentration, or osmotic pressure, without reference to the effects of the salt constituents separately. It should be pointed out, however, that possible synergistic or antagonistic interactions between mixed salts in solution may cause the effects of salts in combination to be different from those of salts separately, and that the presence of poisonous salts (such as nitrates, sulfides, and fluorides) can render dangerous for use waters whose total solids concentration is apparently within acceptable limits.

- 2. Cross References. Distilled Water, Specific Electric Conductance, Chapter V.
 - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The 1962 USPHS Drinking Water Standards (2036) specify that the total dissolved solids should not exceed 500 mg/l if more suitable supplies are, or can be made, available. This limit was set primarily on the basis of taste thresholds. The 1958 WHO International Standards (2328) set the "permissible limit" at 500 mg/l and the "excessive limit" at 1500 mg/l, but no "maximum allowable limit" is given. The 1961 WHO European Standards (2329) do not include limits for total dissolved solids.

Many communities in the United States and in other countries use water containing from 2000 to 4000 mg/l of dissolved salts, when no better water is available (32, 620, 621, 622, 1545, 3469). Such waters are not palatable, may not quench thirst, and may have laxative action on new users. However, no harmful physiological effects of a permanent nature have been called to the attention of health authorities. On the other hand, there appears to be no proof that mineral waters have any beneficial or therapeutic value resulting from their mineral content (623, 624, 625), although life at spas and similar resorts may be undeniably healthful and wholesome for other reasons. One team of workers has found allergic diseases higher in frequency where water was low in dissolved salts (626).

Waters containing more than 4000 mg/l of total salts are generally considered unfit for human use, although in hot climates higher salt concentrations can be tolerated than in temperate climates (627). Waters containing 5000 mg/l or more are reported to be bitter and act as bladder and intestinal irritants (295). In one village in British Somaliland, the water contains 10,000 mg/l of salts, of which 4400 mg/l are sulfates (1546). Volhardt and Schutte (1547) described a series of experiments in the course of which eleven healthy young men on dry diets drank only 500 ml of sea water daily for 5-6 days, while continuing with their usual jobs. Although marked loss of weight and changes in the composition of blood and urine occurred, recovery from these disturbances was rapid nevertheless.

It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l; however, higher concentrations may be consumed without harmful physiological effects and may indeed even be

more beneficial. Each water with a total salt concentration over 1000 mg/l should be judged on the basis of the local situation, alternative supplies, and the reaction of the local population.

An interesting influence of total dissolved solids on domestic water supply is discussed by Buswell and Upton (3470). When a fire hose is directed onto a highvoltage power line, the firemen are in danger of electrical shock. The current that will flow down the host stream will depend on the voltage of the power line and the specific electrical conductance of the water, which is a function of the dissolved solids.

b. Industrial Water Supplies. Dissolved solids in industrial waters can cause foaming in boilers and interference with clearness, color, or taste of many finished products. Water with extremely low dissolved solids is desirable for atomic power reactor cooling systems (3395). High contents of dissolved solids also tend to accelerate corrosion (3471). Concentrations that have been recommended for various industrial water uses are shown in the following tabulation. For further details, see Chapter V.

LIMITING CONCENTRATIONS OF DISSOLVED SOLIDS FOR INDUSTRIAL WATERS

Industry and Use of Water	Limiting Concentration, mg/l
Boiler feed water	- 50-3000 (according to pressure)
Brewing, light beer	= 500
Brewing, dark beer	1000
Brewing and distilling, general.	500–1500
Canning and freezing	850
Carbonated beverages	850
Confectionery	_ 50- 100
Dairy washwaters	_ 850
Food equipment washing	850
Food processing, general	850
ice manufacture	_ 170-1300
Plastics, clear	_ 200
Paper manufacture	
Fine papers	_ 200
Groundwood papers	_ 500
Kraft paper, bleached	_ 300
Kraft paper, unbleached	_ 500
Soda and sulfate pulp	_ 250
High-grade paper products	_ 80
Lower-grade products	_ 150 200
Rayon manufacture	_ 100- 200

c. Irrigation Water. The total concentration of dissolved solids in irrigation waters generally varies from 150 to 1500 mg/l and in a few cases is found to be as high as 5000 mg/l, a concentration tolerated by only the most salt-resistant plants (285, 635). Some varieties of barley will produce grain satisfactorily even though irrigated over most of the life cycle with water containing 20,000 mg/l of salt (3472). High salinities may be deleterious to plants directly, or indirectly through their effects on the soil; but their harmfulness may be modified by a number of factors, such as the kind of crop, character of soil, drainage conditions, types of salts found in the water, climate, etc. (For a detailed discussion, see Irrigation, under Chapter V.)

There is abundant literature on the effects of dissolved salts on irrigation in general and upon specific crops for given soils under certain conditions of application (267, 271, 282, 636, 637, 638, 639, 1548, 1549, 1550, 1912, 2135, 2200, 2383, 2384a, 2385, 2387, 2391, 3472, 3474, 3475, 3476, 3477, 3478). To tabulate or abstract these references

beyond the scope of this report. Much of the work has been correlated or summarized by the Salinity Laboratory of the U.S. Department of Agriculture at Riverside, California, as reviewed in Chapter V.

Chapman, Wilcox, and Hayward (267) consider 1000 mg/l a concentration "approaching the limit for best crop growth." Irrigation waters in California have been classified (263, 269) according to salt content as follows:

Classification	Concentration in mg/l
Freellent	175 or less
Good	175-525
Permissible Doubtful	
Injurious	2100 or more

In other references (246, 274) three classes have been given in this manner:

Salt Concentration, mg/l

Class	Suitability Sal	t Concentration, m
Ι	suitable under almost all conditions	under 700
II.	suitability dependent on crop, soil,	700-2100
III	unsuitable under most conditions -	over 2100

d. Stock and Wildlife Watering. Livestock and poultry may be injured by drinking water that contains excessive dissolved solids. Continuous use of such water may cause general loss of condition, weakness, scouring, unthriftiness, reduced milk or egg production, bone degeneration, and death. However, animals can drink temporarily highly saline waters that would be harmful if used continuously. Animals can also adjust gradually to the use of waters with a higher solids concentration than that which they normally drink, although sudden change from slightly to highly mineralized waters causes acute distress and diarrhea of varying severity. The limits of tolerance depend upon the kind of salts present, the species of animal, its diet, age, physiological condition, season of year, climate, etc. (282, 284, 288, 290, 640, 2398). For further details, see Chapter V, Stock and Wildlife Watering.

The following tabulation shows the reported effects of various concentrations of total salts on animals:

various co	Heartranous or	COURT BELLOS OIL COLLEGE	•
Concentra- tion in mg/l	Animals	70000	Reference
2,860	poultry	safe upper limit	282
3,000	livrestock	injurious	6.41
3,600-5,756	cattle	deleterious	643
4,000	livestock	injurious	289, 290
4,000	rats	no deleterious effect	2398
4.290	pigs	safe upper limit	282
4,546-7,369	NOMA NIPO	no harmful effect	Z91
5,000	livestock	interim threshold limit	3373
5,000	cattle	tolerated	2397
5,700	horses	satisfactory	287
	horses	thrived	2395
6,260 6,435	horses	safe upper limit	282
7,000	cattle	roduced weight	2398
7,150	dairy cattle	safe upper limit	282
7,150	cows	reduced milk production	2393
7,800	horses	safe upper limit	2395
7,865	horses	thrived	642
8,000	sheep	tolerated	2397
9,100	horses	harmful	287
9,100	cattle	lost condition	642
9,400	cattle	safe upper limit	2395
	beef cattle	safe upper limit	282
10,000 10,000	rats	deleterious	2398
10,000	white rats	toleratedloss of weight2	290, 641
10,000	livestock	loss of weight2	90, 295, 642
11,000	cows and sheep	satisfactory	287
11,400	adult dry sheep	safe upper limit	282
12,900	horses	sustained without work	642
13,500	sheep	thrived	642
14,700	farm animals, dry	satisfactory upper limit	288
15,000	lactating cows and		
15,000	mion -	injured	288
15 000	horses cattle sheep	fatal during long periods	284
15,000	sheep	safe upper limit	2395
15,600	cattle	thrived	642
18,000 18,600	sheep	thrivedused temporarily	2393
70,000	висор		

A maximum permissible concentration of dissolved solids in water of 2500 mg/l has been recommended by Tobisca (285), while Stander (3373) has suggested an interim threshold limit of 5000 mg/l. In Montana, the following arbitrary standards are used for livestock waters: up to 2500 mg/l, good; 2500 to 3500 mg/l, fair; 3500 to 4500 mg/l, poor; over 4500 mg/l, unsatisfactory (297).

e. Fish and Aquatic Life. It has been reported (310) that among inland waters in the United States supporting a good mixed fish fauna, about 5 percent have a dissolved-solids concentration under 72 mg/l; about 50 percent under 169 mg/l; and about 95 percent under 400 mg/l.

The blood of fresh-water fishes has an osmotic pressure approximately equal to six atmospheres, or about 7000 mg/l as sodium chloride, and fresh-water fish have been able to live well in sea water diluted to this level (307, 311, 313, 644). The antagonistic effects of mixtures of salts in sea water and brines makes it possible for fish to tolerate higher concentrations of individual salts in mixed than in pure solutions (307, 313, 645). In practical pollution work any effluents with an osmotic pressure greater than six atmospheres may be expected to be deleterious to fresh-water fish. Limiting concentrations of dissolved solids for fresh-water fish are not definitely known, but may range from 5,000 to 10,000 mg/l, according to species and prior acclimating (1552, 3068). The Aquatic Life Advisory Committee of ORSANCO (2414) described the many factors affecting tolerance to salinity but did not recommend limiting values.

Some fish are adapted to living in more saline waters, and a few species of fresh-water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l (646). Fish can become acclimatized slowly to higher salinities than those to which they are accustomed (644), but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil-well brines (645, 647, 648).

Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness metals. Chromates, copper, cyanides, detergents, phenolic compounds, zinc and several other substances are generally more toxic in distilled water than in hard water of high dissolved solids. For details, see the specific substances in Chapters VI and X.

Clemens et al. (3479, 3480) investigated the toxicity of brine water from oil wells toward a variety of aquatic life, both fish and invertebrates. A wide range of the median threshold toxicity values was found.

f. Shellfish Culture. Inasmuch as oysters grow in brackish waters, decreases in salinity following floods or other heavy discharges of fresh water into shellfish-growing areas have interfered with feeding, fattening, and reproduction of oysters (320, 321, 649), and have sometimes resulted in heavy mortalities (322, 650, 651, 652). Although oysters can live within a wide range of salinities, the tolerable limits of salinity differ with the species; and under unfavorable conditions changes in salinity equivalent to a density change of 0.002 (approx. 1000)

mg/l) may be significantly harmful, especially during the spawning season (316).

In the literature reviewed here the concentrations of dissolved solids in oyster-growing waters have been reported in the following different ways: (a) in terms of the density of the water (315, 316); (b) as a percentage of the salinity of sea water (320, 321, 650); (c) as grains per gallon (314); and (d) as parts per thousand or parts per million (318, 322). For the purpose of coordinating the available data on dissolved solids in water, all these types of reference have been converted, roughly, to mg/l. Density has been changed to mg/l of total solids on the basis of a sea-water density of 1.026 for 35,000 mg/l of salinity and 20°C. Sea water has been assumed to have an average salinity of 35,000 mg/l, and the conversion of percentages of salinity has been based on this figure. In the paragraph below, both the original references as given by the authors, and their approximate equivalents as mg/l are listed.

Oysters could tolerate a salinity as low as 5000 mg/l for only 20 days (322). Oysters stopped fattening at salinities below 20 percent of sea water (approximately 7000 mg/l) (321). The optimum salinity for Ostrea virginica is 25 to 29 percent (8750 to 10,150 mg/l); for Ostrea angulata, 28 to 35 percent (9800 to 12,250 mg/l) (320). Oysters are found in water with densities between 1.002 and 1.025 (2700 to 33,800 mg/l), thrive best at densities from 1.011 to 1.022 (14,800 to 30,000 mg/l) and cannot tolerate densities less than 1.007 (9500 mg/l) for more than short periods (315). The most favorable salt content of water for oyster culture is about 1800 grains per gallon (30,800 mg/l) composed largely of chlorides (314). Dissolved salts concentrations from 10,000 to 27,000 mg/l are satisfactory for oysters (318). Oysters can tolerate salinities between 20 and 50 percent of sea water (7000 to 17,500 mg/l) (319).

Oysters can withstand significant variations in salinity, living as they do in regions where such variation is normal. However, all species do not have the same salinity preference. In general the larger oysters, genus Crassotrea, prefer somewhat lower salinities than the flat oysters, Ostrea. The optimum salinity for the eastern oyster, C. virginica, and the Pacific oyster, C. gigas, is commonly said to be about 18,000 to 20,000 mg/l. The optimum for the Olympia oyster, O. lurida, seems to be somewhat higher (2415).

The gaper clam appears to be restricted to a minimum salinity of about 27,000 mg/l while the softshell clam is found almost to the fresh-water line (2417).

In his comprehensive review of the literature about oysters, Korringa (1448) pointed out that there is contradictory information concerning the influence of salinity differences on the development of oyster eggs. Some investigators think that eggs and larvae can withstand a wide range of salinities; others are equally certain that only salinities lower than that of the open sea are suitable for normal development. The salinity ranges found to be suitable for normal development have varied both with the species and the investigators.

g. Recharging Groundwater. The composition of waters stored in underground basins is affected by the source and nature of the recharge waters. Where return irrigation and waste waters are substantial contributors to recharge waters, the salinity has increased to the detriment of ground-water quality (1557). The dissolved-solids concentration of irrigation runoff may be as much as 15 times as great as that in the irrigation supply. The possibility of pollution through irrigation is now receiving wider recognition (1488, 1558).

h. Navigation. For prevention of marine borers, such as *Teredo navalis*, a total salt concentration not exceeding 5,000 mg/l is considered desirable (1486).

4. Summary. On the basis of this literature survey, dissolved solids up to the following limits should not interfere with the indicated beneficial uses:

a. Domestic water supply	1000 mg/l
b. Irrigation	700 mg /I
c. Stock watering	. 2500 mg/l
d. Fresh-water fish and aquatic life	2000 mg/d

DISTILLED WATER

(see also Dissolved Solids, Specific Electrical Conductance)

As processed water, distilled water deserves mention in this report only because solutions made up in distilled water have sometimes been used in studies of the biological effects of chemicals upon fish. The results of such experiments are not strictly comparable with those involving the use of natural or tap waters because the presence and composition of dissolved substances in water may significantly change the toxicity of many pollutants.

Distilled water is generally tasteless and may even be distasteful; dissolved minerals and gases render water palatable (653).

The effects of distilled water on fish and fish food organisms are variable (313); at times distilled water itself has been toxic to fishes (307), owing to the decrease in osmotic pressure. Solutions of copper sulfate and lead chloride have been found to be more toxic to fish-food organisms in distilled water than in tap water; the effect of mercury compounds, on the other hand, has been reported to be the same in both kinds of water (654). For the effects of copper, chromates, cyanides, detergents, phenols, zinc, and other substances in disstilled water, see the specific substance in Chapters VI and X.

DISTILLERY WASTES

(see also B.O.D., Alcohols, Soaps, Synthetic Detergents)

Schaut (362) reported that a 1:240 dilution of a distillery waste (composition or strength not specified) gave high odor, color, and turbidity; and it depleted the oxygen content by 28 percent in one hour. However, minnows exposed at this dilution for one hour showed no visible effects. The major detrimental effects of this waste, insofar as aquatic life is concerned, seem to be its high B.O.D. and its effect upon temperature in the receiving waters (3448). There is also an increase in phosphates, which may increase productivity in the stream.

DI-SYSTON

(see Chapter IX)

DIURON

(see Chapter IX)

DNQ

(see Chapter IX-Dichloronaphthoquinone)

DODECYLACETAMIDODIMETHYLBENZYL AMMONIUM CHLORIDE

(see Chapter X)

DOWPON

(see Chapter IX)

DUPONOL 80

(see Chapter X)

DYES

(see also Nigrosine, Aniline, Chromates)

A complete description of the various types of dyes and their effects upon the color and turbidity of receiving waters is beyond the capacity of this survey. Certain dyes are known to be toxic to bacteria, aquatic organisms, and plant life. In fact, dyes have been used for weed killers and bacterial disinfectants, The following references were uncovered in the course of this survey, but the reader should recognize that these few brief comments only touch on the fringes of a potentially huge field of research.

Dyes used in the textile industry are frequently classified as direct, acid, basic, sulfur, vat, and miscellaneous dyes. The direct, acid, and basic dye wastes are all highly colored and commonly have a higher B.O.D. than that of domestic sewage (1097).

Direct dyes are readily soluble and can be used without a mordant. Where they are used, mordants and adjuvants may prove to be more toxic than the dye itself (611). Used mostly on cotton, rayon and vegetable fibers, direct dyes are azo compounds and are frequently derivatives of benzidine and tolidine. Because of their great solubility, direct dyes are difficult to remove from industrial wastes (1097).

Acid dyes, used on animal fibers such as wool, are salts of color acids and are also azo compounds of benzidine and tolidine. Basic dyes are salts of color bases capable of dyeing animal fibers directly but requiring a tannin mordant for vegetable fibers. Derived principally from analine and its homologues, basic dyes are mainly triphenylmethane dyes.

Sulfur dyes, so called because they comprise sulfur compounds and are used in conjunction with sodium sulfide in the dye bath, are used exclusively on vegetable fibers. They are difficult to treat and their effect upon streams is frequently quite detrimental. Vat dyes are those that acquire their dyeing properties as a result of the reducing action in the dye vat just prior to dyeing. Vat dyes are reduced to a soluble form in the vat by means of a strong reducing agent such as hydrosulfite in conjunction with an alkali. They are generally used with cotton and they may be anthracene, indigo, or carbozol compounds.

The amount, strength, and character of a dye waste from a textile or paper mill depends on the way in which the dye is applied and how often dyes are changed in the operation of each process. When dyes are changed, vats must be dumped and cleaned. At other times, the wastes consist only of the uniform flow of rinses and wash waters (1097).

Dyes in water are detectable to the naked eye at very low concentrations, such as 0.025 mg/l for fluorescein

and 0.02 mg/l for magenta (1756).

Despite the fact that dyes are used extensively in industry and despite the fact that numerous references state that dyes are toxic substances, relatively few specific references dealing with the toxicity of dyes were uncovered in this survey. Schaut (632) found that sulfur-black dye wastes, diluted 1:240 with stabilized tap water, had no noticeable effect on minnows during a one-hour exposure. Wright (1162) used Dye 914, a flavine dye, to inhibit or destroy sulfate-reducing bacteria, in a concentration of 4.0 mg/l.

A lagoon that was used to receive and treat wastes from an ink-pigment manufacturing plant in Pennsylvania broke and discharged its entire contents quickly into a small stream. Dyestuffs used in this plant comprised tobias acid, metanitroparatoluene, eosin, methyl violet, erioglaucine, dichlorobenzedine, rhodamine, brilliant green, Victoria blue, paranitroaniline, and Orange II. Many inorganic salts were also used, but the commonly suspected toxic chemicals were not used. The sudden shock load of wastes killed a great number of fish in the creek, but considering the B.O.D. load and the available dilution, it could be shown that deoxygenation alone would account for the fish deaths. Some of the distressed fish were taken from the stream, kept in clean water and later returned to the stream with apparently no ill after-effects. It was suspected, therefore, that the aforementioned wastes were not directly toxic to fish (7).

Clemens and Sneed (2979, 2981) found the 24-, 48-, and 96-hour TL_m values of Malachite green (zinc oxalate of tetramethylpara-aminotriphenylcarbinol) at 25°C all to be 0.14 mg/l toward fingerling channel catfish. With the dye "Luxantholschwarz G," Lodemann (3449) reported that small guppies were harmed at a concentration of 5 mg/l but for carp, the threshold of harmful effect was 75 mg/l. On the other hand, 100 mg/l of eosin, fluorescein, or uranin (dyes widely used as tracers) were found to be non-toxic to trout and roach (3236).

Experiments in Germany prior to 1900 using tench primarily and carp occasionally led to the results shown in the following table (2977):

Duestuff	$Concentration \ in \ mg/l$	Exposure in days	Effects On Fish
Methylene blue	177.5-217.5	7	lethal
Methylene blue	57.5-157.5	7	lethal
Diamineazobenzene	5.0	0.3	lethal
Bismark brown	8.0	4	lethal
Bismark brown	5.0	4	no effect
Martius yellow	85	4	lethal
Martius yellow	57.5	4	no effect
Indigo blue	471.5	5	no effect
Naphthol black	150	. 3	no effect
Wool black	150	3	no effect
Diamond fuchsin	125	14	no effect
Metanilic yellow	120	14	no effe ct
Congo red	110	5	no effect
Azoarchil	100	4	 no effect
β-naphtholorange	100	14	no effect

Dyestuff	Concentration in mg/l	Exposure in days	Effects On Fish
Naphthol green	100	3	no effect
Dinitrocresol	80	3	no effect
Dinitroresorcinol	80	6	no effect
Diazotobenzide salicylate	60	š	no effect

Bringmann and Kuhn (2158) tested the toxicity of three dyes to Daphnia exposed for two days at 23°C and Scenedesmus for four days at 24°C. Threshold effects were noted at the following concentrations:

	$Threshold\ Concentration,\ mg/l$		
Dye	Daphnia	Scenedesmus	
Congo red	4	0.6	
Fuchsin	20	1.0	
Methylene blue	2 ·	0.1	

EDTA

(see Ethylenediaminetetraacetic Acid)

EMCOL-888

(see Chapter X)

EMULSIFIERS

(see Chapter X)

EMULSIN

(see also Amygdalin)

This carbohydrase is an enzyme that specifically hydrolyzes beta glucosides, such as amygdalin. Schaut (362) reports that 17.1 mg/l of this substance in stabilized tap water was not harmful to minnows during 24 hours of exposure, but the dissolved-oxygen content of the water was lowered 41 percent.

ENDOTHAL

(see Chapter IX)

ENDRIN

(see Chapter IX)

EPN

(see Chapter IX)

ETHYL ALCOHOL

 C_2H_5OH

Industrial ethyl alcohol, produced largely by fermentation of molasses, is widely used in industry, as a starting material for the manufacture of many organic substances, for perfumes, flavors, and drugs; in beverages; for paint and varnish; for fuel; and for many other common purposes. It is a clear, colorless, flammable liquid with a pleasant odor and a burning taste. It is highly miscible with water and many organic liquids. The acute oral toxicity toward rats has been given as 7.4 mg/kg of body weight (3248).

Fish and other aquatic life can apparently withstand high concentrations of ethyl alcohol but, like humans, fish become intoxicated by it. Ellis (313) quotes references to the effect that tench survived a two-hour exposure to 10,000 mg/l in tap water, without injury; but Jones (467) reports that stickleback fish will avoid such a concentration. If forced to remain in tap water containing a 40,000 mg/l of ethyl alcohol, sticklebacks be-

come intoxicated. For gudgeon, a European fresh-water fish, the lethal range is reported (2977) to be 7000 to 9000 mg/l. In contrast, it is interesting to note that only 250 mg/l of ethyl alcohol in distilled water killed goldfish in 6 to 11 hours (313). It is probable that the effect in this instance was attributable to the changes in osmotic pressure when the fish were placed in pure water, i.e., the alcohol may have had no influence.

Toward other aquatic life, ethyl alcohol is similarly toxic only in high concentrations. Anderson (358) showed that the threshold concentration for immobilization of Daphnia magna after prolonged exposure in Lake Erie water at 25°C was 18,400 mg/l. A concentration of 198,000 mg/l was required to stimulate the movement of the water beetle (2956). The following threshold concentrations were reported for organisms in Lake Erie water at 20 to 25°C: Daphnia magna (young), 7,800 mg/l; Daphnia magna (adult), 12,100 mg/l; and Mesocyclops leuckarti, 12,000 mg/1 (2955).

ETHYLAMINE

 $C_2H_5NH_2$

This flammable liquid is miscible with water, producing an ammoniacal odor and an alkaline reaction, probably from its dissociation and the formation of ammonium ion. It is used in oil refining, organic synthesis, and the manufacture of synthetic rubber, dyes, and pharmaceuticals (364). The oral LD_{50} for rats has been

reported as 400 mg/kg of body weight (2978).

Gillette et al. (1442) found that all creek chub, a fish of average tolerance, in well-aerated water at 15-21°C withstood 30 mg/l of ethylamine for 24 hours but all died at 50 mg/l. The approximate 24-hour TLm was about 40 mg/l. Shelford reported that 400 to 800 mg/l in tap water killed orange-spotted sunfish in one hour (313, 363). According to Bringmann and Kuhn (2158, 3343) the toxic threshold for Daphnia during a two-day exposure at 23°C was 140 mg/l, for Microregma it was 40 mg/l, but for Scenedesmus at 24°C for 4 days it was only 10 mg/l. A concentration of 1000 mg/l had no apparent effect on Escherichia coli at 27°C.

ETHYLENE

 $CH_2 = CH_2$

This colorless, flammable gas is prepared commercially from petroleum gases or by dehydration of alcohol, and it occurs naturally in ripening fruit and illuminating gas. It is used to ripen the color of fruits, and in the manufacture of plastics, alcohol, mustard gas, ethylene oxide, and other organics. Shelford (363) reports that orange-spotted sunfish were killed in one hour by a concentration of 22 to 25 mg/l, while Gutsell (463) gives lethal concentrations of 22 to 65 mg/l in an hour or longer.

ETHYLENEDIAMINE

 $\mathrm{NH_{2}CH_{2}CH_{2}NH_{2}}$

Freely soluble in water, this strong alkaline liquid forms a hydrate in water. By dissociation it reacts to form ammonium ions and to raise the pH. It is used industrially as a solvent and emulsifier. The oral LD_{50} in rats is reported as 1.16 grams/kg of body weight.

According to Gillette et al. (1442) the critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 30 to 60

According to Rohlich and Sarles (759), the halogenation of an aromatic series markedly influences tastes and often a change from sweet to bitter is effected. Benoclor, a trade product consisting of a mixture of the nonemulsifiable forms of mono-, di-, and trichlorobenzene, is used in high-pressure subsurface sprays to control aquatic vegetation. It is reported by Goudey (897) to have a pungent odor but to have no physiological effect on humans at odoriferous concentrations.

Straus (890) reports that more than 500 mg/l of Benoclor in water is required to injure crops. According to Goudey (897), Benoclor is toxic to fish, crayfish, and clams, but concentrations are not given. The toxic dose of Benoclor for sheep is 2666 mg/l, according to Straus (890) but the taste is so bad that animals will avoid the

water.

HALOGENATED PHENOLS

1. General. Chlorine, iodine, and bromine have been introduced into the phenol molecule in various manners to produce compounds with toxicities differing markedly from that of phenol. Iodophenols appear to be more toxic than chlorophenols or bromophenols, and of the iodophenols, the para compound is most toxic and the meta the least (613).

2. Cross References. Phenois, Pentachlorophenols, Halogenated Hydrocarbons, Chapter IX.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The chlorination of water supplies containing traces of phenol results in medicinal tastes (see Phenols). The type of chlorophenol formed depends on the concentration of chlorine and phenol, upon temperature, and upon catalytic agents. Rohlich and Sarles (759) quote references to the effect that chlorine in doses up to 0.1 mg/l did not produce odor in water containing up to 0.015 mg/l of phenol. The critical range for chlorophenol tastes was for chlorine dosages from 0.175 to 0.4 mg/l with phenol from 0.002 to 0.017 mg/l. A combination of 0.22 mg/l of chlorine with 0.007 mg/l of phenol caused a strong chlorophenol odor, but heavier dosages of chlorine eliminated the odor.

Several investigators have reported the taste or odor threshold concentrations for various chlorinated phenols. Their results have been summarized and tabulated

helow:

perom:		
	Taste (t) or Odor (d) Threshold	
C	$Concentration \ in \ mg/l$	Reference
Compound o-chlorophenol	.00033 (d) at 30°C	2982
0-cmozopasa	.0001 (t) .002 (d) at 25°C	459 3493
	.0025 (d) at 60°C	2982 3493
	.004 (t) at 25°C	2059
m-chlorophenol	.100 (d) at 60°C	2982 2982
-	.200 (d) at 30°C .900 (t)	2059
	1.0 (t)	459 2982
p-chlorophenol	.033 (d) at 30°C .1204 (d)	3494
	.143 (d) at 60°C	2982 3493
	.250 (d) at 25°C 1.0 (t)	459
	1.35 (t) >1.0 (t) at 25°C	2059 3493
	> = (0) =	

Compound	Taste (t) or Odor (d) Threshold Concentration in mg/l	Reference
2. 4-dichlorophenol	.00065 (d) at 30°C	2982
z, 1-dictiorophenor	.002 (d) at 25°C	3493
	.0065 (d) at 60°C	2982
•	.008 (t) at 25°C	3493
	.02 (t)	459
2, 5-dichlorophenol	.00045 (d) at 60°C	2982
2, 0 didn-01 vp-02-1	.0033 (d) at 30°C	2982
2. 6-dichlorophenol	.002 (t) at 25°C	3493
z, o didziologicz	.003 (d) at 25°C	3493
2, 4, 5-trichlorophenol	.011 (d) at 30°C	2982
-, -, -,	.333 (d) at 60°C	2982
2, 4, 6-trichlorophenol	.10 (d) at 30°C	2982
-, -, 1	.667 (d) at 60°C	2982
	>1.0 (d) at 25° C	3493
	>1.0 (t) at 25°C	3493
trichlorophenol (undesignated)	1.0 (t)	459
2, 3, 4, 6-tetrachlorophenol	.915 (d) at 30°C	2982
-, -, -,	47.0 (d) at 60°C	2982
pentachlorophenol	.857 (d) at 30°C	2982
-	12.0 (d) at 60°C	2982

According to Chamberlin and Griffin (1576) concentrations as low as 0.001 mg/l of mixtures of o-chlorophenol, p-chlorophenol, and trichlorophenol can sometimes be detected in drinking water, and the presence of these compounds may be detrimental to certain industries, such as the manufacture of paper food containers.

- b. Industrial Water Supplies. Halogenated phenols produce tastes and odors in many of the food and beverage industries (179, 223, 225). See Chapter V for more details.
- c. Stock and Wildlife Watering. The oral LD50 for male rats fed 2, 4, 5-trichlorophenol was 2.96 grams per kg of body weight (3490). There was no evidence of adverse effects in rabbits fed 500 mg/kg of body weight or in rats fed 300 mg/kg. McCollister et al. (3490) conclude that this material is not likely to present a health hazard from ingestion.
- d. Fish and Other Aquatic Life. The 96-hour TL_{m} of o-chlorophenol for bluegill fingerlings was found to be 8.4 mg/l. According to Gersdorff and Smith (939), ortho-, meta-, and para-chlorophenols are slightly less toxic to goldfish than is phenol itself, as shown below:

Compound phenol o-chlorophenol m-chlorophenol p-chlorophenol	Relative Products of Concentration and Killing Time 1.00 1.15 1.51 1.89
--	--

In concentrations as low as 0.1 mg/l, chlorophenols may impart a taste to the flesh of fish (656), Henderson et al. (2958) report that 2.0 mg/l of o-chlorophenol gave a taste to the flesh of adult bluegills.

At a concentration of 10 mg/l, 95 to 100 percent of the snails (Australorbis glabratus) that are the intermediate host of Schistosoma mansoni were killed by 2, 4, 6-triiodophenol and its sodium salt, by 2, 4, 6-tribromophenol, by pentabromophenol, and by sodium and copper pentachlorophenates, according to Berry et al. (975).

Applegate et al. (3491) tested several halogenated mononitrophenols against the larvae of sea lamprey and also against three fresh-water fish. Results were as follows:

to 300 lbs of ammonium sulfate per acre; but the liquor must be free of oils and tar, and low in thiocyanates.

GELATIN

(see also Biochemical Oxygen Demand)

This protein, obtained by boiling skin, tendons, ligaments, and bones in water, is used extensively for food products, adhesives, medicines, plastics, and in numerous other ways. Apparently its only detrimental effect in water is its oxygen utilization in decomposition. Schaut (362) reported that 17.1 mg/l in stabilized tap water was not harmful to minnows after 24 hours of exposure, but it lowered the dissolved-oxygen content of the water by 57 percent.

GERMANIUM

Ge

This trace mineral, relatively unimportant until recently, is finding increasing use in industry, especially in electronic devices. It is employed in the manufacture of the semi-conductor triode which consists of a small germanium crystal with three electrical contacts. Germanium is also used in metallurgical processes and in electroplating (364, 2121).

Germanium is present in many soils in trace amounts and it may be picked up by certain forms of vegetation. There is no evidence, however, that germanium is an essential element for plant or animal nutrition. It does not accumulate in animal systems. Although it is readily assimilated it is rapidly excreted in the urine (2121, 2129).

Elemental germanium, the oxide, and the sulfide are relatively non-toxic and pharmacologically inert (2129). Food containing 100 mg/kg or water containing 100 mg/l of neutralized germanium oxide caused some inhibition in the growth of rats and a 50 percent mortality in four weeks (3489). Animals that survived beyond four weeks were able to continue such dosages with ill effects.

GIUTHION

(see Chapter IX)

GLYCERIN

(see Glycerol)

GLYCEROL

CH2OHCHOHCH2OH

A syrupy liquid with a sweet warm taste, glycerol (commonly called glycerin) is miscible with water and alcohol. It is used extensively in food production, printing inks, glues and cements, textile printing, antifreeze and shock absorber fluids, dynamite, and over 1500 other processes (364). In natural waters it appears to exert no inimical effect other than an oxygen demand arising from decomposition. Ellis (313) quotes references to the effect that tench survived a 16-hour exposure to 100,000 mg/l of glycerol in tap water at 8°C without apparent harm.

GLYERCOL MONOLAURATE

(see Chapter X)

GOLD

Au

Widely distributed in nature, gold occurs in trace quantities in many rocks, in sea water, and in copper, lead, zinc, and other ores. The pure metal is extremely inactive, and insoluble in water. A few gold salts are soluble in water, but owing to the fact that the hydroxide, monochloride, monoxide, and several other combinations are insoluble, gold ions are not likely to be found in natural waters. Gold salts are used in photography, for electrogilding, for painting on porcelain and glass, and for therapeutic purposes. Because it has a short half-life and seeks out certain organs of the body, colloidal radioactive gold has been used for the treatment of internal cancer in humans. Gold salts have also been used in the treatment of arthritis (364, 2129).

According to Jones (2941), the lethal concentration limit of gold ions to the stickleback is 0.40 mg/l.

GOLD TRICHLORIDE, ACID

(see Chloroauric Acid)

GREASE

(see Animal and Vegetable Oils, Oil-Petroleum)

GROUNDWOOD PULP MILL WASTES

Wastes from mechanical or groundwood pulping consist chiefly of finely divided spruce, balsam or poplar that escape in the processes of disintegration. Very little dissolved organic matter occurs in these wastes and hence their B.O.D. is low. According to Westfall (673), however, a finely divided wood, like pine, gives a grinding effluent that is toxic to aquatic organisms (see also Sawdust). This waste blankets stream beds, covers spawning beds, and promotes the growth of undesirable fungi and bacteria in harbors. Pulp that has been pretreated with steam leaves toxic soluble substances in the effluent. Young fish often become tangled in mats of fine wood pulp and even adult gills are affected. (For a contrary opinion, see Sawdust).

GUAIACOL

 $\mathrm{CH_3OC_6H_4OH}$

This white or slightly yellow crystalline substance, a methylcatechol, is obtained from guaiac resin or from hardwood tar. It was formerly used for chronic infections of the respiratory tract but it may cause gastrointestinal irritation (364). It is moderately soluble in water.

According to Hoak (2982, 3403), the odor threshold of guaiacol in hot water (60°C) is 0.0025 mg/l and in warm water (30°C) it is 0.002 mg/l. The killing strength of guaiacol to perch is reported to be 70 to 80 mg/l (365). Toward ciliated protozoa it is given as 1520 mg/l (2904).

GYPSUM

(see Calcium Sulfate)

HALOGENATED HYDROCARBONS

There are numerous halogenated hydrocarbons for which the literature reports detrimental effects to benefical uses of water. Most of these compounds are covered elsewhere in this chapter or in Chapter IX as pesticides. containing 400 to 1600 mg/l of formaldehyde, finding

such solutions to be irritating (467).

Toward lower organisms, Bringmann and Kuhn (2158, 3343) reported the median threshold effect of formaldehyde toward Daphnia occurred at 2 mg/l during a twoday exposure at 23°C. Toward Scenedesmus held for 4 days at 24°C, it was 0.3 mg/l, toward Microregma 5.0 mg/l, and toward Escherichia coli at 27°C it was 1.0 mg/l. Gellman (3485) indicated that the toxic concentration of formaldehyde toward aerobic organisms lay between 130 and 175 mg/l while Hermann (2923) found that 740 mg/l inhibited oxygen utilization by 50 percent. It is possible, however, to develop cultures of aerobic organisms that will withstand formaldehyde concentrations of 265 mg/l (660) and 1500 mg/l (3485).

The Mersey River Board in England (2950) has established working standards for sewage and industrial effluents that limit the formaldehyde content to 1.0 mg/l.

FORMIC ACID AND FORMATES

HCOOH

(see also Fatty Acids)

Formic acid is a colorless liquid with a pungent odor. A strong reducing agent, it is dangerously caustic to the skin. It is used as a decalcifier, as a reducer in dyeing wool-fast colors, for dehairing and plumping hides, in tanning, in sizes, and in rubber processing. Sodium formate, HCOONa is used in dyeing and printing operations in textile mills. According to Anderson (352), the threshold concentration of sodium formate for immobilization of Daphnia magna in Lake Erie water at 25°C, after 48 hours of exposure, was approximately 4700 mg/l. This substance is probably toxic only when present in sufficient concentration to exert unfavorable osmotic pressure.

Concentrations of 20,000 mg/l of formic acid or 40,000 mg/l calcium formate in the drinking water of guinea pigs for 30 days caused no apparent changes in growth, blood, or urine (2980). The oral LD50 of formic acid for dogs is given as 4 gm/kg of body weight (3486).

Toward Daphnia, the median threshold concentration of formic acid was 120 mg/l for a two day exposure at 23°C; and toward Scenedesmus 100 mg/l in 4 days at 24°C (2158). A concentration of 1000 mg/l of formic acid had no effect on E. coli (2158) but 550 mg/l inhibited the 5-day BOD of sewage by 50 percent.

FURFURAL

C4H3OCHO

This colorless oily liquid aldehyde, soluble in water, is used in the manufacture of plastics, as a solvent in petroleum refining, in the manufacture of varnishes, and as an insecticide, fungicide, and germicide (364). The oral LD₅₀ for dogs is 2.3 grams/kg of body weight. In the drinking water of albino rats, 10,000 to 50,000 mg/l proved to be lethal in 114 to 548 days (2980). The odor threshold has been reported (2058) as 4 mg/l, above which a musty odor is evident.

Toward the bluegill sunfish, Turnbull et al. (2093) found the 24-hour TL_m to be 32 mg/l at 20°C and the 48-hour TL_m was 16 mg/l. In highly turbid water at 23-24°C, Wallen et al. (2940) reported the 24hour TLm as 44 mg/l whereas the 48- and 96-hour TLm values were both 24 mg/l. According to Ettinger et al. (3487), biochemical degradation of furfural is rapid in rivers seeded with the proper organisms as a result of previous furfural pollution, with up to 25 mg/l disappearing in 5 to 8 days.

GALLIC ACID

 $C_6H_2(OH)_3COOH$

This light-colored, odorless, crystalline solid is used in the manufacture of pyrogallol and ink dyes, as a photographic developer, in tanning, and in analyses. Ellis (313) quotes references to the effect that gallic acid killed goldfish and minnows at a concentration of 143 mg/l. According to LeClerc et al. (2942, 2943), the minimum lethal dose for minnows at 21°C was 30-35 mg/l in hard water and 15-20 mg/l in distilled water during a six-hour exposure.

GAMLEN CW

(see Chapter X)

GAMMEXANE

(see Chapter IX-Benzene Hexachloride)

GASOLINE

(see Oil, Petroleum)

GAS-PLANT WASTES

(see also Ammonia, Cyanides, Hydrogen Sulfide, Phenol, Benzene, Halogenated Hydrocarbons, Halogenated Phenols)

Gas liquors may be detrimental to receiving waters as a result of (a) high B.O.D. (b) direct toxic action of some of the constituents, and (c) tastes and odors (346). The effects of individual substances that may occur in gas-plant wastes are given elsewhere in this report.

As early as 1917, Shelford (363) reported that illuminating gas, gas liquor, and 31 out of 34 representatives of chief groups of compounds found in gas and gas liquors were very toxic to fishes, in concentrations varying from 1.0 to 1500 mg/l. He noted that fish appear to develop a preference for gas-polluted water and are lured into it, only to be harmed. According to Allen et al. (668), the chlorinated effluents of sewage-treatment plants that contained gas-plant wastes were harmful to fish although the unchlorinated effluents were not. It is possible that cyanogen chloride was formed in such effluents.

Wastes from gas works had the following effects upon fish, as recorded by Knight (540).

	· ·	
Percent of Waste By Volume	Type of Fish	Time of Kill
5.0 2.0 0.5	perch perch perch	20 minutes 30 minutes 12 hours
0.5	stickleback	10 days

Schaut (362) found that minnows could possibly tolerate for short periods a 1:2400 dilution of gas liquors from cyanogen scrubbers, but they lost equilibrium after 15 minutes. At a dilution of 1:240 there was a 50 percent mortality after one hour. At this dilution, the water was black, opaque, and strongly odoriferous.

Silcox (3488) reported that the ammoniacal liquor from gas works can be used directly as a fertilizer in agriculture, with 400 gallons (Imperial) being equivalent c. Irrigation Water. Concentrations of fluoride likely to be found in natural waters or in polluted streams apparently will have no detrimental effects on plants. Moreover, fluoride added to soil or water has little or no effect on the fluoride content of plants grown in such soil (1049, 1182, 3457). At high concentrations, fluoride has been reported to produce the following effects:

Uoncentration	. of	
Fluoride, mg		Reference
10	No injury to peach, tomato and buckerhood	t
100	Peach and buckwheat plants severely injured	3458
100-500	Inhibited sprouting of boons	3458
200	time peach, tomato, and buckwheat in short	:
360	INJURIOUS to peach and buckwheat even at nu	3458
	6.5Stunted growth of large bean plants	

The use of fluoride-bearing insecticides appears to cause no harmful concentrations of fluoride in the soil moisture (1182).

d. Stock and Wildlife Watering. The effects of fluorides in drinking water for animals is analogous to those for humans. Table 6-6 lists the reported effects as reported in the survey literature, and indicates that 1.0 mg/l appears to be the threshold value below which no harm results. It is interesting to note that the addition of fluorides to a cow's ration or drinking water had no influence on fluorides in the milk (1181, 1188), and doses of 500 mg/l in the drinking water did not increase the milk fluoride above 0.5 mg/l (1186).

REPORTED EFFECTS OF FLUORIDES IN DRINKING WATER FOR LIVESTOCK

_ Fluoride	g			
Concentrat	tion			
$in\ mg/l$	Dose	Animal	Remarks	Reference
1.0		cattle	harmless	100,000
1.0		sheep	fluoride poisoning	_ 292
1.4-4.5		mice	mottling of teeth_	1183
	0.4 mg per kg	cattle	no mottling	3460
	1 mg per kg	rats	mottled teeth	353
	1 mg per kg	cattle	mottled teeth	- 353
	3 mg per kg	cattle	bone damage and	1190, 3462
	3 . 3	Outlie	doeth	0-0
	5 mg	dogs	death gave hypotension_	353
4.0		sheep	mottled and pitted	3461
		элсер	teath and pitted	
5.0		cows	teeth disliked water	1184
5.0		sheep	slight dental mot-	3457
		p	tling dentat mot-	,
6 to 16		hogs et	tling c. severe mottling	1571
11.78		cows	mottled teeth	1005
15	_	mice	affected thyroid and	1178
			kidney	0.100
18		cows	slowly increasing	3460
			fluorosis	7100
20		sheep	5 707044	1190
	2	ынсер	5 percent reduction	
25-100		Tour	in weight	1571
		young catrle	4. 45 5 4	
44-61	•		recent reprofits	3464
01		sheep	chronic fluoride	
50			poisoning	1184
		hamster	s dental fluorosis in	
55			10 weeks	1185
บอ		cows	disliked such water	~100
			and drank less	1186
	60 mg per day	sheep	affected teeth and	1100
	_		bones	1187
	65 mg per day	dogs	no effect on organs	
	120 mg per day	sheep	threshold for	3452
		~~~	threshold for gen-	
	200 mg per kg	rabbits	eral health	1187
100			lethal dose	353
-		cattle	no economic harm_	3463

e. Fish and Other Aquatic Life. Fluoride ions appear to have direct toxic properties toward aquatic life, and in addition there seems to be a relationship between the fluorides in water and the condition of the teeth of

the fish (1189). The following effects of fluorides on fish have been reported:

Concentration of Fluoride, mg/l	Salt used	Type of fish	Effect	Reference
1.5 2.3-7.3 2.6-6.0 2.7-4.7 5.9-7.5 7.7 64 75-91 100 120 358 419 678 1000	Naf Naf Naf Naf Naf Naf Naf	eggs trout trout trout trout trout minnows earp goldfish goldfish rainbow trout moequito-fish Tinca rulgaris goldfish goldfish	alower and poorer hatching TLm at 18°C. in soft water. TLm at 18°C. in soft water. TLm at 7.5°C. in soft water. TLm at 7.5°C. in soft water. 10-day TLm TLm survived over 4 days. killed in 4 days. toxic in soft water. 96-hour TLm in turbid water. lethal dose. killed in 12 to 29 hours in soft water killed in 60 to 102 hours in hard water.	247 3465, 346 3465, 346 353 2407 3467 353 3468 1756 2940 3271 353 353

For toxicities toward lower aquatic organisms, see Sodium fluoride.

4. Summary. On the basis of the foregoing information, it appears that the following concentrations of fluoride will not interfere with the specified beneficial uses:

a.	Domestic water supply	202-10 -
b.	Industrial water supply	0.7 to 1.2 mg/i
c.	Irrigation water	1.0 mg/l
d.	Stock watering	10.0 mg/l
	Stock wateringAquatic life	$1.0  \mathrm{mg/l}$
٠.	Addatte me	15 mg/l

# FORMALDEHYDE

нсно

This simple aldehyde is formed by the oxidation of methyl alcohol by air in the presence of metallic silver or copper at high temperatures (300°C). It results also from the incomplete combustion of many organic substances and is found in the atmosphere over cities. It also occurs in some tannery wastes, penicillin wastes, and effluent from the manufacture of plastics and resins. At ordinary temperatures it is a colorless, flammable gas with a pungent suffocating odor, and it is intensely irritating to mucous membranes. It is very soluble in water, and a 37-40 percent solution in water is sold as "formalin". Because of its toxicity to lower forms of life, formaldehyde is used for preserving biological specimens.

The odor of HCHO is reported to be detectable at 50 mg/l (2983) and also at 20 mg/l (3483). The oral  $\rm LD_{50}$  for rats is given as 800 mg/kg of body weight (3484).

In a concentration of 10 mg/l, formaldehyde had no apparent effect on rainbow trout in three days but 50 mg/l killed them in one to three days of exposure (659). For killing shiners in 120 hours at 18°C, the minimum lethal concentration was also 50 mg/l (190, 344). In stabilized tap water saturated with oxygen, minnows were harmed by a short exposure to 146 mg/l (362). For rainbow trout, the critical level of formaldehyde was reported (2091) as less than 31.8 mg/l and for young chinook salmon less than 28.2 mg/l. Clemens and Sneed (2979, 2981) investigated the toxicity of formalin (37 percent formaldehyde by weight) toward fingerling channel catfish. They found the 24-hour TL_m to be 32 mg/l as formaldehyde while the 48- and 96-hour  $TL_m$ concentrations were 25 mg/l. All fish survived at 18 mg/l as formaldehyde. If they are given a chance to do so, during short-term exposure, fish will avoid solutions

ion in drinking water to aid in the reduction of dental decay, especially among children. A review of such treatment processes is not relevant to this report, but it is significant to note that the presence of about 1.0 mg/l of fluoride ion in natural waters may be more beneficial than detrimental.

There is evidence to support the contention that fluorides in excess of the threshold for mottling of teeth and up to 5 mg/l produce no harmful effects other than mottling (1463, 1564, 1566). Radiologic surveys of 114 persons who had lived for over 15 years at Bartlett, Texas where water had 8 mg/l of fluoride revealed minimal evidence of an increase in density of bones of only 12 percent of those examined, but in no case was there found any interference with the use of bones or joints. Comparisons of mortality rates from nephritis, heart disease, or cancer in high or low fluoride areas has failed to show an association of these diseases with the fluoride content of water (1563, 1564). It has been estimated that daily intakes of about 15-20 mg of fluoride over a period of several years are required to induce chronic fluorosis in an adult man (1567).

The taste of sodium fluoride is salty, but less so than sodium chloride. A solution of sodium fluoride at a concentration of 2.4 mg/l of fluoride can be distinguished from distilled water (1568).

Shay (729, 730) used statistical evidence to show that the incidence of poliomyelitis is lower in districts where the surface waters contain over 1.0 mg/l of fluoride than in areas where the fluoride content is lower. Fellenberg (1163) investigated the correlation between goiter incidence and fluoride in the drinking water, but reached no definite conclusions.

The USPHS Drinking Water Standards (2036) of 1962 set a mandatory limit on fluorides that is based on the annual average of maximum daily air temperatures in accordance with the following table. It is reasoned that children drink more water in warm climates and hence the fluoride content of the water should be lower to prevent excessive total fluoride consumption (1563, 1564, 1565).

Annual Average of Maximum Daily Air Temperatures, °F		Recommended Control Limits of Fluoride Concentrations, mg/l		
Daily An 1emper	usan ous, I	Lower	Optimum	Upper
50.0-53.7 53.8-58.3 58.4-63.8 63.9-70.6 70.7-79.2 79.3-90.5			1.2 1.1 1.0 0.9 0.8 0.7	1.7 1.5 1.3 1.2 1.0 0.8

The WHO International Drinking Water Standards (2328) of 1958 do not set a limit on fluoride concentration, but the WHO European Drinking Water Standards (2329) of 1961 prescribe a recommended limit of 1.5 mg/l.

# TABLE 6-5 REPORTED EFFECTS OF FLUORIDES IN DRINKING WATER FOR HUMANS

	WATER FOR HOWARD	
Concentration of Fluorides, in mg/l	Reported Effect R  Mottled teeth in 1 percent of children No effects at this concentration, or lower	eference 1164 555
0.6 0.7	Mild dental fluorosis in 8.5 percent	
0-8	No effects at this concentration, or lower	1165
0.8 to 0.9 0.8 to 1.5	Threshold for mottling of teeth	219

Concentration of Fluorides, in mg/l	Reported Effect Reference
0.9	assid mottling of teeth 1165, 1167
0.9	Mattling accurred as a result of
	high water use 353 Critical concentration for mottling 555, 1168
0.9	Critical concentration for mottling 555, 1106
1.0	Threshold for mottling of teeth 741
1.0	10 percent of children had mottled teeth 1169, 1164 90 percent of children had 1170
	mottied teetii 1200,
. 1.0	
1.0 to 2.0	
1.0 10 2.0	
1.4	No skeletal schlerosis loung
1.5	Limiting concentration for
<del>_</del>	Limiting concentration for drinking water
1.7 to 1.8	50 percent of children nad
	mottled teeth real weakening of
2.0	tooth structure 1172
0.04-0.0	
2.0 to 3.0 2.0 to 3.0	
2.0 to 3.0	75 to 80 percent children
2.9	had mottled teeth 555, 1169
2.5	75 to 80 percent children had mottled teeth No evidence of skeletal fluorosis 3452
3 to 4	
3 to 6	Gave severe mottling 1165
3.5 to 6.2	No adverse effect on carpol bones of children 3453
4.0	as managet of children had mottled teeth 1164
4.0	No dicordary other mail nement motivities of the
4.0 4.4 to 12	
4.4 (0 12	Caused chromic nuorosis and altected skeletal system 1175, 1176 This concentration had no effect on
5.0	This concentration had no effect on
6.0	
6.0	100 percent of children had mottled teeth 1164
6.0	Gave pitting and chipping of tooth enamel1165
8.0	3490
10	
11.8	Cove abronic fluoring infoxication
11.0	40 ndvilta 1110
12	Affects deciduous teeth 1179
13.7	100 percent of children had
_	
115	Sub-lethal in drinking water 152 Toxic to man in drinking water 555
180	Lethal dose in drinking water 152
. 2000	richiai dose in dimining massi-

b. Industrial Water Supplies. Excessive fluorides may be harmful in certain industries, particularly those involved in the production of food, beverages, pharmaceutical and medical items, according to Bratton (1569). If wet milling of corn is carried on with water containing one mg/l of fluoride, it is estimated that the concentrated steep water will contain more than 6 mg/l and the corn syrup more than 5 mg/l. Malt syrup made with similar water may contain up to 8 mg/l of fluoride. Weir (1570) points out that fluoride up to 10 mg/l in dough water has no effect on bread, that one mg/l stimulated the yeast fermentation of malt, that 10 mg/l may stimulate or depress yeast fermentation, and that 25 mg/l inhibits yeast activity.

In brewing, fluoride concentrations of 1 to 5 mg/l appear to stimulate yeast metabolism. Continued re-use of yeast in wort containing 10 mg/l of fluoride results in severe deterioration after six fermentations (2349). Concentrations of fluoride permissible in domestic water should have no deleterious effects on brewery processes

(2348).

Fluoride concentrations of 1.0 mg/l caused no change in the amount or rate of corrosion of iron, copper, or lead (3482). Fluoride limits have been recommended for some industrial processes, as described in Chapter V and tabulated below:

	Recommended Threshold
Use	Values in mg/l
Brewing	1.0
Corbonated beverages	0.2 to 1.0
Food comming and freezing	1.0
Food equipment washing	1.0
Food processing, general	1.0

year-old girl was caused by ingestion of 1500 mg of FeCl₂.

# FERROUS OXIDE

FeO

Using highly turbid water at  $16-23^{\circ}$ C and the mosquito-fish (Gambusia affinis) as the test organism. Wallen et al. (2940) found the 96-hour  $TL_m$  of ferrous oxide to be over 10,000 mg/l.

# FERROUS SULFATE

FeSO₄ and FeSO₄·7H₂O

- 1. General. The anhydrous and crystalline forms of this substance are highly soluble in water, and the salts are used in many industrial operations. Sources of pollution by ferrous sulfate include canneries, tanneries, textile mills, mines containing pyrites, and metal-cleaning operations involving the use of pickling liquors. Ferrous sulfate is sometimes used as a coagulant in water and sewage treatment.
- 2. Cross References. Iron, Distilled Water, Sulfates, and other iron salts.
  - 3. Effects Upon Beneficial Uses.
- a. Fish and Other Aquatic Life. The threshold concentration of ferrous sulfate for immobilization of Daphnia magna in Lake Erie water was found to be less than 152 mg/l (358).

The following concentrations of ferrous sulfate have been harmful or lethal to fish in the time specified:

	a- Type of			
	/l Water		Species of Fish	Reference
2.9	distilled	4-24 hours	shiners, suckers, carp_	
6.4		24 hours	shiners, suckers, carp_	359
100		24 hours	minnows, goldfish.	203
			trout	959
100		4.2-7 days	hace	359
		2.5-3.5 days	bass	1035, 1030
133		24 hours	sunfish	1035, 1030
315	distilled	3 hours	brook trout	359
500		1.3-5 days	minnows	313
1,000		9-23 hours	goldfish	1030
1,000		48 hours	bass	1030
1,000			very young carp	1459
2,000		5-30 hours	goldfish	1030
1.000	hard	2.5-9 hours	bass	1030
1.390	naru	2-10 hours	goldfish	313
2.721		144 minutes	minnows	991
6.950	tap	31-66 minutes	trout, salmon	313
	<del>-</del> -	104 minutes	minnows	991
10,000		1 week	tench	1459
10,000		1 day	other fish	1459
13,900		68 minutes	minnows	991

The following concentrations of ferrous sulfate have been reported as not harmful to fish within the time specified:

Concen- tration in mg/l	Type of Water	Time of Exposure	Species of Fish	Reference
5		24 hours	carp, shiners, suckers	359
17.1		1 hour	minnows	362
50		7 days	bass, bluegills	1459
50		24 hours	trout	950
100 100 100 380	hard  	96 hours 7 days 7 days 185 minutes	bass, sunfish goldfish goldfish goldfish carp, tench minnows	1035, 1030, 359 313 1035, 1030 1459 1459 353
1,000			mature fish	1459

Ferrous sulfate has also been reported to be lethal to fish at the following concentrations of iron:

Concentration of iron, mg/l	Type of Water	Time of	Type of	
		Exposure	Fish	Referen <b>ce</b>
1.28 368	distilled	24 hours	fish	
300		2-10 hours	goldfish	1466

On the other had, 37 mg/l of iron has not been harmful to goldfish in 100 hours (1466).

The effects of disposal of as much as 3000 tons per day of acid ferrous sulfate solution at sea have been investigated independently by Arnold and Royce (1466) and Redfield and Walford (1467, 1561). They found no evidence of significant changes or harmful results among the aquatic life in the areas studied.

#### FERROUS SULFIDE

r_og

This black solid is highly insoluble in water. Wallen et al. (2940) reported its 96-hour TL_m toward mosquito-fish in highly turbid water at 20-26°C to be over 10,000 mg/l. Undoubtedly the ferrous sulfide remained in suspension or settled out of suspension, for it would not be expected to go into solution.

# FERROUS SULFITE

 $FeSO_3 \cdot 2\frac{1}{2}H_2O$ 

Using highly turbid water at 20-21°C, Wallen et al. (2940) found the 24-, 48-, and 96-hour  $TL_m$  concentrations toward the mosquito-fish (Gambusia affinis) to be 350 mg/l.

# FERTILIZER MANUFACTURING PLANT WASTES

Ellis (611) reported that wastes from a fertilizer manufacturing plant in Mississippi constituted no hazard to fish.

# FLUORIDES

F-

1. General As the most reactive non-metal, fluorine is never found free in nature but it is a constituent of fluorite or fluorspar, calcium fluoride, in sedimentary rocks and also of cryolite, sodium aluminum fluoride, in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters (152).

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other minor uses (364). While not normally found in industrial wastes, they may be present in traces, or in higher concentrations resulting from spillage.

- 2. Cross References. Hydrogen Fluoride and various fluoride salts.
  - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms and 4.0 grams causing death (364). The fatal dose has also been reported (1161) as 0.5 gms per kg of body weight and as 2.5 grams (3481).

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children and a few papers pertaining to skeletal damage. The effects reported in many of these references, summarized in Table 6-5, lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects.

Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride

# FERRIC CHLORIDE

FeCl₃ and FeCl₃ 6H₂O

- 1. General. Highly soluble in water, this substance has an acid reaction and imparts a brownish-yellow or orange color. Potential sources of pollution by ferric chloride include mining, ore milling, the chemical and dyeing industries, and water and sewage works. The oral  $\dot{\text{LD}}_{50}$  for rats is given (364) as 900 mg/kg of body weight.
  - 2. Cross References. Distilled Water, Iron, Chlorides.
  - 3. Effects Upon Beneficial Uses.
- a. Fish and Other Aquatic Life. The following concentrations of ferric chloride have been reported to be harmful or lethal to fish:

Concentration of FeCls in mg/l	Type of Water	Time of Exposure	Species of Fish	Reference
0.6 1.2 4.35 9 20 74 100 540 2700 5400	tap tap tap distilled tap turbid soft	days days days hours hours hours hours hours hours hours hours minutes minutes minutes minutes	goldfish stickleback goldfish goldfish mosquito-fish goldfish minnows minnows	598 1459 313 1459 2940 598, 313 991 991

The following concentrations of ferric chloride were reported to be not harmful to fish:

Concentration in mg/I 1 5 10 100 270	Tupe of Water tap soft hard	Time of Exposure 10 days 50 hours 96 hours 96 hours 90 minutes	Species of Fish stickleback young eels goldfish goldfish minnows	Reference 598 1459 313 313, 593 353
--------------------------------------------------------	-----------------------------------------	----------------------------------------------------------------	------------------------------------------------------------------------------------	----------------------------------------------------

Jones suggested that the toxic effect of FeCl3 might be due principally to the increasing acidity of the solutions as the concentration of ferric chloride was increased (1459). In ferric chloride solution containing 1.0 mg/l of Ferra (at pH 5), Jones' fish lived for 10 days, as long as the controls (1459).

The threshold concentration of ferric chloride for immobilization of Daphnia magna in Lake Eric water was found to be 130 mg/l (358); and in another case less than 18 mg/l, for a 64-hour period (598). For Polycelis nigra the threshold for toxicity was 58 mg/l (608).

The following threshold concentrations of ferric chloride toward lower organisms in Lake Erie water at 20ide toward 10wei organization (2955):
25°C have been reported (2955):
Threshold Concentration mg/l

Organism	for Immobiliz
- ·	***
Daphnia magna, young	
Cyclops vernalis	116
Diaptomus oregonensis	126

# FERRICYANIDES AND FERROCYANIDES

(see Potassium Ferricyanide and Sodium Ferricyanide)

# FERRIC OXIDE

 $Fe_2O_3$ 

(see also Iron and other iron salts)

This insoluble substance is used as a polishing powder for glass and metal, in ceramics, and as a pigment in iron paints. It is also a component of iron rust. For ice making, ferric oxide concentrations in excess of 0.14 to 0.20 mg/l are considered to be objectionable (168, 228, 231) and for carbonated beverages the limit is 0.3 mg/l, as Fe₂O₃. Nielson (1159) reports that concentra-

tions of 2.0 mg/l of ferric oxide are sufficient to kill trout, salmon, and roach by blocking their gills, but small crustaceans are more resistant.

# FERRIC POTASSIUM SULFATE

 $FeK(SO_4)_2$ 

(see also Iron and other iron salts)

Ellis (313) quotes references to the effect that ferric potassium sulfate, used as a mordant for dyeing and printing calico, was not fatal to tench during a oneminute exposure at a concentration of 10,000 mg/l. The maximum concentration of this salt tolerated by young eels for over 25 hours was reported (1459) to be about 14 mg/l.

# FERRIC SULFATE

 $Fe_2(SO_4)_3$ 

(see also Iron and other iron salts)

This compound, slowly soluble in water, is used in dyeing, in ink manufacture, and in water and sewage treatment. Ellis (313) quotes a reference to the effect that a concentration of 0.716 mg/l in distilled water killed shiners, carp, and suckers in 12 to 24 hours. In a solution of ferric sulfate in distilled water, a concentration of only 0.1 mg/l of iron was reported to have killed certain fish within 24 hours (1459). (see also Distilled Water).

In highly turbid water at 19-23°C, Wallen et al. (2940) found the 24-, 48-, and 96-hour TLm concentrations for the mosquito-fish Gambusia affinis, to be 133 mg/l. In Lake Huron water at 12°C, a concentration of 5.0 mg/l of iron sulfates (valence not given) had no effect on rainbow trout, bluegill sunfish, or sea lamprey during a 24-hour period (2976).

# FERROUS CARBONATE

FeCO₂

(see also Iron and other iron salts)

Insoluble in normal water and soluble only in water containing appreciable carbon dioxide, ferrous carbonate is seldom found in surface waters but occurs in some ground waters (364). According to Klut (945) a concentration of 0.3 mg/l of iron carbonate gives water an inky taste. Thresh (32) says that no potable water should contain more than 0.5 mg/l of iron as carbonate, but this amount cannot possibly have any effect upon health.

# FERROUS CHLORIDE

FeCl₂

(see also Iron and other iron salts)

Ferrous chloride is used in dyeing and printing fabrics, and in metallurgy. It is highly soluble in water (364). The threshold concentration of ferrous chloride for immobilization of Daphnia magna in Lake Erie water has been reported to be less than 38 mg/l for a 64-hour period. Concentrations of 1000 mg/l in hard water have killed goldfish within 10 hours; concentrations of 10 mg/l in hard water have not been harmful to goldfish in 96 hours (598). The highest concentration of ferrous chloride tolerated by young eels for more than 50 hours was reported to be about 13 mg/l (1459).

The ingestion of 200 to 800 mg of ferrous chloride daily by dogs induced no noteworthy changes in physiclogical behavior (353), but an acute poisoning of a 21/2mg/l, i.e. all fish survived 30 mg/l but all died at 60 mg/l. Bringmann and Kuhn (2158, 3443) reported that the toxic threshold for *Daphnia* exposed for 48 hours at 23°C to ethylenediamine hydrochloride occurred at 8 mg/l, while for *Scenedesmus* the threshold concentration was 20 mg/l. *Echerichia coli* at 27°C showed an adverse response at 200 mg/l, and *Microregma* (a protozoan) at 30 mg/l.

# ETHYLENEDIAMINETETRAACETIC ACID (EDTA)

The sodium salt of this acid, a soluble white powder, is used as a chelating agent under trade names such as Versene, Sequestrene, and Komplexon. One gram complexes 201 mg of calcium carbonate. Clemens and Sneed (2981) tested its effect on fingerling channel catfish in University of Oklahoma tap water at 25°C. They found the 24-, 48-, and 96-hour TL_m to be 167, 133, and 129 mg/l respectively. During each period, all fish withstood 100 mg/l and all succumbed at 316 mg/l.

# ETHYLENE DICHLORIDE

(see Dichlorethane)

# ETHYLMERCURIC BROMIDE

# ETHYLMERCURIC PHOSPHATE

# ETHYLMERCURIC OXALATE

(see Mercuro-Organic Compounds)

# ETHYL PHTHALATE

C12H14O4

A colorless, practically odorless, oily liquid with a bitter disagreeable taste, this substance is used in the manufacture of celluloid and as a solvent for cellulose acetate in varnishes and dopes. It is also known as diethyl phthalate and it is nearly insoluble in water (364). Fish exposed in a fish bowl to cellulose acetate material known to contain ethyl phthalate died within a few hours, despite the low solubility of this substance. One drop of ethyl phthalate in 50 ml of water, corresponding to a concentration of about 1.2 mg/l killed a goldfish within 30 minutes (1559).

# EXPLOSIVES

(see also Trinitrophenol, TNT, Toluene, Tetryl)

Liquid wastes from the manufacture of munitions and other explosives may contain mixtures of many substances, such as ammonium picrate, picric acid, toluene, mono-nitro-toluene, TNT, nitrobenzene, and orthodichlorobenzene. The principal detrimental effects of such substances appear to be their tastes and odors, although in higher concentrations they are inimical to aquatic life.

During World War II, according to Bandt (616) "bitter-almond" tastes in fish flesh were frequently caused by waste water from factories producing explosives, the main cause being traces of mononitrotoluene, nitrobenzene, and orthodichlorobenzene, which causes tastes when present in concentrations much smaller than those causing damage to the health of fish. Ruchhoft and Norris (655) reported on the concentration of ammonium

picrate in wastes from shell-loading plant, pointing out that 0.5 mg/l of this substance can be tasted in water and that 1.0 mg/l is objectionable.

Red-liquor wastes from TNT-manufacturing plants are highly alkaline and contain toluene, sodium salts, and some TNT, but exhibit no B.O.D. Degani (544) shows that the threshold concentration to fish occurs when the increase in total-solids content from red liquor was 87.5 mg/l. A concentration of 1750 mg/l killed minnows in 130 to 500 minutes but did not kill carp or bullheads. At 7000 mg/l, however, minnows were killed in 37 to 120 minutes, carp in 126 minutes, and bullhead in 254 minutes.

The chief objectionable pollutants in wastes from a small-arms ammunition plant were soap solutions, cleansers, lubricants, acid liquors, and rinse waters containing copper and zinc (657).

# FATS

(see Animal and Vegetable Oils, Oil-Petroleum)

# FATTY ACIDS—GENERAL

RCOOH

(see also Acetic Acid, Formic Acid, Oleic Acid)

Fatty acids, so named because two of the higher members of the series—palmitic and stearic acid—are prepared frem animal fat, belong to the homologous series that may be represented by the general formula RCOOH, where R indicates a saturated hydrocarbon chain. The series starts with formic acid, HCOOH, and acetic acid, CH₃COOH, and runs through stearic acid, C₁₇H₃₅COOH. The higher fatty acids are used extensively in the soap industry and occur in wastes from laundries, bottle-washing processes, chemical plants, and pulp and paper mills. The limiting or threshold concentrations of a few specific fatty acids are given elsewhere in this chapter, but a few references have dealt with the fatty acids as a group.

Gehm (344, 658) summarizes literature to the effect that the sodium salts of fatty acids have a minimum lethal dose, MLD, for fish of 5.0 mg/l. Sodium oleate has a MLD of 5.0 mg/l and sodium linolate has a MLD of 10.0 mg/l. Van Horn et al. (190, 574) report that the sodium salt of the fatty acid fraction of crude soap from sulfate pulp mills had MLD of 5.0 mg/l for killing shiners and minnows in 120 hours at 18°C. For Daphnia, however, the MLD was only 1.0 mg/l. With sodium oleate and shiners, the MLD was also 5.0 mg/l in 120 hours at 18°C.

According to Grin (3450), synthetic fatty acids affect the organoleptic properties of water. Concentrations of 3-4 mg/l inhibits nitrification. He recommends that the limiting concentration of all synthetic fatty acids in domestic water supply reservoirs be considered as 0.1 mg/l.

# FATTY AMINO COMPOUNDS

(see Chapter X)

#### **FENURON**

(see Chapter X)

# FERBAM

(see Chapter IX)

	Concentration in mg/l to Kill	in m	centratio g/l Causi nt Morta	ng
Compound	all larvae of Sea Lamprey	Rainbow Trout	Brown Trout	Bluegill Sunfish
2-bromo-4-nitrophenol sodium salt	<u>5</u>	. 13	11	
3-bromo-4-nitrophenol	5	15 11		$\bar{1}\bar{5}$
5-chioro-2-nitrophenol 2, 5-dichloro-4-nitrophenol _	3	5 13	5	
sodium salt		17	- 1	
3, 4, 6-trichloro-2-nitrophene sodium salt	ol 5	$^{17}_{23}$	15	
3-trifluoromethyl-4-nitropher	nol _ 2	43 9	7	
sodium salt	2	7		

e. Shellfish Culture. Water polluted with chlorophenols to the extent of 0.001 mg/l imparted a taste to oysters (3492).

# HARDNESS

1. General. The term "Hardness" is applied to the soap-neutralizing power of a water. Any substance that will form an insoluble curd with soap causes hardness; but since iron, manganese, copper, barium, lead, zinc and other trace elements are seldom present in appreciable concentration in natural waters, hardness is attributable principally to calcium and magnesium ions.

Soap will not cleanse, nor lather, until all of the hardness is precipitated as insoluble salts of the fatty acids. This property of soap is used in an accepted test for hardness, whereby a standard soap solution is added to an aliquot portion of water until a persistent lather forms (469). The soap-neutralizing power, or hardness, is then expressed in terms of an equivalent concentration of calcium carbonate. In recent years, however, the "versenate" test for hardness has been perfected and it has largely supplanted the more-cumbersome soap test in standard laboratory procedure.

While hardness is caused only by cations such as calcium and magnesium and consequently is independent of the anions in the solution, the terms "temporary hardness" and "permanent hardness," or the corresponding terms "carbonate hardness" and "noncarbonate hardness," have been used extensively. Where carbonates or bicarbonates are present in concentrations equivalent to or greater than the calcium and magnesium, the scale that will form upon evaporation or heating will consist primarily of calcium carbonate and magnesium hydroxide. Such hardness is termed "carbonate" or, because the scale can be removed with acid, "temporary." Where alkalinity is low, the more-soluble sulfates and chlorides may form scales that cannot readily be dissolved by acid, and such hardness is called "non-carbonate" or "permanent."

Hardness in water may be caused by the natural accumulation of salts from contact with soil and geological formations, or it may enter from direct pollution by industrial wastes such as beam-house liquors from tanneries. Some industrial wastes have an indirect effect upon hardness in ground water by increasing the carbonic-acid content and favoring the solution of calcium and magnesium salts. Return flow from irrigation drainage also increases hardness.

The detrimental effects of hardness, as described hereinafter, include excessive soap consumption in homes and laundries; the formation of scums and curds in homes, laundries, and textile mills; the gallowing of fabrics; the toughening of vegetables cooked in hard water; and the formation of scales in boilers, hot-water heaters, pipes, and utensils.

The references described below deal with literature in which the detrimental effects of calcium and magnesium are grouped and described only as "hardness", without regard to the concentrations of the constituents. For other references, where specific pollutants are given, see the appropriate substance.

- 2. Cross References. Alkalinity, Bicarbonates, Calcium, Carbonates, Magnesium, and Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The literature contains numerous statements relating to the desirable limits for hardness in municipal water supplies. Some of them are condensed in the following paragraph. Hardness over 100 mg/l becomes increasingly inconvenient, for it results in a waste of soap and the incrustation of utensils (330). In a few hard-water areas, a commonly prescribed limiting hardness is 140 mg/l (36). In good water, the total hardness is usually below 250 mg/l (632). The hardness of waters of "good" quality should not exceed 270 mg/l (630). In France, hardness in excess of 300 mg/l is considered suspicious and possibly indicative of pollution (32). In England, it is believed that water with a hardness in excess of 315 mg/l should be softened, primarily to remove harmful magnesium salts; but the use of water with 315 mg/l hardness without preliminary softening has been sanctioned by the government. Hardness above 500 mg/l is considered unsuitable for general domestic purposes (32, 36). In Germany, natural carbonate hardness above 350 mg/l is seldom found, and water with hardness above 448 mg/l is considered to be polluted (839).

The major detrimental effect of hardness is economic. Prior to the amount of synthetic detergents (see Chapter X), many studies showed that the decreased cost of soap alone justified the expense of municipal water softening. Now that syndets are widely used in lieu of soap products, there is a common misconception that hardness is no longer an economic factor. Aultman (34) dispelled that illusion by showing that the annual cost of cleansing agents for a family of five doubles as the hardness increases from zero to 375 mg/l. In a comprehensive economic analysis, De Boer and Larson (3151) found that the savings for soaps, syndets, general household cleansers, scouring compounds, bleaches and other additives were \$1.15 per capita per year for each 100 mg/l reduction in hardness (based on 1960 costs).

Since calcium is absorbed and assimilated only in the presence of other essential nutritional factors, such as phosphorus and vitamin D, it is questionable whether calcium in water can be utilized by the body. However, it has been suggested that calcium in water may partially compensate for calcium deficiency in modern foods (330), and from several parts of the world have come reports that the incidence of tooth decay is lower in hard water areas than in soft water areas (629, 868, 921, 938, 1041, 1047). On the other hand, at least one study has found no significant correlation between hardness and caries (36).

Hard waters have had no demonstrable harmful effects upon the health of consumers (32, 36, 653, 947, 1047).

There is no conclusive proof that hardness causes urinary concretions or other diseases of the kidney or bladder (629, 1194, 1195); or biliary calculi, arteriosclerosis, dyspepsia, goiter, diarrhea, constipation, rheumatism, or stomach disorders (623, 1196); but the drinking water of an area may be considered as one of the factors predisposing to formation of calculi (3365). The role of hard water in the formation of urinary concretions is still controversial (1194); Rosenau (629) has cited a reference indicating a higher frequency of calcification of arteries among hard water users; and Murray et al. (1197) have suggested that iodine concentrations that are sufficient in soft waters to prevent goiter may not be adequate in hard waters.

Several investigators (3368, 3369, 3370, 3516, 3517) have found a negative correlation between hardness in the drinking water of an area and death rates from degenerative cardiovascular disease, i.e., softer water was associated with higher death rates. These variations are unexplained on dietary, racial, or social bases. They have been observed in Japan, England, South Africa, the Canary Islands, Australia, and the U.S. Although the correlation appears to exist, its causative factors re-

mained unexplained as of 1961.

Water with a bicarbonate hardness in excess of 90 mg/l is reported to cause formation of a film in tea (1160). A study of the effects of different types of waters on the blanching of vegetables indicated that the greatest loss of ascorbic acid occurred in peas blanched in hard water. The highest calcium contents were found in vegetables blanched in hard waters with high calcium concentrations (220). A study of the effects of hard water used for cooking purposes revealed no changes in weight and composition of feces that could be related to the hardness of the water used for cooking legumes (1198).

Waters with a "temporary" hardness below 57 mg/l are often corrosive to metals (32). Poisonous concentrations of lead in drinking water are generally due to the corrosive action on lead pipes of water with an oxygen concentration below 6 mg/l, pH below 7, and carbonate hardness below 125 mg/l (1073, 1199). Waters with a hardness greater than 125 mg/l form protective coating on lead pipes within a few weeks, thereby limiting the solution of lead (1200); however, hardness does not absolutely prevent plumbosolvency (36, 1201). For further information on the relationship between hardness, carbonate equilibria, and corrosion, see Langelier (692).

b. Industrial Water Supplies. Excessive hardness is undesirable in water for laundries, carbonated beverages, metal finishing, dyeing and textile industries, food processing, paper and pulp, bottle washing, and photography, leather goods, and other industrial processes.

In laundries, if the total hardness of the raw-water supply is more than 286 mg/l, or if the temporary hardness is much more than 214-228 mg/l, water softened by ordinary base-exchange methods contains so much bicarbonate that yellow stains are formed on clothes during drying and finishing (237). In wool-washing, waters with zero hardness remove grease more readily from wool than waters of 57 to 72 mg/l of total hardness; but, owing to the formation in wool of lime soaps

which absorb dirt and fatty acids, moderately hard waters yield a cleaner, softer product. The optimum hardness varies with the water and materials (260).

In baking, medium-hard water strengthens gluten, causing it to retain carbon dioxide better, and produces a finer-grained structure. Soft waters soften the gluten, thus producing a sticky dough and soggy bread. Very hard waters significantly retard fermentation (160). In the canning of fruits and vegetables, salts of calcium and magnesium may combine with pectous substances forming insoluble pectides that toughen the product (224). Hard water toughens peas and some varieties of beans (164, 217), when the hardness exceeds 200 mg/l. Hard water does not toughen corn and its use sometimes results in a product with a more desirable color than soft water. Hard water, with hardness below 350 mg/l, does not toughen beets, but may cause a white coating on the surface of the beets (217). Hardness tends to decrease water absorption in the reconstituting of dehydrated fruits and vegetables (3518).

A survey of paper mills indicated that water supplies in use at different factories varied in hardness from zero to 766 mg/l (243) (for recommendations, see the following tabulation).

Distilled water, with no hardness, has a disintegrating effect on Portland cement (1202). Water with a hardness greater than 10 to 20 mg/l will not attack cement if the CO₂ is less than 10 mg/l. If the pH is greater than 6.5, natural waters will attack concrete only if the hardness is less than 50 mg/l. With low hardness (less than 10 mg/l) attack occurs even when or the pH is as high as 7.5 or the CO₂ is negligible (360). When filtered through powdered cement, more lime was removed by hard water than by water free from carbonates (1203). The effect of hard waters on concrete varies with the pH and carbon-dioxide content of the water (1204). Hardness in mixing water had no effect on the "air-entrainment" properties of concrete because the hardness of the aqueous portion of a concrete mixture is so great that it is not appreciably affected by the hardness of the water supply (194).

The levels of hardness tolerable or desirable in water for various industrial purposes are given in Chapter V and summarized in the following tabulation:

# RANGE OF RECOMMENDED VALUES FOR HARDNESS IN INDUSTRIAL WATER SUPPLIES

Limiting or Recommended Values, in mg/lIndustry and Process Boiler feed water: at 0-150 psi ___ at 150-250 psi ______at 250-400 psi ______over 400 psi _____ 200-300 Carbonated beverages Cooling .... Food canning and freezing: general _____ Food equipment washing _____ 10 Food processing, general 10-250

Industry and Process	Limiting or Recommended Values, in mg/l
Pulp and paper making:	vic mg/ v
groundwood pulp	200
soda pulp	100
kraft pulp, bleached	100
kraft pulp, unbleached	200
fine paper pulp	
Rayon:	
pulp production	8
cloth manufacture	55
Steel manufacturing	
Synthetic rubber	50
Tanning:	
beam house	513
tan house	50-135

Textile manufacture _____

c. Irrigation. After lime-soda softening, the water at Columbus, Ohio, appeared to have no effect either on the soil reaction or on the development of greenhouse plants (1205). Softened Colorado River water with a high content of sodium produced more bushy and compact begonia, fuschia, and camellia plants than unsoftened water with a high salt content (636). It has been reported that no injury to plants grown in calcareous soils result from watering with hard water; injury caused by applying hard water to acid soils can be prevented by adding a trace of borax (921).

Schroder reports that cyclamen sprinkled with tap water containing excessive hardness as CaCO₃ (186 mg/l) deposited a white crust of the carbonate and showed poor growth. Well water with 70 mg/l of carbonate hardness, but with considerably higher non-carbonate hardness, showed no plant injury because the calcium was held in solution as sulfate and bicarbonate (921, 1206). Spurway (1207) maintains that carbonates in hard water may produce alkalinity in greenhouse soils, thereby adversely affecting the growth of plants.

Wilcox stated that hard water is superior to soft water for irrigation (269). For a detailed discussion of the effects of calcium and sodium in irrigation water, see Chapter V.

d. Fish and Other Aquatic Life. The growth of fish in aquaria may be limited by the hardness of the water (1208). The concentration of calcium in vertebrae of fish is not affected by the hardness of the water (1209).

Soft water solutions increase the sensitivity of fish to toxic metals; in hard waters toxic metals may be less dangerous (313, 1111, 1210, 2154, 2936, 2942, 2943, 2944, 2954, 3519). For example, in hard water copper sulfate is less dangerous to fish than in soft water (602). In hard water insoluble copper compounds are precipitated. thereby removing some of the toxicity (600, 900, 1011, 1211). Tarzwell and Henderson (2154) reported that certain beryllium uranyl, zirconium, titanium, vanadium, cadmium, lead, and copper salts were more toxic in soft water than in hard. Dichromates and non metallic compounds such as ammonia, phenol, and naphthenic acid have also been shown (2936, 2954) to be less toxic in hard water than in soft. LeClerc et al. (2942, 2943, 2944) ran numerous fish toxicity tests in distilled water and hard water, finding in most instances that hard water raised the minimum dose causing death to minnows.

Sigler and his colleagues (3465, 3467) reported that the effects of fluorides on fish are counteracted by calcium and magnesium.

e. Stock and Wildlife Watering. Experiments with calves and chicks have indicated that those supplied with hard water developed somewhat better than those supplied with distilled water (1047).

The role of hard waters in the development of urinary concretions is still controversial. (see Domestic Water Supplies, above).

# **HEAVY METALS**

- 1. General. The heavy metals included under this heading comprise copper, lead, zinc, and others of non-specific designation that may originate in sewage and industrial wastes. All of the references relating specifically to such substances are covered elsewhere in this chapter under the designated metal. This section deals only with references that group heavy metals into one category.
  - 2. Cross References. Each heavy metal, by name.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Goudey (992) has suggested an upper limit of 5.0 mg/l for heavy metals in Class AA and A waters; 10 mg/l for Class B and C waters.
- b. Industrial Water Supplies. Aluminum has been damaged by water supplies containing high concentrations of salts of heavy metals (562). Heavy metals are undesirable in water for use in the textile industry (256). The upper limit recommended for heavy metals in water to be used in rayon industries is 0.01 mg/l (405, 550).
- c. Irrigation Waters. The presence in water of low concentrations of heavy metals may be beneficial for irrigation (563). An upper limit of 10 mg/l has been suggested by Goudey (992) for heavy metals in ground waters to be classified as safe for irrigation use.
- d. Fish and Other Aquatic Life. River Boards in England have specified that heavy metals, individually or in total, shall not exceed 0.5 mg/l (1756) and 1.0 mg/l (2950) in sewage or industrial effluents discharged to the watershed.

# HEPTACHLOR

(see Chapter IX)

#### HEPTANE

CHCH₃(CH₂)₅CH₃

(see also Hydrocarbons-General)

One of the saturated (paraffin) hydrocarbons, heptane is a volatile, flammable liquid, used as a standard in testing knock of gasoline engines. It may occur in gasoline or other petroleum wastes. It is soluble in water to the extent of 52 mg/l at 15.5°C (911). Hubault (461) reports that the concentrations of n-heptane required to kill white roach in one to four hours at 21°C was 30 mg/l. In contrast, Wallen et al. (2940) tested the effect of heptane on mosquito-fish (Gambusia affinis) in highly turbid water at 20-27°C. They found the TL_m values

after 24, 48, and 96 hours all to be 4924 mg/l. Turbidity was not reduced by this concentration of heptane.

#### HEXACHLOROCYCLOHEXAN

(see Chapter IX—Benzene Hexachloride)

## HEXANE

 $\mathrm{CH_{3}(CH_{2})_{4}CH_{3}}$ 

This colorless, volatile liquid is soluble in water to the extent of 138 mg/l at 15.5°C (911). According to North et al. (2108), 10 mg/l of n-hexane showed little or no effect on the photosynthetic activity of the giant kelp (Macrocystis pyrifera) during a 96-hour exposure.

# HEXAVALENT CHROMIUM

(see Chromium)

# HEXADECANOL

(see Cetyl Alcohol)

# HUMIC ACID

This collective term is used to describe the acid product resulting from the decomposition of organic matter, particularly dead plants. It is a dark-brown dust-like powder that is slightly soluble in water. Sartorius and Wever (674) state that the presence of humic acid in sufficient quantities to cause color is not dangerous in itself but bacteria live longer in such water and *E. coli* increase in numbers. Humic acid from various sources interfered with chlorination, according to Moiseev (675) but the extent of interference varied with the sources of acid. In some cases, no interference resulted until the concentration of humic acid approached 100 mg/l; in other cases, interference occurred at 0.1 mg/l. Iron humate in a concentration of 0.5 mg/l gives water a marshy, earthy taste (945).

# HYAMINE

(see Chapter X)

# HYDRAZINE

 $NH_2NH_2$ 

(see also Hydrogen Peroxide, Phenylhydrazine)

Hydrazine is a fuming oily liquid with a penetrating odor, extremely explosive and a violent poison. It is used in rocket fuels. Hydrazine hydrate, NH₂NH₂.H₂O, a fuming refractive liquid with a faint characteristic odor, is miscible with water and alcohols. It is used as a reducing agent and as a solvent for inorganic materials; also, to decompose hydrogen peroxide in V-2 rockets.

Southgate (659) reported that waste waters from the testing of rocket motors contained hydrazine hydrate, of which 0.7 mg/l caused fingerling trout to lose equilibrium in less than 24 hours. On the other hand, hydrazine hydrate and hydrazine sulfate, NH₂NH₂·H₂SO₄, had no effect on sea lampreys exposed for 24 hours at a concentration of 5 mg/l (2976).

Corti (146) reports that rainbow trout exposed to 146 mg/l of NH₂NH₂ at pH 8.35 and 13.5°C demonstrated an adverse reaction after 14 to 18 minutes and succumbed completely in 22 to 35 minutes.

The oral LD₅₀ for rats and mice is reported as 60 mg/kg (3495, 3496). Confronted with drinking water

containing 100 mg/l of hydrazine, white rats restricted their fluid intake and with higher concentrations they were even more reluctant to drink the water. Apparently white rats will not ingest voluntarily sufficient hydrazine in drinking water to bring about pathological changes usually associated with hydrazine intoxication (3496).

For industrial process waters, hydrazine has been used in boiler-feed-water treatment as an oxygen scavenger and bactericide (3497).

# HYDROCARBONS (GENERAL)

(see also Oil (Petroleum), Methane, Heptane, Pentane, and other individual hydrocarbons).

Although they may act as bactericides, fungicides, algicides, insecticides, and weed-killers, and although they may be capable of toxic action toward fish and shell-fish, many gaseous, liquid, and solid hydrocarbons are capable of being attacked and decomposed by certain bacteria, yeasts, and molds, of which about 100 species have been identified by Zobell (676).

There is a possibility that leaks from natural-gas transmission lines will affect water supplies that are near enough to become polluted, according to Soule (1577). The natural gas tested comprised 94.40 percent methane, 3.37 percent ethane, 0.98 percent propane, 0.36 percent butanes, 0.09 percent pentanes, and 0.19 percent hexanes by volume, the remainder being N₂ and CO₂. It was found by experiment that natural gas will impart to water an odor similar to benzene, the odor being dependent on the volume of gas, the volume of water, and the period of contact.

# HYDROCHLORIC ACID

(see Hydrogen Chloride)

# HYDROFLUORIC ACID

(see Hydrogen Fluoride)

# HYDROGEN CHLORIDE

HCl

(see also Acidity, Chlorides, pH)

This strong acid, with innumerable industrial applications, is highly soluble in water, dissociating as hydrogen and chloride ions. Inasmuch as chloride ions are relatively innocuous, the principal effect of HCl lies in changing the hydrogen-ion concentration, except in highly buffered waters. Only when the pH value is depressed to 5.0 or lower will HCl prove lethal to fish (361). Cairns and Scheier (2933, 2934, 2935) show that the 96-hour TL_m at 20°C for the bluegill sunfish occurs when the pH value is lowered to 3.6 by HCl. Corresponding lethal pH values of 4.0 and 4.6 have been reported for goldfish and sticklebacks respectively (2920). At pH 5.0, sticklebacks survived 9 days in water to which HCl had been added, at pH 4.0 only 10.5 hours, and at pH 3.0 only 80 minutes (2941).

It is the resulting pH rather than the concentration of HCl that governs lethality toward aquatic life; hence the discrepancies in the following reports of lethal doses of HCl toward fish.

Concentro tion of HO in mg/l		Species of Fish	Remarks Refe	erenc <b>e</b>
3.6	48 hours	sunfish	lethal in distilled	
3.65	24 hours	carp, shiners.	water	313
0.00		suckers	lethal	359
4-6	6 hours	minnows	MLD in distilled	
			water	2942
8.0	24 hours	sunfish	lethal -	359
10	24 hours	trout	MLD ·	359
67.5		whitefish,		
		pickerel	toxic threshold	359
80	24 hours	creek chub	lethal	1442
100-110	6 hours	minnows	MLD in hard water	2942
166	4-7 hours	goldfish	killed in hard water	313
200		perch, roach	collapsed in dis-	
		<b>P</b> ,	tilled water	313
282	96-hour	mosquito-fish	turbid water	2940
	$TL_m$	-		
1000	2-5 minutes	trout	overturned in	
			tap water	31 <b>3</b>

In contrast, Belding (359) reports that 20 mg/l had no effect on minnows and goldfish. According to Ellis (313) in hard water 157 mg/l did not injure goldfish in over 100 hours of exposure. Gillette et al. (1442) indicate that creek chub survived 60 mg/l for 24 hours, but succumbed at 80 mg/l.

The toxic threshold of HCl toward Daphnia magna has been reported at 56 to 62 mg/l in soft water and Lake Erie water respectively (313, 358).

It has been reported that HCl can be tasted at a concentration of about 32 mg/l in water (1578) although it is apparent that this threshold is dependent upon the buffering power of the water.

# HYDROGEN CYANIDE

HCN

1. General. This colorless gas or liquid boils at 26°C and is highly soluble as a gas or miscible with water as a liquid (364). It is used for exterminating rodents and insects in ships and buildings, or for killing insects on trees (677). For this literature review, HCN is particularly significant because it forms in water whenever soluble NaCN or KCN are added thereto. In water HCN dissociates into hydrogen and cyanide ions according to the reaction:

$$HCN \rightleftharpoons H^+ + CN^-$$

the degree of dissociation being governed by the equilibrium equation:

$$\frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 7.2 \times 10^{-10}$$
, at 25°C

or by rearranging

$$\frac{[\text{CN}^-]}{[\text{HCN}]} = \frac{7.2 \times 10^{-10}}{[\text{H}^+]}$$

It is evident from this equilibrium that the ratio of cyanide ion to undissociated HCN is a function of pH. At pH values of 7 or below, less than 1 percent of the cyanide molecules are in the form of cyanide ion; at pH 8, only 6.7 percent; at pH 9, only 42 percent; and at pH 10, 87 percent of cyanide is dissociated (911).

When NaCN or KCN is added to water in dilute concentrations, the salts dissociate immediately but the CN-ions react with H⁺ ions in the water to form HCN with a resulting rise in pH. It is now generally recognized that undissociated HCN is more toxic toward aquatic life than the cyanide ion (1539, 1580, 2109); but South-

gate (346) found that there was no appreciable change in toxicity within a pH range of 6.0 and 8.5. For more discussion of this point, see Cyanides.

2. Cross References. Cyanides, Cyanogen Chloride, Nitriles, Ammonium Thiocyanate, Potassium Cyanate, Potassium Cyanide, Potassium Ferricyanide, Potassium Thiocyanate, Sodium Cyanate, Sodium Cyanide, Sodium Ferricyanide, Sodium Thiocyanate.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The average fatal dose for man by ingestion is 50 to 60 mg (364, 1117). A dose of 161 mg was fatal to man in 15 minutes (353). No information on the effect of a daily intake of HCN was uncovered, but for cyanide ions, 2.9 to 4.7 mg per day were reported as not harmful (922), with 37.8 mg or over being fatal. The average fatal dose for HCN ingestion by man has also been given as 50-60 mg (2963, 3498). Carson (1483) states that the average fatal dose of HCN for a man is 0.7 to 3.5 mg per kg of body weight. On this basis, the fatal dose for a man weighing 165 pounds would be about 52 to 260 mg. See Cyanides for a discussion of drinking water standards.

b. Stock and Wildlife Watering. Toxic and lethal doses of HCN have been reported (353) as follows:

 Animal
 Dose of HCN
 Animal
 Dose of HCN

 Cow
 0.39 to 0.92 grams
 Horse
 0.39 grams

 Sheep
 0.04 to 0.10 grams
 Dog
 0.03 to 0.04 grams

For sheep, toxic doses have also been given as 1.05 mg per kg of body weight. Samples of water fatal to cows and ducks contained 103 mg/l of hydrogen cyanide (353, 1118). Rats fed for two years with food containing 100 to 300 mg/kg of HCN showed no signs of cyanide toxicity. There were no hematological or pathological evidences of adverse effects (3499).

c. Fish and Other Aquatic Life. Most of the literature on the effects of HCN and other cyanides expresses toxicity effects in terms of the cyanide ion (see Cyanides). Garrett and Daugherty (1441, 2959, 2960) used the marine pin perch (Lagodon rhomboides) as a test animal and found the 24-hour TL_m to be 0.069 mg/l, while all fish died at 0.10 mg/l. They concluded that it would be unsafe to discharge HCN to ocean waters when it resulted in a concentration greater than 0.05 mg/l. According to Czensny (1575) concentrations of 0.10 to 0.15 mg/l of HCN are toxic to trout. For further experimental results, see Cyanides.

# HYDROGEN FLUORIDE

(see also Fluorides)

This colorless gas is very soluble in water, dissociating to hydrogen and fluoride ions (see Fluorides). Hydrogen fluoride, per se, is reported to be harmful to fish at 40 mg/l and lethal at 60 mg/l (353).

# HYDROGEN ION

(see pH)

# HYDROGEN PEROXIDE

 $H_2O_2$ 

(see also Hydrazine)

This colorless, unstable liquid with a bitter taste is miscible with water and is sold commercially as a 3 percent solution for medical use. In the pure state it is used in rocket fuels and has occurred in waste waters from the testing of rocket motors. Southgate (659) showed that over 40 mg/l of hydrogen peroxide was toxic to fingerling trout, but less than 40 mg/l had no harmful effect in 48 hours. Concentrations of 200 mg/l are bactericidal but do not impart a taste to water. Higher dosages cause very unpleasant tastes (1581).

# HYDROGEN SULFIDE

 $H_2S$ 

1. General. This flammable, poisonous gas with a characteristic odor of rotten eggs is highly soluble in water, to the extent of about 4000 mg/l at 20°C and one atmosphere. Upon solution it dissociates according to the reactions:

$$H_2S \rightleftharpoons HS^- + H^+$$
  
and  
 $HS^- \rightleftharpoons S^{--} + H^+$ 

The dissociation equilibria are such that, at 18°C, the ratios between H₂S, HS⁻, and S⁻⁻ are as follows:

$$\frac{[\text{HS}^{-}]}{[\text{H}_2\text{S}]} = \frac{9.1 \times 10^{-8}}{[\text{H}^{+}]}$$

$$\frac{[\text{S}^{--}]}{[\text{HS}^{-}]} = \frac{1.2 \times 10^{-5}}{[\text{H}^{+}]}$$

Thus, at pH 9 about 90 percent of the sulfide is in the form of HS-, at pH 7 it is about equally divided between HS- and H₂S, and at pH 5 less than 1 percent is present as HS-; consequently, H₂S will escape to the air. Only at pH 10 and above is sulfide ion present in appreciable proportions.

The sources of hydrogen sulfide in water include natural processes of decomposition, sewage, and industrial wastes such as those from tanneries, paper mills, textile mills, chemical plants, and gas-manufacturing works.

In the presence of certain sulfur-utilizing bacteria, sulfides and hydrogen sulfide can be oxidized to colloidal sulfur, and these bacteria or their deposits may be considered as corollary pollutants.

- 2. Cross References. Sulfur, Gas-plant Wastes, pH, Chapter VII-Sulfur Bacteria.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Hydrogen sulfide is present in many municipal supplies as a result of the anaerobic decomposition of underground organic deposits. While generally considered undesirable because of their odors, such waters are sometimes prescribed or recommended for respiratory, metabolic, and skin disorders, especially in Europe where health resorts have been founded upon such waters (e.g. Spa, Bad Wiessee) (653). The minimum concentration of hydrogen sulfide detectable by taste in drinking waters is given as 0.05 mg/1 (2059).
- b. Industrial Water Supplies. The concentration of hydrogen sulfide in certain industrial waters, especially those used for foods and beverages, is frequently limited. These restrictions are described in Chapter V, from which the following material was condensed.

Industrial Use	Range of Recommended Threshold Values in mg/l
Baking	0.2
Boiler feedwater	
0 to 150 psi	5
150 to 250 psi	3
over 250 psi	0
Brewing	0.2
Carbonated beverages	0.0 to 0.2
Confectionary	0.2
Cooling Water	5.0
Food canning and freez	ing 1.0

In preparing photographic developers, H₂S is particularly bad impurity, according to Crabtree and Mathews (242).

c. Fish and Other Aquatic Life. The following concentrations of hydrogen sulfide have been reported as toxic to fish within the time specified:

Concentra- tion of H ₂ S in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
0.86		24 hours	trout	359, 311
1.0			minnows, shiners	190, 3500
1.0			king salmon, cutthroat trout	3501, 3502
1.0 1.0 1.2 1.38 3.3 3.8 4.3 4.9 to 5.3 5-6 6.25 8-12	15°C	24 hours	trout 362 salmon silver salmon fathead minnows carp suckers goldfish sunfish goldfish fish minnows carp carp	, 1046, 658 1582 3501, 3502 359, 311 363, 313 463, 311 362, 359, 311 362, 1046
10	hard	96 hours	goldfish	313, 367
10	tap	15 minutes	trout	313 359
25		24 hours 3 hours	goldfish tench	313
100	tap	a nours	tencu	010

In contrast, the following concentrations of hydrogen sulfide were survived by the test fish:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
0.3		king salmon	3503
0.5		cutthroat trout	3503
0.7	. ==	silver salmon	3503
4.6	24 hours	minnows	. 362

According to Haydu et al. (1582) the maximum concentration of  $\rm H_2S$  tolerated without injury by the most sensitive fish was about 0.3 mg/l, while Nellist (1466) considers 1.0 mg/l to be the limiting toxic concentration. Murdick (1460) sets the critical concentration at 0.5-1.0 mg/l.

For Daphnia magna, the minimum lethal concentration has been given as 1.0 mg/l (190, 313, 574); for mayfly larvae, 1.0 mg/l; and for chironomous larvae 750 mg/l (190, 3500). Hydrogen sulfide is toxic to most algae (1452); however, hundreds of species of plant microorganisms have been found thriving in stagnant ditches containing 0.22 to 0.45 mg/l of H₂S.

d. Shellfish Culture. According to Oliveira (1215), the hydrogen sulfide generated by a deposit on the bottom of a bay was an important factor in causing the death of young oysters.

# HYDROQUINONE

 $C_6H_4(OH)_2$ 

(see also Benzene Derivatives, Phenol, Pyrocatechol, and Resorcinol)

Known also as p-dihydroxybenzene, this crystalline substance is highly soluble in water. It is used as an antioxidant, as a reducer in photographic developing, and as a chemical reagent in phosphate tests. The oral  $LD_{50}$  for rats is given as 320 mg/kg of body weight (364).

According to Sollman (1474), the approximate 48-hour  $TL_m$  for goldfish was 0.287 mg/l. In Lake Huron water at 12°C, rainbow trout succumbed to 5 mg/l of hydroquinone in 4 hours, bluegill sunfish in 6 hours, and sea lampreys in 14 hours (2976). Threshold concentrations of hydroquinone have been given by Bandt (2904) as 0.2 mg/l for earp, perch, and stickleback at 16°C in moderately hard water.

For lower organisms in River Havel water, Bringmann and Kuhn (2158, 3343) determined the threshold concentrations for adverse effect to occur as follows:

Organism	$Temperature,\ ^{\circ}C$	Threshold Concentration
		mg/l
Daphnia	23	0.6
Microregma .		2.0
Scenedesmus	24	4.0
E. coli	27	50.0

Bandt (2904) reports the toxic threshold for the water flea, Gammarus, to occur at 1.5 mg/l.

#### HYDROXIDES

OH-

(see also Alkalinity, Carbonates, Bicarbonates, pH, and cations that form hydroxides, such as calcium, potassium, and sodium).

The concentration of hydroxyl ions in any solution is indicated by the pH value (see pH). Hydroxides also contribute to the alkalinity of water and markedly influence carbonate equilibria (see Alkalinity, Carbonates, and Bicarbonates). The hydroxyl-ion concentration is given by the relations:

$$\begin{array}{l} [\mathrm{OH^-}] \ = \ \frac{10^{-14}}{[\mathrm{H^+}]} \ \mathrm{in \ mols \ per \ liter} \\ \\ \mathrm{or \ Hydroxides} \ = \ \frac{17,000 \times 10^{-14}}{[\mathrm{H^+}]} \ \mathrm{in \ mg/l \ as \ OH^-} \\ \\ \mathrm{or \ Hydroxides} \ = \ \frac{50,000 \times 10^{-14}}{[\mathrm{H^+}]} \ \mathrm{in \ mg/l \ as \ CaCO_3} \end{array}$$

Thus, at pH 10, the alkalinity attributable to hydroxide ion is only 5.0 mg/l and at lower pH values the concentration of hydroxyl ions in relations to other forms of alkalinity is insignificant.

While not present in appreciable concentrations in natural streams, hydroxides may be increased materially by the discharge of alkaline industrial wastes such as those from beam-houses in tanneries, soda and sulfate pulping mills, cotton kiering, wool scouring, and finishing in textile mills.

Most of the references dealing with the effects of hydroxides on the beneficial uses of water express concentrations in terms of salts such as KOH, NaOH, and Ca(OH)₂. Such literature is covered under the appropriate cation in this report. Only those references in which hydroxide is reported as such are discussed below.

The N.E.W.W.A. Committee on Water Quality Tolerances for Industrial Uses (159) suggests the following limits for the hydroxide-ion concentrations in boiler feed waters:

Pressure, in psi	Hydroxide, in mg/l
0-150	50
150-250	40
250-400	30
400 and over	15

In testing the relative toxicities of the various anions of sodium salts toward *Polycelis nigra*, a flatworm, Jones (354) found the toxic threshold of hydroxide to be 13 mg/l. For toxicities of hydroxides to fish and other organisms, see the specific salts.

#### HYDROXYLAMINE

 $NH_2OH$ 

This hygroscopic solid is very soluble in water with an alkaline reaction, apparently from dissociation and the formation of ammonium ions. Corti (146) tested rainbow trout (Salmo irideus) at a concentration of 150 mg/f of hydroxylamine and a temperature of 13.5°C. The fish displayed their first adverse reaction in 5 to 10 seconds, turned over in 4 to 6 minutes, and made their last motion in 9 to 10 minutes.

# HYPOCHLORITES

(see Calcium Hypochlorite, Chlorine, Sodium Hypochlorite)

# HYPOCHLOROUS ACID

(see Chlorine)

# IGEPAL CA

# IGEPON T

(see Chapter X)

# INDOLE $C_8H_7N$

This highly odoriferous compound occurs in coal tar, feces, and some plants. Soluble in hot water, it produces a pleasant odor in dilute concentrations; hence it is used in perfumes. In Lake Huron water at 12-13°C, exposure to 5 mg/l of indole for ten hours produced death or obvious distress to trout, but the same concentration for 24 hours had no effect on bluegill sunfish or sea lamprey (1976).

# INSECTICIDES

(see Chapter IX)

# IODINE

Elemental iodine and iodides occur only as traces in fresh natural waters, but their concentration in sea water is somewhat higher. There iodine is absorbed by certain seaweeds, the ash of which constitutes a source of sodium iodide and iodine for commercial use. Because they are used only sparingly in industry, e.g. for medicines, germicides, and analytical chemistry, iodine and iodides are not likely to occur in polluted waters in significant concentrations. There is a possibility, however, that radioactive iodine from medical and research institutions may be discharged accidentally (see Chapter VIII).

In contrast with chlorine, elemental iodine is only slightly soluble in water, except in the presence of iodides, and it is not appreciably hydrolyzed in weak acid solution. Its disinfecting power, therefore, is not attributable to the HOI molecule or to iodide, but rather to molecular iodine or possibly to tri-iodides (1216). Extensive unpublished research on the mechanism of disinfection by iodine and the effects of iodine upon human physiology has been performed by Fair and others at Harvard University. Iodine has been used successfully for the disinfection of water in swimming pools (3504) with residual concentrations of free iodine in the range of 0.2 to 0.6 mg/l.

There is extensive literature dealing with the relationship between iodine deficiencies in water or food and the incidence of goiter, but a thorough review of it is not within the province of this survey. To overcome an iodine deficiency and to minimize goiter in the community, Rochester, New York, added iodine to its water supply from 1923 to 1933; but, owing to economic factors, the availability of a superior vehicle (salt) for the dispersing of iodine, and the adverse effect upon certain individuals sensitive to iodine, the Rochester experiment was abandoned and further mass treatment for iodine deficiency was discouraged (152, 330). The iodine content of blood appears to be independent of the iodine in domestic water supplies (3505, 3506).

It has been reported (1586) that 8 mg/l of iodine destroys all forms of water-borne pathogens, but no adverse affects were noted when personnel in the tropics used drinking water containing NaI at a rate of 12 mg of iodine per man per day for 16 weeks and 19.2 mg per day for the next 10 weeks (1587).

Ellis (313) quotes references to the effect that 28.5 mg/l of iodine killed minnows and goldfish.

With the advent of nuclear testing and the extensive use of radioisotopes in medicine and industrial research, radioiodine (I-131) has become a significant environmental factor. The maximum permissible level of I-131 in drinking water has been given as 0.03 microcurie per liter (3375, 3507, 3508). Algae and other plankton concentrate radioiodine from water by factors in excess of 100,000 within a few days after the iodine becomes available (3509). For further information on concentration factors, see Chapter VIII.

# IODOACETIC ACID

CH₂ICOOH

This white crystalline substance is highly soluble in water. Hiatt et al. (3350) found that 10 mg/l of iodoacetic acid produced a moderate irritant activity in marine fish.

# IPC

(see Chapter IX)

## IRON BACTERIA

(see Chapter VII)

#### IRON

 $\mathbf{Fe}$ 

1. General. Metallic iron and its common alloys are of interest in this survey primarily because they are corroded by water in the presence of oxygen. The resulting products of corrosion, in which the iron is in the ionic or molecular state, may in themselves be pollutants of water. In addition to corrosion products, natural wa-

ters may be polluted by iron-bearing industrial wastes such as those from pickling operations and by the leaching of soluble iron salts from soil and rocks, e.g. acidmine drainage and iron-bearing ground water.

Although many of the ferric and ferrous salts such as the chlorides are highly soluble in water, the ferrous ions are readily oxidized in natural surface waters to the ferric condition and form insoluble hydroxides (3510). These precipitates tend to agglomerate, flocculate, and settle or be absorbed on surfaces; hence, the concentration of iron in well-aerated waters is seldom high. In ground water, the pH and Eh may be such that high concentrations of iron remain in solution (3510, 3520).

The following material deals with references to iron or iron ions when no designation of a salt or anion has been made. For literature covering the various ferric and ferrous salts, see the cross references.

- 2. Cross References. Ferric Chloride, Ferric Oxide, Ferric Potassium Sulfate, Ferric Sulfate, Ferrous Carbonate, Ferrous Chloride, Ferrous Sulfate, Chapter VII-Iron Bacteria.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The 1962 Drinking Water Standards of the USPHS (2036) included a recommended limit of 0.3 mg/l for iron. The 1958 WHO International Standards (2328) contain a "permissible limit" of 0.3 mg/l and an "excessive limit" of 1.0 mg/l but prescribe no maximum allowable limit. The 1961 WHO European Standards set a recommended limit of 0.1 mg/l for iron. Some authorities (1217, 1218) maintain that drinking water should not contain more than 0.1 mg/l of iron.

The WHO and USPHS limits are based not upon physiological considerations, for iron in trace amounts is essential for nutrition. Indeed, larger quantities of iron are taken for therapeutic purposes (555, 1077). The daily nutritional requirement is 1 to 2 mg, and most diets contain 7 to 35 mg per day, with an average of 16. Consequently, drinking water containing iron in unpalatable and unesthetic concentrations, say 1.0 mg/l, would have little effect on the total daily intake.

Instead of physiological reasons, therefore, the limit is based on esthetic and taste considerations. Iron and manganese tend to precipitate as hydroxides and stain laundry and porcelain fixtures. It has also been reported (1160) that ferric iron combines with the tannin in tea to produce a dark violet color.

The taste threshold of iron in water has been given (3511) as 0.1 and 0.2 mg/l of iron from ferrous sulfate and ferrous chloride respectively. It has also been reported (3300) that ferrous iron imparts a taste at 0.1 mg/l and ferric iron at 0.2 mg/l. In contrast, Lockhart et al. (3241) indicated that the taste threshold of ferric sulfate was 10 mg/l of iron. Using a statistically controlled taste panel, Cohen et al. (3301) found that the median taste threshold for ferrous sulfate in spring water occurred at 1.8 mg/l of iron, but for the most sensitive individuals it was 0.12 mg/l. Similarly, for ferrous sulfate in distilled water, the median taste threshold concentration was 3.4 mg/l of iron but the most sensitive individuals tasted 0.04 mg/l.

/l

Iron in domestic water supplies containing organic matter may be present in chelated form and consequently will not precipitate readily (2338, 3510, 3512). Furthermore, it may occur in microbial protoplasm as described under part 3e, following.

b. Industrial Water Supplies. The ranges of recommended threshold values for iron in process and cooling waters are given in Chapter V. Most of this information has been reassembled and tabulated below:

·	Range of Recommended
Industrial Use	Threshold Values in mg
Baking	_ 0.2
Brewing	
Carbonated beverages	
Cooling water	_ 0.5
Confectionary	
Electroplating	_ traces
Food canning and freezing	
Food equipment washing	0.2
Food processing, general	_ <b>0.2</b> .
Laundering	0.2-1.0
Oil-well flooding	0.1
Photographic processes	0.1
Pulp and paper making	
Ground wood pulp	_ 0.3
Soda pulp	_ 0.1
Kraft pulp, bleached	_ 0.2
Kraft pulp, unbleached	_ 1.0
Fine paper pulp	0.1
Rayon manufacture	_ 0.0 to 0.05
Sugar making	0.1
Tanning processes	_ 0.1 to 2.0
Textile manufacture	_ 0.1 to 1.0

- c. Irrigation. Iron is one of the minor constituents of irrigation water, usually occurring in low concentrations. It is generally of little importance in irrigation practice (268). Chelated iron has been used to combat chlorosis in plants.
- d. Stock and Wildlife Watering. Iron is an essential constituent of animal diets (553), but animals are sensitive to changes in iron concentration (945). Cows will not drink enough water if it is high in iron, and consequently, milk production is affected (549).
- e. Fish and Other Aquatic Life. Most of the references dealing with this beneficial use are expressed in terms of specific iron salts (see cross references). When iron is added to water in the form of chlorides, sulfates, or nitrates, the salt dissociates but the resulting ferrous or ferric ions combine with hydroxyl ions to form precipitates. Hence, very little of the iron remains in solution; but if the dosage is sufficient and the water is not strongly buffered, the addition of a soluble iron salt may lower the pH of the water to a toxic level. Furthermore, the deposition of iron hydroxides on the gills of fish may cause an irritation and blocking of the respiratory channels. Finally, heavy precipitates of ferric hydroxide may smother fish eggs (346, 2109, 3513).

Knight (540) tested the effects of wastes from nail-making plants on trout, stickleback, and perch. These wastes contained high concentrations of chloride, hydrogen, ferric, and ferrous ions, but the pH values were not specified. Concentrations of 1000 mg/l of these mixed salts killed most fish within a few hours, but hardy stickleback were not killed until five hours exposure to 2500 mg/l. Much of the killing action was attributed to coatings of iron oxide or hydroxide precipitates on

the gills. According to Southgate (346), the toxicity of iron and iron salts depends on whether the iron is present in the ferrous or ferric state and whether it is in solution or suspension. The following limiting concentrations have been noted:

Concentration of Iron, in mg/l	Remarks	Reference
0.2	Threshold concentration for lethality to three types of	
0.9	Carp will die at this con- centration if pH is 5.5 or	1023
1.0	lower	306
1-2	Death of pike, tench, and trout at pH 5.0-6.7	1459, 1588
1-2	No deaths among dogfish	
1-2	during one week Indicative of acid pollution and other conditions unfa-	3415
	vorable to fish	247
5	Killed dogfish in 3 hours	3514
10	Caused serious injury or death to rainbow trout in	
	5 minutes	604
40	Not lethal to fingerling channel catfish in 96 hours when added as ferrous di-	•
	sodium versanate	2981
50	Upper limit for fish life	801

Waters that support good fish fauna in the United States, according to Ellis (310), have the following concentrations of iron:

Concentration of	Percent of Waters Having
Iron, in $mg/l$	This Concentration, or Less
0.0	5
0.3	50
0.7	95

Crenothrix, Gallionella, and other iron bacteria utilize iron as a source of energy and store it in their microbial protoplasm. They may accumulate in wells, treatment plants, pipelines, and other waterworks structures; or they may pass into the distribution system and cause customer complaints (2700, 2701, 2705). At Wilmington, California, where the residual iron content was only 0.025 mg/l, Wilson (1219) found growths of Crenothrix. Trouble with this organism is experienced frequently when the iron exceeds 0.2 mg/l.

Radioactive iron, Fe-59, may be concentrated by certain microorganisms in aquatic and marine environments. For further details on concentration factors for radionuclides, see Chapter VIII. The following concentration factors have been reported for Fe-59:

Concentration		
Factor	Organism	Reference
720-1030	flagellate, Platymonas	3386
1000	vertebrates, soft parts	2440
1550-4480	alga, Ochromonas	3386
4220	diatom, Navicula conf.	3386
5000	vertebrates, skeleton	2 <b>44</b> 0
5533	diatom, Nitzschia	3386
6000	flagellate, Chlamydomonas	3386
7500	flagellate, Rhodomonas	3386
10,000	fish	2436
10.000	invertebrates, soft parts	2440
20,000	algae, non-calcareous	2440
100.000	insect larva	2436
100.000	filamentous algae	2436
100,000	invertebrates, skeleton	2440
200,000	phytoplankton	2436

- 4. Summary. On the basis of the foregoing information, the following concentrations of iron should not be deleterious to the designated beneficial uses:

#### IRON HUMATE

(see Humic Acid)

#### ISODRIN

(see Chapter IX)

#### ISOPRENE

 $C_5H_8$ 

This unstable, oxidizable liquid, insoluble in water, is used in the manufacture of synthetic rubber (364). According to Klimkina (3413), it has an odor threshold in water at a concentration of 0.005 mg/l. For warmblooded animals, the threshold limit in drinking water is 5 mg/l, but deoxygenation of wastes is not inhibited by 30 mg/l.

### IVORY SNOW

(see Chapter X)

#### **JAUNDICE**

(see Chapter VII-Infectious Hepatitis)

## KELTHANE

(see Chapter IX)

#### KEROSENE

(see Oil, Petroleum)

#### KRAFT PULP MILL WASTES

1. General. Certain types of wood, primarily coniferous, are pulped in digesters with a strong caustic solution containing sodium hydroxide, sodium sulfate, and sodium sulfide. This procedure is known as the "Kraft" process. When sulfur compounds are not used, as in the pulping of deciduous wood, the digestion is known as the process. In either process, the concentrated alka-'soda' line wastes that are drained and washed from the pulped wood are known as "black liquor". Economy of operation dictates that such black liquors be kept as concentrated as possible and that they be processed for the recovery and re-use of the sodium salts. In well-operated soda or Kraft mills, therefore, the only liquid wastes result from rinse or wash waters that are too dilute to be recovered economically.

Black liquors from Kraft mills, although having a much lower B.O.D. than sulfite waste liquors, have been shown to be much more toxic to aquatic life (465, 683, 684). This toxicity appears to be related to the sulfur compounds, especially the mercaptans, and the resinous and fatty-acid components (685). Kraft-mill black liquors contain mercaptans, dimethyl sulfide, turpentine, methyl alcohol, ammonia, lignin, fatty and resinous acids, formic acid, acetic acid, lactonic acid, and sodium salts of organic and inorganic acids. Most of the organic constituents of black liquors are derived from the cellulose-binding substances in the wood, such as the lignins, pectins, and hemicelluloses.

2. Cross References. Sulfite Waste Liquors, Soaps, Resins, Mercaptans, and other substances noted above.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Kraft-mill wastes discolor water, cause tastes and odors, and raise the pH. A report by the Technical Association of the Pulp and Paper Industries (686) states that a Kraft-mill waste contained 33 mg/l of sulfide and 12 mg/l of mercaptans. To render it odorless, a dilution of 1:50,000 was required; but after chlorination of the waste to a 1.5 mg/l residual, the required dilution was only 1:40. Insofar as domestic water supply is concerned, the elimination of tastes and odors appears to be the controlling factor.

b. Irrigation. Stabilized Kraft-mill effluents have been used directly for spray irrigation of several crops. The yield of crops was increased and there was no damage to the soil resulting from continued application for several years (3522).

c. Fish and Other Aquatic Life. Most of the references dealing with effect of Kraft-mill wastes on fish are expressed in terms of dilution, and inasmuch as the strengths of the wastes are not known the results in the following table are not strictly comparable.

Dilution	Aquatic Organism	Remarks	Reference
1:2	Fish	Killed in 7 minutes	683
1:20.8	Sockeye salmon	Maximum non-	V00
		lethal concentration	3521
1:200	Fish	Killed	687
1:200	Fish	Killed	311. 688
1:500	Fish	Irritated but not killed	311. 688
1:500 to			,
1:1000	Fish	Killed in 10 days or less	673
1:1000	Fry and	242224	0.0
	fingerlings	Killed .	1225
1:2000	Fish	Killed	689

The Department of Fisheries of the State of Washington (2091) conducted tests with synthesized Kraftmill effluents and salmon. It was found that older chinook salmon in flowing sea water were least tolerant, requiring a dilution of 60 to 1 to prevent a kill. Silver salmon in flowing fresh water required only 30 to 1. For black liquor, itself, chinook salmon required a dilution of 1093 to 1 in aerated sea water.

In a report of the National Council for Stream Improvement, (690, 3523) the toxicities of various components of Kraft mill waste were compared, as shown in the following table:

	Minimum 1	ethal Conce	entrations, mg/l
Waste Component	Minnows	Daphnia	Insect Larvae
Sodium hydroxide	100	100	125-1000
Sodium sulfate	100	5000	
Sodium sulfide	3	10	2-1000
Sodium carbonate	250	300	
Sodium sulfite		300	
Methyl mercaptan	0.5	1	50
Crude sulfate soap	5.0	5-10	50
Resin acid soap	1.0	3	50-100
Hydrogen sulfide	1.0	1	

In a subsequent report (3501, 3503) the N. C. S. I. listed the minimum lethal concentrations (for 100 percent kill) and the maximum concentrations for no kill of seven components of the Kraft-mill effluents toward king salmon, silver salmon, and cutthroat trout. The results are shown herein under the specific chemicals, viz, hydrogen sulfide, methyl mercaptan, sodium sulfide, sodium sulfhydrate, sodium hydroxide, sodium carbonate, and sodium sulfate.

Extrom and Farner (691) studied the toxicities of effluents from a sulfate mill and the effluents after dilution in the river, using largemouth bass, bluegills, and sunfish. At 50 percent of the concentration of the mill effluent, with 80,000 mg/l of total solids and 3300 mg/l of sodium sulfide, all bass died in 9 days and sunfish in 15 days. Wastes being tested were aerated to keep the dissolved-oxygen content above 4.0 mg/l, so that toxicity was not attributed to oxygen deficiencies. After dilution by the river, such that the concentrations of sodium sulfide were only 0.099 mg/l, none of the fish died.

Jones et al. (3524) showed that chinook salmon tried to avoid concentrations of Kraft-mill effluent, while coho salmon and steelhead trout were less sensitive to this waste.

For the N. C. S. I., Gehm (344, 658, 692) summarized the work of many people to show the effects of sulfate liquors and their components on fish. The critical concentration (minimum lethal dose) for each component is shown by the following table:

•	Critical
Component	Concentration, mg/l
Sodium hydroxide	100
Sodium sulfide	3
Methyl mercaptan	0.5
Hydrogen sulfide	1.0
Formaldehyde	
Crude sulfate soap	5.0
Unsaponifiable fraction of sulfate soa	p 6.0
Sodium salts of saponifiable fraction	
of sulfate soap	3.0
Sodium salts of fatty acids	5.0
Sodium salts of resin acids	1.0
Sodium oleates	5.0
Sodium linoleate	
Sodium salts of abietic acid	3.0
Phytosterol	
Sodium thiosulfate	
Sodium sulfate	
Sodium chloride	
Sodium hydrogen sulfide	
Sodium sulfide (as sulfide)	
MOUTUIL DELINES (ND BUILDE)	

c. Shellfish Culture. Galtsoff et al. (693) report that the threshold concentration of sulfate-pulp-mill effluents dumped into the York River, Virginia, occurred at a dilution of 1:2000, for oysters. At this dilution, there was a decrease in feeding. The toxic factor in these wastes tends to concentrate in the soap portion, resin acids, and sodium and calcium salts.

#### KURON

(see Chapter IX)

## LACTATES

(see Lactic Acid, Mercury)

### LACTIC ACID

CH₃CHOHCOOH

(see also Dairy Wastes)

This organic acid occurs in sour milk and other sour foods, such as sauerkraut, as the result of bacterial decomposition of the milk sugar, lactose. It also occurs in blood and urine. Industrial uses include numerous processes in food and beverage production and medicine, in dyeing baths, as a mordant in textile printing, in tanneries, and as a solvent. Hence it may occur in wastes from any of these processes.

Ellis (313) reports that 430 mg/l of lactic acid in hard water was not lethal to goldfish in over 100 hours, but 654 mg/l at 18-23°C killed them in 6 to 43 hours. At low dissolved-oxygen contents, lactic acid was even more toxic (311). In soft water, which is generally weakly buffered, the toxic limit appears to be lower. Leclerc et al. (2942, 2943) exposed minnows for 6 hours to water at 20°C containing lactic acid. In hard water the minimum lethal dose was 470-480 mg/l but in distilled water it was only 18-20 mg/l. The effect of these dosages upon pH is not indicated. For Squalius leuciscus the lethal level is 1000 mg/l and for Salmo irideus it is 400 mg/l, but harmful symptoms develop at 100 mg/l. For trout, 100 mg/l is lethal in about 18 hours (2977).

Doudoroff and Katz (361) claim that lactic acid can be directly lethal to fully developed fish only when the pH value is reduced to 5.0 or lower. This explanation agrees with the antagonistic effect of hardness and al-

kalinity toward the toxicity of lactic acid.

According to Westfall (3525) the lethality of lactic acid to goldfish is independent of the oxygen level. Inasmuch as no precipitate of mucus was observed on the gill filaments except in very strong solution, he suggested that lactic acid diffuses into the blood and death results from systemic effects of the absorbed acid.

For Daphnia magna, Ellis (313) reports a toxic limit of 170 mg/l in 26 to 72 hours in soft water whereas Anderson (358), gives the threshold concentration of 243 mg/l for immobilization in Lake Erie water after pro-

longed exposure at 25°C.

#### LACTONITRILE

CH₃CH(OH)CN

(see also Cyanides, Hydrogen Cyanide)

Among the common organic cyanides, lactonitrile is unique in that it dissociates appreciably in water to release cyanide ion which then combines with hydrogen ion to form the toxic HCN principle. According to Henderson et al. (2958) the cyanide ion released is almost equivalent to the CN content of the lactonitrile. Renn (2968) reported that lactonitrile yielded tolerance values only slightly less than those for potassium cyanide, both expressed as N. Consequently, it is not surprising that several investigators report this compound to be highly toxic.

The critical concentration of lactonitrile for a mixed population of common fish was reported by Renn to be about 0.09 mg/l as N (or 0.457 mg/l as lactonitrile). Garrett (2959, 2960) found the 24-hour  $TL_m$  for pin perch to be 0.215 mg/l and all fish were killed at 0.50 mg/l. Daugherty and Garrett (1441) postulated that it would be unsafe for marine fish such as pin perch if the lactonitrile concentration in sea water exceeded 0.10 mg/l.

Henderson et al. (2958) conducted bioassays using three species of common fish in both hard and soft water saturated with oxygen at 25°C. Their results as shown below are expressed as median toxic limits based on commercial lactonitrile.

Wind of	Tupe of	$TL_m$ in $mg/l$		
Kind of Fish Fathead minnows Fathead minnows Bluegills	Water hard soft soft	24-hour 0.90 0.90 0.90	48-hour 0.90 0.90 0.90	96-hour 0.90 0.90 0.90 1.37
Gupples	soft	1.37	1.37	1.37

Adult bluegills exposed up to four weeks in water containing 0.25 mg/l of lactonitrile did not pick up any organoleptic properties that could be detected by a taste panel (2958).

#### LANTHANUM

La

(see also Chapter VIII—Radioactivity)

This rare-earth metal occurs in nature chiefly as the oxide in several minerals, frequently associated with cerium. It is used as a weighting agent for silk and rayon, in the manufacture of glass and ceramics, and in "flint" lighters (364, 2121). The chloride, hydroxide, and nitrate salts are highly soluble in water; but the carbonate, oxide, and sulfate are insoluble. Hence, lanthanum ions in waste waters are likely to be precipitated and removed by sedimentation or adsorption, as carbonates or sulfates.

Lanthanum is not recognized as a toxic element for man or animals. The  $\rm LD_{50}$  values for rats, in terms of lanthanum were reported (3526, 3527) as 4440 mg/kg for lanthanum acetate, 1450 mg/kg for the nitrate, 2450 mg/kg for the sulfate, and over 8500 mg/kg for the oxide.

Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of lanthanum acetate on four organisms. For Daphnia exposed for 48 hours at 23°C, the median threshold effect occurred at 160 mg/l, expressed as lanthanum. For Scenedesmus exposed for 4 days at 24°C, the median limit was only 0.15 mg/l of lanthanum; for E. coli at 27°C it was 0.4 mg/l, and for a protozoan (Microregma) it was 24 mg/l.

#### LARVICIDES

(see Chapter IX)

# LAURYL DIMETHYL BENZYL AMMONIUM CHLORIDE

(see Chapter X)

# **LEAD** Pb

1. General. Some natural waters contain lead in solution, as much as 0.4-0.8 mg/l, where mountain limestone and galena are found. In the U.S.A., lead concentrations in surface and ground waters used for domestic supplies range from traces to 0.04 mg/l averaging about 0.01 mg/l (3528). Lead may also be introduced into water as a constituent of various industrial and mining effluents, or as a result of the action of the water on lead in pipes.

In the examination of waters for various beneficial uses, their action on lead may be of great importance and should always be considered since lead is frequently used for service and domestic pipes and water-storage chambers. The factors that determine the action of plumbo-solvent waters are complex and not yet fully understood. Practically all waters have a slight action on new lead pipes, although in most cases it is only transient and insufficient to be harmful. Normally the internal lead surfaces quickly acquire a protective coating, after which no further lead is dissolved by the water.

With certain types of water, however, no such protective covering is developed, or its formation may be so slow that the solution of lead can go on for a long time. The characteristics of water, soft or hard, that appear to be conducive to plumbo-solvency include comparative absence of calcium and magnesium bicarbonates, low pH, high dissolved oxygen, and high nitrate content (36, 1199, 1226).

The following material was gathered from references in which the effects of lead were given without details of the entire compound, if any. Where specific lead salts were mentioned, the data were listed under the appropriate salt. Certain lead salts, such as the acetate and chloride, are readily soluble, but owing to the fact that the carbonate and hydroxide are insoluble and the sulfate is only sparingly soluble, lead will not remain long in natural waters.

- 2. Cross References. Dissolved Oxygen, pH, Lead Acetate, Lead Arsenate, Lead Chloride, Lead Fluoride, Lead Nitrate, Lead Sulfate, Tetraethyl Lead.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Foreign to the human body, lead is a cumulative poison. It tends to be deposited in bone as a cumulative poison. The intake that can be regarded as safe for everyone cannot be stated definitely, because the sensitivity of individuals to lead differs considerably. Typical symptoms of advanced lead poisoning are constipation, loss of appetite, anemia, abdominal pain, and tenderness, pain, and gradual paralysis in the muscles, especially of the arms. A milder and often undiagnosed form of lead poisoning also occurs in which the only symptoms may be lethargy, moroseness, constipation, flatulence, and occasional abdominal pains (36). Lead poisoning usually results from the cumulative toxic effects of lead after continuous consumption over a long period of time, rather than from occasional small doses. Immunity to lead cannot be acquired, but sensitivity to lead seems to increase (1227). Lead is not among the metals considered essential to the nutrition of animals or human beings (2121).

Lead may enter the body through food, air, and tobacco smoke as well as from water and other beverages. Consequently, the total intake of lead must be considered in setting standards for water. The exact level at which the intake of lead by the human body will exceed the amount excreted has not been established, but it probably lies between 0.3 and 1.0 mg per day (152). The mean daily intake of lead by adults in North America is about 0.33 mg. Of this quantity, 0.01 to 0.03 mg per day are derived from water used for cooking and drinking (3528, 3529). A total intake of lead appreciably in excess of 0.6 mg per day may result in the accumulation of a dangerous quantity of lead during a lifetime. Lead in an amount of 0.1 mg ingested daily over a period of years has been reported to cause lead poisoning (1228, 1229). The daily ingestion of 0.2 mg lead is considered excessive by one authority (1230). On the other hand one reference considered 0.5 mg per day safe for human beings, and a daily dose of 2.0 mg for a one-year period apparently did not affect the health of one adult (353).

Lead poisoning among human beings is reported to have been caused by the drinking of water containing lead in concentrations varying from 0.042 mg/l to 1.0 mg/l or more (27, 29, 32, 36, 629, 997, 1231, 1232, 1233, 1234, 1235, 1236, 1237, 1238, 1239, 1240, 1241, 1242, 1243, 1244, 1245, 2326, 3530, 3531). On the other hand, concentrations of 0.01 to 0.16 mg/l have been apparently non-poisonous over long periods of time (1077, 1201, 3532). However, there is a feeling that 0.1 mg/l may cause chronic poisoning if the water is used continuously, especially among hypersensitive persons (29).

For many years, the mandatory limit for lead in the USPHS Drinking Water Standards was 0.1 mg/l; but in the 1962 Standards, the limit for lead was lowered to 0.05 mg/l. In the WHO International Standard and WHO European Standards (see Chapter V) the limit for lead has been set at 0.1 mg/l. In the past, the Netherlands and Germany have permitted a temporary lead concentration up to 0.3 mg/l in water that had been in pipes for 24 hours (997, 1229, 3530). Uruguay, on the other hand, has used a standard as low as 0.02 mg/l (1457). Several countries use 0.1 mg/l as a standard.

Owing to the fact that the total intake of lead from food, inhaled atmosphere, and tobacco smoke in industrial urban areas appears to be increasing, with little chance of regulation and diminution, and inasmuch as the concentration of lead in drinking water can be controlled without undue hardship on water purveyors, the USPHS Drinking Water Standard for lead was lowered to 0.05 mg/l in 1962 (2062, 2672). It is significant, however, to note that the U.S. Government has also established a tolerance of lead in food at 7 mg/kg, more than 100 times the limit for drinking water (3533).

b. Industrial Water Supplies. Traces of lead in metal-plating baths will affect the smoothness and brightness of deposits (214).

c. Irrigation. Inorganic lead salts in irrigation water may be toxic to plants and should be investigated further (269, 1014). Klintworth (1493) stated that lead is harmful to plants at all concentrations. On the other hand, the addition of 2.0 mg of lead per kg of dry soil in pot tests increased the nitrogen content of peas (2926). In the culture of oats and potatoes, lead nitrate in concentrations of 1.5 to 25 mg/l had a stimulating effect, but at concentrations over 50 mg/l all plants died in a week's time (2997). See also lead salts.

Lead at a concentration of 51.8 mg/l of nutrient solution was slightly injurious to sugar beets grown in sand culture (1473). Germination of cress and mustard seeds in solution culture was completely inhibited by a 2760 mg/l lead solution, during an exposure period of 18 days. Germination was delayed and growth was retarded by 345-1380 mg/l of lead (1479).

d. Stock and Wildlife Watering. Farm animals are poisoned by lead from various sources, including paint, more frequently than by any other metallic poison (1247). It is not unusual for cattle to be poisoned by lead in the water; the lead need not necessarily be in solution, but may be in suspension, as, for example, oxycarbonate (36). Chronic lead poisoning among animals has been caused by 0.18 mg/l of lead in soft water (1232); and by concentrations under 2.4 mg/l (1238). Chronic changes in the central nervous system of white rats were observed after an ingestion of 0.005 mg of lead per kg of body weight (3534). Most authorities agree

that 0.5 mg/l of lead is the maximum safe limit for lead in a potable supply for animals (1238).

Allcroft (1589) reported that calves given as much as 2.0 grams of lead daily have survived for 2 to 3 years. Calves have tolerated daily doses of 8 mg and 6 mg of lead per kg of body weight for, respectively, many months and up to three years. Doses of 0.2-0.4 grams of lead per kg body weight caused death within a few days (1590). When a calf was given drinking water containing lead nitrate at a concentration of 100 mg/l of lead, it survived for only four months. It was suggested that nitrate was partly responsible for the death (1589). Geese have been reported to have contracted lead poisoning from the ingestion of mine tailings (3535).

e. Fish and Other Aquatic Life. The toxic concentration of lead for aerobic bacteria is reported to be 1.0 mg/l; for flagellates and infusoria, 0.5 mg/l. The bacterial decomposition of organic matter is inhibited by 0.1 to 0.5 mg/l of lead (576, 2977, 3324, 3534).

Carpenter and others have studied the effects of small concentrations of heavy metals, particularly lead, upon fish. Such studies indicate that in water containing lead salts, a film of coagulated mucus forms, first over the gills, and then over the whole body of the fish, probably as a result of a reaction between lead and an organic constituent of mucus. The death of the fish is caused by suffocation due to this obstructive layer (346, 991, 1248, 2411). In soft water, lead may be very toxic; in hard water equivalent concentrations of lead are less toxic (311). Calcium in a concentration of 50 mg/l has destroyed the toxic effect of 1.0 mg/l of lead (353).

Wilder found that lobsters died within 20 days when kept in lead-lined tanks; however, in steel-lined and other control tanks they survived for 60 days or longer (1530). Small sticklebacks appeared to be slightly more sensitive to lead than the larger fish (1460).

The Water Pollution Research Board (74) in England conducted extensive experiments to determine the effects of lead salts on rainbow trout in hard and soft waters. In water of the lowest hardness used, 14 mg/l as CaCO₃, all of the lead added as lead nitrate remained in solution and produced a curvilinear relationship of lead concentration vs time of survival. A similar curve was obtained for a water with a total hardness of 27 mg/l as CaCO₃, although some precipitation of PbCO3 occurred with lead concentrations greater than 8.0 mg/l. In solutions with a total hardness of 53 mg/l as CaCO3 the maximum concentration of lead remaining in solution was approximately 1.6 mg/l, and the median period of survival of the trout exceeded two days even at lead dosages in excess of 20 mg/l. It seems probable, therefore, that precipitated lead carbonate is not effective as a lethal agent. For further evidence that insoluble lead is not highly toxic to fish, see Lead Oxide.

A chart submitted by the Water Pollution Research Board (74) indicates that the median period of survival of rainbow trout in soft water containing dissolved lead, at 18.5°C, was 18 to 24 hours at 1.6 mg/l and only 10 to 12 hours at 4.0 mg/l.

The Water Pollution Research Board has also shown that the toxicity of lead toward rainbow trout increases with a reduction of the dissolved-oxygen concentration of the water (74, 88, 3321, 3322). The following table

shows factors by which the threshold concentration of lead must be multiplied to determine concentrations of equal toxicity at lower dissolved-oxygen tensions:

Dissolved oxygen (percent of saturation) 100 80 60 40 Factor 1.0 0.95 0.85 0.71

The following concentrations of lead have been reported toxic or lethal to fish in the time specified (see also the various lead salts):

Concentration				
of lead.	Type of	Time of		
in mg/l	water	exposure	Species of fish	Reference
in ing/i	water			
0.1			Fish	353, 573, 1249
0.1			Sticklebacks	1460, 2920, 2941
0.1			Sticklebacks	1459
0.1-0.2	very soft		Fish	3319
0.2	soft		Guppy	2921
0.21	,	- <b>-</b>	Fish	598
0.25	fresh		Minnows, brown trout	000
0.33		· ·	and sticklebacks	271 212 253 2020
		40.1 TIT	Sticklebacks and coho	3536
0.34	of dissolved	48-hour TLm	salmon salmon	3330
	solids	26-48 hours	Minnows	1459
0.4	distilled		Coho salmon	3536
0.41	1000-3000 mg/l	24-hour TLm	Cono salmon	5550
	of dissolved solids			
0.53	1000-3000 mg/l	24-hour TLm	Sticklebacks	3536
0.00	of dissolved			
	solids	į.		
0.75	BOLIUS		Minnows	353
1.0	!	long-term	Carp	3327
1.0	}	8.5 days	Sticklebacks	1444, 1460
	soft	18-24 hours	Rainbow trout	74
1.4		48-hour TLm	Bluegill sunfish	2093
1.4	tap	24-hour TLm	Bluegill cunfish	2093
2.0	tap	96-hour TLm	Bluegill sunfish Fathead minnows	2154, 2125
2.4E	soft	4-16 hours	Minnows	313
2.7	distilled	4-10 nours	Fish	2931
2.8	fresh	10-12 hours	Rainbow trout	74
4.0	soft	10-12 nours	Fish	313
4.0	]	1		313, 598, 609
5.5	stream water		Trout.	313
5.5	distilled		Goldfish	919
6.3	tap	24 & 48-bour	l <b>.</b> .	0000
• • • •	} · •	TLm	Bluegill sunfish	2093
10.0			Goldfish	1459, 2920
17	l	1	Goldfish	
27	tap	16-183 days	Catfish	1459
40	1 .	80 hours	Goldfish	1466
63		80 hours	Goldfish	1466
75E	hard	96-hour TLm	Fathead minnows	2154, 2125
1915	I ISOLU	20 20 M		I
	1	<del></del>	·	

E = exploratory test only

The following concentrations of lead have not visibly harmed fish within the time specified:

Concentration of lead, in mg/l	Type of water	Time of exposure	Species of fish	Reference
0.62 0.7 1.0 4.0	soft tap water very soft	48 hours 3 weeks indefinitely	Trout	1459 1459 1459 1459

Toward the giant kelp, Macrocystis pyrifera, North and Clendenning (2107) found that lead was less toxic than mercury, copper, hexavalent chromium, zinc, and nickel. Lead nitrate produced no deleterious effect on the rate of photosynthesis of kelp in sea water during a four-day exposure at 4.1 mg/l of lead.

The Mersey and Severn River Boards in England have established "working standards" for several streams whereby the total concentration of all heavy metals, including lead, cannot exceed 1.0 mg/l.

4. Summary. In view of the 1962 Drinking Water Standards of the USPHS, setting a mandatory limit of 0.05 mg/l on lead in water delivered to the consumer,

and in light of the fact that lead concentrations as low as 0.1 mg/l have been deleterious to fishlife, especially in soft waters, it is evident that the dissolved lead content of surface waters should be restricted to 0.1 mg/l where these two beneficial uses are involved.

#### LEAD ACETATE

 $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 

- 1. General. Known also as "sugar of lead", this freely soluble lead salt is used in printing and dyeing operations, in the weighting of silk, and in the manufacture of other lead salts.
- 2. Cross References. Acetate, Lead, and other lead salts.
  - 3. Effects Upon Beneficial Uses.
- a. Irrigation. When lead acetate was tested, 1000 to 10,000 mg/l of lead severely stunted the growth of water hyacinths in water culture; and 1 to 100 mg/l retarded growth (1525). In nutrient solution containing lead acetate, 1500 to 20,000 mg/l of lead inhibited the germination of cress and mustard seeds; however, even after 18 days of exposure to lead, the seeds germinated when they were transferred to water cultures (1479).
- b. Fish and Other Aquatic Life. Dawson (1459) found evidence of injury to blood cells of catfish exposed for 16 to 183 days to a 50 mg/l solution of lead acetate (27 mg/l of Pb) in tap water, renewed at 48-hour intervals. Minnows were killed in 26 to 48 hours by 0.4 mg/l of lead in a solution of lead acetate in non-toxic distilled water, renewed at regular intervals during the observation period.

It has been reported that lead acetate concentrations of 10 mg/l in stream water killed trout (313, 598, 609). In distilled water, 5.0 mg/l of lead acetate killed minnows in 4 to 16 hours; and 10 mg/l in distilled water renewed every second day, killed goldfish in 12 days (313). The Washington Department of Fisheries (2931) reported that lead acetate at a concentration of 2.8 mg/l of lead killed fish in fresh water; but Fujiya (3327) maintained that long-term exposure of carp to a much lower concentration of lead acetate (1.0 mg/l as Pb) resulted in a harmful effect to their serum.

#### LEAD ARSENATE

PbHAsO₄

- 1. General. Lead arsenate sprays are used for insect control on crop lands, especially for the gypsy moth and boll weevil; but it is believed that such use has not resulted in the contamination of water supplies derived from treated watershed areas (152). Fortunately, lead arsenate is highly insoluble in water.
- 2. Cross References. See Lead, Arsenic, other arsenic compounds.
  - 3. Effects on Beneficial Uses.
- a. Domestic Water Supplies. Lead arsenate is more toxic to humans than lead carbonate. A total of 100 mg of lead arsenate ingested by two individuals over a period of 10 days caused no apparent harm (353).
- b. Stock and Wildlife Watering. In doses of 1.3 to 56.7 grams per day, lead arsenate killed 18 out of 31 chickens, but the survivors showed no symptoms of poisoning. Drinking water containing about 4800 mg/l of lead arsenate caused no harm to 10 birds after a 60-day

period (1013). Toward male rats, the  $\rm LD_{50}$  value of lead arsenate has been reported as 1050 mg/kg. The daily consumption by one cow of 6.48 grams of lead arsenate for an unspecified period was not harmful (1014).

c. Fish and Other Aquatic Life. A concentration of 25 mg/l of lead arsenate has killed trout within 24 hours (359), but a concentration of 17.1 mg/l in stabilized tap water did not harm minnows during a one-hour exposure (362).

### LEAD CHLORIDE

PbCl₂

(see also Chlorides, Lead and other lead salts)

This relatively soluble lead salt is used in the manufacture of certain lead paints and as a solder and flux. The following concentrations of lead chloride have been reported as deleterious toward aquatic life:

Concentration of Lead Chloride, mg/l	Type of water	Time of exposure	Type of organism	Reference
0.01 to 1.0 0.33 0.58 1.25 3.2E 10.0 >100E 128	many kinds  Lake Erie Lake Erie soft distilled hard Lake Erie	10 days 96-br. TLm 24 hours 96-br. TLm	Daphnia magna tresh-water fish whitefish fry. Daphnia magna Fathead minnows. Daphnia magna Fathead minnows. Cyclops vernalis.	598 598 2955 2955 2154, 2125 654 2154, 2125 2955

E = exploratory test only

It was also reported (654) that *Daphnia magna* withstood 10 mg/l of lead chloride for 5 hours, but succumbed in 24 hours.

#### LEAD OXIDE

PbO

This insoluble white powder is used extensively in paints. Wallen et al. (2940) tested its toxicity toward the mosquito fish (Gambusia affinis) in water having a turbidity from soil suspension of 315 mg/l, a pH range of 7.1 to 7.2, and a temperature range of 18 to  $20^{\circ}$  C. He found that the 96-hour TL_m was greater than 56,000 mg/l and there was no significant decrease in turbidity as a result of the addition of lead oxide. Apparently insoluble lead is not toxic to fish.

#### LEAD NITRATE

 $Pb(NO_3)_2$ 

(see also Lead, Nitrates)

Used in the manufacture of matches and special explosives, as a mordant in dyeing and printing of textiles, as an oxydizer in the dye industry, and in photography and engraving, this lead salt is highly soluble in water (364).

For tadpoles in tap water, 1.6 mg/l of lead nitrate is deleterious to growth and 3.3 mg/l is lethal (313). Fish appeared to try to avoid, i.e., react negatively, to solutions of lead nitrate varying in strength from 0.33 to 644 mg/l, but reacted positively to a 6640 mg/l solution after a temporary initial negative reaction (1046).

Westfall found that concentration of dissolved oxygen has a significant effect on the response of goldfish to lead nitrate, for example, all the fish tested survived a 2-hour exposure to 5 mg/l of lead nitrate in the presence of 6.2 mg/l of oxygen, but all the fish tested died within 2

hours in the presence of only 1.4 mg/l of dissolved oxygen (1459).

In fresh water, 3 mg/l lead nitrate has been fatal to Fundulus within 12 hours (1459). Using lead nitrate, Jones found the lethal concentration limit of lead for sticklebacks to be 0.1 mg/l. At different concentrations of lead, the average survival times of the fish were as follows: one day at 1.0 mg/l, two days at 0.7 mg/l, four days at 0.3 mg/l, and one week at 0.2 mg/l (1460). However, goldfish died only after an 80-hour exposure to 63 mg/l of lead (1466). Minnows died within 48 hours when exposed to 0.4 mg/l of lead in a solution of lead nitrate in non-toxic distilled water (1459).

The following concentrations of lead nitrate have been reported to have killed fish:

Concen-					
tration of					
Lead Ni-					
trate, in	Type of	Time of	Type of		
mg/l	water	Exposure	Fish	Refe	rence
0.16	tap		stickleback	2920	, 598
0.53	tap		minnows, sticklebacks.		,
			and brown trout		920
10	natural	2.5 hours	trout		598
10	tap	24 and 48-hr	bluegill sunfish	4-0	2093
		$TL_m$			-020
10	hard	4 days	goldfish		353
16	tap		goldfish		2920
16.6		20 hours	minnows		353
100	hard	80 hours	goldfish		
165	distilled	oc mound	fish		313
240	highly		11911		313
<b>410</b>	turbid	96-hr TLm	manaulte Cel		
250	distilled	4-5 days	mosquito-fish		2940
250			goldfish		313
	distilled	2-3 hours	minnows		313
830		3 hours	minnows		991
3320		2.2 hours	minnows		991
8300		1.5 hours	minnows		991
16600		1.4 hours	minnows	991,	
44000		44 minutes	minnows		1248
53000		40 minutes	minnows		1248

On the other hand, 10 mg/l of lead nitrate in hard water has not harmed fish during a 96-hour exposure period (313).

Bringmann and Kuhn (2158, 3343) tested the effects of lead nitrate in River Havel water at pH 7.5 and a temperature of 24°C against several organisms during an exposure of 4 days. The threshold concentrations for deleterious action were as follows:

Test $Organism$	Threshold Concentration in mg/l of Lead
Daphnia magna	5.0
Scenedesmus	2.5
Escherichia coli	1.3
Microregma	1.25

Cleland (3328) found that lead nitrate in a concentration of about 200 mg/l in sea water produced abnormalities in the eggs of sea urchins.

### LEAD SULFATE

PbSO₄

(see also Lead, Sulfates)

Sparingly soluble in water, this salt is used as a paint pigment, for weighting fabrics, in lithography, and in galvanic batteries. In distilled water 25 mg/l of lead sulfate killed goldfish in 4 days and killed minnows in 2 to 3 hours (313). Jones (2920) reports the lethal concentration for goldfish as 26 mg/l.

### LEAD TETRAETHYL

 $Pb(C_2H_5)_4$ 

Used as an additive in motor fuels to prevent knocking, this lead compound might occur in the effluents from refineries. Turnbull et al. (2093) conducted bioassays with this substance in Philadelphia tapwater, using bluegill sunfish (*Lepomis macrochirus*) as the test fish. They found a 24-hour  $TL_m$  of 2.0 mg/l as lead and a 48-hour  $TL_m$  of 1.4 mg/l. They estimated the safe concentration at 0.20 mg/l.

### LIGNASAN

(see Mercuro-Organic Compounds)

## LINOLEIC ACID AND LINOLEATES

(see Fatty Acids)

# LISSAPOL (NONYLPHENOL ETHYLENE OXIDE CONDENSATE)

(see Chapter X)

#### LIME

(see Calcium Hydroxide)

#### LINDANE

(see Chapter IX-Benzene Hexachloride)

#### LITHIUM

Li

(see also Lithium Chloride)

As one of the alkali metals, related to sodium and potassium, lithium is not widely distributed in nature, being found in a few minerals and in certain spring waters. Being very active, the metal does not occur in the elemental state and when purified as such it must be protected from water or oxygen. It is used in metallurgy, in medicinal waters, in some types of glass, and as lithium hydroxide in storage batteries. Hibbard (250) recommends, without references, that lithium in water for drinking and cooking purposes should not exceed 5 mg/l.

Lithium toxicity in citrus has been identified in Santa Barbara County, California. In green-house experiments, 2 and 5 mg/l of lithium sulfate (in air-dried soil) caused the appearance of toxic symptoms in orange seedlings within 6 months. In the field, 1, 2, and 4 mg/l of lithium chloride in the soil have caused symptoms of lithium toxicity.

Various irrigation waters in the area were found to contain 0.045-0.080 mg/l of lithium. Possibly lithium poisoning has resulted from the accumulation in ground of toxic concentrations over a long period of time. Aldrich (1591) and his collaborators are making further studies of the effects of 0.05-0.1 mg/l of lithium in irrigation water.

#### LITHIUM CARBONATE

 $\text{Li}_2\text{CO}_3$ 

This light white alkaline powder, quite soluble in water, is used in the production of glazes on ceramic and electrical porcelain (364). It was reported in 1923 that concentrations of 295-516 mg/l of lithium carbonate retarded larval and pupal development of *Drosophila melanogaster* (1592).

## LITHIUM CHLORIDE

LiCl

(see also Lithium)

A white deliquescent crystalline solid, lithium chloride is highly soluble in water. It is used in pyrotechnics and in the soldering of aluminum. It is also used in the manufacture of mineral waters and it may be found in some natural mineral springs (364).

In a concentration of 3750 mg/l, lithium chloride in distilled water killed goldfish in 22 to 27 hours (313). For mature small fresh-water fish, the lethal concentration in 24 hours of exposure was found to be 2600 mg/l. The data gathered by Powers and by Iwao indicate that lithium chloride at concentrations between 1950 and 3770 mg/l can kill fresh-water fish in about one day, or sooner at warmer temperatures (1459). In contrast with these high concentrations required for lethal effect, one German publication (2977) reports that 100 mg/l of LiCl is toxic but 33 mg/l is harmless to fish.

The threshold concentration for immobilization of Daphnia magna in Lake Erie water was found to be less than 7.2 mg/l (598); but in River Havel water at 23°C the threshold of poisonous effect was observed at 16 mg/l during 48 hours contact (2158). With the protozoan Microregma as the test organism, food intake was inhibited at 66 mg/l (3343). Toward Scenedesmus and Escherichia coli, no toxicity was evident at concentrations less than 1000 mg/l (2158). In order to evoke stimulation and movement of the water beetle, Laccophilus maculosis, a LiCl concentration of 19,500 mg/l was required (2956).

It has been reported that dilute concentrations of LiCl are deleterious to the eggs of various aquatic organisms, retarding their development and producing monstrosities (1467). King demonstrated that concentrations of 848 mg/l were highly toxic to fly larvae, preventing emergence of offspring and retarding development of both larvae and pupae (1592).

## LITHIUM FLUORIDE

LiF

This moderately soluble salt is used as a flux for soldering and welding aluminum and in the manufacture of vitreous enamels and glazes (364). The oral LD₅₀ for guinea pigs is 200 mg/kg of body weight (3271). The lethal dose in 48 hours for the fish, *Tinea vulgaris*, is reported as 20,000 mg/l (3271).

### LITHIUM SULFATE

(see Lithium)

## LOROL METASODIUM SULFOBENZOATE

(see Chapter X)

### **MAGNESIUM**

Mg

1. General. As one of the most common elements in the crust of the earth, constituting about 2.1 percent of it, magnesium is widely distributed in ores and minerals (364). Because it is very active chemically, it is not found in the elemental state in nature. With the exception of the hydroxide at high pH values, its salts are very soluble; even the carbonate will dissolve to the extent of 100 to 300 mg/l at normal temperatures (364, 911). The solubility of magnesium hydroxide is governed by the equation:

[Mg**] 
$$[OH^-]^2 = 1.2 \times 10^{-11} \text{ at } 18^{\circ}\text{C}$$

Thus, at pH 7, magnesium ions theoretically can be present to the extent of 1200 mols per liter or 28,800

grams per liter, but at pH 10 the maximum possible concentration of magnesium ions would be 28.8 mg/l and at pH 11 only 0.288 mg/l. This phenomenon is useful in treatment processes to remove magnesium from water, but insofar as natural waters are concerned it is described herein merely to show that at common pH values magnesium ion may be present in high concentrations despite the apparently low solubility product.

The industrial and commercial uses of magnesium and its salts are many, as described hereinafter for the salts. Magnesium metal is used as a constituent of light alloys, in other phases of metallurgy, and in the manufacture of electrical and optical apparatus (364). Magnesium ions are of particular importance in water pollution in that they occur in significant concentration in natural waters, and along with calcium form the bulk of the hardness reaction (see Hardness).

The literature decribed herein deals with articles in which magnesium ions were referred to without mention of associated cations. Where salts were tested and described, the material is covered under the appropriate salt.

- 2. Cross References. Calcium, Hardness, Dissolved Solids, Tastes.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Magnesium is an essential mineral element for human beings, the daily requirement of magnesium is about 0.7 grams (295). Magnesium is considered relatively non-toxic to man and not a public-health hazard because, before toxic concentrations are reached in water, the taste becomes quite unpleasant (633) (see also Tastes). At high concentrations, magnesium salts have a laxative effect, particularly upon new users, although the human body can develop a tolerance to magnesium over a period of time.

The 1946 USPHS Drinking Water Standards recommended a limit of 125 mg/l but there is no limit in the 1962 standards (2036). The 1958 WHO International Standards (2328) have a "permissible limit" of 50 mg/l and an "excessive limit" of 150 mg/l, but no maximum allowable concentration. The 1961 WHO European Standards (2329) have a recommended limit of 125 mg/l, but if the sulfate exceeds 250 mg/l, the magnesium is limited to 30 mg/l.

Limits ranging from 100 to 200 mg/l have also been proposed for domestic water supplies (942, 1059). Hibbard recommended a limiting concentration of magnesium of 10 mg/l in water for drinking and cooking; 5 mg/l for washing; and no magnesium for laundry (250). Baylis suggested limiting concentrations of magnesium ranging from 50 to 150 mg/l for four grades of drinking water (499). In his system for classifying ground waters, Goudey suggested limits from 15 to 125 mg/l, according to domestic and industrial uses (992).

The taste threshold for magnesium (in  $MgSO_4$ ) has been reported (3241) as 100 mg/l and for the average individual it is given as about 500 mg/l (3392).

The negative correlation between hardness in water and cardiovascular disease does not appear to hold for magnesium as it does for calcium (3368, 3369); yet one investigator (3537) reports the favorable use of magnesium sulfate to treat such cases and claims that mag-

nesium, rather than calcium, is the beneficial element in reducing cardiovascular attacks (see Hardness).

b. Industrial Water Supplies. Like calcium, magnesium in small amounts is beneficial in the mash water for pale beer (175, 1074, 3344). Magnesium in water used for preparing developer solutions causes spots on films, if it is precipitated out of solution (242).

The limiting or threshold concentrations of magnesium that have been recommended for various industrial waters are described in Chapter V. The following table is extracted from that chapter:

	Recommended Limits, in mg/l for			
Process	Magnesium	Masos	MaCla	Ma(HCO2)s
Brewing	20		100-200	
Ice manufacture		130-300	171-300	50
Soda pulp Sugar making	12			
Towards making	10			<del></del> :
Textile manufacture	5			

- c. Irrigation. Magnesium is essential to normal plant growth (635); and magnesium and calcium cations in irrigation water tend to keep soil permeable and in good tilth (268, 281, 348, 1252). It has been reported that magnesium in water in concentrations up to 24 mg/l will probably not affect seriously the condition of underground water basins, growth of trees, or condition of the soil (1060). In very high concentrations (3000-5000 mg/l) MgCl₂ and MgSO₄ have been toxic to the bean plant (3376).
- d. Stock and Wildlife Watering. Animals require magnesium salts in their diet. According to Maynard, calves require about 0.6 grams of magnesium per 100 lbs. body weight, or 600 mg/kg in the dry ration. Chicks require about 400 mg/kg of magnesium in the dry ration. The specific needs of other animals are not known (995).

In the body, calcium and magnesium are antagonistic to a certain degree and calcium may alleviate symptoms of magnesium excess. Diets high in magnesium and low in calcium can cause rickets (284, 295). Provided that both calcium and phosphorus in the diet are sufficient, however, the ingestion of a moderate excess of magnesium in the food or water will not markedly disturb calcium retention, although it may increase the calcium requirement (284, 295).

Magnesium salts act as cathartics and diureties among animals as well as human beings, and high concentrations in drinking water may cause scouring diseases among stock. Water containing less than 5000 mg/l of magnesium compounds is harmless to cattle which have become accustomed to it (292). An interim threshold limit of 500 mg/l has been suggested by Stander (3373). Ingestion of mixtures of sodium salts and magnesium and nitrate ions caused poisoning among ducks (288).

e. Fish and Other Aquatic Life. The relative concentrations of magnesium and calcium in water may be one factor controlling the distribution of certain crustacean fishfood organisms, such as copepods, in streams (1085). Hart et al. cite a report that among U.S. waters supporting a good fish fauna, ordinarily 5 percent have less than 3.5 mg/l of magnesium; 50 percent have less than 7 mg/l; and 95 percent have less than 14 mg/l (310).

Magnesium chloride and nitrate can be toxic to fish in distilled water or tap water at concentrations between 100 and 400 mg/l as magnesium. However, magnesium chloride, nitrate, and sulfate, at concentrations between 1000 and 3000 mg/l as magnesium have been tolerated for 2-11 days. Some fresh-water fish have been found in very saline lake water containing over 1000 mg/l of magnesium as well as additional sodium and calcium salts (1459).

As magnesium nitrate, 400 mg/l of magnesium is toxic to a flatworm, *Polycelis nigra*, as magnesium chloride (353). A concentration of 300 mg/l of magnesium has been reported to be toxic to stickleback (353, 2941). Magnesium salts in water affect the toxicity of copper toward fish (1076). For further details on fish toxicity, see the specific magnesium salts.

f. Shellfish Culture. Magnesium was found to be more toxic than calcium to mussels but less toxic than sodium and potassium (353).

## MAGNESIUM ACETATE

 $Mg(C_2H_3O_2)_2 \cdot 4H_2O$ 

(see also Magnesium, Acetates)

This colorless salt is freely soluble in water. Heller found that 15,000 mg/l of magnesium acetate in drinking water permitted satisfactory growth and reproduction among rats (287, 2980).

# MAGNESIUM BICARBONATE

(see Magnesium)

## MAGNESIUM CHLORIDE

MgCl₂·6H₂O

- 1. General. Highly soluble in water, magnesium chloride may occur in water either naturally or as a component of waste waters from oil wells, road run-off, and industry. It is used in manufacturing chemicals, artificial leather, cements, fire extinguishers and fireproofing materials, sweeping compounds, and road coverings (364).
- 2. Cross References. Hardness, Magnesium, Taste, Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of magnesium chloride in water has been reported to be 200 to 750 mg/l (621). Steyn et al. recommended that in order to prevent unpleasant salty tastes and possible appetite disturbances, water should not contain more than 168 mg/l of magnesium chloride (284). Thresh states that much smaller quantities of magnesium chloride, even 40 to 50 mg/l, can render a water useless for many domestic purposes because of its hardness (32).
- b. Industrial Water Supplies. Magnesium chloride in water may interfere with its suitability for some industrial uses. In boiler waters it is corrosive (855).

The following maximum concentrations have been recommended:

Concentration in mg/l	Reference
•	173
100	170
171	173

c. Irrigation Use. Irrigation with effluents of high magnesium chloride content did not appreciably affect the yields and composition of hay (1253). At concentrations in excess of 2000 mg/l, MgCl₂ inhibited the growth of bean plants (3376) and guayule (3378).

d. Stock and Wildlife Watering. In experimental animals 4.0 grams of magnesium chloride per 100 grams of diet causes diarrhea, loss of appetite and even death (295). It has been reported that daily oral administration of 20 grams of magnesium chloride to pigs; 60 grams to sheep; and 400 grams to horses had no detrimental effects. A dose of 1.5 grams has been toxic to ducks (284).

Magnesium chloride in water had no effect on tooth decay among rats (1069). Water containing 10,000 to 15,000 mg/l of magnesium chloride interfered with the growth of rats (287). Water containing 10,000 mg/l of magnesium chloride and 5000 mg/l of calcium chloride was not harmful to mature rats, although it did interfere with lactation (287). Water containing 5000 mg/l of magnesium chloride and 20,000 mg/l of sodium chloride inhibited rat growth (284). Concentrations of MgCl₂ up to 9500 mg/l in the drinking water had no effect on the food or water intake of male rats (2398).

e. Fish and Other Aquatic Life. Garrey found that magnesium chloride added to water decreased the toxicity of calcium and potassium chlorides toward freshwater fish, and that calcium chloride decreased the toxicity of magnesium chloride (307).

The following concentrations of magnesium chloride have been reported to have killed fresh-water fish:

Concentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
476	distilled	4-6 days	minnows	313
5000		96.5 hours	golden shiners	645
6757	distilled	3-21 days	goldfish	313
8132			carp	3538
10000		4.6 hours	shiners	645
15000		0.8 hours	shiners	645
16500	turbid	96-hour TLm	mosquito fish	. 2940
20000		0.5 hours	shiners	645
23800		24 hours	Orizias	1459

The highest concentration of MgCl₂ tolerated by young eels for more than 50 hours was reported to be about 9500 mg/l (1459). Some fish-food organisms, such as *Daphnia* and other cladocera, are less tolerant of magnesium chloride and have been immobilized or killed within two days by concentrations of magnesium chloride from 740 to 3500 mg/l (598).

f. Shellfish Culture. In 1890, Dean reported that the most favorable salt content for oyster growth is about 30,800 mg/l of chlorides, of which magnesium and potassium chlorides constitute about 20 percent (314).

## MAGNESIUM FLUORIDE

 $MgF_2$ 

This colorless salt is soluble in water only to the extent of 87 mg/l at  $18^{\circ}$ C. It finds commercial application in the ceramics and glass industries. The oral LD₅₀ for guinea pigs is 1000 mg/kg of body weight (364). To kill tench, a concentration of 10,000 mg/l was required (3271).

## MAGNESIUM NITRATE

 $Mg(NO_3)_2 \cdot 6H_2O$ 

(see also Magnesium, Nitrates)

This freely soluble compound is used in pyrotechnics. The taste threshold of magnesium nitrate in water is reported to be 500 to 800 mg/l (621). The following

concentrations of magnesium nitrate have been reported to kill fish:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
300	long-time	stickleback	1460
400		stickleback	2920
500	4 days	stickleback	1460
1500	2 days	stickleback	<b>1460</b> .
1820	14-16 hours	stickleback	598
2000	one day	stickleback	1460
12500		goldfish	313

## MAGNESIUM OXIDE

MgO

(see also Magnesium)

Known in the dry state as "magnesia", this oxide combines with water to form magnesium hydroxide, which is sparingly soluble at high pH values. It is used medicinally as an antacid and laxative, in doses of 0.25 to 3.0 grams. One authority (1254) reports that drinking water should contain some magnesium and calcium oxides; the most satisfactory ratio of calcium oxide to magnesium oxide is said to be 7:1. In the soft-drink industry, magnesium oxide in the wash water gradually "clouds" the bottles, causing unsightliness (180).

## MAGNESIUM SILICOFLUORIDE MgSiF₆·6H₂O

This highly soluble salt is used for mothproofing fabrics. The oral  $LD_{50}$  in guinea pigs is given as 200 mg/kg of body weight (364). A concentration of 50 mg/l is reported to kill tench (3271).

## MAGNESIUM SULFATE

 $MgSO_4 \cdot 7H_2O$ 

- 1. General. Known also as Epsom salt, this compound is freely soluble in water. It occurs in natural deposits and soils, thereby contributing to the concentration in natural waters. It is used in weighting cotton and silk, in dyeing and printing calico, in tanning processes, and in fertilizers, explosives, and matches (364).
- 2. Cross References. Dissolved Solids, Magnesium, Sulfates.
  - 3. Effects on Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of magnesium sulfate is 400 to 600 mg/l (621, 3241). A dose of 30 grams of magnesium sulfate is toxic and 120 grams fatal for man (284).

Magnesium sulfate in excessive concentrations in drinking water may have purgative effects (623). The most sensitive individuals are affected at about 400 mg/l and the average person at about 1000 mg/l (3392). Waters containing 1200 mg/l of magnesium sulfate and 500 mg/l of sodium sulfate have caused diarrhea in humans. Ordinarily, according to Taylor (36) waters containing half this quantity would be regarded as unsuitable for domestic use.

Dosages of 1 to 2 grams of magnesium sulfate have a purgative effect; therefore, in drinking-water standards magnesium sulfate should be limited to 1000 to 2000 mg/l. Concentrations below this limit are physiologically harmless (621).

b. Industrial Water Supplies. The following concentrations of magnesium sulfate have been recommended for industrial waters:

	Concentration, $mg/l$		
Process	Optimum	Maximum	Reference
Brewing, pale ales, I	60-90		170
pale ales, II	60-120		170
mild ales	60		170
stout	60		170
Brewing	100		170
Brewing, light or dark		200	173
Ice, raw water	1	130	173

c. Irrigation. See Calcium, Hardness, and Chapter V-Irrigation.

d. Stock and Wildlife Watering. High concentrations of magnesium sulfate in the drinking water of rats and other small animals have retarded growth, caused emaciation, rough coat, diarrhea, and increased mortality among the young (284, 287, 640). Concentrations from 10,000 to 25,000 mg/l have been harmful to rats. A combination of 5000 mg/l of magnesium sulfate and 20,000 mg/l of sodium chloride has inhibited the growth of rats (640) (see also Dissolved Solids). On the other hand, 5000 mg/l in drinking water has not been harmful to rats (287). Livestock will tolerate 2050 mg/l of magnesium sulfate without laxative effects (2394). In drinking water, 12,000 mg/l had no effect on the water and food consumption of male rats (2398).

e. Fish and Other Aquatic Life. The following concentrations of magnesium sulfate have been reported to have killed fish:

Concentration	Type of	Time of	Type of R	eference
$in\ mg/l$	Water	Exposure	Fish	
15,500	turbid	96-hour TLm	mosquito-fish	2940
20,900-28,400	cistern	14 days	perch	<b>644</b>
24.500-27.500	well	78 days	perch	644

The maximum concentration of magnesium sulfate tolerated by young eels for over 25 hours was reported to be about 12,000 mg/l (1459).

## **MALATHION**

(see Chapter IX)

## MALEIC ANHYDRIDE

 $C_4H_2O_3$ 

This solid dissolves readily in water, forming maleic acid, HOOCHC = CHCOOH. It is used in the manufacture of alkyd-type resins, dye intermediates, and pharmaceuticals (364). Wallen et al. (2940) exposed mosquito-fish (Gambusia affinis) to maleic anhydride in turbid water at 20-23°C. They found the 24- and 48-hour TL_m values to be 240 mg/l and the 96-hour TL_m was 230 mg/l. The pH value was lowered from 8.0 to 5.8 and the 128 mg/l of turbidity was coagulated and removed by this compound. Using bluegill sunfish (Lepomis macrochirus) in Philadelphia tap water at 20°C, Turnbull et al. (2093) found the 24-hour TL_m to be 150 mg/l and the 48-hour TL_m to be 138 mg/l. They estimated a safe concentration to be 35 mg/l.

## MANGANESE

 $\mathbf{M}\mathbf{n}$ 

1. General. Manganese metal is not found pure in nature, but its ores are very common and widely distributed. The metal or its salts are used extensively in steel alloys, for dry-cell batteries, in glass and ceramics, in the manufacture of paints and varnishes, in inks and dyes, in matches and fireworks, and in agriculture to

enrich manganese-deficient soils (2121). Like iron, it occurs in the divalent and trivalent form. The chlorides, nitrates, and sulfates are highly soluble in water; but the oxides, carbonates, and hydroxides are only sparingly soluble. For this reason, manganic or manganous ions are seldom present in natural surface waters in concentrations above 1.0 mg/l. In ground water subject to reducing conditions, manganese can be leached from the soil and occur in high concentrations. Manganese frequently accompanies iron in such ground waters and in the literature the two are often linked together.

- 2. Cross References. Iron, Manganese Salts, Potassium Permanganate, Turbidity, Tastes.
  - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The 1962 Drinking Water Standards of the USPHS (2036) set a recommended limit for manganese of 0.05 mg/l. The 1958 WHO International Standards (2328) prescribe a "permissible limit" of 0.1 mg/l and an "excessive limit" of 0.5 mg/l, but no maximum allowable limit is given. The 1961 WHO European Standards have a recommended limit of 0.1 mg/l.

These limits have been established on the basis of esthetic and economic considerations rather than physiological hazards. Manganese is essential for the nutrition of both plants and animals (2121, 2129). Diets deficient in manganese result in impaired or abnormal growth, symptoms of central nervous system disturbance, anemia, and possibly interference with reproductive functions (2121, 2129). The daily intake from a normal human diet is about 10 mg (2129). It is absorbed very slightly and deposits mainly in the liver and kidneys (2129).

In concentrations not causing unpleasant tastes, manganese is regarded by most investigators to be of no toxicological significance in drinking water (633, 1077). However, some cases of manganese poisoning have been reported in the literature. A small outbreak of an encephalitis-like disease, with early symptoms of lethargy and edema, was traced to manganese in the drinking water in a village outside of Tokyo; three persons died as a result of poisoning by well water contaminated by manganese derived from dry-cell batteries buried nearby (36, 1225). Excess manganese in the drinking water is also believed to be the cause of a rare disease endemic in Manchukuo. That manganese may be toxic is also indicated by the reports that 0.5 to 6.0 grams of manganese per kilogram of body weight administered daily to rabbits had stunted growth and interfered with bone development (921).

Despite the possible toxic effects of manganese under unusual circumstances, it cannot be considered a physiological hazard because the normal dietary intake is far higher than the amount that would be tolerated esthetically in drinking water.

Manganese is undesirable in domestic water supplies because it causes unpleasant tastes, deposits on food during cooking, stains and discolors laundry and plumbing fixtures, and fosters the growth of some micro-organisms in reservoirs, filters, and distribution systems (1593, 3539, 3540, 3541, 3542) (see Fish and Other Aquatic Life, below).

It has been reported by one observer that manganese salts impart a metallic taste to water at concentrations above 0.5 mg/l (945); and by another reference at above 20 mg/l (759). Cohen et al. (3301) found the taste threshold for manganous ion in spring water to occur at about 180 mg/l for the median of a large panel, but at 32 mg/l for the most sensitive members. In distilled water the taste thresholds were much lower, about 35 mg/l for the median and about 0.9 mg/l for the most sensitive panel members (3301). Manganese in excess of 0.15 mg/l has also been reported to cause turbidity in water (1594).

For domestic water supplies a maximum concentration of manganese, or of iron and manganese together, as low as 0.017 mg/l has been recommended (1256). Concentrations as low as 0.1 mg/l are reported to cause laundry trouble (219, 284); concentrations of 0.2 to 0.4 mg/l are likely to cause complaints (36); and, in general, limiting concentrations from 0.02 to 0.5 mg/l have been recom-

mended (499, 555, 628, 1257, 3541).

b. Industrial Water Supplies. Excessive manganese is undesirable in water for use in many industries, including textiles (255, 256, 257); dyeing (261); food processing, distilling, and brewing (240, 224, 284); ice (234); paper (212, 879); and many others (see Chapter V). The following tabulation summarizes the recommendations as to maximum permissible concentrations of manganese in industrial waters:

	Maxim	um Permissible Conc	entration
Ĭ	langanese	Iron + Manganese	Reference
Industrial $Use$	$in\ mg/l$	in $mg/l$	
Air conditioning	0.5	0.5	162
· ·	0.5		152
Baking	0.2	0.2	162, 152
Brewing, light and dan	k 0.1	0.1	162, 152
Canning	0.2	0.2	162, 152
Carbonated beverages	0.2	0.2	162, 152, 184
-		0.1	179
Confectionary	0.2	0.2	162, 152
Cooling water	0.2	0.2	152
	0.5	0.5	162
Dyeing	0	0	36
Food processing	0.2	0.2	162, 152
Ice	0.2	0.2	162, 152, 234
Milk industry	0.03-0.1		2344
Paper and pulp	0	0	36
Groundwood	0.5	1.0	162, 152
	0.1		244
Kraft pulp	0.1	0.2	162, 152
Soda and sulfate	0.05	0.1	162, 152
•	0.05		245
Highgrade paper	0.05	0.1	<b>162,</b> 152
Fine paper	0.05	0.1	350
Kraft paper	2.5	•	
bleached	0.1		351
unbleached	0.5		351
Photography	0	0	36
Plastics (clear)	0.02	0.02	162, 152
Rayon and viscose			
Pulp production	0.03	0.05	162, 152
Manufacture	0	0	162, 152
	0.02		550, 405
Tanning	0.2	0.2	162, 152
Textiles, general	0.25	0.25	162, 152
		0.1	852
	0.1	0.05	256
dyeing	0.25	0.25	162, 152
wool scouring	1.0	1.0 0.2	162, 152 162, 152
bandages	0.2	0.2	104, 104

c. Irrigation. Manganese is essential for plant growth, apparently as an enzyme activator (3543). It is especially abundant in the reproductive parts of plants, seeds being highest while woody sections contain the least manganese (3544). Nuts contain the highest concentrations (22.7 mg/kg) and sea foods the lowest (0.25 mg/kg). Tea diffuses enough so that the normal liquid has 1 to 7 mg/l (2121). Manganese has been used to enrich soil, yet in some concentrations it may be phytotoxic (219, 277, 563).

Manganese in the nutrient solutions has been reported to be toxic to many plants, as grown in solution cultures. The sensitivity and response of the plants to the presence of manganese varies both with the species of plant and the composition of the nutrient solution. Symptoms of manganese injury have been intensified in the presence of molybdenum, vanadium (1595), or nitrate (1596). Symptoms of manganese injury have been diminished in the presence of cobalt (1499), iron, molybdenum, aluminum, phosphorus deficiency (1458), ammonium or ammonium nitrate (1596). The following concentrations of manganese have been reported to be harmful to plants in solution culture:

Concentration of Manganese in mg/l	Type of Plant	Reference
0.5	Various plants	1597
1-10	Various legumes	1597
- 3.5	Various plants	1597
5	Orange and mandarin seedlings	1524
5-10	Tomatoes	1499
10-25	Soybean, flax	1595
25-100	Flax	1458
50	Flax	1596
62.5	Various plants	1597
150-500	Oats	1462

It has also been reported that 0.25 mg/l of manganese has permitted good growth of tomatoes, and that up to 5.0 mg/l of manganese has reduced the severity of cobalt poisoning in tomatoes (1499). In the presence of ammonium or of ammonium nitrate, 50 mg/l of manganese was not harmful to flax, although this concentration was harmful in the presence of nitrate without ammonium (1596). Manganese sulfate, at a concentration of 100 mg/l as manganese caused no apparent injury to oat plants (1462).

d. Stock and Wildlife Watering. A deficiency of manganese in animals produces ovarian disfunction, testicular degeneration, poor lactation, lack of growth, bone abnormalties, and symptoms of central nervous disturbance (2121). Cattle are reported to have received dosages of 50 to 600 mg/kg in the diet for 20 to 45 days without serious effects. Birds have received single oral dosages of up to 600 mg/kg without adverse effects, but the continuous excess of manganese in fodder was suspected as an etiological factor in the occurrence of infectious anemia in horses. Manganese appears to oxidize vitamin B in the horse body, producing avitaminosis (1049).

The metabolism of manganese is closely related to that of calcium, phosphorus, iron, copper, and possibly other minerals, and the proper balance must be maintained. The manganese requirement for chicks has been reported to be 30-50 mg/kg (dry ration); for hens, 40-50 mg/kg.

However, 1000 mg/kg in the dry ration was not toxic (1551).

e. Fish and Other Aquatic Life. The toxicity of manganese toward fish is dependent upon many factors. Jones (2941) gives the lethal concentration for the stickleback as 40 mg/l; however, the toxic action is slow and manganese does not appear to precipitate the gill secretions. According to Oshima (3545) and Iwao (3546) the toxicities of manganous chloride and manganous sulfate are slight, being about 2400 and 1240 mg/l of manganese respectively. Manganese appears to be somewhat antagonistic to the toxic action of nickel toward fish (1468).

The following concentrations of manganese have been tolerated by fish under the stated conditions:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
1		river crayfish	2977
15	7 days	tench, carp, trout	2151
40*	4 days	fingerling catfish	2981
50**	3 days	stickleback	1459
2700	50 hours	eels	1459

* from manganese disodium versenate **from manganese sulfate

Manganese and iron in concentrations above 0.1 mg/l stimulate the growth of certain organisms, such as *Crenothrix*, Gallionella, and other related forms in reservoirs, filters, and distribution systems (152, 921, 945, 1258). The addition of as little as 0.0005 mg/l of manganese resulted in increased growth and multiplication of various microbiota in sea water (1259). Guseva (584, 1260), on the other hand, found that concentrations of manganese above 0.005 mg/l had a toxic effect on some algae.

The threshold concentration of manganese for the flatworm *Polycelis nigra* has been reported to be 700 mg/l as manganese chloride and 660 mg/l as manganese nitrate (608). Crustacea, worms, and insect larvae were not harmed by 15 mg/l of manganese during a 7-day exposure (2151).

The permanganates are much more toxic to fish than the manganous salts. Permanganates killed fish in 8 to 18 hours at concentrations of 2.2 to 4.1 mg/l of manganese (3545, 3546). However, permanganates are not stable for long in water.

4. Summary. On the basis of the literature surveyed, it appears that the following concentrations of manganese will not be deleterious to the stated beneficial uses:

a. Domestic water supply	$0.05 \mathrm{mg/l}$
b. Industrial water supply	0.05  mg/l
c. Irrigation	0.50  mg/l
d. Stock watering	
e. Fish and aquatic life	1.0 mg/l

#### MANGANESE CHLORIDE

MnCl₂ and MnCl₃

(see also Manganese, Chlorides)

This highly soluble salt, occurring generally in the manganous form, is used in dyeing operations, in disinfecting, in linseed oil driers, and in electric batteries (364). In fresh water, 12 mg/l has been reported as fatal to minnows (Fundulus) within six days (1459), but other fish have been found to be much more tolerant of MnCl₂. For the small fresh-water fish (Orizias), the 24-hour lethal concentration was about 7850 mg/l (1459) and for other fish 5500 mg/l (3545, 3546). The highest concen-

tration tolerated by young eels for 50 hours was 6300 mg/l (1459). The first toxic effects of MnCl₂ for fish were observed at 330 mg/l but the lethal concentration

did not occur until 800 mg/l (2977).

Toward lower organisms there is similarly a wide variation in reported toxicity. For immobilization of Daphnia magna in Lake Erie water, the threshold concentration was found (598) to be 50 mg/l of MnCl₂. In River Havel water at 23°C, the threshold effect of MnCl₃ occurred at 50 mg/l of manganese (2158). For the flatworm, Polycelis nigra, the threshold concentration of MnCl₂ was reported to be 700 mg/l (608).

## MANGANESE DIFLUORIDE

MnF₂

(see also Manganese, Fluorides)

This highly soluble manganous salt is reported to be lethal to tench in 48 hours at a concentration of 500 mg/1 (3271).

#### MANGANESE NITRATE

 $Mn(NO_3)_2 \cdot 4H_2O$ 

This manganous salt is very soluble in water. For sticklebacks in tap water, the minimum lethal concentration of manganese nitrate has been reported to be 40 mg/l as manganese (598, 1460). The average survival times of the fish in different concentrations was as follows: one week at 50 mg/l, four days at 100 mg/l, two days at 150 mg/l and only one day at 300 mg/l, all measured as managanese (1460). For the flatworm, Polycelis nigra, the threshold concentration has been reported to be 660 mg/l as manganese nitrate (608).

## MANGANESE SULFATE

 $MnSO_4 \cdot H_2O$ 

This pale-pink manganous salt, highly soluble in water, is used in dyeing, porcelain glazing, varnishes, and specialized fertilizers (364). In culture solution, 100 mg/l as manganese caused no apparent injury to oat plants, 150-200 mg/l caused chlorosis, and 500 mg/l produced injury (1462).

Toward fish, the toxicity of manganous sulfate is slight. In tap water, 50 mg/l as manganese did not kill sticklebacks within three days (1459). Young eels tolerated 1500 mg/l as manganese sulfate for more than 25 hours. The first influence of this salt toward fish is reported to occur at 500 mg/l as Mn, and at 1000 mg/l as Mn the salt is lethal (2977). Japanese investigators (3545, 3546) report the toxicity of this salt at 3400 mg/l.

#### MANOXOL OT

(see Chapter X)

## MASONITE MANUFACTURING WASTES

Ellis (611) investigated wastes from a Masonite plant in Mississippi, containing chemical compounds, fibers, pigments, and an unidentified substance with a high B.O.D. that was toxic to fish in one to three days at 1:100,000 dilution. Loose fibers menaced fish for 12 miles below the plant.

## MERCAPTANS, GENERAL

(see also Methanethiol)

Mercaptans (RSH) are the sulfur analogs of the alcohols (ROH) and phenols (R'OH). They are generally odoriferous and can be detected in very small concentrations. They occur in coal tar and in the wastes from

Kraft-process pulp mills.

The threshold concentration for taste and odor of mercaptans from Kraft mill wastes has been reported at less than 0.02 mg/l (686). The untreated waste from the mill, containing 12 mg/l of mercaptans, required a dilution of 1:50,000 to render it odorless, i.e., down to a concentration of 0.00024 mg/l; but after chlorination to a residual of 1.5 mg/l, the required dilution was only 1:40, i.e.

down to a concentration of 0.3 mg/l.

Gersdorff (695) shows that phenyl mercaptan, C6H5SH (thiophenol), a liquid with a repulsive, penetrating, garlic-odor, and tolyl mercaptan CH₃C₆H₄SH (thioeresol) have a similar toxic effect on goldfish, but the toxic action differs from that of phenol. Metatolyl mercaptan is about four times as toxic, o-tolyl mercaptan about five times, and p-tolyl mercaptan about 8.5 times as toxic as phenol (see Phenols). The relative toxicities of m-o-, p-tolyl mercaptans are in the ratios 1 to 1.19 to 2.19, a relationship nearly the same as that found for the corresponding cresols. The replacement of the oxygenation of the cresol molecule by sulfur appears to cause a fourfold increase in the toxicity of the compound to goldfish (695).

## MERCURIC ACETATE

(see Mercuro-Organic Compounds)

### MERCURIC CHLORIDE

 $HgCl_2$ 

- 1. General. This salt is soluble in water at 20°C to the extent of 61,000 mg/l (911). It is used in embalming, disinfecting, preserving, printing of fabrics, tanning, electroplating, manufacturing ink, and numerous other processes (364). It may occur in wastes from any of these industries, or in lead mining and chemical wastes
- Cross References. Mercury, Other Mercury Salts, Mercuro-Organic Compounds, Chlorides, and Chapter V —Fish and Other Aquatic and Marine Life.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The ingestion of 1.0 to 2.0 grams of mercuric chloride is frequently fatal to human beings.
- b. Stock and Wildlife Watering. The lethal dose for dogs has been reported as 10 to 15 mg per kg of body weight (353). The LD₅₀ value of mercuric chloride for rats was given as 37 mg/kg while that for mercurous chloride (Calomel) was 210 mg/kg (3009, 3067).
- c. Fish and Other Aquatic Life. From a study of the relation between concentration of the salt and period of survival, it appears that mercuric chloride is infinitely toxic to fish, i.e. that infinitesimal traces of the compound will be toxic if exposure continues long enough (3547). The following concentrations of mercuric ion from chloride have been shown to injure or kill fish in the time indicated:

Time of Exposure	Species of Fish	Reference
	sticklebacks	1460, 2941
	sticklebacks	2962, 2920
80-92 days	minnows	1459
	sticklebacks	598
	guppies	2921
	Exposure  	Exposure Fish  sticklebacks sticklebacks 80-92 days minnows sticklebacks

Concentration of Mercury, in mg/l	Time of Exposure	Species of Fish	Reference
0.02	19-47 days	minnows	1459
0.02	7 days	sticklebacks	1460
0.027	50 hours	young eels	1459
0.05	1 day	minnows	1459
0.1	8 hours	minnows	1459
0.2	4 days	sticklebacks	1459
3.2		minnows	362
4.0 to 30		fish	468
7.4	15 minutes	sticklebacks	1459
7.4	106 minutes	sticklebacks	1264
9.2 to 37	24 hours	trout	359
10.0	42 minutes	minnows	313
12.6	15 minutes	minnows	362
30	31 minutes	fish	467
370	54 minutes	trout	313
1000	20.5 minutes	minnows	991
5000	12 minutes	minnows	991

*Threshold value for deterimental effect

In varying concentrations, sodium chloride exhibits first a synergistic effect, then an antagonistic effect toward the toxicity of mercuric chloride. The presence of 1,000 mg/l of NaCl decreased the survival time of fish in a solution of 10 mg/l of mercuric chloride from 106 minutes to 54 minutes, but concentrations of 15,000 mg/l of NaCl prolonged the survival time to as much as 190 minutes (1264, 1265). According to Jones (467), fish show no special ability to detect or avoid toxic concentrations of mercuric chloride.

Anderson (598) reports that the threshold concentration for immobilization of Daphnia magna in Lake Erie water at 25°C was found to be less than 0.006 mg/l in 64 hours. For Polycelis nigra, a flat worm, the threshold of toxicity in 48 hours was 0.2 mg/l of mercury, or 0.027 mg/l of mercuric chloride, according to Jones (608). The effect of mercuric chloride on Marinogammarus marinus, an amphipod, was measured by Hunter (1266) who found that 0.1 mg/l of mercury killed in 510 minutes and 1.0 mg/l in 390 minutes. Low concentrations of copper increase appreciably the toxicity to mercury solutions.

Toward the larvae of bivalves, Woelke (2989) reported mercuric chloride to be lethal at a concentration of 0.027 mg/l (0.02 mg/l as Hg). Bringmann and Kuhn (2158, 3343), using River Havel water, determined the concentrations of mercury added as mercuric chloride that produced threshold effects upon four organisms as follows:

Organism	Threshold Concentration of $Hg$ in $mg/l$		
Microregma	0.15		
Escherichia coli			
Daphnia magna	0.03		

In a concentration of 3.0 mg/l, mercuric chloride killed 100 percent of water snails (Australorbis glabratus), while at a dosage of 1.0 mg/l only 30 percent were killed (exposure time not specified) (3548). Other inorganic mercury salts were approximately equal in effectiveness.

Mercuric chloride at a concentration of 0.61 mg/l causes a 50 percent decrease in the 5-day utilization of oxygen by synthetic sewage (2923) and at a concentration of 2.0 mg/l there is complete bacteriostasis (3549).

Clendenning and North (2106, 2107) found that 0.05 mg/l of mercury, added as mercuric chloride, caused a

50-percent inactivation of photosynthesis of the giant kelp (Macrocystis pyrifera) during a four-day exposure, while 0.1 mg/l caused a 15-percent decrease in photosynthesis in one day and complete inactivation in four days. Mercury was more toxic than copper, hexavalent chromium, zinc, nickel, and lead.

#### MERCURIC CYANIDE

 $Hg(CN)_2$ 

Highly soluble in water, mercuric cyanide has been used as a diuretic, as a topical antiseptic, and as a disinfectant for surgical instruments (364). Bringmann and Kuhn (2158, 3343) tested its effectiveness in water from the River Havel toward four organisms. Concentrations of mercury added as Hg (CN)₂ required to cause a median threshold effect were reported as follows:

	Threshold Concentration		
Organism	of $Hg$ in $mg/l$		
Daphnia magna	0.02		
Scenedesmus	0.15		
Escherichia coli	0.20		
Microregma	0.16		

### MERCURIC NITRATE

 $Hg(NO_3)_2 \cdot H_2O$ 

This soluble salt is used in the manufacture of explosive caps, felt, and the treatment of skin diseases. In very soft water, it killed sticklebacks in one week at a concentration of 0.02 mg/l as Hg (2977). Toward guppies the LD₅₀ value was also reported as 0.02 mg/l as Hg (2921). A concentration of 3.0 mg/l gave a 90-percent mortality among water snails, while 1.0 mg/l showed a 30 percent reduction (3548). Klock and Pearson (2314) reported the 48-hour TL_m toward the stickleback (Gasterosteus aculeatus) as 1.7 mg/l. The concentrations producing the first apparent significant response for three organisms were as follows:

	(NOs): in mg/l
Isopod (Neospheroma oregonensis)	0.015
Fish (Gasterosteus aculeatus) Polychaete (Mercierella enigmatica)	

## MERCURO-ORGANIC COMPOUNDS

Organic mercury compounds are used in herbicides, fungicides, and medical treatment of animals and humans. They have been used extensively to control slimes in paper mills and consequently they may be present in discharged white waters. Phenylmercuric acetate is used extensively as a herbicide for the control of crabgrass.

Van Horn (974) tested the survival time of fish in organic mercury compounds and other proprietary substances used for slime control in paper mills. He found that the critical concentrations, i.e., the concentrations that will sooner or later be fatal to fish, were as follows:

	Concentration in $mg/l$ for		
$Trade\ Name$	Minnows	Shiners	
Santobrite	0.3 to 0.4	0.2	
Merfenel	0.02	0.02 to 0.06	
Lignasan	1.0	0.8	
Nalco 23	1.4	1.4	
Nalco 21	<del>-</del> _	0.4	

Van Horn and Balch (3550) investigated the toxicity of slime control agents to minnows. The minimum lethal concentration was 0.15 mg/l for pyridylmercuric acetate and 0.04 mg/l for pyridylmercuric chloride.

Ellis (1267) found that in water at a pH value of 7.7 to 7.8 containing 0.5 mg/l of phenylmercuric lactate, all fish died in 16 hours or less. The lowest concentration causing death was about 0.10 mg/l. In terms of the content of mercury, phenylmercuric lactate is more than twice as toxic as mercuric chloride.

Phenylmercuric acetate (Scutl) in concentrations of 0.02 mg/l was fatal to young salmon in less than five days, according to Vallin (357), and the maximum safe concentration was found to be 0.01 mg/l. For mercuric acetate, the safe concentration was 0.02 to 0.05 mg/l. Daphnia pulex was found to be more sensitive than fish to phenylmercuric acetate, the safe concentration lying between 0.005 and 0.01 mg/l.

Pyridylmercuric acetate in very small concentrations (about 0.14 mg/l) was found to be beneficial to the health of fish, probably by suppressing the micro-organisms in the water (356). According to Van Horn and Katz (1268), 96 percent of Lake Emerald shiners survived a concentration of 0.15 mg/l but higher concentrations are toxic to fish.

Pyridylmercuric acetate successfully controlled the growth of a fluorescent species of Pseudomonas, which had infected yearling blueback salmon, when the fish were immersed for one hour in a solution containing 10 mg/l without harming the fish (1598). This same concentration, however, has been found toxic to other species, being more toxic to rainbow trout fingerlings than to brown or brook trout. Toxicity was manifested by losses of appetite, and it increased with temperature (1599).

A concentration of 5 mg/l for one hour was not toxic to rainbow trout fingerlings less than three inches in length, but it was toxic to larger fingerlings of the same species (1467). A concentration of 2 mg/l applied for one hour to yearling trout resulted in the death of 13 percent of the fish. Two weeks later a repeated treatment caused death of 10 percent of the fish. No fish died after a third treatment when the fish were not fed for 24 hours (1600).

Clemens and Sneed (2981) investigated the toxicity toward fingerling channel catfish of numerous compounds used in fish management and in agriculture. The results for organic mercury compounds in tap water are summarized below:

$T_{PT}$	mperature		$TL_m$ in $mg/l$		
Chemical	$\overset{\circ}{\circ}\overset{\circ}{C}$	24 hrs.	48 hrs.	72 hrs.	96 hrs.
Phenylmercuric acetate	19	4.1	3.4*	3.3	3.3
Pyridylmercuric acetate	24	3.8		0.49	
Ceresan M (a)	19	1.8	1.8	1.6	1.6
Lignasan (b)	19	2.0**	$\frac{2.2}{0.78}$	1.7 0.60	$\frac{1.3}{0.58}$
Tag 10% solution (e)	20	1.5	0.18	0.60	0.00

Bond and Nolan (3548) found that 13 organic compounds of mercury were 90 to 100 percent fatal to snails (Australorbis glabratus) at concentrations of 1.0 mg/l and several were highly toxic at 0.3 mg/l. Toward phytoplankton, the minimum lethal concentration of ethylmercuric bromide, phenylmercuric chloride, and ethylmercuric oxalate was found to be about 0.3 mg/l. Zooplankton were killed by this concentration in 22 minutes (3552). Lignasan (ethylmercuric phosphate, 6.25 percent) is an effective algicide at 1.0 mg/l (3551).

#### MERCURY

1. General. Although elemental mercury occurs as a free metal in some parts of the world, it is rather inert chemically and insoluble in water; hence, it is not likely to occur as a water pollutant. It is used in scientific and electrical instruments, in dentistry, in power generation, in solders, and in the manufacture of lamps (364, 2121).

Mercuric salts occur in nature chiefly as the sulfide HgS, known as cinnabar, but numerous synthetic organic and inorganic salts of mercury are used commercially and industrially, e.g. as medicinal products, disinfectants, detonators, pigments, and photoengraving. Many of the mercuric and mercurous salts are highly soluble in water.

Most of the references dealing with mercury express concentrations in terms of specific mercuric salts; hence they are covered under that heading. The data in this section relates only to the mercuric compounds for which the anion was not specified.

- 2. Cross References. Mercuric Salts, Mercuro-Organic Compounds.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The drinking water standards of the USPHS and the WHO do not include limits for mercury but for over a decade the maximum permissible concentration of mercury or mercuric ions in drinking water in the USSR has been set at 0.005 mg/1 (460, 3107).

Mercury and mercuric salts are considered to be highly toxic to humans (353, 364, 2121). They are readily absorbed by way of the gastro-intestinal tract, and fatal doses for man vary from 3 to 30 grams (2121). According to Smith (922), adults may safely drink water containing about 4 to 12 mg of Hg per day and a fatal dose of such water would be about 75 to 300 mg per day.

b. Fish and Other Aquatic Life. Mercuric ions are considered to be highly toxic to aquatic life. For freshwater fish, concentrations of 0.004 to 0.02 mg/l of Hg have been reported harmful (2409). For the stickleback (Gasterosteus aculeatus) the lethal concentration limit has been found to be 0.008 mg/l (353, 1460, 2941). Mercury salts, such as the unstable compounds mercuric sulfate and nitrate, have killed minnows at a concentration of 0.01 mg/l as mercury, after 80-92 days. At concentrations of 0.05 and 0.1 mg/l as mercury, fish were killed in 6 to 12 days (1459). For further details, see the mercuric salts.

In contrast, Schweiger (2151) reported that 0.2 mg/l of mercury was not harmful to one- and two-year-old tench, carp, rainbow trout, and char, nor to fish-food organisms such as crustacea, worms, and insect larvae.

For phytoplankton, the minimum lethal concentration of mercury salts has been reported (3552) to range from 0.9 to 60 mg/l of Hg. The toxic effects of mercuric salts are accentuated by the presence of trace amounts of copper (3313).

The Severn and Mersey River Boards in England have adopted working standards that limit the total concen-

^{*} At 45 hours ** At 28 hours (a) Ethyl mercury p-toluene sulfonantilide, 7.7 percent (total mercury as metallic, 3.2 percent)

⁽b) Ethylmercuric phosphate, 6.25 percent (c) Phenylmercuric acetate, 10 percent

tration of heavy metals, including mercury, to 1.0 mg/l (1756, 2950).

#### METAL-PLATING WASTES

(see also Chromates, Cyanides, Zinc, Iron, Acidity)

Pickling liquors from metal-plating works contain principally sulfuric acid, chromates, and iron. Schaut (362) found that a 1:240 dilution of such wastes gave a yellow color and an opaqueness to water, with an iron content of 470 mg/l and an acidity of 30 mg/l. At this dilution, minnows were harmed in 15 minutes and had a 50-percent mortality in one hour. For a dilution of 1:2400 the water was murky yellow in appearance but minnows were normal after one hour of exposure.

#### **METAPHOSPHATES**

(see Phosphates and Phosphoric Acids)

#### METASYSTOX

(see Chapter IX)

#### METHANE

 $CH_{4}$ 

(see also Hydrocarbons, General)

A gaseous saturated (paraffin) hydrocarbon, methane is odorless and flammable. It is a product of anaerobic decomposition of organic matter in marshes, mines, and sludge-digestion tanks. Wastes from natural-gas and petroleum plants may contain methane dissolved in water. According to Shelford (363), methane does not appear to be toxic or harmful to sunfish and Schaut (362) reported that a saturated solution (about 65 mg/l) had no effect on minnows after two hours of exposure.

### METHANETHIOL

CH₃SH

Known also as methyl mercaptan, this flammable gas with an odor of rotten cabbage occurs in coal tar and wastes from pulp mills. At a concentration of 1.0 mg/l in lake water it has been reported to kill white bass in 105 minutes, smallmouth blue bass and blue gills in 6 to 8 hours and rock bass in 11 hours (311, 313, 688, 696). In Kraft-pulp-mill wastes the minimum lethal concentration for shiners in 120 hours at 18°C was given as 0.5 mg/l (190, 344, 658). For minnows, the minimum lethal concentration was also reported as 0.5 mg/l (3523).

Haydu et al. (3501, 3502, 3503) reported on the minimum lethal concentration (defined as the minimum concentration giving complete kills) and the critical concentration (defined as the maximum concentration that caused no mortality) for three species of fish as follows:

Condition	King Salmon	Silver Salmon	Cutthroat Trout
Temperature of test, °C	15.5-19.5	12-18	9-15
Minimum concentration for			
complete kill mg/l	0.9	1.75	1.2
Maximum concentration for			
no kill, mg/l	0.5	0.7	0.9

For Daphnia magna and may-fly larvae, the minimum lethal concentration is given as 1.0 mg/l (190, 574) but for the larvae of *Chironomus*, the minimum lethal dose is only 50 mg/l. The toxicity of methanethiol to chironomous larvae was reported as follows (690):

Concentration in mg/l	Survival in percent
5 to 20	100
50	50
100	25
200	0

#### **METHOXYCHLOR**

(see Chapter IX)

### METHYL ALCOHOL

 $CH_3OH$ 

This colorless, clear, flammable liquid is obtained from the destructive distillation of wood or by hydrogenation of carbon monoxide. It is used extensively in chemical syntheses, as a fuel, as a solvent, and in the commercial manufacture of many products. The acute oral toxicity to rats has been reported (3248) as 9.1 mg/kg of body weight.

For human consumption it is very toxic. Small amounts will lead to blindness and 10 ml has caused death (364). Aquatic life, however, is much more tolerant to this substance. Trout withstand 10,000 mg/l in tap water for two hours without apparent injury; but in distilled water with 250 mg/l goldfish died in 11 to 15 hours (313). The same effect was noted with ethyl alcohol. For fingerling trout in natural waters, up to 8100 mg/l of methyl alcohol had no harmful effects in 24 hours.

Anderson (358) reports that in Lake Erie water the threshold concentration for immobilization of *Daphnia magna* after prolonged exposure at 25°C was 32,000 mg/l. To evoke a reaction (stimulation of movement) in a group of water beetles (*Laccophilus*) a methyl alcohol concentration of 115,000 mg/l was required (2956).

#### METHYLAMINE

CH₃NH₂

Occurring in nature as a degradation product of proteinaceous matter, methylamine is a gas at ordinary temperatures and pressures. It is highly soluble in water. Industrially, it is used in tanning and in organic synthesis (364).

According to Gillette et al. (1442) the critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 10 to 30 mg/l, i.e., all fish survived 10 mg/l but all died at 30 mg/l. Corti (146) tested rainbow trout (Salmo irideus) at a methylamine concentration of 141 mg/l. The resulting pH was 10.2 and the temperature 13.0-13.5°C. The fish showed their first reaction in about two minutes, turned over in 5 to 8 minutes, and made their last movement in 19 to 23 minutes. Bringmann and Kuhn (2158, 3343) found that the toxic threshold for methylamine hydrochloride occurred at a concentration of 4 mg/l for Scenedesmus and 50 mg/l for Microregma during a 4-day exposure at 24°C. For Daphnia at 23°C for 2 days, the threshold was 480 mg/l, while for E. coli at 27°C concentrations up to 1000 mg/l had no deleterious effect.

## METHYL CHLORIDE

CH₃Cl

This colorless gas with an ethereal odor is used as a refrigerant. It is soluble in water to the extent of 4000 mg/l at 20°C or about 9000 mg/l. Yant et al. (3554) investigated the possibility of poisoning by methyl chloride pollution of water fed to dogs. The taste of water

saturated with methyl chloride at 20°C is sharp, sickening, and sweetish when first taken into the mouth, followed almost immediately by a burning sensation. The

water was frequently refused by the dogs, but they had no other water supply. Ingestion of water with an average methyl chloride content of 5950 mg/l caused no apparent symptoms of poisoning or changes in the hemoglobin or blood cells (3554).

### METHYL CYANIDE

(see Acetonitrile)

## **METHYLCYCLOHEXANE**

(see Cyclohexane)

# METHYL DODECYL BENZYL TRIMETHYL AMMONIUM CHLORIDE

(see Chapter X)

## METHYL ETHYL KETONE

CH₃COC₂H₅

Known also as 2-butanone, this flammable liquid is highly soluble in water. It is widely used as a solvent in industry and for the manufacture of smokeless powder and synthetic resins (364). The oral  $LD_{50}$  dose for rats is given as 3.98 grams/kg of body weight (3244).

Turnbull et al. (2093) exposed bluegill sunfish (Lepomis macrochirus) to methyl ethyl ketone in Philadelphia tap water at 20°C. They found the 24-and 48-hour TL_m values both to be 5,640 mg/l, but the fish were visibly affected at 3,380 mg/l. Using highly turbid water and the mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values all to be 5,600 mg/l. This ketone had no clarifying effect on the turbidity.

## METHYL MERCAPTAN

(see Methanethiol)

## **METHYLNAPHTHOQUINONE**

 $C_{11}H_8O_2$ 

(see also Naphthoquinone and Dichloronaphthoquinone)

This bright-yellow crystalline solid with a faint acrid odor, also known as Menadione and by other trade names, is almost insoluble in water, but soluble in organic liquids. It is used in vitamin K therapy. Fitzgerald et al. (1542) report that it was toxic to fish in 24-48 hours at concentrations of 0.3-0.6 mg/l, or about the same concentration necessary to kill blue-green algae.

## METHYL PARATHION

(see Chapter IX)

### METHYL SALICYLATE

HOC₆H₄COOCH₃

This oily liquid, known also as oil of wintergreen, is used in medicine topically as a counter-irritant. It is also used in perfumery and for flavoring (364). At 30°C it is soluble in water to the extent of 740 mg/l. According to Helbig (3494) the threshold odor of methyl salicylate in water is 0.035 mg/l.

#### MOLLUSCACIDES

(see Chapter IX)

#### MOLYBDENUM

Μo

- 1. General. This metal and its salts are not considered to be significant in water pollution at the present time. Although the element occurs in some minerals such as molybdenite, MoS₂, and wulfenite, PbMoO₄, it is not widely distributed in nature. The metal and its salts are used principally for metallurgy and for electrical and electronic apparatus. It is also used in the glass and ceramic industries, for the production of pigments, and as a constituent of fertilizers for leguminous crops.
- 2. Cross References. Ammonium Molybdate, Copper, Selenium.

3. Effects Upon Beneficial Uses.

a. Irrigation. Molybdenum in very low concentrations has been found to be essential for healthy growth of a number of plants (1493, 1498, 1601, 1602, 1603, 3555, 3556), and for certain microbiological systems, where it apparently plays a role in the enzymatic catalysis of nitrate reduction (3557). At higher concentrations it has been injurious to the growth of many kinds of plants in solution or sand culture. The following concentrations of molybdenum have been reported to be injurious to plants:

Concentration o Molybdenum in m		Effect	Reference
0.5-100	Flax	Abnormal growth	1458
5.0	Clover, lettuce	Toxic effect	1601
10-20	Soybean, flax	Toxic effect	1595
25-35	Cotton	Slight effect	1604
50	Oats	Slight effect	1462
100	Oats	Chlorosis	1462
200	Oats	Stunted growth	1462

It has also been reported that 40 mg/l of molybdate  $(MoO_4^{--})$  in nutrient solution was slightly injurious to

sugar beets in sand culture (1473).

On the other hand, 0.1 mg/l of molybdenum has caused no injury to soybean and flax plants (1595). Molybdenum in small amounts reduced the symptoms of manganese, cobalt, and nickel poisoning in flax (1458), and nitrate injury in tomatoes (1596). There is some evidence that 1.0 mg/l of molybdenum in the water applied to cotton plants will reduce chlorosis (3556). The application of molybdenum to soil has overcome necrosis in hops (3555). Peas and beans grown with nitrate as nitrogen source appear to require molybdenum for completion of their life cycle, inasmuch as molybdenum is essential in the nitrogen-fixing mechanism (2121). Recovery of molybdenum deficient plants was effected by the application of 100 mg/l of molybdenum in molybdate solution (1603).

d. Stock and Wildlife Watering. Molybdenum appears to be an essential trace mineral for rats (1605), 2121). The toxic dose for rats has been reported to be 0.4 mg of molybdenum as molybdate (1498). Browning (2121), however, reported the oral LD₅₀ for rats to be 125 mg/kg for molybdenum trioxide, 101 mg/kg for calcium molybdate and 333 mg/kg for ammonium molybdate. Comparison of the effects of various molybdenum compounds showed that 500 mg of molybdenite (MoS₂) ingested daily was non-toxic, but animals receiving molybdenum trioxide, calcium molybdate, and ammonium molybdate showed anorexia, listlessness, and loss of weight. In the drinking water, 5 mg/l of molybdenum

increased the mortality rate among rats fed a ration

containing 11 mg/l of selenium (1481).

Upon addition to the gross ration 0.1 percent molybdenum (as sodium molybdate, Na2MoO4·2H2O) has produced toxic symptoms among rabbits (1606). When 1.2 g/kg of ammonium molybdate was given orally to rats and guinea pigs anorexic, colic, trembling, incoordinated movements, and dyspnea resulted (2121). In the diet of chicks, 300 mg/l (on a dry basis) of molybdenum has resulted in a reduced rate of growth of the chicks during a 4-week observation period (1493), and 200 mg/l depressed growth at eight weeks (3311), although copper appears to reduce the toxicity of molybdenum.

The principal detriment of molybdenum, like that of selenium, arises from the fact that it is picked up by plants and concentrated in foliage in pastures. Watersoluble molybdenum compounds in herbage cause cattle to scour severely (1269, 1270, 3557, 3558). Soil from pastures in which cattle had scoured contained 20 to 100 mg/l of molybdenum while non-injurious fields contained less than 5 mg/l. The herbage content of molybdenum varied with species on the same soil (1049).

Barley hay containing 89 mg/l of molybdenum (dry weight) caused symptoms similar to selenium poisoning in livestock, and molybdenum has also been suggested as a cause of bovine hematuria in parts of Australia. Studies are being conducted in Australia to determine the significance of molybdenum (1049). In an area of Florida where molybdenum poisoning among cattle has been common, the molybdenum content of the herbage has been as high as 26 mg/l (dry basis), while the molybdenum content of the water has ranged from 0 to 85 mg/l (1607). The toxic symptoms of molybdenum poisoning appear to be reduced by copper (3311, 3558) and molybdenum appears to affect copper metabolism (1271). Many studies have been undertaken to clarify the metabolic relationships between molybdenum and copper, as well as other minerals (1498, 1575, 1607, 1608, 1609, 1610, 2121, 3311). Copper glycinate has been injected into cattle to overcome the toxic effects of molybdenum (3558)

e. Fish and Other Aquatic Life. Tarzwell and Henderson (2154), in an exploratory test with fathead minnow. found the 96-hour TLm for molybdic anhydride (MoO3) to be 70 mg/l in soft water (pH = 7.4, total alkalinity = 18, hardness = 20) and 370 mg/l in hard water (pH = 8.2, total alkalinity = 360, hardness = 400). Molybdenum appears to be essential for the growth of Scenedesmus (1602) and indeed the threshold concentration for deleterious effect upon this alga occurs at 54 mg/l (2158). Escherichia coli and Daphnia tolerate concentrations of 1000 mg/l without perceptible injury (2158). Several species of algae concentrate molybdenum from water by factor of 2 to 15 (2442).

## MONOBUTYL BIPHENYL SODIUM MONOSULFONATE

## MONOBUTYL PHENYLPHENOL SODIUM MONOSULFONATE

## MONOBUTYL PHENYL SODIUM MONOSULFONATE

(see Chapter X)

### MONOCHLORO PHENOL

(see Halogenated Phenols)

## MONONITRO BENZENE

(see Nitrobenzene)

#### MONONITRO PHENOL

(see Nitrophenol)

#### MONONITRO TOLUENE

(see Nitrotoluene)

#### MUSTARD GAS

ClCH2CH2SCH2CH2Cl

(see also Chemical Warfare Agents)

This oily liquid, a deadly vesicant with a weak, sweet, agreeable odor, is sparingly soluble in water (about 480 mg/1). Direct contact of eyes with the unhydrolyzed liquid may cause conjunctivitis or blindness, and serious effects are noted with the respiratory tract and skin. Ingestion of contaminated material may cause nausea and vomiting (364). When hydrolyzed in water, however, mustard gas becomes almost innocuous (697) and nontoxic to man (466). In rabbits, gastro-intestinal inflammation is caused by water containing 500 mg/l of mustard gas (i.e. some unhydrolyzed liquid) and at 650 mg/l the mortality is 33 percent. The skin of man has about the same threshold sensitivity as the gut of a rabbit (697).

In a mustard-gas concentration of 5 mg/l in tap water, guppies become sluggish, and at a concentration of 20 mg/l, guppies died within 15 minutes (698).

## NACCONOL NRSF

## NALCO 21

(see Chapter X)

#### NALOAM

(see Chapter IX)

#### NAPHTHA

(see Petroleum Benzin)

#### NAPHTHALENE

 $C_{10}H_{8}$ 

The most abundant single constituent of coal tar, naphthalene is a white solid with the odor of moth balls. It is soluble in water at 20°C to the extent of about 30 mg/l. The use of naphthalene in organic syntheses and dye manufacture is extensive, and hence it may occur in wastes from refineries, coal-tar plants, textile mills, and chemical industries.

Shelford (363) and Gutsell (463) report that 4 or 5 mg/l of naphthalene kills sunfish in one hour, but Demyanenko (431) and Ellis (313) set the lethal concentration at 10 mg/l. During an exposure of one hour, 17.1 mg/l did not kill minnows but it caused them to stop eating. A concentration of 4.3 mg/l had no effect (362). For perch, the killing strength has been given as 40 mg/l (365, 699) and as 20 mg/l (2920).

Le Clerc (2942) exposed minnows for 6 hours to naphthalene in distilled water and hard water. The minimum lethal dose in distilled water at 19°C was 11-13 mg/l and in hard water at 16°C it was 15-18 mg/l. Using highly turbid water and the mosquito-fish (Gambusia affinis), Wallen et al. (2940) found the TL_m values at 22-24°C to be 220 mg/l at 24 hours, 165 mg/l at 48 hours, and 150 mg/l at 96 hours. The naphthalene did not clarify the turbid water. In aerated seawater, the critical level for fingerling silver salmon during a 72-hour exposure was reported (2091) to be between 1.8 and 3.2 mg/l.

In a dilution of 1:2400, commercial naphtha solution made minnows stop eating after 15 minutes of exposure; but the effect was temporary because the naphtha evaporated quickly (362). A concentration of 1.0 mg/l influenced the taste of the flesh of bleak (2904).

#### NAPHTHALIC ACID

 $C_{10}H_6(COOH)_2$ 

Ellis (313) quotes references to the effect that naphthalic acid and other naphthalene derivatives from refinery wastes showed the following lethalities in tap water:

Lethal Concentration				
Species	in mg/l	Killing Time		
percoid fish	3	6 to 12 hours		
pickerel	5	36 to 48 hours		
minnows	5	72 hours		
carp	20	26 to 36 hours		
goldfish	20	8 to 16 hours		

#### NAPHTHOL

 $C_{10}H_7OH$ 

This hydroxynaphthalene is used in the manufacture of dyes, intermediates, perfumes, medicinals, and anti-oxidants for synthetic rubber. The  $\alpha$ -naphthol is slightly soluble in water and has an oral LD₅₀ in rabbits of 9000 mg/kg of body weight. The  $\beta$ -naphthol is soluble to the extent of about 1000 mg/l. Its oral LD₅₀ for rabbits is given as 3800 mg/kg of body weight.

According to Nesmeyanova (3402) the odor threshold of naphthol in water occurs at 7 mg/l; but in chlorinated water at 0.5 mg/l Hoak (2982, 3403) gives the odor thresholds of  $\alpha$ -naphthol as 0.455 mg/l at 60°C and 0.500 mg/l at 30°C. For  $\beta$ -naphthol the corresponding thresholds occur at 5.0 and 3.33 mg/l.

Bandt (2904) reports the following effects of naphthols upon fish and the taste of fish flesh:

	Concentration in $mg/l$		
Effect Upon Fish	a-Naphthol	β-Naphthol	
Thresholds of toxicity for:		•	
bleak	<b>2</b>	2	
bream	3	2	
carp	<b>4</b>	2	
Threshold of taste in flesh:			
bleak	0.5	_	
bleak and carp		1	

### NAPHTHENIC ACID

(see Cyclohexanecarboxylic Acid)

## NAPHTHOQUINONE

 $C_{10}H_6O_2$ 

(see also Methylnaphthoquinone and Dichloronaphthoquinone)

These oxygenated products of naphthalene occur as 1,2-naphthoquinone and 1,4-naphthoquinone. The former is highly soluble in water, but the latter only sparingly so (364).

In Lake Huron water at 12°C, 1,2-naphthoquinone at a concentration of 5 mg/l killed rainbow trout, bluegill sunfish, and sea lampreys in 2, 3, and 4 hours respectively while a concentration of 1.0 mg/l killed them in 3, 4, and 12 hours respectively. A concentration of 0.1 mg/l had no effect in 24 hours.

According to Fitzgerald et al. (1542), 1,4-naphthoquinone was toxic to fish in 24-48 hours at a concentration of 0.3 to 0.6 mg/l. This concentration was also toxic to blue-green algae.

#### NASCENT OXYGEN

(see Ozone and Dissolved Oxygen)

## NATURAL GAS WELL WASTES

(see also Hydrocarbons, Specific Electrical Conductance, Mercaptans)

Ellis (611) reports that waste waters from naturalgas wells are detrimental to aquatic life owing to (a) osmotic action of brine water, inasmuch as a specific conductance of  $4000 \times 10^{-6}$  mhos at 25°C is approximately the upper limit tolerable by fish, (b) toxic action of calcium and magnesium salts, and (c) toxic action of hydrocarbons, mercaptans, and other organic compounds.

## NEOTRAN

(see Chapter IX)

### NICKEL

Ni

1. General. Elemental nickel seldom occurs in nature, but nickel compounds are found in many ores and minerals. As a pure metal it is not a problem in water pollution because it is not affected by, or soluble in, water. Many nickel salts, however, are highly soluble in water and since they are used in metal-plating works they may be discharged to surface or ground waters.

Although metallic nickel does not merit serious consideration as a water pollutant, nickel ions may be detrimental to beneficial uses. Where concentrations mentioned in the literature are expressed as nickel, they are summarized below; but when nickel salts are described, the results are discussed under the appropriate salt.

- 2. Cross References. See also Nickel Acetate, Nickel Chloride, Nickel Nitrate, Nickel Sulfate, and Nickel Ammonium Sulfate.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The USPHS Drinking Water Standards (2036) do not place any limit on nickel but Kirkor (460) reports that in Russia the maximum permissible concentration is 1.0 mg/l. According to Sawyer and Brown (561) the existence of 0.09 mg/l of copper, 0.08 mg/l of cobalt and 0.03 mg/l of nickel in public water supplies containing 80 to 90 mg/l of total solids, 4.4 mg/l of chlorides and with a pH of 3.8 to 4.5 caused pitting of aluminum in the kettles. Without these traces, no pitting occurred.

No data on the toxicity of nickel to man were revealed, but the toxicity is believed to be very low (353). Systemic poisoning of human beings by nickel or nickel salts is almost unknown (2121).

b. Irrigation. According to literature cited by the Chilean Nitrate Educational Bureau (921), experiments

performed in 1899 upon horse beans and corn showed that the effect of nickel salts upon the growth of plants was very injurious no matter how small the quantity. This contention is shared by Wilcox (3559).

Nickel is extremely toxic to citrus plants. It is found in many soils in California, generally in insoluble form, but excessive acidification of such soil may render soluble, causing severe injury or death of plants (1445).

Nickel at a concentration of 0.5 mg/l was toxic to flax grown in water culture, but the symptoms were somewhat reduced in the presence of molybdenum (1453). Concentrations of 15.9-29.4 mg/l of nickel, in nutrient solution were injurious to sugar beets, tomatoes, potatoes, oats, and kale grown in sand culture (1473).

- e. Stock and Wildlife Watering. An average daily dose of 2 mg of nickel did not harm rats but for dogs doses of 10 to 20 mg per kg of body weight proved lethal (353). Administered in the drinking water, 5 mg/l of nickel caused an increase in mortality among rats fed a ration containing 11 mg/l of selenium (1481). Nickel in the water supply of amphibia, reptiles, birds, and mammals hinders the growth of the liver (3560).
- d. Fish and Other Aquatic Life. Nickel appears to be less toxic to fish and river crabs than copper, zinc, brass, and iron (575). For sticklebacks, however, the lethal limit has been reported as 0.8 mg/l of nickel (2941) (see also Nickel Salts). Kaemmerer and Ericksen found that nickel was more toxic to fish than iron and manganese (1468). They also found fish living in water polluted with mine effluent and containing 13-18 mg/l of nickel (1459).

The Mersey and Severn River Boards in England have established standards for industrial wastes that limit the concentration of nickel alone, or in combination with other heavy metals, to 1.0 mg/l (1756, 2950).

Nickel combines readily with cyanide to form a nickelcyanide complex that is relatively stable. It can be present in water at concentrations greater than 100 mg/l as cyanide without harm to fish life if the water is moderately alkaline. In acid waters, however, the complex breaks down and releases HCN (2109, 2154, 2157, 2410, 2412, 2973, 3561, 3562, 3563)

## NICKEL ACETATE

 $Ni(C_2H_3O_2)_2$ 

This green crystalline salt of nickel is highly soluble in water. Cats and dogs, fed daily with 4 to 12 mg of nickel acetate per kg of body weight were unaffected in 200 days (353).

#### NICKEL AMMONIUM SULFATE

 $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ 

This bluish-green crystalline salt, highly soluble in water, is used in electroplating baths. The threshold of deleterious effect toward *Daphnia magna*, according to Bringmann and Kuhn (2158, 3343) is 6 mg/l of nickel. Toward *Scenedesmus* the threshold of toxicity is 0.09 mg/l, toward *E. coli* 0.1 mg/l, and toward *Microregma* 0.07 mg/l as nickel.

A nickel concentration of about 27 mg/l from nickel ammonium sulfate caused a 50 percent reduction in the oxygen utilization from synthetic sewage (2949).

### NICKEL CHLORIDE

 $NiCl_2 \cdot 6H_2O$ 

Occurring generally as the green crystalline solid, NiCl₂·6H₂O, this salt is highly soluble in water and is used for nickel plating and the manufacture of sympathetic ink (364).

Cats and dogs that received 4 to 12 mg of NiCl₂ per kg of body weight per day for 200 days were unaffected (353).

The tolerance of fish toward NiCl2 varies widely, depending on synergism, species, pH, and other factors. In soft water, goldfish survived a concentration of 100 mg/l of NiCl₂ · 6H₂O for 19 to 50 hours and 10 mg/l for 200 to 210 hours. Jones (2920) reports the lethal concentration of NiCl₂ · 6H₂O for goldfish to be 10 mg/l. In tap water, 8.1 mg/l NiCl₂ · 6H₂O killed the top minnow Fundulus in a few hours but the same species survived 259 mg/l of NiCl₂ ·  $6H_2O$  in salt water (313, 598, 1459). Toward the guppy, the median lethal concentration of NiCl₂ · 6H₂O was reported as 4.8 mg/l (2921). It has also been reported (1466) that nickel chloride at a concentration of 4.5 mg/l as nickel killed goldfish in 200 hours. Exploratory tests by Tarzwell and Henderson indicated that the 96-hour TLm for fathead minnows was 4.0 mg/l in soft water and 24 mg/l in hard water, expressed as  $NiCl_2 \cdot 6H_2O$ .

Using water of the River Havel from which test organisms were taken, Bringmann and Kuhn (2158) found the threshold of toxic effects toward Daphnia magna to be 6.0 mg/l as nickel. Anderson (598) had previously determined the threshold concentration for immobilization of this organism in Lake Erie water at 25°C to be less than 0.7 mg/l in 64 hours of exposure. In similar studies, Bringmann and Kuhn (2158, 3343) set the threshold concentration for Scenedesmus at 1.5 mg/l, for Escherichia coli at 0.1 mg/l and for Microregma at 0.05 mg/l as nickel.

The biochemical oxidation of sewage was inhibited 50 percent by 15 mg/l of nickel added as nickel chloride (2922), by 9.4 mg/l of N: (2949) and by 12 to 16 mg/l of nickel (3411).

#### NICKEL NITRATE

 $Ni(NO_3)_2$ 

This salt of nickel occurs generally as the green deliquescent crystal Ni(NO₃)₂ · 6H₂O which is highly soluble in water. It is used for nickel plating and the manufacture of brown ceramic colors (364). According to Anderson (598), the threshold concentration for stickleback in tap water was 2.44 mg/l of Ni(NO₃)₂. Jones (608) gives the threshold concentration of nickel nitrate for toxicity to a flatworm (Polycelis nigra) as 45 mg/l measured as nickel.

The lethal concentration limit of nickel nitrate for sticklebacks was reported to be 0.8 mg/l of nickel. At higher concentrations, the survival times were as follows: one week at 1.0 mg/l, four days at 1.5 mg/l, and only one day at 10 mg/l, as nickel (1460). Jones (2920) indicates that the lethal concentration of nickel nitrate toward sticklebacks at 15-18°C is 1.0 mg/l as nickel.

A nickel concentration of about 13 mg/l from nickel nitrate caused a 50 percent reduction in the oxygen utilization from synthetic sewage (2949).

### NICKEL SULFATE

NiSO₄·6H₂O

Occurring generally as a green crystalline salt, NiSO₄ 6H₂O, this compound is highly soluble in water. It has a sweet astringent taste and it is used in nickel plating, dyeing, and printing of fabrics (364). Applied in a culture solution it was slightly toxic to oat plants at a concentration of 1.0 mg/l as nickel. At 2.5-5.0 mg/l as nickel it was severely toxic and markedly reduced growth (1462).

The maximum concentration of nickel sulfate tolerated by young eels for an average of 31 hours was found to be about 16 mg/l. In a tap water solution of nickel sulfate, 50 mg/l (as nickel) killed sticklebacks in 49-60 hours. A rainbow trout was not affected by one mg/l of nickel in a 51-hour period of exposure (1459).

In water culture, 2.5 mg/l of NiO from nickel sulfate caused plants to wilt or die (2977).

North and Clendenning (2107) measured the effects of many heavy metals on the rate of photosynthesis by the giant kelp, *Macrocystis pyrifera*. They found that zinc sulfate showed no appreciable effect at 1.31 mg/l as zinc but gave a 50 percent reduction in photosynthesis in 4 days at 13.1 mg/l.

A nickel concentration of 3.6 mg/l from nickel sulfate caused a 50 percent reduction in the oxygen utilization from synthetic sewage (2949).

## NICOTINE

(see Chapter IX)

### **NIGROSINE**

(see also Dyes, Aniline, Weed Killers)

Nigrosine is an aniline dye that has been used to control weeds in fish-hatchery ponds. It tends to destroy the coarse weeds and to favor the growth of waterbloom. Apparently it is absorbed by plants and used up within a short period of time (700). At concentrations of 10 to 25 pounds per acre, used to control weeds, nigrosine does not harm fish or benthal organisms. Daphnia magna successfully survived 7.2 mg/l (about 20 lbs per acre feet of water) for five days. In a dirt-bottomed pond, 10 lbs of nigrosine applied weekly for four weeks caused benthos to increase, but zooplankton decreased.

## NITRAMINE

(see Tetryl)

## **NITRATES**

 $NO_3$ 

1. General. Nitrates are the end product of the aerobic stabilization of organic nitrogen, and as such they occur in polluted waters that have undergone self-purification or aerobic treatment processes. Nitrates also occur in percolating ground waters as a result of excessive application of fertilizer (1032) or leachings from cesspools. In a few instances, nitrates may be added to a stream or ground water by natural degradation or directly by inorganic industrial wastes, but such sources are relatively insignificant. Wastes from chemical fertilizer-producing plants (apart from fertilizers in the field) are an increasingly important source of nitrate pollution.

In spite of their many sources, nitrates are seldom abundant in natural surface waters, for they serve as an essential fertilizer for all types of plants, from phytoplankton to trees. Photosynthetic action is constantly utilizing nitrates and converting them to organic nitrogen in plant cells. In deep ground waters, however, this action is not possible and, consequently, it is in such waters that excessive and deleterious concentration of nitrates are often found.

- 2. Cross References. Ammonia, Albuminoid Ammonia, Nitric Acid, Nitrites, and Nitrogen.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Until 1962, the USPHS Drinking Water Standards (2036) did not have a requirement for nitrates. At that time, however, a recommended limit of 45 mg/l as nitrates was established. The WHO European Drinking Water Standards (2329) have a recommended limit of 50 mg/l as nitrates. No limit has been set for the WHO International Standards (2328). These limits were established because of the relationship between high nitrates (or nitrites) in water and infant methemoglobinemia. No cases of such poisoning have been evident in the U.S. when the water consistently contained less than 45 mg/l of nitrate as NO₃ or 10 mg/l as nitrogen.

Infant methemoglobinemia, a disease characterized by certain specific blood changes and cyanosis, may be caused by high nitrate concentrations in the water used for preparing feeding formulae. Since the disease often does not occur even where the water is very high in nitrate content, however, it seems likely that not all infants are susceptible to nitrate poisoning, but that some are predisposed to it by physiological conditions such as low gastric acidity or other unknown factors. Many well waters containing over 500 mg/l of nitrate nitrogen have never been linked with reported cases. Most cases, however, have been associated with the use of water containing 50 mg/l or more of nitrate nitrogen. While it is still impossible to state precise concentration limits, it has been widely recommended that water containing more than 10 mg/l of nitrate nitrogen should not be used for infants. The references dealing with nitrates and methemoglobinemia are far too numerous to discuss in detail in this report; however, the following were reviewed: (36, 152, 353, 630, 944, 1273-1283 incl., 1611-1617 incl., 2028, 3530, 3564, 3565, 3566, 3567, 3568, 3569, 3570, 3571, 3572, 3573).

Nitrates are rated among the poisonous ingredients of mineralized waters, with potassium nitrate being more poisonous than sodium nitrate (284). Excess nitrates cause irritation of the mucous linings of the gastrointestinal tract and bladder, with symptoms of diarrhea and diuresis. Drinking one liter of water containing 500 mg/l of nitrate can cause such symptoms (629).

Studies of nitrate-bearing water, both artificial and authentic, seeded with coliform bacteria indicated that when the nitrate-nitrogen concentration was 100 mg/l or higher, the standard presumptive tests for the presence of coliforms gave unreliable and ambiguous results (1618, 1619).

b. Industrial Water Supplies. Nitrates are injurious to the dyeing of wool and silk fabrics (261). Nitrates are

harmful to fermentation processes and cause disagreeable tastes in beer (165, 167, 240, 1094, 2347). For brewing, the nitrate concentration of water should be less than 30 mg/l (170), or less than 15-20 mg/l (3574). In the brewing industry, according to Bonnet (2344), nitrates are partially reduced to nitrites during fermentation; hence they are poisonous toward yeast. They also give a bad taste to the beer when present in large amounts. Nitrates and free nitric acid at concentrations of 15 to 30 mg/l render water harmful for various industrial purposes (855). On the other hand, two mg/l of nitrate in some water protects metal in boilers from intercrystalline cracking (1284).
c. Irrigation. Excess nitrate tends to reduce soil per-

meability. Nitrates may sometimes accumulate to toxic concentrations in the soil solution, but their effect is usually osmotic (246). In general, nitrates are desirable

for their fertilizing value.

d. Stock and Wildlife Watering. Outbreaks of nitrate poisoning (methemoglobinemia) have been reported among cattle following their consumption of hay containing 30,000 to 70,000 mg/l of potassium nitrate (1049), although fodder containing 20,000 mg/kg was without effect. Campbell et al. (3575) report methemoglobinemia among cattle that received water containing 2790 mg/l of nitrate.

Nitrates in the drinking water of rats and livestock have been harmful in lower concentrations than mixtures of chlorides and sulfates of the alkaline metals (286, 641). Where "duck disease" occurs, the soil contains a high concentration of nitrates. Oral feeding to ducks of mixtures of salts with nitrates has resulted in duck poisoning (1285).

Nitrate in water and food consistently inhibited dental decay among a group of experimental rats (1069).

Special attention should be paid to the concentration of nitrates in stock waters, especially when the total salt concentration exceeds 570 to 1000 mg/l (284).

Although the drinking water administered to two cows over a 10-day period contained 114 mg/l of nitrate nitrogen, no positive test for nitrates could be demon-

strated in the milk (1277).

e. Fish and Other Aquatic Life. High nitrate concentrations in effluents, and water stimulate the growth of plankton and aquatic weeds (380, 584, 1286, 1287, 1288). By increasing plankton growth and the development of fish food organisms, nitrates indirectly foster increased fish production (1288).

Hart et al. report references to the effect that among United States waters supporting a good fish life, ordinarily 5 percent have less than 0.2 mg/l of nitrates; 50 percent have less than 0.9 mg/l; and 95 percent have less than 4.2 mg/l (310).

The toxic threshold concentration of nitrate, as sodium nitrate, for the flatworm Polycelis nigra is reported to be 2670 mg/l (354).

NITRIC ACID  $HN0_3$ 

1. General. One of the most-widely used acids in industrial processes, nitric acid is a clear, colorless liquid that is very hygroscopic and miscible with water. It dissociates completely into hydrogen ions and nitrate ions with a resulting tendency to lower the pH value. Its principal deleterious effect, therefore, is its acid reaction. For further information about the effects of acids, see Acidity and pH; and for further data pertaining to the nitrate ions, see Nitrates.

- 2. Cross References. See also Nitrates, Acidity, pH.
- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Rudolf has reported that free nitric acid and nitrates in concentrations of 15 to 30 mg/l render water harmful or dangerous for domestic, drinking, and industrial purposes (855).
- b. Industrial Water Supplies. Nitric and nitrous acids in high concentrations are injurious to the dyeing of wool and silk fabrics; they not only color the fabrics yellow, but may also react with some of the dyes (261).
- c. Fish and Other Aquatic Life. The threshold concentration of nitric acid for the immobilization of Daphnia magna in Lake Erie water at 25°C is reported to be 107 mg/l (358).

Doudoroff and Katz (361) cite references to the effect that nitric, as well as other strong acids, are directly lethal to fully developed fish only when they reduce the pH to 5.0 or less. The lethal threshold concentration of nitric acid for stickleback is reported to be 0.01 mg/l of hydrogen ion (353), i.e. a pH value of 5.0. The following concentrations of nitric acid have been cited as toxic or lethal to fish:

Concentration in mg/l			Time of Exposure	Type of Fish	Reference
1.6				Trout	353
1.56-20				Fish	359
15.6			24 hours	Trout	359
72	6.2	Turbid	96-br TL _m	Mosquito-fish	2940
98.5 (threshold				Pickerel	353
113 (threshold)	)			Whitefish	353
200				Minnows,	
750	3.4	Hard	⅓-1 hr.	goldfish Goldfish	359 313, 353
1000		Тар	4 hr.	Trout	313
1000	4.4		7 hrs.	Minnows	313

In contrast, the following concentrations of nitric acid have not been harmful to fish within the time specified:

Toncentration in mg/l	Resulting pH	Time of Exposure	Type of Fish	Reference
5.75	5.2		Minnows	313
5.75	· ·		Shiners	359
5.75-20			Fish	359
20			Carp, goldfish,	
			suckers	359
200		> 100  hrs.	Goldfish	313
200	4.9	>4 days	Goldfish	35

## NITRILES

(see Acetonitrile, Acrylonitrile, Adiponitrile, Benzonitrile, Cyanides, Lactonitrile, Oxydipropionitrile).

#### NITRITES

1. General. In water, nitrites are generally formed by the action of bacteria upon ammonia and organic nitrogen. Owing to the fact that they are quickly oxidized to nitrates, they are seldom present in surface waters in significant concentrations. In conjunction with ammonia and nitrate, nitrites in water are often indicative of pollution. However, the presence of nitrite does not always signify pollution (155).

- 2. Cross References. See also Nitrates, Nitrogen, Ammonia.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Nitrites are poisonous compounds, but in the minute amounts ordinarily found in drinking waters they can scarcely have a pharmacological effect (629, 630). Old Swiss standards for drinking and mineral waters required the complete absence of nitrites (944). A generally accepted limit for nitrites in domestic water supplies is 2 mg/l (170), however, another reference states that the ammonia and nitrite content of drinking water should not exceed 0.1 mg/l (855). In southern Bavaria, 70 poisonings including 18 deaths have been attributed to the use of nitrites in the foodstuff industry (3576).

b. Industrial Water Supplies. Nitrite is undesirable in waters for use in brewing (1094, 2344), and in the dyeing of wool and silk fabrics (261). Nitrite containing waters are objectionable in brewing because (a) they show the presence of organic matter in decomposition, (b) the preservation of beer is poor, (c) nitrites are poisons for the yeast, and (d) they are not suitable for malting as they cause an invasion of the malt by molds

and bacteria.

c. Irrigation. Nitrite usually occurs in very low concentrations in irrigation water and is of little signifi-

cance (268).

d. Fish and Other Aquatic Life. Nitrite and nitrate stimulate the growth of plankton in reservoirs (1287). For further details, see Nitrogen and Nitrates. Tests with minnows showed that a concentration of 50 mg/l of sodium nitrite could be fatal in 14 days, while 10,000 mg/l destroyed the minnows in 1.5 hours (3577). The snail hosts of schistosomes *Planorbis glabratus* and *Bulinus contortus* were killed in 24 hours by 10,000 mg/l of sodium nitrite or potassium nitrite (3578).

## NITROANILINE

 $C_6H_4NH_2NO_2$ 

(see also Dyes, Analine)

This compound exists with the NO₂ group in the metaortho-, or para-position. They are all used as dyestuff intermediates. Meta- and paranitroaniline are moderately soluble in water but the ortho-form is only slightly soluble. Bringmann and Kuhn (2158) found the threshold of harmful effect toward Daphnia occurred at 24 mg/l and toward Scenedesmus at 20 mg/l. A concentration of 100 mg/l had no effect on E. coli at 27°C.

#### NITROBENZENE

 $C_6H_5NO_2$ 

(see also Dinitrobenzene and Trinitrobenzene)

Moderately soluble in water, this oily liquid with an almond odor is used in the manufacture of analine, soaps, and shoe polishes. The oral  $LD_{50}$  for rabbits is given as 700 mg/kg of body weight (364). The approximate concentration in water that results in a faint odor has been reported as 0.03 mg/l (1756).

Hiatt et al. (3350) indicate that 10 mg/l of nitrobenzene in sea water produced a slight irritant activity in marine fish. According to LeClerc (2942), the minimum lethal dose for minnows during a 6-hour exposure in distilled water at 22°C was 20-24 mg/l, and in hard water

90-100 mg/l.

Toward lower aquatic life, Bringmann and Kuhn (2158, 3343) found the thresholds of toxicity to be 28 mg/l for Daphnia, 30 mg/l for Microregma, 40 mg/l for Scenedesmus, but 600 mg/l for Escherichia coli. Herman (2923) reported that 630 mg/l caused a 50 percent decrease in oxygen utilization in the BOD test.

## NITROCHLOROBENZENE

C₆H₄ClNO₂

This yellow crystalline compound is insoluble in water in the o- and p-isomers. It is used in dye chemistry (364). Orthonitro-chlorobenzene has been detected in river waters and has been observed to persist for many weeks (3102, 3356).

#### NITROGEN

N

(see also Albuminoid Ammonia, Ammonia, Cyanides, Nitrates, Nitriles, Nitrites, Nitrogen Gas, Organic nitrogen)

Nitrogen occurs abundantly in nature, constituting 78.06 percent by volume of the atmosphere. It is also an essential constituent of protein in all living organisms, and it is present in many mineral deposits as nitrates (364). In organic matter it undergoes changes of decomposition from complex proteins through amino acids to ammonia, nitrites, and nitrates; and also changes of synthesis from nitrates into plant and animal forms. This so-called nitrogen cycle in nature is dependent upon bacterial action for decomposition and upon photosynthesis for reconstitution of organic matter. In natural or polluted waters, nitrogen may be present in many forms, but the ones that are measured by the common tests include ammonia, albuminoid ammonia, organic nitrogen, nitrites, and nitrates (469). Results of investigations that are expressed in terms of a particular form of nitrogen are presented elsewhere in this chapter under the appropriate term. The references described below deal with the term "nitrogen" without reference to the form. In some instances total nitrogen is involved.

In water suitable for most beneficial uses, the total concentration of nitrogen compounds should be less than 10 mg/l according to an anonymous German reference (632). This same limit has been recommended for critical low flows in the Miami River from Dayton to its mouth (929). For irrigation purposes, however, nitrogen in any form is seldom deleterious; in fact, it is usually beneficial, for nitrogen compounds form the basis of most organic and chemical fertilizers (1289, 1290, 1291, 1292).

Toward algae, crustacea, and other fish-food organisms, the total concentration of nitrogen is not as important as the form in which it exists. Organic nitrogen, amino acids, and ammonia may inhibit biological growth whereas nitrates stimulate phytoplankton (1293) (see also Ammonia). Some green plants apparently do not need to depend upon complete nitrification but can utilize nitrogen from ammonia or nitrites (1294). Extensive studies have been made of the effects of nitrogen and phosphorus in three Wisconsin lakes upon the nuisances from odors caused by algal "blooms" (375, 377, 1295). According to Sawyer (374), the critical concentration of nitrogen, below which algal growths were not troublesome, was 0.30 mg/l provided that phosphorus was kept below 0.015 mg/l. Fish production is highest in ponds

and streams containing the most organic nitrogen

(1296).

Sawyer et al. (1450) reported that for some algae, the optimum nitrogen: phosphorus ratio appeared to be about 30 to 1; for other algae, ratios of 15-18:1 were evident. The presence of 0.01 mg/l of phosphorus and 0.30 mg/l of inorganic nitrogen in ponds or lakes at the time of the spring overturn would probably foster the production of nuisance blooms. Gerloff and Skoog (2209, 2210, 2211) suggest that in many instances nitrogen, rather than phosphorus, may be the limiting element in growth of algae. Imhoff (2170) and Mueller (3579, 3580) point out that enormous growth of plants in streams and lakes does not occur if the nitrate as N is kept below 0.3 mg/l and the total nitrogen as N is below 0.6 mg/l.

## NITROGEN GAS

Natural waters in equilibrium with air contain dissolved nitrogen gas as well as dissolved oxygen in accordance with Henry's Law. Although nitrogen is considerably less soluble than oxygen, it constitutes about 78 percent by volume of normal air, and hence water in equilibrium with air at 20°C will contain about 15.6 mg/l of dissolved nitrogen gas (911). Unlike oxygen, however, dissolved nitrogen is inert and it is not consumed in biological stabilization; consequently, the dissolved-nitrogen-gas content of surface waters is not likely to fluctuate other than in accordance with temperature changes.

No literature was uncovered to describe the effects of dissolved nitrogen gas on beneficial uses of water other than for fish and aquatic life. Under normal conditions of saturation, no detrimental effects toward fish are anticipated, and extreme supersaturation or undersaturation is not likely to occur in surface waters. When nitrogen gas occurs in excess of saturation, gas bubbles may form on rough and warm surfaces, producing gas-bubble disease in fishes (3553). It has been reported (3581) that supersaturation of nitrogen above 130 percent may be

fatal to fish.

#### NITROGEN TRICHLORIDE

 $NCl_3$ 

(see also Chlorine and Chloramines)

Known also as agene, this compound may be produced in waters treated by breakpoint chlorination, if ammonia or nitrogenous organic compounds are present and if the pH is below 5.0. It may cause unpleasant odors in treated waters (1620, 1621).

## NITROPHENOL

C₆H₄OHNO₂

Metanitrophenol is highly soluble in cold water, p-nitrophenol moderately so, and o-nitrophenol only sparingly soluble. The ortho isomer is used in chemical manufacturing (364). According to Le Clerc et al. (1560, 2942) the minimum lethal doses toward minnows during a 6-hour exposure at 22°C in distilled or hard water were as follows:

	Minimum Lethal Dose in mg/l		
Isomer	In Distilled Water	In Hard Water	
m-nitrophenol	9-10 4-6	125-130 20-22 30-33	

Lammering and Burbank (3582) used bluegill sunfish and standard bioassay procedures at  $20^{\circ}\mathrm{C}$  to determine the effects of o-nitrophenol. They found the 24-hour TL_m to be 66.9 mg/l and the 48-hour TL_m to be 46.3 to 51.6 mg/l.

Toward lower organisms in River Havel water, Bringmann and Kuhn (2158, 3343) found the following

thresholds of toxic effect:

		Concentratio	n of Nitroph	enol in mg/l
Organism	$Temp.$ $^{\circ}C$	Ortho-	meta-	para-
Daphnia	23	60	24	14
Scenedesmus	24	36	28	72
Microregma		40	20	20
Escherichia c	oli 27	>1000	300	100

Applegate et al. (3491) tested the effects of several halogenated nitrophenols toward the larvae of sea lamprey and the adult form of three fresh water fishes. Results were as follows:

	Concentration in mg/l to	Concentration in mg/l to cause 10 percent fish kill		
Compound	kill all sea lamprey larvae	Rainbow Trout		
2-bromo-4-nitrophenol	5	13	11	
3-bromo-4-nitrophenol	5	11		15
5-chloro-2-nitrophenol	3	5	5	
2, 5-dichloro-4-nitropher	nol 3	13		
3, 4, 6-trichloro-2-nitrop	henol 5	17	15	
3-trifluoromethyl-4-nitre	ophenol 2	9	7	

#### NITROTOLUENE

NO₂C₆H₄CH₃

(see also Trinitrotoluene)

Metanitrotoluene is moderately soluble in water but o- and p-nitrotoluene are almost insoluble. These compounds are used in the manufacture of dyes and other chemicals (364). According to Le Clerc (2942) the minimum concentrations producing death to minnows in 6 hours at 23°C in distilled water or at 21-22°C in hard water were as follows:

	Minimum Lethal Concentration, mg/l			
Isomer	in distilled water	in hard water		
o-nitrotoluene	18-20	35-40		
m-nitrotoluene p-nitrotoluene		25-30 45-50		

# NONYLPHENOL ETHYLENE OXIDE CONCENTRATE (Lissapol)

NOPALCO

NOPCO 2272-R

NOPCOGEN 14-L

(see Chapter X)

OCTADECENYL DIMETHYL ETHYL AMMONIUM BROMIDE

(see Chapter X)

OCTOPHENOL

(see Chapter X)

#### OCTYL ALCOHOLS

 $C_8H_{17}OH$ 

Octyl alcohol is a generic term that includes a number of isomeric alcohols of which 2-ethyl hexanol and n-octyl alcohol are industrially the most common. The octyl alcohols are colorless liquids, generally with a penetrating aromatic odor. They are used in the manufacture of perfumes and esters, in mercerizing textiles, and as a solvent for dyes, resins, and oils. Ellis (313) reports that among 23 octyl alcohols, the least toxic produced paralysis in goldfish in four hours at 200 mg/l. Primary octyl alcohol produced paralysis in 15 minutes at a concentration of 67 mg/l. A concentration of 5 mg/l had no effect on the sea lamprey during a 24-hour exposure in Lake Huron water at 12°C (2976).

#### N-OCTYL SODIUM SULFATE

(see Chapter X)

#### ODOR

(see also Tastes)

Disagreeable odors and tastes in water are associated with the presence of any of a great variety of objectionable substances, particularly living microscopic organisms or decaying vegetation, including weeds, bacteria, fungi, actinomycetes, and algae; decaying organic matter; sewage; and industrial-waste products. Problems of odor and taste are very complex because the senses of smell and taste are intimately related and their responses are often difficult to differentiate clearly. In addition, it is frequently difficult, if not impossible, to identify the specific cause of an odor or taste, for many substances can cause what appears to be the same effect, or because mixtures of substances may be involved.

It would be impractical to attempt to make a complete list of all the types of industry whose waste products are potentially odoriferous in water supplies, but among them are the following: pulp and paper; explosives; petroleum, gasoline, and rubber; wood distillation; coke and coal tar; gas; tanneries, meat-packing and glue; chemicals and dyes; and milk products, canneries, beet-sugar, distillation and other food products. Among the chemicals responsible for tastes and odors are halogens, sulfides, ammonia, turpentine, phenols and cresols, picrates, various hydrocarbons and unsaturated organic compounds, mercaptans, tar and tar oils, detergents, pesticides, and innumerable others, many of unknown identity. For odor and taste threshold concentrations of specific substances, see each potential pollutant in this chapter and also Chapters VII, IX, and X. Odor thresholds of many compounds have been tabulated by Hoak (2982, 3403), Nesmeyanova (3402), Baker (2058), and Filicky et al. (2040).

Odorous substances in water must be vaporizable in order to be smelled. While such substances may often also be tasted, the sense of smell is generally much more acute than that of taste (759) and in water-works practice the separation of odor and taste is rarely made. Standard Methods for the Examination of Water and Wastewater (469) does not prescribe a procedure for taste determination. For a discussion of the complexities of the odor-taste differentiation problem, see the paper by Rohlich and Sarles (759).

Odors can be caused by volatile substances in concentrations too small to be detected by ordinary analytical techniques; therefore, reliance must be placed upon the

sense of smell, in spite of its subjectivity and lack of precision (3584). Methods devised for determining the presence of odor in either cold or hot water are described in Standard Methods (469). Results are reported in terms of "threshold odor numbers" (TON) calculated from the amount of sample in the most diluted portion giving perceptible odor. The threshold odor number equals the volume of the dilution divided by the volume of the sample in the dilution. The 1962 Drinking Water Standards of the USPHS (2036) indicate that the threshold odor number should not exceed 3. In the literature on odor and taste in water are also found many references to the "threshold concentrations" of odor and taste-producing substances, i.e. the lowest concentrations, in mg/l giving perceptible odor and/or taste. The variety of odors possible is almost numberless, and although many descriptive terms have been assembled (16, 469, 759) they are still considered to be inadequate.

Knowledge about the sources of odors in water was enhanced considerably by the development at the R. A. Taft Sanitary Engineering Center of the carbon-filter technique for separating and identifying organic components in dilute concentrations (1622, 1623, 2983, 3004, 3102, 3354, 3355, 3356, 3357, 3358, 3583, 3585, 3586, 3587, 3588, 3589, 3590, 3591). Studies of numerous surface waters indicate that hydrocarbons are a major source of taste and odors. Among the hydrocarbons, the neutral fractions have the highest threshold odor numbers. For more detail, see Carbon Chloroform Extract and Oils, Petroleum, or the original references.

Odor and taste problems may be aggravated by the impounding of water (962, 2314) or by the sedimentation of suspended solids, resulting in the trapping of decaying matter on lake or stream bottoms (780). In addition, chlorination of waters polluted by even very low concentrations of TNT wastes, algae and protozoa, detergents, or phenolic or cresolic compounds may result in the production of foul odors and tastes. On the other hand, chlorination may reduce the odors and tastes caused by some wastes, such as Kraft mill wastes, sulfides, mercaptans, and turpentine (686). Treatment methods for combating odors and taste vary in effectiveness with the substances involved and the composition of the water.

Waters free from odor and taste nuisance are desirable for drinking and domestic use, industry, irrigation, fish production and fishing, shellfish culture, and recreation (345, 964, 965). Odors and tastes are particularly undesirable in waters for drinking and domestic purposes, beverages, dairying, distilling, brewing, and other food-processing industries (173).

Offensive odors and tastes may be imparted to fish and shellfish from polluted waters by algae, petroleum products, turpentine, resins and resin acids, vegetable and mineral oils, insecticides, wastes from synthetic rubber and explosives factories, petroleum refineries, phenols, and cresols. Phenol in concentrations of 15 mg/l (431) to 25 mg/l (935) and cresols in concentrations of 10 mg/l have rendered fish unpalatable.

Many state and interstate water-pollution-control agencies have included references to odors and taste in their standards, but such requirements are qualitative and not quantitative. For details and exact statements, see Chapter III and its appendices.

#### OIL, PETROLEUM

1. General. A comprehensive report on "Oily Substances and Their Effects on the Beneficial Uses of Water" was published in 1956 by the California State Water Pollution Control Board (3596) as Publication No. 16. Much of the following material appears in that reference, but for a thorough analysis of oils in relation to beneficial uses the reader should consult the full publication.

Potential contributors to oil pollution are all agencies engaged in production, transportation, handling, and use of oil, such as ships, oil wells, oil-loading points, refineries, railroads, civic dumps, salvage dumps, garages, and industries (981). Garland (982) lists the principal sources of oil pollution of seas and harbors as (a) the discharge of oil-contaminated ballast and bilge, (b) cleaning and flushing of oil tanks at sea, and (c) accidents to oil lines in fueling. The average oil content of such wastes is 2 to 3 percent and the average ship contains 1000 to 2000 tons of such material.

The British Minister of Transport appointed a committee to consider and report on practical measures to prevent oil pollution of seas (1624). The report indicated that fouling of seas, hundreds of miles offshore, damages flora and fauna of the coast line and open ocean. There is evidence that the oils causing the worst pollution are very stable. There may be very slow oxidation, so slow as almost to defy detection, but the oils keep floating almost indefinitely. In experimental tanks, oil on water floated for nearly 18 months until the water had evaporated. Experiments on the behavior and drift of oil discharged on the sea indicated that 15 tons of fuel oil covered an area of 8 square miles six days after discharge and drifted about 20 miles in an eight-day period. Wind and tide influence the drift.

Sources of pollution include unburned fuel oil escaping through funnels of ships as well as crude oil residues, leakage, breakage, and the discharge from ballast tanks. Damage caused by oil may involve (a) spoiling of beaches and coastal resorts, (b) destruction and injury of sea birds, (c) fouling of boats, fishing gear, and quays, (d) the risk of fire in harbors and other enclosed areas, and (e) damage to marine flora and fauna. The disappearance of eel-grass is believed by some to be a result of such pollution. Large areas of eel-grass provided special habitat for fish and food for waterfowl; the long fronds were effective as breakwaters. Where large areas of eel-grass have disappeared there has been a great decrease in molluscs and crustaceans, wild fowl have moved elsewhere, and coastline erosion has often followed (1624).

The Oil Pollution Act of 1924 of the U.S. Congress forbids the discharge or dumping of oil by any means into navigable coastal waters in which the tide ebbs and flows (614). Oil may also reach inland surface waters from industrial processes such as machining operations (983) and from garages and filling stations.

Oil films may interfere with gas exchange, coat bodies of birds and fish, impart a taste to fish flesh, exert a direct toxic action on some organisms as a result of watersoluble components, and interfere with fish-food organisms and the natural food cycle (614, 1624, 3535, 3592, 3593, 3594, 3595). Oil from surface films becomes adsorbed on clay particles, settles to the bottom, and there remains a source of pollution, for it may be stirred up to float again or may leach toxic principles (614). Experiments in England (2001, 2518) have shown that films of oil less than 10⁻⁴ cm thick do not affect the rate of solution of oxygen.

The American Petroleum Institute (984) investigated the spreading of oil on water surfaces and presented the following tabulation of thicknesses and descriptions.

Gallons of Oil Per Square Mile of Surface	Approximate Film Thickness, Inches	Appearance
25	$1.5 imes10^{-6}$	Barely visible under most favorable light conditions
. 50	$3.0 imes10^{-6}$	Visible as a silvery sheen on surface of water
. 100	$6.0 imes 10^{-8}$	First trace of color may be observed
200	$12.0  imes 10^{-6}$	Bright bands of color are visible
666	$40.0 imes10^{-6}$	Colors begin to turn dull
1332	$80.0  imes 10^{-6}$	Colors are much darker

Films up to  $3.0 \times 10^{-6}$  inches do not persist for more than five hours on agitated water surfaces. A slug of oil at sea required 40 to 100 hours to thin out to  $40 \times 10^{-6}$  inches but thereafter disappeared entirely in less than 24 hours. The API reports that oil may be discharged uniformly at a rate of 10 gallons per hour per square mile without becoming visible, but a rate of 28 gallons per hour per square mile would result in a continuous iridescent film (984) (see also Hydrocarbons).

In well waters, as little as 10-6 mg/l of oil has been detected by a fluorescence test (3597).

- 2. Cross References. Animal and Vegetable Oils, Hydrocarbons, Tars, Tastes and Odors, Chapter IX.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supply. The potential deleterious effects of oily substances upon domestic water supplies may be grouped into the following categories: (a) hazards to the health of consumers, (b) the production of tastes and odors, (c) the presence of turbidity, films, or iridescence and (d) the increased difficulty of water treatment. The first two categories are discussed in detail in the following sections of the report. The third category is one involving esthetic problems that are unlikely to arise inasmuch as the taste and odor of oily wastes become objectionable at much lower concentrations of oil than those required to produce turbidity, iridescence, or films (3596).

The fourth category is an outgrowth of the second and third. Floating or emulsified oil in raw-water supplies will complicate the coagulation, flocculation, and sedimentation processes at a treatment plant. Oil-coated floc may not settle properly. If free or emulsified oil reaches sand filters or ion-exchange beds it will coat the grains, decrease the effectiveness of filtration, and interfere with backwashing. Taste- and odor-producing compounds will require the greater use of activated carbon or heavy

chlorination. Again, however, the taste-and-odor factor will control the threshold or limiting concentration of oily material acceptable in a domestic water supply (3596).

An exhaustive search of literature to determine the toxic concentrations of the components of refinery waste waters toward humans revealed a paucity of toxicological data on the ingestion of such substances by humans or by test animals (2980). From the approximate order of magnitude based on data from the fields of occupational health and industrial hygiene, it was concluded that any tolerable health concentrations for oily substances far exceed the limits of taste and odor. It appears, therefore, that hazards to human health will not arise from drinking oil-polluted waters, for they will become esthetically objectionable at concentrations far below the chronic toxicity level (2980).

The principal detriment of petroleum oils toward domestic water supplies lies in their tastes and odors. This effect has been reported as the threshold odor concentration (TOC) in mg/l and as the threshold odor number (TON), the dilution ratio at which odor is just detectable (see Tastes and Odors). Kirkor (460) reports the TOC of refined petroleum in water to be 1.0 to 2.0 mg/l, and for raw petroleum 0.1 to 0.5 mg/l. According to Halstrick (952) mineral oil imparts a taste to water at a concentration of 5.0 mg/l and an odor at 2.5 mg/l. The odor of gasoline is more easily detected than that of crude oil, but the latter is tasted more quickly. Aging causes petroleum odors to become musty, probably as a result of biochemical decomposition. Cohen et al. (2984) give the TOC of deodorized kerosene as 0.082 mg/l. Melpolder et al. (3589) report the TOC of commercial gasoline in water as 0.005 mg/l, with 0.010 mg/l giving a strong odor.

By far the most comprehensive work in relation to the odors of oily substances has been that of Ruchhoft, Middleton, Ettinger, Braus, and Rosen at the R. A. Taft Sanitary Engineering Center in Cincinnati (459, 1469, 2983, 3353, 3354, 3358, 3585, 3586, 3588, 3591). These investigators developed the carbon-filter techniques to remove minute concentrations of odor-producing substances from surface waters and liquid wastes. The materials adsorbed on the carbon filters are eluted with an organic solvent and then separated into acidic, basic, amphoteric, phenolic, neutral, and water-soluble groups. The neutral group consists primarily of the aromatic and aliphatic hydrocarbons, and closely related compounds that do not form salts with acids or bases. The acidic group comprises a mixture of organic acids including fatty acids; and the basic group is derived largely from nitrogen bases such as the pyridines.

Numerous tests of effluents from refineries and of river water and lake water known to be polluted by oily substances by Ruchhoft and his colleagues have shown that the neutral fractions are the most odoriferous, with TOC values as low as 0.003 mg/l.

Other investigators have reported the odor of oily substances in terms of the threshold odor number (TON), or the dilution ratio at which odor is just detectable. Gibbons (953) tabulated the dilutions required to reach the threshold odor for various petroleum products as follows:

Petroleum	Threshold Odor Number (Dilution Ratio)		
Product	Hot (65°C)	Cold (20°C)	
Gasoline		5,000,000	
No. 1 heating oil	4,000,000	1,500,000	
No. 2 heating oil	12,000,000	3,000,000	
No. 4 heating oil	10,000,000	2,000,000	
Bunker C fuel oil	7,600,000	2,000,000	
20 W lubricating oil	80,000	40,000	

Mueller (1739) notes that some persons can detect gasoline in water at a TON of 1,100,000, most people notice it at 500,000, and it is quite evident at 100,000. Gibbons (953) recorded a TON of 5,000,000 for gasoline while Halstrick (952) gave a TON value of 400,000 for petroleum oil. German authors (1739, 3598, 3599, 3600, 3601) report on the pollution of ground water and its effect on the odor of drinking-water supplies. TON values as high as 5,000,000 were indicated. In one of these cases (1739), the gasoline contained lead, but in only one sample of ground water was the lead concentration as great as 0.5 mg/l and in other samples it was 0.1 mg/l or less. No danger of lead poisoning was present.

Coincident with the appearance of gasoline in wells. nitrates could no longer be determined, and only traces of nitrites were found. As the gasoline odor diminished, nitrates gradually increased to their normal value. Gasoline in the soil appears to be oxidized first by atmospheric oxygen and then by means of nitrates with the aid of catalytic or biological processes. When the groundwater table is lowered, the lighter gasoline were absorbed by the soil, but they became evident again when the

water table rose.

b. Industrial Water Supplies. In steam production, the presence of oil in boiler feed water may cause foaming, priming, overheating of tubes resulting in blistering or failure, and poor transmission of heat from the metal to the water. As a result, the American Boiler Manufacturers Association in its standard guarantee on steam purity specifies that "the total quantity of oil or grease, or substance which is extractable either by sulfuric ether or by chloroform, shall not exceed 7 ppm in the boiler water when the sample being tested is acidified to 1 percent hydrochloric acid, or 7 ppm in the feed water when the sample being tested is first concentrated at low temperature and pressure to the same ppm total solids as the boiler water."

Powell (212) recommends that "No oil should be present in boiler feedwater. Serious damage has resulted from only a few parts per million of oil in feedwater fed to high-pressure boilers. When oil is present in the feedwater, it forms deposits on the boiler tube surfaces. preventing proper heat transfer, thus causing overheating and final failure of the metal.'

Cooling waters may be used once and discarded, but the trend is toward water conservation by recirculation through cooling towers. In this process, evaporation will cause impurities in the water to become more concentrated. Moreover, aeration over huge surfaces favors biological action so that cooling waters tend to become slimy, especially when organic pollutants and nutrient materials are present. Oily substances in cooling water may possibly retard corrosion of metal in some instances, but their disadvantages in cooling waters outweigh this possible advantage. Powell (212) reports that "waters

contaminated by oil and grease are highly objectionable when used as cooling water for heat exchangers, surface condensers, and similar types of equipment."

Oil in water used for hydraulic transport or buoyancy may coat the product being transported (e.g. fruit or vegetables in a cannery) or the containing vessels or flumes. Biological slimes may result from presence of

such oily substances in flowing waters.

For many processing and production operations, the major deleterious effect of oily substances is the possibility of taste and odor in the manufactured product. This is especially true for brewing, carbonated beverages, bakeries, food canning and freezing, ice manufacture, sugar production, and food-equipment washing. While the literature dealing with food and beverage processes does not specify numerical concentrations for oil, the recommended threshold or limiting values for oil, taste and odor, or organic matter are given as "none," "low," "infinitesimal," or "barely noticeable."

Oil is detrimental in water used for paper making in that it may adhere to the stock, form slick spots on the paper, or promote the growth of undesirable organisms. The Portland Cement Association (191) states that water used for making concrete should be free of acids,

alkalies, and oil.

c. Irrigation Waters. Aromatic solvents of petroleum origin have been used to kill weeds in irrigation ditches. According to the United States Bureau of Reclamation (890), a concentration of 300 mg/l in the stream for 30 minutes will kill weeds without harming crops that are subsequently irrigated, owing to volatilization and dilution. Roberts (986) claims that oil films do not prevent the growth of fresh-water plants. It has been reported (667), however, that pollution by oil from ships is a possible contributing factor to the disappearance of eel grass from European and American coastal waters.

The phytotoxic mode of action of oils is described by McKee (3596) based on the work of van Overbeak and his colleagues. Instances are also cited where crude petroleum, added directly to the soil, appeared to improve rather than interfere with crop production. Heavy applications (4-5 percent in the soil) inhibited the rate of growth of some plants, presumably by interfering with

the availability of soil moisture.

From the foregoing information it appears that the pollution of irrigation waters by oil is not likely to be-

come a serious problem.

d. Stock and Wildlife Watering. Literature dealing with the effects of oily wastes in water on livestock and wildlife is both scant and inconclusive. In 1935, Ferguson and his committee (3602) stated that some cattle, sheep, and hogs develop a liking for crude oil and suffer adverse physiological effects from ingestion of oil-polluted waters. The adverse effects may have been due to laxative properties or possibly to toxicity. Whatever the cause, the animals failed to thrive and have been reported to die as a result.

Bruns et al. (2873 describe tests with guinea pigs to determine the possible ill effects of an emulsion containing 400 and 800 mg/l of aromatic hydrocarbons (mostly xylene). The animals consumed considerably less treated water than untreated, and they almost refused to drink the 800 mg/l water until the third day when they became

very thirsty. After three days of confinement on treated water, none of the 32 animals showed ill effects. It is believed that the strong odor and disagreeable taste of water heavily polluted with hydrocarbons make it unlikely that animals will drink such water. Where an occasional heavy dose occurs, animals will postpone drinking until the water clears up or an alternate source is available.

The oral LD₅₀ of kerosene for rabbits has been given

(3603) as 28,350 mg/kg of body weight.

Floating oil may smear birds so that they cannot fly (615, 981, 3592). The wrecking of the oil tanker Frank H. Buck off San Francisco in March 1937 proved disastrous to many species of aquatic birds along the coast (987), but sea gulls escaped.

Unwin (988) describes effluent standards set up by the Ohio Department of Health for Mills Creek, including a limit of 30 mg/l for emulsified oils, because the creek is

used for grazing cattle.

e. Fish and Other Aquatic Life. Oily substances may possibly be harmful to fresh-water aquatic life in the

following manners:

1. Free oil and emulsions may act on the epithelial surfaces of fish, i.e. they adhere to the gills and interfere with respiration. Within limits, however, fish have a defensive mechanism to combat such action. They can secrete a mucous film to wash away irritants. If the concentration of oil is too heavy, oil will accumulate on the gills and cause asphyxia (311).

2. Free oil and emulsions may coat and destroy algae and other plankton, thereby removing a source of fish food. The coated organisms may agglomerate with suspended solids and settle to the bottom of the stream.

3. Settleable oily substances may coat the bottom, destroy benthal organisms, and interfere with spawning areas.

4. Soluble and emulsified material, ingested by fish, taint the flavor of the flesh.

5. Organic materials may deoxygenate the waters suffi-

ciently to kill fish.

6. Heavy coatings of free oil on the surface may interfere with the natural processes of reaeration and photosynthesis. Very light coatings would not be detrimental in this respect, however, for wave action and other turbulence would maintain adequate reaeration.

7. Water-soluble principles may exert a direct toxic action on fish or fishfood organisms. Such toxicity may be acute or chronic. Acute toxicity will produce death or debility in 96 hours or less. Chronic toxicity exerts a long-time effect, through an accumulative action or through subtle changes in the ecology. By its very nature, chronic toxicity is difficult to detect and generally even more difficult to prove. The material presented below deals primarily with acute toxicity attributable to soluble principles (3596).

Certain petroleum products appear to have no soluble poisonous substances, but when emulsified by agitation with water, such oils prove deadly to fish (463). Chipman and Galtsoff (615) report that crude oil in concentrations as weak as 0.4 ml per liter (i.e., about 0.3 mg/l) is extremely toxic to fresh-water fish. Kerosene applied as an insecticide at a rate of 25 gallons per acre had no effect on fresh-water fish (612). The lethal limit of gasoline

for rainbow trout has been reported as 100 mg/l (2977). After 15 minutes exposure at 50 mg/l, rainbow trout show irritation and after 60 minutes they are tired. The toxic threshold is about 40 mg/l (2977). Agitated solutions of automobile gasoline and jet aviation fuel were found to be lethal to fingerling salmon at concentrations of 100 and 500 mg/l respectively (2218).

Turnbull et al. (2093) tested the toxicity of commercial cutting oils toward bluegill sunfish at 20°C in tap water. They found 24-hour TL_m values of 5540 and 14,500 mg/l for No. 1 and No. 2 soluble cutting oils respectively. For a commercial dissolved and floating

kerosene, the 24-hour TLm was 2990 mg/l.

Albersmeyer and Erichsen (3404) found that carbolated oil and light oil, both dephenolated, imparted a taste to fish flesh more pronounced than that caused by naphthalene and methyl naphthalene. They concluded that the hydrocarbons were more responsible for tastes

in fish flesh than were the phenolic compounds.

Oils are toxic to mosquito larvae and also to the microorganisms on which the larvae feed (877). Crude oil, diesel oil, and Navy-grade special fuel oil in sea water are toxic to the hydrozoan *Tubulareacrocea*, to barnacles, and to the embryos of toadfish (615). Shaw and Timmons (3604) note that the concentration of emulsified aromatic hydrocarbons used to destroy weeds in irrigation ditches (300 mg/l) was sufficient to eliminate crayfish. Other fish were also killed.

The biochemical oxidation of hydrocarbons can be accelerated by the use of seeding material. With 28 mg/l of motor oil at the start of a test, 52 percent disappeared in 6 days with the use of a seed developed from a refinery cooling-tower effluent. With 70 mg/l initially present, 72 percent destruction occurred in 17 days with seed developed from oil-saturated soil. Both seeds gave approximately 50 percent reduction in 6 days (1625).

Petroleum oils are used extensively as solvents or vehicles for pesticides. While the oil may not in itself be toxic, it frequently increases the toxicity of the pesticide.

For further details, see Chapter IX.

Toward the giant kelp, Macrocystis pyrifera, North and Clendenning (2106, 2866, 2867) found that 100 ml/l of boiler fuel oil and diesel fuel oil was injurious in 12 to 48 hours and concentrations of emulsified fuel oils above 10 ml/l were deemed to be deleterious.

f. Shellfish Culture. The heavy mortality of oysters in 1932-33 in certain areas of Louisiana was believed to be due to oil-well wastes, according to McConnell (319) and Gowanloch (967). In laboratory tests at that time, sea water that had been in contact with oil caused a 90 percent mortality of oysters in three months as compared with 17 percent for unpolluted sea water. The oil itself was not in contact with the oysters but the sea water extracted toxic substances from the oil. Sedentary animals such as clams may be destroyed by direct contact with oil (615).

According to Speer (317) surface films of floating oil can kill free-swimming larvae in a few hours and heavier portions are deposited on the bottom where oysters are killed by direct contact. Oil destroys plankton, especially diatoms, diminishes aeration at surface, destroys spawning grounds, and gives offensive tastes to oysters. Galtsoff (989) reports that oil imparts a taste to oyster flesh

that makes the meat unsalable. Also, oysters in oil-polluted water show a decreased glycogen content.

g. Swimming and Other Recreational Uses. Oil slicks are visible when the concentration reaches 50 gallons of oil per square mile (984) and higher concentrations may coat bathers. Mixtures of brine and oil cause skin irritation to bathers (985) and the fire hazard to a water front is increased by oil pollution.

## OLEIC ACID AND OLEATES

(see Fatty Acids)

## OLEYLPOLYOXYETHYLENE GLYCOL ETHER

(see Chapter X)

## ORGANIC NITROGEN

(see Nitrogen)

## ORGANIC PHOSPHATES

(see Chapter IX)

## **OMAZENE**

(see Chapter IX)

#### ORTHOPHOSPHATES

(see Phosphates and Phosphoric Acids)

#### OSMOTIC PRESSURE

(see Dissolved Solids, Specific Electrical Conductance, Distilled Water)

#### **OVATRAN**

(see Chapter IX)

#### **OXALATES**

-00C-C00-

(see also Oxalic Acid)

The salts of oxalic acid are likely to occur in the same industrial wastes that contain oxalic acid. Inasmuch as many oxalates dissociate readily and inasmuch as oxalic acid is a weak acid, the net effect is an increase in pH. Consequently, the result of adding oxalates to water is just the opposite of adding oxalic acid, insofar as pH is involved.

Jones (354) tested the threshold of toxicity of sodium oxalate to *Polycelis nigra*, a flatworm, and found that at 15-18°C the threshold occurred when the concentration of oxalate ion was 970 mg/l. In Lake Erie water at 25°C, however, Anderson (352) reports that 214 mg/l of sodium oxalate immobilized *Daphnia magna* in 48 hours. Toxicity appeared to have been due to factors other than osmotic pressure.

Using turbid water at 19-23°C and mosquito-fish (Gambusia affinis) as the test animal, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values for sodium oxalate to be 1350 mg/l. This compound had very little effect on the turbidity.

### OXALIC ACID

H00C-C00H

(see also Oxalates)

This simple organic acid occurs widely in plants and vegetables, for it is one of the products of metabolism

of many molds. As a dihydrate, the crystalline solid sublimes readily into fumes that irritate the respiratory tract (364). It is highly soluble in water and in this form it is used extensively in industrial processes, such as those of the textile, leather, ceramic, paper, and rubber industries.

According to Doudoroff and Katz (361) oxalic acid cannot be toxic to fully developed fish without lowering the pH to 5.0, i.e. toxicity is not attributed to the undissociated acid. Consequently, the pH value is a good index of serious pollution by oxalic acid. Furthermore, a given dose of oxalic acid would be less likely to cause harm in a highly buffered water than in a relatively pure water.

Ellis (313) reported that 200 mg/l of oxalic acid in hard water was not lethal to goldfish after 100 hours, but 1000 mg/l in hard water killed goldfish in 30 minutes. German authorities (2977) report that 100 mg/l is lethal for fingerlings of trout in 20 to 50 minutes. For other fish the threshold of toxicity lies at about 20 mg/l.

In Lake Erie water, according to Anderson (358), the threshold concentration for immobilization of *Daphnia magna* after prolonged exposure at 25°C was 95 mg/l. Herman (2923) indicates that 43 mg/l of oxalic acid inhibits the 5-day BOD of sewage by 50 percent.

## OXYDIPROPIONITRILE

(CH₃CH₂CN)₂O

(see also Cyanides, Hydrogen Cyanide)

Henderson et al. (2958) conducted bioassays using three common species of fish in both hard and soft water saturated with oxygen at 25°C. Commercial oxydipropionitrile was used as the test compound. Apparently it does not dissociate measurably in water for little if any of the toxic principle, HCN, is formed. The following median toxic limits were reported:

	Type of		$TL_m$ in $mg/l$	
Kind of Fish	Water	24-hour	48-hour	96-hour
Fathead minnows	Hard	5700	5700	3900
Fathead minnows	Soft	4650	3850	3600
Bluegills	Soft	4300	4200	4200
Guppies	Soft	7350	7350	4450

Adult bluegills exposed up to four weeks in water containing 100 mg/l of oxydipropionitrile did not pick up any organoleptic properties that were apparent to a taste panel (2958). For rats, the oral LD₅₀ dose of this compound was reported (2978) as 2830 mg/kg.

#### OXYGEN

(see Dissolved Oxygen)

#### OXYGEN CONSUMED

1. General. Like acidity, alkalinity, and BOD, this term is applied not to a specific pollutant but to a measure of the strength or character of many substances. The full name of the test, oxygen consumed from permanganate, refers to the amount of oxygen used by the sample when digested for 30 minutes in a boiling bath with a definite strength of acid or alkaline permanganate. Although potassium permanganate oxidizes the carbon but not the nitrogen in organic matter, the test does not indicate the total amount of carbonaceous organic matter, for the carbon in nitrogenous organic matter (e.g., proteins) is not so readily oxidized as that in carbonaceous organic matter (e.g., sugars). Furthermore, the

test does not differentiate directly the carbon present in unstable organic matter from that in fairly stable organic matter (469, 3605). Thus, it measures primarily the readily oxidizable carbonaceous organic matter. Formerly popular and routine for analyses of water and sewage, it is used less frequently now, having been replaced by the more significant test for BOD. According to Phelps (330), "The test is no longer regarded as having any significant value as an index of pollution in the sanitary water analysis". It is of value, however, in estimating the strength of certain industrial wastes in conjunction with, or in lieu of, the BOD test. Although many of the references cited below are outdated, they are presented for what they are worth; but the reader should weigh them against the significance of the oxygen-consumed test.

- 2. Cross References, BOD.
- 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. As described by Taylor (36), if the oxygen absorbed from NaOCl is greater than the oxygen absorbed from permanganate, animal pollution is indicated, but if it is less, then organic pollution is probably of vegetable origin. Beger (630) considers a water to be of good quality when it contains, among other things, not more than 12 mg/l of organic matter expressed as oxygen consumed from permanganate.

b. Industrial Water Supplies. The Progress Report of the N.E.W.W.A. Committee on Water Quality Tolerances for Industrial Uses (159) suggested the following limits for the oxygen-consumed test for boiler feed waters.

Pressure in psi	Oxygen consumed, mg/l
0-150	15
150-250	10
250-400	4
400 and over	3

For ice making and refrigeration a threshold concentration of 3.0 mg/l has been recommended (229) and polluted water with a potassium-permanganate demand of more than 8.0 mg/l is reported to impart a bad odor to textiles washed in it (259). Water having an oxygenconsumed value greater than 3.0 mg/l caused trouble when used in making synthetic rubbers at a plant on the Kanawha River in West Virginia (1213). The limit recommended (184) for carbonated beverage is 1.5 mg/l. Schwalbe (552) proposed a tentative specification for the quality of water used in pulp and paper manufacturing. For higher-grade products he proposed a standard of 10 mg/l for oxygen consumed from permanganate and for lower-grade papers a permissible tolerance of 20 mg/l. In discussing water for brewing, Laufer (170) indicates that the generally accepted limit for oxygen consumed is 0.5 to 2.0 mg/l with a maximum of 5.0 mg/l.

### OZONE AND NASCENT OXYGEN

 $O_3$  and O

Although it is the most reactive form of oxygen and deteriorates rapidly into oxygen and nascent oxygen according to the reaction,

$$O_3 \rightarrow O_2 + O$$
 (nascent)

ozone is found in the atmosphere in varying amounts (about 0.05 mg/l by volume at sea level), inasmuch as

it is produced continuously in the outer layers of the atmosphere by the action of solar ultra-violet radiation on the oxygen of the air (364). It can also be produced in the laboratory or commercially by passing dry air between plate electrodes charged by an alternating current. The commercial product is used as a disinfectant for water and air, and for bleaching paper pulp, textiles, waxes, and oils. Its occurrence in wastes from these processes is extremely unlikely, however, for ozone is the strongest oxidizing agent known and consequently is converted rapidly to oxygen and oxidized products.

Owing to its powerful oxidizing action, ozone has been used as a bactericide and cysticide. Kessel et al. (1297) report that the time required to destroy cysts of Entamoeba hystolytica and bacteria was less for solutions containing 0.3 mg/l of ozone than in solutions of 0.5 to 1.0 mg/l of chlorine. According to Chang (742), ozone concentrations of 0.1 to 0.3 mg/l killed these cysts in a few minutes.

Toward fish, ozone and nascent oxygen have been shown to be extremely deleterious. Ellis (313) reports that minnows and shiners may be killed by 0.033 mg/l of nascent oxygen and fish are irritated by ozone in concentrations less than 0.01 mg/l (311, 361, 2920).

#### PALLADIUM CHLORIDE

 $PdCl_2$ 

This dark-brown crystalline salt, occurring as PdCl₂·2H₂O, is highly soluble in water. It is used in photography, toning solutions, indelible ink, and galvano-coating of precision parts (364). The lethal concentration of PdCl₂ for three mature small freshwater fish (*Orizias*) exposed for 24 hours to only 20 ml of test solution, was reported to be about 7 mg/l (1459).

## PAPER MILL WASTES

(see Kraft Pulp-Mill Wastes, Groundwood Pulp-Mill Wastes, Paper Mill White Waters, Sulfite Waste Liquors)

### PAPER MILL WHITE WATERS

The so-called "white waters" from paper mills, which may be highly colored at times, consist primarily of the water that is drained or drawn from the paper stuff on the paper machines. Such water contains fine fibers that escape the machine or occur in clean-up wastes, sizing materials, alum, clay, other weighting substances, dyes, and bactericidal or slime-controlling agents. The fine cellulose fibers may cause difficulty in a stream by blanketing the bottom and killing important fish-food organisms (684, 701). Schaut (362) reported that a 1:240 dilution of a white waste in stabilized tap water gave a white turbidity and caused minnows to stop feeding. At a 1:2400 dilution, there was no noticeable effect on minnows.

## PARADICHLOROBENZENE

(see Dichlorobenzene)

## PARA-OXON

(see Chapter IX)

## PARATHION

(see Chapter IX)

## PARIS GREEN (COPPER ACETOARSENITE)

(see Chapter IX)

### PENETRANTS

(see Chapter X)

### PENTABORANE

(see Boron)

#### PENTABROMOPHENOL

(see Halogenated Phenols, Chapter IX)

# PENTACHLOROPHENOL AND PENTACHLOROPHENATES

(see Chapter IX)

## PENTANE

 $C_5H_{12}$ 

(see also Hydrocarbons, General)

This flammable liquid, one of the saturated (paraffin) hydrocarbons, occurs in natural petroleum and as a constituent of petroleum benzin. It is soluble in water to the extent of 360 mg/l at 16°C. The concentration required to kill fish (white roach) at 20.2°C is given by Hubault (461) at more than 60 mg/l.

#### PENTENE

 $C_5H_{10}$ 

Shelford (363) found that amylene (1-pentene) which occurs in some gas-manufacturing wastes and coal tar, killed sunfish in one hour when the concentration of this colorless liquid in tap water was 655 mg/l.

## PEPTONE

Peptone is the product of the pancreatic digestion of meat, the dried powder containing about 15 percent nitrogen and 4 percent ash. It is highly soluble in water. According to Schaut (362), 17.1 mg/l of peptone in stabilized tap water produced no noticeable effect on minnows after 24 hours of exposure, but the dissolved-oxygen content of the water decreased 58 percent.

#### PERTHANE

(see Chapter IX)

#### PETROLEUM

(see Oil, Petroleum)

## PETROLEUM BENZIN

(see also Pentane, Hexane)

Known also as petroleum ether, benzin, or naphtha, petroleum benzin consists chiefly of hydrocarbons of the methane series, principally pentanes and hexanes. It is clear, nonflourescent, colorless, highly flammable liquid with a characteristic odor, used as a solvent for fats and waxes, as a detergent, in paints and varnishes, as fuel, and as an insecticide.

## pН

1. General. The symbol "pH" is used to designate the logarithm (base 10) of the reciprocal of the hydrogen-ion concentration. Thus, if  $[H^+] = 10^{-5}$  mols per

liter, then pH = 5. Inasmuch as an excessive concentration of hydrogen ions may adversely affect water for one or more beneficial uses, pH is a measure of a potential pollutant.

Not only is the hydrogen ion a potential pollutant in itself; it is also related intimately to the concentration of many other substances, particularly the weakly dissociated acids and bases. A few of the common equilibria in which hydrogen ions are involved are shown below:

## Reaction

#### Reaction

$$H_2O \rightleftharpoons H^+ + OH^ H_2S \rightleftharpoons H^+ + HS^-$$
  
 $H_2CO_3 \rightleftharpoons H^+ + HCO_3^ HS^- \rightleftharpoons H^+ + S^{--}$   
 $HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$   $HOCl \rightleftharpoons H^+ + OCl^-$   
 $H_2BO_3^- \rightleftharpoons H^+ + H_2BO_3^ H_2PO_4^- \rightleftharpoons H^+ + H_2PO_4^-$ 

The foregoing reversible reactions are but a few of the ones involving hydrogen ions in natural waters, but they illustrate that the concentration of hydrogen ions, i.e., the pH, controls the degree of dissociation of many substances; and since the undissociated compounds are frequently more toxic than the ionic forms, pH may be a highly significant factor in determining limiting or threshold concentrations (361). For an example, see Ammonia.

Conversely, the concentration of weakly dissociated acids and bases markedly affects the pH value and the ease with which it can be altered. For this reason, pH should not be confused with acidity and alkalinity. The presence of carbonates, phosphates, borates, and similar ions give water a buffering power so that the addition of an acid or base is less likely to be deleterious.

Owing to their origin in municipal water supplies, most domestic sewages are neutral or slightly alkaline, with a strong buffering action. Many industrial wastes, on the other hand, are so strongly alkaline or acid that they have a marked effect upon the pH of receiving waters. Among the acid wastes may be included tan liquors, acid dyes, coal-mine drainage, sulphite waste liquors, pickling liquors, and some brewery wastes; and among the strongly alkaline wastes are beam-house effluents, kier liquors, wool-scouring wastes, soda- and sulfate-pulp rinse waters, laundry wastes, and bottle wash waters.

Most of the state and interstate agencies that have established stream standards or effluent standards have included limits for the pH values. For details of stream standards for specific states and agencies, see Chapter III and its appendices. Where effluent standards have been promulgated, they are generally expressed in terms of the resulting pH of the stream. The standards for the discharge of industrial wastes to public water courses in Russia (460) state that the wastes shall not lower the pH below 6.5 nor increase it above 8.5.

- 2. Cross References. Acidity, Alkalinity, Ammonia, Bicarbonates, Carbonates, Chlorine, Hydrogen Sulfide, Hydroxides, Phosphates, Protozoa.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The hydrogen-ion concentration of a raw-water source for domestic water is

important in that it affects taste, corrosivity, efficiency of chlorination, treatment processes such as coagulation, and industrial applications. The United States Public Health Service Drinking Water Standard of 1962 (2036) set no limits to pH in domestic waters.

Butterfield et al. (493) have shown that the killing power of chlorine diminishes with increasing pH values and, consequently, it is advantageous to apply chlorine to a water with a pH value of 7 or less. On the other hand, Langelier (692) has demonstrated that high pH values favor corrosion control. Natural waters do not dissolve lead if their pH value is above 8.0, according to Holl (1073). Water acquires a "sour" taste at pH 3.9 or below, except in highly buffered solutions, according to Rohlich and Sarles (759). The optimum dosage of coagulating chemicals is influenced by the pH as well as by the buffering action of the water (387, 711). In a lighter vein it is interesting to note that during Prohibition days waterworks operators received many complaints from customers who preferred water with a pH below 7.0 for home brewing (164).

b. Industrial Water Supplies. Recommended threshold values of pH for various industrial process waters are given in Chapter V, from which the following table has been abstracted:

Industrial	Recommended pH Values		
Process	Minimum	Range	
Boiler feed water:			
0 to 150 psi	8.0		
150 to 250 psi			
250 to 400 psi	9.0		
400 psi and over			
Brewing	<del>-</del>	6.5 to 7.0	
Confectionary	<b></b> 7.0		
Food canning and freezing			
Laundering		6.0 to 6.8	
Oil-well flooding	7.0		
Rayon manufacturing		7.8 to 8.3	
Steel making		6.8 to 7.0	
Tannery operations		6.0 to 8.0	

In addition to the foregoing tabulations, the following observations are of interest. Collins (164) states that distilled water is not satisfactory for making hard candies because it is likely to have a pH of 6.1 to 6.5 which favors inversion of sucrose and makes the candy sticky. According to Behrman (1017), the optimum pH range for waters used in carbonated beverages is 2.7 to 3.5. Medberry (404) sights problems of foaming of carbonated beverages when the pH was above 8.0, but none when the pH was below 7.0. For higher-grade pulp and paper, Schwalbe (552) proposed that the pH of the water supply be 7.0 and for lower-grade products 6.7 to 7.3.

Low pH values increase the corrosion action of water toward concrete (see Chapter V). Antill (1298) states that caution should be observed for corrosion of concrete if the water has a pH below 7, and Tremper (1299) reports that the degree of attack is inversely proportional to the pH value in waters ranging from pH 6.0 to 7.0. Attack is negligible at pH values greater than 7.0. According to Ley (694), ground water with a pH less than 6.0 is potentially dangerous to concrete through corrosive properties. The corrosion of concrete is not a function of

pH alone but varies with the content of hardness and alkalinity constituents, with free carbon dioxide being particularly detrimental (see Carbon Dioxide). Low pH values favor the formation of carbonic acid from bicarbonates (360, 1204).

c. Irrigation. The optimum pH for irrigation water depends on the type of crops to be grown and the physical and chemical properties of the soil. In the western United States, where alkaline soils predominate, waters with low pH values are desirable. Wilcox (269) reports that waters with pH values over 9.0 are unsuitable for irrigation use. In eastern acid soils where liming is practiced, waters of moderately high pH are not detrimental for most crops. However, Stevens (1300) noted that a cranberry crop in Wisconsin improved when the fields were flooded with waters of pH 5.3 and 6.8 in contrast with the normally alkaline water used on such fields. In the other direction, the yield of corn grown in culture solution at pH 4.5 was about half of that grown at pH 6.0 (1447).

d. Fish and Other Aquatic Life. Ellis (313 reports that the pH values of most inland waters containing fish range between 6.7 and 8.6, with extremes of 6.3 and 9.0; but Cole (311) states that fish are euryionic and can live in a wide pH range, with limits as broad as 4.7 to 8.7. Of United States waters that support a good fish fauna, only 5 percent have a pH less than 6.7; 50 percent have a pH less than 7.6; and in 95 percent the pH is less than 8.3 (310).

The permissible range of pH for fish depends upon many other factors such as temperature, dissolved oxygen, prior acclimatization, and the content of various anions and cations. The pH value determines the degree of dissociation of weak acids and bases, some of which may be more toxic in the molecular than ionic form (361). For example, Jones (1046) showed that the toxicity of sodium sulfide to trout tends to increase with acidity as the pH changes from 9 to 6, i.e., as sulfide and HS- ion are converted to H₂S (see Hydrogen Sulfide). The tolerance of fish to low concentrations of dissolved oxygen varies markedly with pH (1301, 3650, 3701). The toxicity of nickel cyanide increased over 1000-fold as the pH of the solution was decreased from 8.0 to 6.5 (1632) (see also Cyanide). The toxicity of sodium sulfide to fish increased as the pH decreased; 8.0 mg/I of sodium sulfide was lethal at pH 8.2, but at pH 5.2, as little as 0.55 mg/l was lethal (1468). Stiemke and Eckenfelder (270) presented an empirical formula to relate lethality, pH, and total acidity of common acids for predicting survival of fish (see Acidity). Fish that can tolerate pH values as low as 4.8 will die at pH 5.5 if the water simultaneously contains 0.9 mg/l of iron (306, 1023).

The Aquatic Life Advisory Committee of the Ohio River Valley Water Sanitation Commission (2408) concluded that direct lethal effects of pH are not produced within a range of 5 to 9.5, but from the standpoint of productivity it is best to maintain the pH in the range of about 6.5 to 8.2.

Some of the minimum and maximum pH values, and recommended ranges in pH, as reported in the literature, are given in the following tabulation for fish.

Limiting	pH Values		-
Minimun	Maximum	Remarks	References
3.3	10.7	Trout survived without adverse effects	1467
3.6		Tench survived two weeks but carp died	1302
3.6	10.5	96-hour TL _m range for bluegill sunfish	2934
3.8	10.0	Fish eggs could be hatched, but abnormal young were produced	
4.0	10.0	of extreme pH's  The most resistant fish can tol- erate such extreme pH values	1468
4.0	10.1	indefinitely after acclimatization Limits for the most resistant	
4.0	10.4	species Limits for bluegill sunfish with	361
4.1	8.5	HCl and NaOH Range tolerated by speckled	3606
		trout in nature	1467
4.1	9.5	Range tolerated by trout	862
4.3		Carp died in 5 days	1303
4.4	8.7	Toxic limits for trout	3609
4.5	8–9	Trout eggs and larvae develop	
		normally	1636
4.6	9.5	Toxic limits for perch	3609
4.6	÷	Tench died in two days	2977
4.8		Lower limit for trout	1304
4.8		Illness and early death for carp	2977
4.8	9.2	Toxic limits for fish	1305
5.0		Toxic limit for sticklebacks	2941
5.0	9.0	Tolerable range for most fish 361,	2409, 3009
	8.7	Upper limit for good fishing water	717
5.4		Lower limit for carp and tench	$\frac{1306}{2977}$
	9.2	Upper limit for trout and perch	2911
5.5		Lower limit for general fish pro- tection	1307
5.4	11.4	Fish avoided waters beyond	1046
6.0	11.0	these limits Fish did not avoid waters in	1040
0.0	11.0	this range	1046
6.0	7.2	Optimum range for fish eggs	1468
6.5	8.4	Range tolerated by most fresh-	
		water fish	1466
For other	r aquatic orga	nisms, ranges were reported as foll	ows:
1.0		Mosquito larvae destroyed at this value	1308
2.5		Tolerated by Chlamydomonas, Fragilaria, Asterionella, Apha-	01/00
3.3	4.7	nizomenon  Mosquito larvae thrived in this range	2168 1309
4.0		Toxic for Paramecium, Volvox, Asplanchna	2977
7.5	8.4	Good range for plankton production	1021
	8.5	Algae are destroyed above this	

Wiebe (3607) investigated the effects of rapid changes of pH on fish. A majority of the species tested tolerated extensive and rapid changes in pH, e.g. from 7.2 to 9.6 and from 8.1 to 6.0.

value

When the pH falls below 5.0, specialized flora and fauna develop (3608) and some species have been observed at pH values as low as 2.9

e. Shellfish Culture. According to Loosanoff and Tommers (323), oysters live in brackish waters of which the pH is usually above 7.0. At pH values of 6.5 or lower, the rate of pumping and the time shells remained open were decreased 90 percent. With respect to high pH values, Gaarder (324) found that oyster larvae are injured

Reference

at pH 9.0 and die at pH 9.1 in a few hours. For crabs,

the upper limit of pH is 10.2 (2977).

Loosanoff and Tommers found that oysters pumped normally at pH 7.75. At pH values of 6.75-7.00 they pumped vigorously for a few hours, but then fell behind the controls. At pH 6.5 the rate of pumping was markedly reduced; and at pH 4.14 the pumping rate was off 90 percent (1448).

f. Swimming and Other Recreational Uses. A decrease in the pH of swimming pool water from 8 to 7 resulted in an increase in the number of cases of eye irritation

among swimmers in a controlled pool (1104).

#### PHAGES

(see Chapter VII—Bacteriophages)

### PHENANTHRENE

C14H10

(see also Coal-Tar Wastes)

This solid, highly insoluble in water, is found in some coal-tar manufacturing wastes. Shelford (363) reports that concentrations of 1.02 to 2.0 mg/l killed sunfish in one hour, while Gutsell (463) gives 4.0 to 5.0 mg/l as the lethal concentration for fish during one hour exposure. In Lake Huron water at 12°C, 5.0 mg/l killed rainbow trout and bluegill sunfish in 24 hours but had no effect on the sea lamprey (2976).

## PHENOL $C_6H_5OH$

1. General. This colorless, crystalline substance with a characteristic odor is commercially obtained from coal tar and is widely used as a disinfectant, for the manufacture of synthetic resins, medical, and industrial compounds, and as a reagent for chemical analyses. It is highly soluble in water (one gram per 15 ml) and in alcohol, benzene and other organic solvents (364). Phenolic wastes arise from the distillation of wood, from gas works, coke ovens, oil refineries, chemical plants, sheep dips, and from human and animal refuse (923).

Despite the fact that it is used as a bactericide in strong concentrations, weak phenol solutions are decomposed by bacterial and biological action in streams (924). Mischonsniky (925) reports that, in the presence of earth and aquatic plants, phenol is decomposed at a rate of 3.0 to 5.0 mg/l per day with an accompanying decrease in dissolved oxygen. In the absence of earth and plants, decomposition is only 2.0 mg/l per day.

In a concentration of 1.0 mg/l, phenol has been found to be biologically dissimilated at 20°C in 1 to 7 days under aerobic conditions (1538). At 4°C, complete dissimilation required 5-19 days. Under anaerobic conditions, dissimilation occurs but at a slower rate (1538).

In tests conducted by the San Bernardino County Flood Control District (926) wastes containing 24 mg/l of phenols were leached through columns of soil 50 inches long and 12 inches in diameter. The concentration of phenol in the effluent rose gradually from 0.31 mg/l to 22 mg/l with 23 gallons of flow. Then distilled water was added and the concentration of phenol in the effluent decreased gradually to 3.6 mg/l with 37 gallons. The lagooning of water containing 3.0 mg/l of phenol reduced the phenols to 0.28 mg/l in seven days and to 0.02 mg/l in 14 days. Sayre and Stringfield (927) report that

phenols from the Ohio River have not affected the wells at Parkersburg, W. Virginia, although the wells are only 150 feet from the river.

State and interstate agencies that have promulgated stream standards frequently limit phenol concentrations in the waters. For details, see Chapter III.

- 2. Cross References. Halogenated Phenols, Cresols, Nitrophenols, Pentachlorophenol, Chapter III.
  - 3. Effects Upon Beneficial Uses.

Threshold Concentration in mg/l

a. Domestic Water Supplies. The ingestion of concentrated solutions of phenol will result in severe pain, renal irritation, shock and possibly death. A total dose of 1.5 grams may be fatal (364). It is not likely, however, that harmful concentrations of phenol will be consumed in drinking water because such concentrations are much higher than taste considerations would allow. The 1962 USPHS Drinking Water Standards (2036) limit the concentration of phenolic compounds to 0.001 mg/l, because of tastes resulting from the action of chlorine on such waters. The 1958 WHO International Standards (2328) set a permissible limit of 0.001 mg/l and an excessive limit of 0.002 mg/l. The 1961 WHO European Standards (2329) have a recommended limit of 0.001 mg/l. Bean (1745) recommends that the concentration of phenolic substances in drinking water be limited to 0.0005 mg/l.

Other authorities have reported that the threshold concentrations for taste or odor are as follows:

# 

· · · · · · · · · · · · · · · · · · ·	2000
B. For Phenol in Chlorinated Water	
0.00001-0.001	3610
0.0005-0.001	3 <del>4</del> 02
0.001	459, 499, 687
0.002	871, 930, 946
0.002-0.010	931
0.005	932
0.005-0.020	460, 3611
	•

Kinney (3584) points out that the method of analysis for phenol measures not phenol alone but a whole series of organic compounds that are called "phenolics"; yet it does not measure all phenol-like compounds. Phenolics are found not only in discharges from coke plants and refineries but also in mountain streams from decaying vegetation, in the urine of rabbits and pregnant mares, and in countless other sources (3612). Strong medicinal odors may occur when phenol concentration is 0.002 mg/l, yet at other times when the phenol concentration was over 0.050 mg/l there were no tastes or odors (3584).

b. Industrial Water Supplies. Phenol is deleterious in many of the food and beverage industries (see Chapter V) and may cause obnoxious tastes and odors (179, 223). Kohman (225) reports that pears packed in syrups made from chlorinated river waters had "iodoform" tastes. On the other side of the ledger, however, Pickett (934)

reports that refineries discharge wastes containing up to 60 mg/l of phenol into Dominguez Channel in Los Angeles County without harmful effects and that a beneficial action occurs in that the phenol retards development of objectionable marine growths in the harbor. Similar discharges elsewhere might be highly objectionable

- c. Irrigation Waters. Phenol in irrigation water is not considered to be deleterious to crops. In Germany, a municipal sewage containing 40-50 mg/l of phenol from a gas plant was used for irrigation without any damaging effect on the crops (2977).
- d. Stock and Wildlife Watering. According to Heller and Pursell (941) rats that drank water containing phenol from 15 to 1000 mg/l showed no deleterious physiological effects. In concentrations up to 5,000 mg/l, phenol did not interfere with digestion, adsorption, or other metabolic functions. Above 7,000 mg/l, growth was stunted and many young died at birth. The authors conclude that appreciable concentrations of phenol are not toxic to animals.
- e. Fish and Other Aquatic Life. Phenolic compounds may affect fish in two ways: first, by a direct toxic action and second, by imparting a taste to the fish flesh. There are numerous references concerning the effects of phenolic compounds on aquatic life, especially fish. The reported lethal concentrations vary widely not only because of the common variables such as species, temperature, time of contact, dissolved oxygen and mineral quality of water but also because of synergistic and antagonistic effects of other substances in the water. Some of the tests have been run on pure phenols, but others were conducted with phenolic wastes for which the phenol equivalent is given. Many phenolic compounds are more toxic than pure phenol and consequently mixed phenolic compounds may have a lower lethal limit than phenol itself. For this reason, the Aquatic Life Advisory Committee of ORSANCO (2109) recommends that any criterion for toxicity to fish be set for phenolic compounds as a group rather than for phenol itself. Indeed, much of the toxicity of a phenolic waste may be due to non-phenolic substances such as cyanide.

The following concentrations of phenol have been reported as lethal or damaging to fish:

Concentra- tion in mg/l	Time of Exposure	Type of Water and Tem- perature.°C	Type of Fish	Reference
• • •				•
0.079	30 minutes	River	Minnows	936
0.28		River	Mixed fish	3613
0.4-0.6	8.5 hours		Fish	313
0.5 - 1.0			Trout	3405
0.71	1 hour		Sunfish	311
1-5			Tench	3405
3-5			Fish	3614
4.3	12 hours	River	Trout	3615
5.0	10 hours	Lake	Trout	2976
5.0	24 hours		Trout	359
5.0			Perch	827
5.0	24-hour TLm	18°	Salmonide embryos	3404
5-10			Fish	311
5-10			Trout	311
5-20	1 hour	Aerated	Sunfish	311
6.0			Perch	3405
6.0			Rainbow trout	2920
6.2	24 hours		Brook trout	359
7.5-12.5	60 minutes	12°	Yearling trout	3245
9		<u> </u>	Perch	365
9-10			Trout	1637
9.5	156 minutes		Brook trout	3616
10	156 minutes		Dobule	3616
îŏ	72 hours	Hard	Goldfish	313
10		, ,	Fish	247
10			Tench	311
10-15			Fish	935

Concentra-	Time of	Type of Water and Tem-		
tion in mg/l		perature.°C	Type of Fish	Reference
10-20		Non-aerated	Fish	937
11.5-20	96-hour TLm	Standard, 20°	Bluegili sunfish	2933
12	oo man xmm		Perch	1637
12	156 minutes		Perch	3616
13.5	96-hour TLm	Soft. 18°	Bluegill sunfish	2936
14.2	24 hours		Minnows	359
14.5	24-hour TLm	18°	Tench	3404
15.5	48-hour TLm		Stickleback	2985
15.5	48-hour TLm	Synthetic, 15°	Stickleback	3617
16-20			<b>Fi</b> sh	313
16.7	96-hour TLm	Тар	Fingerling catfish	2981
17			Minnows	1637
17	156 minutes		Minnows	3616
17	20 minutes		Perch	3405
18-20	6 hours	Hard, 17°	Minnows	2942
19	48-hour TLm	Aerated, 20°	Bluegill sunfish	2093
19.3	96-hour TLm	20°	Bluegill sunfish	3618
20	110 minutes	21°	Roach	910
20		·	Fish	431
20	1 hour		Sunfish	311
20		17°	Minnows	2920
20	16.2 minutes		Minnews	3405
20-25		Aerated	Fish	937
20.2	96-hour TLm	Hard, 18°	Bluegill sunfish	2936
22.2	48-hour TLm	Synthetic, 20°	Bluegill sunfish	3582
23	10 minutes		Perch	3405
24	96-hour TLm	Soft, 30°	Bluegill sunfish	2936
24-28	6 hours	Distilled, 19°	Minnows	2942
24.9	24-hour TLm	18°	Carp	3404
28.5	96-hour TLm	Hard, 30°	Bluegill sunfish	2936
28.9	48 hours	Tap	Goldfish	1474
30	150 minutes	9.5°	Roach	910
40	30.7 minutes		Eels	3405
40	48-hour TLm		Fathead minnows	3335
51	90-140 minutes	Distilled	Goldfish	313
56	96-hour TLm	Turbid, 23-26°	Mosquito-fish	2940
70- <b>7</b> 5	1 hour	Тар	Sunfish	363
100 or less	I hour		Fish	463
100		18-23°	Goldfish	2920
333	24 hours		Goldfish	359
400	15 minutes		Trout	614
1600	Brief	Tap	Trout, perch	1638
1900	Brief	River	Roach	1467

The following concentrations of phenol have been reported not to harm fish in the indicated time of exposure:

Concentration	Time of	Type of	
$in \ mg/l$	Exposure	Fish	Reference
0.002		Mixed	3613
0.079		Goldfish	936
0.10		Fish	. 938
0.5		Fish	935
1.0	100 hours	Goldfish	313
1.3	<del>_</del>	Trout	3619
2.7		Bluegills	1639
3.0	48 hours	Stickleback	2985
5.0	24 hours	Bluegills and	
		lamprey	2976
9.0	156 minutes	Brook trout	3616
10	6 hours	Carp	936
10		Fish	925
15		Fish	313, 431
17.1	24 hours	Minnows	362
20	90 minutes	Eels	
19,000	Brief	Carp	1467, 1638

On the basis of the foregoing tabulations it is evident that there is a wide spectrum of toxic levels and considerable overlap between the lethal or damaging concentrations and those that have not harmed fish in the designated times. Much of the reliable information relating to pure phenol under earefully standardized conditions indicates that the 24-, 48-, and 96-hour TL_m concentrations are in the general range of 10-20 mg/l at 20°C. The threshold concentration, however, may be considerably lower.

The Halsbands (3619) attempted to determine the "threshold of disturbance" of phenol toward trout. They maintained that lethal action toward fish and fish-food organisms should not be the criterion but rather any

disturbance that has a pathological effect on the animal. For trout, they found that the threshold of disturbance lies at 1.3 mg/l. Phenol appears to act as a nerve poisoning, causing too much blood to get to the gills and to the heart cavity of the fish (3620). Threshold responses were also noted for stickleback at 3.0 mg/l (2985) and 0.6 mg/l (3617). Kalabina (3613) found an abundant and diversified fish fauna in a river containing 0.02 mg/l of phenolic compounds, but found no fish in parts of the river where phenolic compounds were 0.28 mg/l. On the basis of the foregoing figures, 3.0, 1.3, 0.6, and 0.28 mg/l as threshold concentrations, it is apparent that somewhere in the vicinity of 1.0 mg/l represents a threshold effect for fish.

The toxicity of phenol toward fish increases as the dissolved-oxygen concentration is diminished (3321, 3322), as the temperature is raised (3405), and as the hardness is lessened (2904, 2036). The effect of combinations of different phenolic compounds is additive (610, 3405).

The second major effect of phenolic substances on fish relates to the odor imparted to flesh. Mixed phenolic substances appear to be especially troublesome in this respect (2109). Chlorophenols produce a bad taste in fish flesh even at concentrations far below lethal or toxic doses (2904). Mineral oils also give a bad taste to fish meat by way of the fish-food organisms living in oilcontaining muds (2904). The relationship between true phenols and taste in fish flesh is far from clear. In experiments carried out with fish exposed for 36 hours at concentrations below the TLm, no connection between the phenol uptake of the fish and the impairment of taste could be found. It was concluded that the phenols occurring in waste waters of phenol-working industries could not be considered as the intrinsic cause of socalled phenolic tastes in fish. On the other hand, there was in intense impairment of taste from carbolated oil and light oil, both dephenolated. It was concluded that taste was due to non-phenolic materials accompanying the phenols in waste water (3404).

Tests carried out on the sperm of carp and the eggs of this fish and the stickleback indicate that the propagation products of fish are not damaged by phenol concentrations tolerated by fish (3404).

Over a concentration range of 4 to 400 mg/l of phenol, minnows appear to have little or no power of discrimination between phenol and water; hence they will swim into the solution and become intoxicated (1535). While it is possible that a slight degree of pollution may do no harm if the effluent is highly diluted immediately to a maximum degree, the possibility does exist that if phenolic pollution mixes only slowly with the stream and forms pools where solution of comparably high concentrations may be found, fish may venture into these regions and be harmed. Solutions of phenol cause a fish to lose its sense of balance and capability of coordinated movement. The time the solutions take to produce this effect is much shorter than the survival time (1535).

Phenols appear to be less toxic toward fish-food organism and other lower aquatic life than towards fish. The following concentrations of phenol have been reported to be damaging or deleterious toward lower organisms:

Concentration	n		
$in \ mg/l$	Organism	Effect	Reference
1	Platymonas	Limits photosynthesis	3621
3	Mytilias edulis	Threshold effect	3617
5	Daphnia (young)	Threshold effect	2955
8-10	Daphnia magna	Killed	313
14	Daphnia (adult)	Threshold effect	2955
15	Tubeworm	Threshold effect	3617
15	Isopod	Threshold effect	3617
16	Daphnia	Threshold effect	2158
25	Gammaridae	Lethal	935
30	Microregma	Threshold effect	3343
40	Scenedesmus	Threshold effect	2158
40-50	Culex larvae	Threshold effect	3404
50	Isopod	Threshold effect	2985
<b>50-60</b>	Daphnia	Threshold effect	3404
94	$Daphnia\ magna$	Immobilization	358
94-100	Snail	Toxic action	2936
100 - 120	Pionocypris	Threshold effect	3404
108	Diaptomus		
	oregonensis	Threshold effect	2955
122	Cyclops vernalis	Threshold effect	2955
150 - 180	Cyclops and		
	Sayomia larvae	Threshold effect	3404
200	Tubifex	Toxic action	2889
200	Crustacea	Toxic effect	2904
200	Molluses	Toxic effect	2904
251 - 261	Navicula	Toxic effect	2936
800-1000	Culex pupae	Threshold effect	3404
1000	Protozoa	Toxic action	2904
1000	Rotifers	Toxic action	2904
1600	Bacteria	Toxic action	2923

At a concentration of 4.3 mg/l, phenol was not damaging to Gammerus pulex, Tubifex, or Chironomid larvae in 12 hours (3615).

Toward algae, phenol is less toxic than cresol, but more so than catechol. The toxic effect of phenol toward algae is essentially attributable to its undissociated molecule and to the tendency to form compounds with the albumen of the protoplasm (940).

Bringmann and Kuhn (2158, 3343) tested the effect of several phenolic compounds toward four species of lower aquatic life in River Havel water. The concentrations showing threshold effects are shown below:

_	Thre	shold Concer	itration in mg	/l for
Phenolic Compound (	Daphnia a crustacean)	Scenedesmus	Microreoma	
	(23°C)	(24°C)		(27°C)
Phenol	16	40	30	>1000
p-Aminophenol	0.6	6	2	8-10
p-Butylphenol	8	10	10	>100
o-Cresol	16	40	50	600
m-Cresol	28	40	20	600
p-Cresol	12	6	10	>1000
o-Nitrophenol	60	36	40	>1000
m-Nitrophenol	24	28	20	300
p-Nitrophenol	14	72	20	100
2, 4-Dinitropher	oI 6	40		>100
Dinitro-o-cresol	8	36	30	100
o-Xylenol	16	40	10	500
m-Xylenol	24	40	70	>100
p-Xylenol	10	40	50	>100
Resorcinol	0.8	60	40	>1000
Hydroquinone	0.6	4	2	50
Pyrocatechol	4	6	6	90
Pyrogallo	18	8	50	30

As this table indicates, many of the phenolic compounds are more toxic than pure phenol toward these lower organisms.

Clendenning and North (2106, 2866, 2870) tested the effect of phenol on the giant kelp, *Macrocystis pyrifera*. They found that 10 mg/l caused a 50-percent inactiva-

tion of photosynthesis in bottom kelp fronds during a 4-day exposure, but 1.0 mg/l had no apparent effect.

The Mersey River Board in England (2950) has recommended that sewage and industrial wastes discharged to rivers should not contain more than 1.0 mg/l of phenolic compounds.

4. Summary. On the basis of the foregoing information, it appears that the following concentrations of phenol will not interfere with the designated beneficial

a. Domestic water supply	0.001  mg/l
h Irrigation	$50.0 \mathrm{mg/I}$
c. Stock watering	1000.0  mg/l
d. Fish and aquatic life	$0.2~\mathrm{mg/l}$

#### PHENYL ETHER

 $C_6H_5OC_6H_5$ 

Used in perfuming soaps and for organic synthesis, this liquid is only slightly soluble in water (364, 911). According to Middleton et al. (2983, 3356) it is detectable in water by odor or taste at a concentration as low as 0.013 mg/l.

## PHENYLHYDRAZINE

C₆H₅NHNH₂

(see also Hydrazine)

This combination of benezene and hydrazine is only sparingly soluble in water. It is used in the manufacture of dyes and as a reagent for sugars, aldehydes, and ketones (364). The oral lethal dose for rats is reported as 550 mg/kg of body weight (364). In a concentration of 108 mg/l, phenylhydrazine retards fermentation and at 1080 mg/l decomposition processes are almost completely stopped (2977).

## PHENYL MERCAPTAN

(see Mercaptans, General)

## PHENYLMERCURIC ACETATE

## PHENYLMERCURIC LACTATE

(see Mercuro-Organic Compounds)

## PHOSPHATES

1. General. In addition to the phosphates formed from ortho-, meta-, and pyro-phosphoric acids, anhydrous salts may be produced in which the hydrogen of the acid is replaced only partially by univalent or bivalent metals. Regardless of the condition of the anhydrous salt, the water solution of this salt will contain primarily H₂PO₄- or HPO₄-, depending on the pH of the solution (see Phosphoric acid). The sodium, potassium, and ammonium phosphates are soluble, but of the calcium salts only monocalcium phosphate is soluble. Most of the numerous magnesium phosphates are only slightly soluble (911).

Phosphates may occur in surface or ground waters as a result of leaching from minerals or ores in natural processes of degradation or from agricultural drainage, as one of the stabilized products of decomposition of organic matter, as a result of industrial wastes, as a constituent of cooling waters that have underground phosphate treatment and as a major element of municipal sewage as a result of utilization of syndets. In surface

waters, however, phosphates are seldom found in significant concentrations because they are utilized by plants and converted into cell structures by photosynthetic action. Higher concentrations are likely to occur in ground waters that receive leachings from excessive application of fertilizer, from cesspools, or from the recharge of cooling waters.

2. Cross References. Phosphorus, Phosphoric Acid, Sodium and Potassium Salts, Mercuro-Organic Compounds, Chapter VIII—Radioactivity, Chapter IX—Pesticides, Chapter X—Surface Active Agents.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Polyphosphates have been used in municipal water works and especially in boiler-feed-water treatment to prevent scale formation and to inhibit corrosion. There are numerous references dealing with such treatment, the preferred compounds, the optimum doses, and the results; but a review of such treatment is beyond the scope of this report. The subject is relevant to this survey, however, in that such treated waters may be discharged to streams or underground basins. In the concentrations encountered in water treatment, these polyphosphates do not appear to have any physiological significance. They do tend, however, to encourage aftergrowths of organisms in treated water by serving as a nutrient (152, 1311).

According to Konrich and Haase (1312), excessive phosphate is undesirable in water used for preparing food, as it has a buffering action on the acids of the

stomach

Jones (1313) discusses the physiological effects of hexametaphosphates and points out that in the acid condition of the stomach, they are rapidly changed to H₃PO₄ (see Phosphoric acid). In sufficient concentration, they can cause vomiting and diarrhea. Safe doses for oral ingestion were given as follows:

Safe Dose, in Grams, f	
Rabbit	Man
15 3 4	450 90 120
	Rabbit 15

For rats, amounts up to one-tenth of the total diet, or 200 mg/kg had no ill effects (1314). Manz (3626) reported an incident where sodium polyphosphates added to culinary water in a concentration of 450 mg/l produced diarrhea but no permanent illness. He considered that 50 mg/l should not be exceeded.

In raw-water sources, polyphosphates are detrimental in that they interfere with coagulation, flocculation, and the lime-soda treatment of water (204). Sodium tripolyphosphate and tetrasodium pyrophosphate are the principal builder compounds of synthetic detergents. As such they are appearing increasingly in polluted water and in raw water sources for domestic supply. Several papers (2050, 3622, 3623, 3624, 3625) have reported that phosphate concentrations of 0.5 to 1.5 mg/l interfere markedly with coagulation. Cohen et al. (2049), report that concentrations of sodium tripolyphosphate as low as 0.025 mg/l have an adverse effect on synthetic turbid water being coagulated with 10 mg/l of ferric sulfate. A concentration of 0.4 mg/l virtually prevented any removal of turbidity.

Campbell et al. (2059) reported the taste threshold of trisodium phosphate in water to be 225 mg/l, while Lockhart et al. (3241) found a taste threshold in distilled

water at 180 mg/l.

b. Industrial Water Supplies. Owing to their weekly dissociated acid reaction and their inhibitory effects upon scale formation, phosphates are seldom frowned upon in industrial-process or cooling waters. Where they encourage biological aftergrowths, however, they are detrimental (1311). In brewing water, according to LeClerc (166), primary phosphates are converted into secondary phosphates, making the wort more alkaline and deleteriously affecting the aroma and the resistance of the beer to bacterial actions.

c. Irrigation. Phosphates are one of the minor constituents of irrigation waters and are of little importance in irrigation practice (268). Where they do occur, they are likely to be beneficial in increasing the fertility of the soil moisture (905, 1291, 1315). Blueberry plants grown in nutrient water of low phosphate content (1 to 5 mg/l of P) showed signs of phosphorus deficiency and were only three-fourths as large as plants grown with more P. On the other hand, plants that received 60 mg/l of phosphorus showed signs of incipient iron chlorosis. A high P content in the nutrient solution appears to lower the available inorganic iron and thereby produces chlorosis in the blueberry plant (3627).

d. Fish and Other Aquatic Life. The discharge of excessive amounts of phosphates to streams or lakes may result in an overabundant growth of algae with concomitant odors and detriment to fish (373, 374, 1910) (see Phosphorus). In themselves, however, phosphates seldom exhibit toxic effects upon fish and other aquatic life (1316, 1317, 1318) and may be beneficial to fish culture

by increasing algae and zooplankton (367).

A mixture of sodium tripolyphosphate and sodium pyrophosphate was not toxic to fingerling rainbow trout during a 24-hour exposure to a concentration of 545 mg/l expressed as phosphate, but a concentration of 1090 mg/l produced death to all fish. Exotic phosphate compounds may be considerably more toxic, owing undoubtedly to the cation employed. For example, Surber (898, 3628) found that tributylphosphate was toxic to bluegill sunfish at concentrations exceeding 15 mg/l. Also, a substituted fluorophosphate was toxic to carp at 20 to 40 mg/ kg in fish bait (2529). Diethyl phosphate is toxic toward Scenedesmus at concentrations exceeding 250 mg/l, to the protozoan Microregma at 100 mg/l in 24 hours, and to Daphnia at 25 mg/l in 48 hours (2977). Dimethyl phosphate, on the other hand, is more toxic to Scenedesmus (toxic at 12.5 mg/l in 4 days) and less so to Microregma (withstanding 500 mg/l for 24 hours) and Daphnia (withstanding 125 mg/l for 48 hours) (2977).

Organic phosphates are used extensively in pesticides, and as such exhibit selective toxicity to many forms of aquatic life. For details, see Chapter IX—Pesticides.

According to Eldridge (2826), phosphate is the major factor controlling the growth of Sphaerotilus, but extremely small amounts (0.01 mg/l) of phosphate are required to implement the growth of Sphaerotilus. Since the Columbia Basin Irrigation Project was initiated, the average phosphates in the Columbia River have doubled, owing perhaps to the use of fertilizers.

#### PHOSPHINE

 $PH_3$ 

(see also Phosphorus)

This colorless gas with a garlic-like odor is analogous chemically to ammonia, but unlike ammonia it does not form a base with water. It is less soluble, less basic, and more toxic than ammonia (1224). At 17°C it is soluble to the extent of 260 cc per liter, or about 397 mg/l (911). As a gas, it is extremely toxic to man, with the maximum allowable concentration in the atmosphere being given as 0.05 mg/l (364).

Doudoroff and Katz (361) cite a reference to the effect that a concentration of 3.6 mg/l of phosphine in hard water was lethal to rainbow trout.

#### PHOSPHORIC ACIDS

HPO₃, H₄P₂O₇, H₃PO₄

(see also Phosphates, Phosphorus, Phosphorus Salts, Chapter VIII, Chapter IX—Pesticides, Chapter X—Surface Active Agents)

With a valence of +5, phosphorus forms three types of phosphoric acids, viz HPO₃, metaphosphoric acid;  $H_4P_2O_7$ , pyrophosphoric acid; and  $H_3PO_4$ , orthophosphoric acid. In water solution, the meta and pyro forms tend to change to the more stable ortho condition. Orthophosphoric acid, hereinafter referred to as phosphoric acid, is of interest in this survey in that in water it dissociates in three steps, to  $H_2PO_4$ ,  $HPO_4$ , and  $PO_4$  with corresponding release of hydrogen ions. At  $18^{\circ}$ C, the constants for these dissociations are  $1.1 \times 10^{-2}$ ,  $7.5 \times 10^{-8}$ , and  $4.8 \times 10^{-13}$ , respectively (911). The degree of dissociation, therefore, is a function of pH and the proportion of phosphate ions in each of the four conditions is computed to be as follows:

Approximate Percentage of Phosphate Ions

pH	21 pp/03	at 18°C in Form of			
Value	$\overline{H_3PO_4}$	$H_2PO_4^-$	HPO.	PO.	
1	90.0	9.9			
2	47.6	52.4			
3	8.3	91.7			
4	0.89	99.1	0.01		
5	0.08	99.2	0.72		
6		93.0	7.0		
7		57.2	42.8		
8		11.8	88.2		
9		1.3	98.64	0.04	
10		0.12	99.40	0.48	
11			95.42	4.58	
12			67.6	32.4	
13		<del></del>	17.1	83.9	

Between pH 2 and 7, therefore, most of the phosphate ions in water will exist as  $H_2PO_4^-$  ions, and between pH 7 and 12, most will be in the form of  $HPO_4^-$  ions. This concept of dissociation is important for an understanding of what occurs when soluble phosphates are added to water. Also it illustrates the effect of phosphates in adding to the buffering power of water.

Phosphoric acid, per se, is used as an acidulant in beverages, in dental cements, in process engraving, and in several other industrial applications (364), but its occurrence in the partially dissociated states in polluted waters is more likely to result from the use of soluble

phosphates in industry, in cooling waters, and in synthetic detergents (see Phosphates).

Doudoroff and Katz (361) report that phosphoric acid can be directly lethal to fully developed fish in most natural waters only when the pH is reduced to 5.0 or lower. For stickleback, the lethal limit of phosphoric acid has been given as 0.01 mg/l of hydrogen ion, i.e., at pH 5 (353). In distilled water, to which phosphoric acid had been added, Gasterosteus aculeatus (a stickleback) survived eight hours when the pH was reduced to 4.0, but only 15 to 57 minutes when the pH was 2.2 to 3.4 (353).

Using highly turbid water and the mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m concentrations at 22-24°C to be 138 mg/l.

#### **PHOSPHORUS**

(see also Phosphates, Phosphoric Acid, Phosphine, Chapter VIII—Radioactivity, Chapter IX—Pesticides, and Chapter X—Surface Active Agents).

This active element does not occur free in nature, but is found in the form of phosphates in several minerals and it is a constituent of fertile soils, plants, and the protoplasm, nervous tissue and bones of animal life. It is an essential nutrient for plant and animal growth, and like nitrogen it passes through cycles of decomposition and photosynthesis (1319). It combines directly with oxygen, sulfur, hydrogen, the halides, and many metals (1224). For references dealing with the combined forms of phosphorus, see the specific cross reference. The literature cited below is that in which phosphorus has been mentioned without reference to its particular combined form or with the understanding that it pertains to total phosphorus in all forms.

Newcombe (781) discusses the loss of phosphorus as a result of silt pollution, pointing out that the Mississippi River annually removes about 62,000 tons of soluble phosphorus plus  $7,500 \times 10^6$  cubic feet of suspended matter containing 0.15 percent phosphorus in the combined form. Obukhov (1320) states that more than 0.2 mg/l of phosphorus in ground or surface waters indicates that some phosphorus of sewage origin is present.

Extensive studies have been made of the effects of nitrogen and phosphorus in three Wisconsin lakes upon the nuisances from odors caused by algal "blooms" (375, 377, 1295). According to Sawyer (374), excessive growths of algae developed in these lakes when the average concentration of inorganic phosphorus was over 0.01 mg/l. Gardiner (1321) points out that in lakes and tarns where food supplies are scanty, the addition of nitrogen and phosphorus fertilizers has increased the amount of food available to trout and hastened the rate of growth of trout. The total fish productivity of Minnesota lakes was shown to rise linearly from 100 to 400 lbs per acre as the phosphorus was increased from 0.2 to 1.4 mg/l (3629). It appears, also, that the rate of decomposition of organic matter in fresh water depends on the concentration of phosphorus in the water  $(\bar{4}32)$ .

Nitrogen and phosphorus concentrations of water appear to be most important factors regulating the biological productivity of a group of 17 Wisconsin lakes. Nitro-

gen-phosphorus ratios of 30:1, and of 15-18:1 have been reported as optimal for the growth of algal blooms. Sawyer (1450) and Curry and Wilson (3630) suggest a concentration of 0.01 mg/l of inorganic phosphorus as a maximum value permissible without the danger of supporting undesirable growths. It is pointed out that detergents are an increasingly important source of phosphorus pollution

Total phosphorus determinations were made in regions where a heavy Gymnodinium "red tide" occurred off the Florida coast in November, 1952. It was found that although the phosphorus content was high in areas of definite bloom, nevertheless certain other areas minus bloom had much higher phosphorus values, as much as 10 times normal (1640). On the other hand, Ketchum (2727) reported that the total phosphorus in "red-tide" waters was 10 to 20 times that of adjacent unaffected waters.

Isom (3631) studied the toxicity of elemental phosphorus to the bluegill sunfish at 26°C, using yellow phosphorus, in distilled water adjusted to pH 7. When colloidal phosphorus was removed by filtration through a membrane filter, all fish lived for more than 6 days, but when the colloidal material was added, the fish died within 24 hours. He concluded that the TL_m of colloidal P₄ is not greater than 0.105 mg/l at 48 hours nor less than 0.025 mg/l at 163 hours.

Studies of radioactivity have revealed that phosphorus-32 is often the most abundantly concentrated radioisotope in aquatic environments. On the Columbia River below Hanford, for example, the concentration of P-32 in the caddis-fly larvae of the genus Hydropsyche was 370,000 times that of the water and in shiners the concentration factor was 165,000 (2535). Waterfowl that have fed from the Columbia River are reported (3702) to have concentrated phosphorus-32 by a factor of 75,000. The freshwater alga Spirogyra was found to concentrate P-32 by a factor of 850,000 (3273). For further details about concentration factors, see Chapter VIII—Radioactivity.

#### PHOSDRIN

(see Chapter IX)

#### **PHYGON**

(see Chapter IX, Dichloronaphthoquinone)

#### PHYTOSTEROL

Phytosterols are complex alicylic alcohols that occur in plants, in contrast to other alcohols, the cholesterols, which occur in animals. Phytosterol is present in some wastes from Kraft process pulping mills. The minimum lethal concentration to kill shiners in 120 hours at 18°C has been reported to be 3.0 mg/l (190, 344, 3632).

#### PICOLINE

C5NH4CH3

(see also Pyridine)

Found in coal tar, bone oil, the urine of horses, and some industrial wastes, the alpha, beta, and gamma isomers of methyl pyridine are all freely soluble in water. A colorless liquid with a strong unpleasant odor, alphapicoline (2-methylpyridine) is used as a solvent and as

an intermediate in the dye industry. Beta-picoline (3-methylpyridine) has the same uses and also is employed in the manufacture of insecticides, waterproofing agents, and nicotinic acid. Gamma-picoline (4-methyl-pyridine) is used similarly (364). The oral LD₅₀ for rats has been given (2978) as 1.29 mg/kg of body weight. The minimum concentration of picolines in water that can be detected by taste or odor is reported (2983) to be 0.5 to 1.0 mg/l.

In Lake Huron water at 12-13°C, a concentration of 5.0 mg/l of alpha-picoline had no effect on trout, bluegill sunfish or sea lamprey during a 24-hour exposure (2976). Picolines are subject to biochemical degradation in surface waters, especially when the proper seed organisms

are present (1641, 3633).

## PICRIC ACID AND PICRATES

(see Trinitrophenol)

### **PICROTOXIN**

C₃₀H₃₄O₁₃

This substance is the active constituent of fish berries that are used by East Indians to stupefy fish. It is also the bitter principle isolated from cockle. Intensely bitter, it is used as a respiratory stimulant for humans, in doses of 1.0 to 3.0 mg. Heavier doses may cause nausea, paralysis, and death.

According to Schaut (362), in stabilized tap water 4.0 mg/l killed 25 per cent of minnows exposed for 24 hours

and 7.0 mg/l gave a 50-percent mortality.

## PLATINIC CHLORIDE

(see Chloroplatinic Acid)

## POLYETHYLENE COMPOUNDS, POLYOXY-ETHYLENE COMPOUNDS, AND RELATED SUBSTANCES

(see Chapter X)

#### **POTASSIUM**

K

1. General. One of the more common elements, potassium constitutes 2.4 percent of the crust of the earth and occurs in many minerals (364). It is one of the most active metals and reacts vigorously with oxygen and water. For that reason it is not found free in nature but only in the ionized or molecular form. Potassium resembles sodium in many of its properties, and potassium salts can be substituted for sodium salts in many industrial applications. The sodium salts, however, are generally less expensive and hence more frequently used. For fertilizers, some varieties of glass, and for a few other purposes, however, potassium salts are indispensable (1224). Owing to the fact that the common salts of potassium, even the carbonate and hydroxide, are extremely soluble, they are not readily separated from water by natural processes other than evaporation.

The references described below are those that deal with the general subject of potassium or refer to potassium ions without mentioning the salt. For other references dealing with specific salts, see the appropriate heading

hereinafter.

2. Cross References. Potassium Salts, Sodium and Sodium Salts, Dissolved Solids, Chapter V, Chapter VII (Protozoa).

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Potassium is an essential nutritional element, but in excessive quantities it acts as a cathartic. A dose of 1 to 2 grams of potassium is cathartic, and 1000 to 2000 mg/l is regarded as the extreme limit of potassium permissible in drinking water (621). According to Lockhart et al. (3241), the taste threshold for potassium from KCl was 340 mg/l and from potassium acetate it was 680 mg/l.

b. Industrial Water Supplies. Foaming may be caused in boilers by more than 50 mg/l of potassium plus sodium in the water (1214). As shown in Chapter V—Industrial Water Supply, potassium ion or potassium salts are not listed among the substances for which limiting or threshold concentrations are given.

c. Irrigation. Potassium in low concentrations is essential for plant nutrition (3634), but for good plant development it must be maintained in proper balance with other mineral requirements, such as phosphorus (269, 1322). In irrigation water, potassium and sodium act alike upon the soil, although potassium is considered less harmful than sodium (268, 348, 3634) (see also Chapter V—Agricultural Water Supply). Potassium in saline irrigation waters appears to prevent the intake of sodium chloride in excess amounts by barley seedlings (1323).

Results of the most recent studies of soil samples at the United States Salinity Laboratory indicate that exchangeable potassium has only a slight or no effect on the physical properties of soil. There is also some evidence that high concentrations of potassium in nutrient or soil solutions may be toxic to some plants; however no

data are given (1642).

d. Stock and Wildlife Watering. Potassium is essential for animal nutrition (295, 995, 1049). The effects of excesses are not clearly understood (284) (see also Dis-

solved Solids)

e. Fish and Other Aquatic Life. The toxicity of potassium to fish is reduced by calcium, and, to a lesser degree, by sodium. Potassium is more toxic to fish and shellfish than calcium, magnesium, or sodium (306). The toxic threshold concentration of potassium for the flatworm *Polycelis nigra* has been reported to be 350 mg/l, as either potassium nitrate or chloride (608). For stickleback, the lethal concentration limit of potassium has been reported to be 50 mg/l (353, 2941).

Several investigators found, independently, that potassium could be toxic to fish in soft or distilled waters at concentrations of 50-200 mg/l when potassium chloride and nitrate were tested. It has also been reported that the threshold concentration of potassium for fish in different kinds of water is about 400 mg/l when potassium chloride, nitrate, or sulfate is used. Young eels could tolerate for more than two days 3900 mg/l of potassium in potassium chloride solution, but survived for only 15-27 hours 1950 mg/l of potassium when the nitrate or sulfate was used (1459).

It has been observed that potassium stimulates plankton growth (1295). The content of potassium in lakes in Germany, Austria, and Scandinavian countries is reported to vary from 0.4 to 1.5 mg/l in oligotrophic and mesotrophic lakes; it runs as high as 5-6 mg/l in very eutrophic lakes (1643, 3635).

For lower organisms, the toxicity level has been reported (2977) as follows: for Gammaridae, 200 mg/l of K; for Chironomidae, 700 mg/l; and for Trichoptera larvae, 1000 mg/l of potassium.

#### POTASSIUM ALUM

(see Aluminum Potassium Sulfate)

#### POTASSIUM BICARBONATE

KHCO₃

(see also Alkalinity, Bicarbonates)

This highly soluble salt is used in baking powders and effervescent antacid salts (364). A concentration of 2000 mg/l of potassium bicarbonate has killed minnows and goldfish (313). It has also been reported (2980) that 50,000 mg/l in the drinking water of sheep daily for 62 days caused a moderate adverse effect on appetite and growth.

#### POTASSIUM BIFLUORIDE

KHF₂

This highly soluble salt is used as a flux for silver solders, for frosting glass, and for treating coal to prevent slag formation (364). Simonin (3271) reports that a concentration of 100 mg/l is lethal to tench.

#### POTASSIUM CARBONATE

 $K_2CO_3$ 

(see also Carbonates, Alkalinity)

Many industrial processes, such as tanning, soap manufacture, utilize this soluble salt. Potassium carbonate is a valuable plant fertilizer (905), but in excess concentrations is highly toxic to plants (264, 268, 635).

#### POTASSIUM CHLORATE

 $KClO_3$ 

This highly soluble salt is used in matches, fireworks, and explosives as an oxygen donor. It is also used in printing and dyeing textiles (364). According to a German reference (2977), 2500 to 3000 mg/l is the threshold of toxicity for perch and bleak in tap water; and 1250 mg/l is the threshold value for pike in distilled water. A concentration of 1000 mg/l kills algae and fungi in 24 hours (2977).

## POTASSIUM CHLORIDE

KCl

- 1. General. Occurring in water as a natural ionized substance or as a component of brines from oil wells and other industrial wastes, potassium chloride is highly soluble.
- 2. Cross References. Chlorides, Hardness, Potassium, Tastes, Dissolved Solids, Distilled Water.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The taste threshold concentration of potassium chloride in water is reported to be 350 to 600 mg/l (621) and 650 mg/l (3241). Adverse effects on the nervous system and kidneys have been reported (2980) at dosages of 80-100 mg of K per kg of body weight.

b. Stock and Wildlife Watering. Most of the information available concerning the effects of potassium chloride in stock water deals with effects of mixtures of salts (287) (see Dissolved Solids, Chlorides). No adverse effects on sheep were observed when 116 grams of KCl per head per day were administered in the drinking water

(1644). Chicks fed water containing 2500 mg/l of KCl for 10 days had a 22 persont martely (2020)

for 10 days had a 33-percent mortality (2980).

c. Fish and Other Aquatic Life. Potassium chloride appears to be the most toxic to fish of the chlorides of sodium, calcium, magnesium and potassium. While calcium and sodium chlorides tend to annul the effect of potassium chloride, potassium chloride has no antagonistic effect upon the toxicity of the others (307).

The threshold concentration of potassium chloride for immobilization of *Daphnia magna* is reported to be 373 to 432 mg/l (358, 598). Concentrations up to 1250 or 1860 mg/l in various types of water have killed *Daphnia* and other related crustacean organisms within a few hours (598). In Lake Erie water at 20-25°C the following threshold concentrations were observed for aquatic invertebrates (2955):

Organism	Threshold Concentration, mg/l for Immobilization
Daphnia magna, young	430
Leptodora kindtii	127
Cyclops vernalis	640
Mesocyclops leuckarti	566
Diaptomus oregonensis	134

The following concentrations of potassium chloride have been reported to have killed fish:

Concentra- tion in mg/l	$egin{array}{c} Type\ of\ Water \end{array}$	Time of Exposure	Type of Fish	Reference
74.6 373 751 920 1360 2010 2300 5500	Distilled Distilled Lake Erie Turbid Well Synthetic	4.5-15 hours 12-29 hours 96-hour TLm 3 days 96-hour TLm 24 hours 24-hour TLm	Goldfish Minnows Pickerel Mosquito-fish Some perch Bluegills Small freshwater fish Bluegills	313 313 353, 2955 2940 644 2936, 3381 1459
10368 12060	Lake Erie	24-hour TLm	Whitefish fry Pickerel	353, 295 <b>5</b> 353

Some perch, on the other hand, have survived exposure for three days at a concentration of 1360 mg/l in well water (644). The highest concentration tolerated by young eels for 50 hours was 7500 mg/l (1459). At a concentration of 5800 mg/l, KCl stimulated 50 percent of the water beetles (*Laccophilus maculosis*) to greater movement (2956). For the snail *Physa heterostropha* the 96-hour TL_m has been reported (2936) as 940 mg/l.

## POTASSIUM CHROMATE

(see Chromium)

#### POTASSIUM CUPRIC CYANIDE

K₃Cu(CN)₆

Using water from the River Havel, from which the test organisms had been recovered, Bringmann and Kuhn (2158) determined the median concentration of potassium cupric cyanide causing a threshold effect on the following organisms:

Organism	$Temperature \ ^{\circ}C$	Time of Exposure	Concentration in mg/l as Cu(CN).
Daphnia	23	2 days	0.4
Scenedesmus	<b>24</b>	4 days	1.2
Escherichia coli	27	1-2 days	12.0

#### POTASSIUM CYANATE

KOCN

(see also Cyanides, Hydrogen Cyanide)

Cyanates are formed when cyanides in waste waters are treated by alkaline chlorination. According to Resnick et al. (2974), cyanates are stable in aerobic water at pH 7 and 20 for at least 10 days. Eventially, cyanates

undergo hydrolysis to yield ammonium carbonate. In anaerobic solutions, cyanates are reduced not to cyanide but to a mixture of ammonia and formic acid.

Minnows exposed for 24 hours to potassium cyanate in stabilized tap water showed no effects at a concentration of 17.1 mg/l according to Schaut (362) or 264 mg/l according to Dobson (1115). The toxic threshold to fish is 125 to 250 mg/l as reported in references quoted by Eldridge (1114).

Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158, 3343) found concentrations producing median threshold effects to be as follows:

Organism	Temperature °C	Exposure Time	Concentration as CNO, mg/l
Scenedesmus	24	4 days	520
Daphnia	23	2 days	23
Escherichia co	li 27	1-2 days	10
Microregma		2 days	21

#### POTASSIUM CYANIDE

KCN

(see also Cyanides, Hydrogen Cyanides, and other cyanide salts)

This highly soluble salt is used in a similar fashion to, but is largely replaced by, sodium cyanide (364). Upon solution in water, the cyanide ions unite with hydrogen ions to form weakly dissociated hydrogen cyanide, thereby tending to raise the pH of the solution. For further explanation of the toxic mechanism of cyanides, see Hydrogen Cyanide.

Herbert et al. (1580, 1645, 3636) ran tests on yearling trout with KCN at 17.5°C with dissolved oxygen near saturation. The pH of the water varied from 7.4 to 8.0. In this range, about 95 percent of the HCN produced by hydrolysis of the added KCN will be undissociated (see HCN).

The mean survival times of the rainbow trout to varying concentrations of cyanide were as follows:

Concentration of Mean Survival Concentration of Mean Survival Cyanide in mg/l Time, in minutes Cyanide in mg/l Time, in minutes

weed on negle	T suce, me members	Cyaniae in mg/i	1 ime, in minute
2.00	2.7	0.14	90
0.30	8.8	0.10	2520
0.25	12	0.09	1620
0.20	12	0.08	3600
0.18	25	0.07	4400
0.16	72		

Toxic concentrations of KCN toward fish have been reported as follows:

of KCN in mg/l	Time of Exposure	Type of Fish	Remarks	Reference
0.009 0.09 0.1 0.1-0.3 0.12 0.14 6.175 0.22 0.25-0.35 0.25-1.0	48 hours 3-4 days 96 hours 1 hour 73 hours 24 hours 6 hours 10-120 min.	Brook trout Brook trout Marine fish Goldfish Bluegill sunfish Trout Rainbow trout Blacknose dace Minnows Fish	Reduced ability to swim TL.m. Irritating Lethal in hard water TL.m., with low DO Helpless at 5°C Succumbed TL.m. Lethal in hard water Lethal in unserated water	2966 2966 3350 313 2954, 2957 1113 2920 2965 2944 1114
0.45-0.57 0.6-1.0 0.7 0.78 1.6 5.0 5.0	96 hours 6 hours 24 & 48 hrs. 43-118 hrs. 43-118 hrs. 1 hour 9 hours	Trout Bivegill sunfish Minnows Bluegill sunfish Goldfish Mosquito fish Trout, sunfish Sea lamprey Tadpoles	Overturned Thm. normal DO Lethal in distilled water Thm Lethal in distilled water Thm in turbid water Lethal in lake water Lethal in lake water Lethal in lake water Lethal	313 2933, 2935 2944 2093 313 2940 2976 2976 313

The toxicity of KCN toward fish is more severe at low tensions of dissolved oxygen (2954, 2957). This effect appears to be most marked in the lower concentrations of KCN (2964).

Toward other aquatic and marine organisms KCN does not appear to be generally as severely toxic as toward fish. A concentration of 1.0 mg/l caused fresh-water mussels to close and lose their ability to attach to fish (313). The 96-hour  $TL_m$  for the pulmonate snail (*Physa heterostropha*) at 18°C was reported by Cairns and Scheier (2957) to 1.08 mg/l in synthetic dilution water with normal dissolved oxygen and only 0.48 mg/l with periodic low dissolved oxygen. Toward bivalve larvae, however, KCN is lethal at 0.014 mg/l.

Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158, 3343) found median threshold effects of KCN to occur as follows:

	Temperature	Exposure	Concentration
Organism	$^{\circ}C$	Time	as CN in mg/l
Scenedesmus	24	4 days	0.16
Daphnia	23	2 days	0.8
E. coli	27	1-2 days	0.4-0.8
Microregma		2 days	0.04

In contrast, concentrations of 65 mg/l of KCN are reported (313) to have killed *Daphnia magna*. Some animal plankton were killed by 40 mg/l of KCN and all by 200 mg/l (1117). Oxygen utilization by synthetic sewage was diminished 50 percent in 5 days by 15 mg/l of KCN (2923). Growth of the amoeba, *Petomyxa carolinensis* was inhibited by 0.0065 mg/l of KCN (10⁻⁷ molar) but 10⁻⁹ molar concentration increased growth.

## POTASSIUM DICHROMATE

(see Chromium)

#### POTASSIUM FERRICYANIDE

K₃Fe(CN)₆

(see also Cyanides, Hydrogen Cyanide, and Potassium Ferrocyanide)

This compound differs from the ferrocyanide in that the iron is trivalent. Potassium ferricyanide is slowly but highly soluble in water, and an aqueous solution decomposes gradually, especially in sunlight (364). The compound is used chiefly for blueprints, but also in textile processes, as an etching liquid, and in electroplating work (364).

According to Schaut (362), minnows exposed to 17.1 mg/l of potassium ferrieyanide for one hour in stabilized tap water showed no harm, and Ellis (313) quotes references to the effect that 2000 mg/l of this compound had no lethal action on minnows and goldfish. It is important to recognize, however, that the ferricyanide and ferrocyanide ions decompose slowly with the release of cyanide ion and the formation of HCN, which is much more toxic than the complex ions. Burdick and Lipschuetz (1324) recognized this phenomenon and demonstrated that concentrations of ferricyanide as low as 2.0 mg/l in the presence of sunlight became toxic to fish life (2412, 2961, 2973, 3409). In hot, bright summer weather, this limit might be even lower, according to the authors (see Potassium Ferrocyanide for details of their tests). A toxic limit as low as 0.5 mg/l of ferricyanide has been reported (353). Hiatt et al. (3350) found that 1.0 mg/l

of potassium ferricyanide produced a slight irritant ac-

tivity in marine fish.

Using water from the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158) found the median threshold effect of potassium ferricyanide to occur as follows:

	Temperature	Time of	Threshold Concentration
Organism	$^{\circ}C$	Exposure	in $mg/l$ as $Fe(CN)_s$
Scenedesmu	s 24	4 days	0.25
Daphnia	23	2 days	2.5
E. coli	27	1–2 days	over 1000

#### POTASSIUM FERROCYANIDE

K₄Fe(CN)₆

(see also Cyanides, Hydrogen Cyanide, Potassium Ferricyanide)

This compound, in which the iron is in the reduced or ferrous condition, is readily soluble in water, but the complex ions decompose slowly to release cyanide ion. The industrial uses of this substance are similar to those

of potassium ferricyanide (364).

Schaut (362) reports that minnows exposed for 70 days to 17.1 mg/l of potassium ferrocyanide in stabilized tap water showed no harmful effects, and Ellis (313) quotes references to show that 2000 mg/l were not lethal to minnows and goldfish. Trout survived a one-hour exposure to 8,723 mg/l in tap water without symptoms (313).

Burdick and Lipschuetz (1324) noted that fish were killed in a New, York stream by the discharge of an industrial waste containing ferro- and ferricyanides when the concentration of the diluted compounds was far less than the generally accepted lethal doses (as noted above). The authors reported that these compounds decompose under the action of sunlight, especially in the presence of dissolved oxygen, to release cyanogen, HCN, and cyanides. Part of the HCN is lost to the atmosphere. In diffuse light, 4000 mg/l of potassium ferrocyanide in solution showed a cyanide content of 0.3 to 0.6 mg/l and killed all fish in 48 hours. This toxic effect is not evident in solutions of 2000 mg/l in diffuse light or in the dark. In direct sunlight, however, the following effects upon fish were noted:

Concentration of Potassium Ferrocyanide in mg/l	Resulting Concentration of Cyanide, mg/l Effects	
1	0.05 to 0.16	No harm in 5 hours
. 2	0.36 to 0.48	Fish died in 0.5 to 1.5 hrs.
3	0.72	Fish died in 25 minutes
5	0.50 to 0.84	Fish died in

Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158) found that the median threshold effect of potassium ferrocyanide occurred as follows:

Test Organism	$Temperature \\ ^{\circ}C$	Time of Exposure	Threshold Concentration in mg/l as Fe(CN).
Scenedesmus	24	4 days	0.2
Escherichia coli	27	1-2 days	over 1000

## POTASSIUM FLUORIDE

KF

Highly soluble in water, this salt is used as an insecticide, for frosting glass, as a flux in soldering, and to

prevent unwanted fermentations (364). The 24-hour oral  $LD_{50}$  for rats has been reported as 245 mg/kg of body weight (3637). For tench, a concentration of 1500 mg/l has been reported as lethal (3271).

#### POTASSIUM HYDROXIDE

KOH

(see also Alkalinity, Hydroxides)

Sources of potassium hydroxide pollution include wastes from soap works; wood industries; dyeing, bleaching and mercerizing of cotton; paint and varnish removers; electro-plating, photoengraving, and lithography; detergents; and printing inks. The salt is highly soluble and hence occurs in water solution as potassium and hydroxide ions.

A dose of 2.6 grams of potassium hydroxide may cause death in man (353). The taste threshold of potassium hydroxide in water is reported to be 1 to 50 mg/l (621).

The following concentrations of potassium hydroxide are reported to have killed fish:

Concentration in mg/l	$Type\ of\ Water$	Time of Exposure	Type of Fish	Reference
28.6		24 hours	Minnows	359
50	<b>-</b>	24 hours	Trout	359, 353
56		24 hours	Bluegills	359
56	Distilled	4½ hours	Bluegills	313
80-85	Turbid	24 & 96-	-	
		hour TL _m	Mosquito-fisl	
140		94 house	Coldfish	250

The following concentrations of potassium hydroxide were not harmful to fish within the period specified:

Concentration	Type of	Time of	Type of	
$in \ mg/l$	Water	Exposure	Fish	Reference
28		24 hours	Bluegills	359
28	Distilled	10 days	Bluegills	313, 359

#### POTASSIUM IODIDE

ΚI

(see also Iodine)

This soluble salt is used in photographic emulsions, in animal and poultry feeds to the extent of 10 to 30 mg/l, in table salt, and in analytical chemistry (364). Like iodine, it may cause iodism in sensitive individuals in doses over 0.3 to 1.3 grams.

The taste threshold of potassium iodide in chlorinated water is reported to be 0.005 mg/l (459). A concentration of potassium iodide of 10,000 mg/l in the drinking water of rats permitted fair growth, but no reproduction (287). The oral LD₅₀ in mice has been reported as 1982-2068 mg/kg of body weight (3638).

Using water from the River Havel, Bringmann and Kuhn (2158) found the toxic threshold of KI to be 7.5 mg/l for *Daphnia*. For *E. coli* and *Scenedesmus*, however, a concentration of 1000 mg/l had no effect.

#### POTASSIUM NITRATE (Saltpeter)

 $KNO_3$ 

- 1. General. This primary source of nitrates is used extensively in industry, for fireworks, fluxes, matches, gunpowder, freezing mixtures, pickling meats, treating tobacco, and for tempering steel (364). It is highly soluble in water.
- 2. Cross References. Nitrates, Potassium, Dissolved Solids, Chapter V.
  - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Potassium nitrate can be a diuretic for man and animals; large doses cause vomiting, diarrhea, muscular weakness, collapse and death (284, 623). The medicinal dose of potassium nitrate is 0.3 grams (629). A dose of 5 grams of potassium nitrate is toxic to man; and 8 to 39 grams, fatal (284).

b. Stock and Wildlife Watering. A dose of 50 grams of potassium nitrate is toxic to horses; a dose of 240 grams is fatal to cows; a dose of 30 grams is fatal to sheep and swine; and 6 grams are fatal to dogs (284,

c. Fish and Other Aquatic Life. The following concentrations of potassium nitrate have killed fish:

Concentration in mg/l	n Type of Water	Time of Exposure	Type of Fish	Reference
127	Natural		Stickleback	598
162	Turbid	96-hour TL _m	Mosquito-fish	2940
181		One week	Stickleback	1460
<b>2</b> 58		4 days	Stickleback	1460
421	Turbid	24-hour TLm	Mosquito-fish	2940
517		2 days	Stickleback	1460
1203	Tap	15 days	Bluegills	313, 598
1290		1 day	Stickleback	1460
3000	Aerated	96-hour TLm	Bluegills	3381
5050		15.7 hours	Young eels	1459

The highest concentration of KNO₃ tolerated by young eels for more than 50 hours was reported (1459) to be about 1000 mg/l.

#### POTASSIUM PERMANGANATE

KMnO₄

(see also Manganese)

Potassium permanganate is a powerful oxidizing agent and it is sometimes used as a bactericide (1325). It is frequently used to disinfect fish tanks and to treat certain fish infections, such as fungus growths (313). In concentrations of 0.2 to 0.5 mg/l it has been effective as an algicide in reservoirs (587).

The threshold concentration of potassium permanganate for the immobilization of Daphnia magna has been reported to be 0.63 mg/l (358). In river water, 5 mg/l has killed various minute crustaceans, including fishfood organisms (313). The following cencentrations of potassium permanganate have been toxic or lethal to

Concentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
3.0			Bluegills	3639
3.2	Tap	24-hour TLm	Fingerling catfis	h 2981
4.0	-		Largemouth bass	3639
5.0			Fathead minnow	s 3639
5.2	U.S.mn.	24-hour TLm	Bluegill sunfish	2093
5.4	U.S.mn.	48-hour TLm	Bluegill sunfish	2093
6.25		24 hours	Trout	359
10	Hard	12-18 hours	Goldfish	313, 2920
11.8		8 hours	Young eels	1459
12	Turbid	24 & 96-hour	*	
22-62		TL _m 30 minutes	Mosquito-fish Fish	2940 1326

Young eels tolerated 8 mg/l for 50 hours (1459). Concentrations of 2.0 to 2.5 mg/l of KMnO₄ have been used in aquaria and in the field to neutralize the toxicity of 0.05 mg/l of rotenone (3639), without harmful effects.

#### POTASSIUM PHOSPHATE, TRIBASIC $K_3PO_4$

This deliquescent crystalline solid is highly soluble in water. Using mosquito-fish (Gambusia affinis) in highly

turbid water at 20-30°C, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m concentrations to be 750 mg/l. This salt reduced the turbidity to less than 25 mg/l.

#### POTASSIUM SILICOFLUORIDE

K₂SiF₆

Used in the manufacture of opalescent glass, porcelain enamels, and insecticides, this solid is only sparingly soluble in water (364). The lethal dose to kill tench has been reported (3271) as 50 mg/l.

#### POTASSIUM SULFATE

 $K_2SO_4$ 

(see also Sulfates)

This soluble salt is used in fertilizers and for the manufacture of potassium alum and other potassium salts. A dose of 45 grams has been reported as fatal for man (364). Potassium sulfate in a concentration of 869 mg/l has killed bluegills and stickleback in four days (313, 598). The 96-hour  $TL_m$  for bluegill sunfish in aerated water was reported by Trama (3381) as 3550 mg/l. The highest concentration of K₂SO₄ tolerated by young eels for more than 50 hours was reported to be about 1300 mg/l (1459).

#### POTASSIUM SULFIDE

 $K_2S$ 

(see also Sulfides, Hydrogen Sulfide)

In waters used for mixing developer solutions, even very low concentrations of potassium or sodium sulfides can cause a chemical fog (242).

#### POTASSIUM THIOCYANATE

KSCN

(see also Cyanides, Hydrogen Cyanide, Sodium Thiocyanate)

Readily soluble in water, this compound has been used in printing and dyeing of textiles, as an intensifier in photography, and in the manufacture of artificial mustard oil (364). It has a high chlorine demand and can interfere with water purification by decreasing the bactericidal effects of chlorination (362). Schaut (362) reports that fish were killed and minnows harmed by exposure for three days to 171.4 mg/l of KSCN. When chlorinated to a 0.02 mg/l residual, however, as little as 6.0 mg/l of KSCN was toxic to fish, owing to the breakdown of the SCN- molecule to cyanide.

A concentration of 97 mg/l of KSCN killed Paramecium aureleaneum in less than 24 hours but did not affect the minnow, Gambusia holbrooki, in 10 days of contact. A concentration of 194 mg/l killed some minnows after two days of exposure and 3880 mg/l killed all in less than two hours (353). The region of harmfulness to fish has also been reported as 1700 mg/l.

Using water of the River Havel, from which the test organisms had been recovered, Bringmann and Kuhn (2158) reported the following median threshold limits for KSCN:

Test Organism	Temperature °C	Time of Exposure	Threshold Concentration in mg/l as SCN
Daphnia	23	2 days	19
Scenedesm	us 24	4 days	120
$E.\ coli$	27	1-2 days	over 1000

#### POTASSIUM XANTHOGENATE

C2H5OCS2K

This substance is very soluble in water, giving a strongly alkaline reaction. It is used in analytical chemistry, in oil flotation, and to free soil from insect pests. According to Ellis (313, 609), goldfish were killed by a concentration of 10 mg/l in hard water in two to four days, and 0.1 mg/l was fatal in five days. Goldfish were also killed by 80 mg/l in 36 hours or less and by 315 mg/l in five to eight hours. Ellis also reports that this compound decomposes rapidly and is not fatal in dilute solutions of 1:100,000 unless constantly renewed. If renewed daily, 1:10,000,000 dilution was toxic to fish. A concentration of 4.0 mg/l stopped the heartbeat of frogs, turtles, and fish immediately, 5.0 mg/l killed crustacea in five days or less, without renewal of the solution, and if renewed daily 0.01 mg/l was detrimental to plankton.

#### PRESSURE

While it may seem to be remote to consider pressure as a potential pollutant, momentary changes in this physical property may be extremely detrimental to one beneficial use of water, namely, the maintenance of fish and other aquatic life. Sudden changes in pressure, therefore, may be classed as a potential pollutant of the physical type.

Underwater charges of violent explosives, such as may be used in explorations for submarine oil, may be very destructive to fish. Large areas can be more or less depopulated by repeated blasts, though repopulation

occurs within a few months (1646).

Fish are resistant to very large and relatively rapid changes in positive pressure, but are very susceptible to negative pressures (i.e., pressures less than atmospheric pressure), and cannot tolerate the almost instantaneous changes induced by high explosives. The tolerance of fish to explosives varies with the nature of the charge and resultant pressure changes. Dynamite and hercomite explosions are very destructive to fish; even when jetted, charges as small as 1.0 to 1.25 lbs. often killed fish; lethal-threshold peak pressures from dynamite explosions varied from 40 to 70 psi.

Black powder explosions are less harmful; charges as high as 45-90 lbs. have not caused excessive loss of fish. Peak pressures of 124-160 psi from black powder explo-

sions did not kill caged fish (1646).

#### PROPIONIC ACID CH₃CH₂COOH

This colorless liquid with a pungent odor is miscible with water. It is employed in the production of propionate mold inhibitors, and in the manufacture of ester solvents, fruit flavors, and perfume (364). According to Doudoroff and Katz (361), propionic acid can be toxic to fish without lowering the pH to 5.0. Its toxicity is attributed primarily to the undissociated acid in solution; hence pH in itself is not a reliable index of dangerous pollution.

#### PROPYL ALCOHOL

 $C_3H_7OH$ 

Normal propyl alcohol is a liquid miscible with water. It is used industrially as a solvent. The oral  $LD_{50}$  for rats has been reported as 1.87 grams/kg of body weight

(2978) and as 3.3 grams/kg (3248). For gudgeon (a European fresh-water fish) the lethal range of n-propyl alcohol is 200 to 500 mg/l; and for isopropyl alcohol the range is 900 to 1100 mg/l (2977). A concentration of 192,000 mg/l was required to evoke a stimulation to movement among 50 percent of a group of water beetles (Laccophilus), according to Hodgson (2956).

#### PULP AND PAPER MILL WASTES

(see Kraft Pulp Mill Wastes, Groundwood Pulp Mill Wastes, Paper Mill White Waters, Sulfite Waste Liquors)

### PYRETHRUM (ALLETHRIN)

(see Chapter IX)

#### PYRIDINE

 $C_5NH_5$ 

(see also Coal Tar and Picoline)

Pyridine is a flammable, colorless liquid with a disagreeable odor and a sharp taste. It occurs in coal-tar and gas-plant wastes and may be washed from recently burned-over areas. It is miscible with water and can be used as a solvent for many organic and mineral substances.

In a concentration of 2.5 mg/l, pyridine produces a characteristic odor in water. At 1.0 mg/l it inhibits biochemical oxidation, but not at 0.5 mg/l. Albino rats fed pyridine doses of 0.125 mg/kg of body weight developed pathological effects. A maximum permissible concentration of 0.25 mg/l of pyridine in water has been suggested (3640).

According to Negus (633), pyridine is a by-product of the ammonium-sulfate treatment of waters when the ammonia is of coke origin; but inasmuch as solutions as high as 10 percent have been used therapeutically for respiratory diseases, any concentrations found in drinking water should be safe for human consumption.

Toward fish and other aquatic life the following effects of pyridine have been reported:

Concentration in mg/l	Type of Organism	Effect	Reference
15	Fish	Toxic action on	311, 753,
40	Daphnia	nervous system Threshold effect	2158
100	Alburnus		2977
100	(fish)	Threshold toxicity	2911
160	Bleak	Threshold toxicity	2904
180	Bream	Threshold toxicity	2904
200	Carp	Threshold toxicity	2904
200	Perch	No damaging effect	3405
200	$m{E}.~coli$	Threshold effect	2158
200	Microregma	Threshold effect	3343
400	Yearling trout	Toxic limit	3245
<1000	Perch	Lethal	
		concentration	2920
1000	Fish	Threshold effect	313, 363, 431
1300	Mosquito-fish	96-hour TLm in	
400 4500		in turbid water	2940
1480-1580	Orange-spotted	Killed in one hour	
4000	sunfish	in tap water	363
1830	Goldfish	Killed in 10-30 hours in distilled	
		water	363
		MUTCOL	500

Pyridine is subject to rapid biochemical degradation in surface waters when the proper seed organisms are

present (1641, 3633). At a concentration of 5.0 mg/l, pyridine influenced the taste of bleak and carp (2904).

### PYRIDYLMERCURIC ACETATE

### PYRIDYLMERCURIC CHLORIDE

(see Mercuro-Organic Compounds)

#### PYROCATECHOL

 $C_6H_4(OH)_2$ 

(see also Phenols, Guaiacol, and Resorcinol)

Highly soluble in water, this solid phenolic-type compound is used in photography and for dyeing fur. To distinguish it from resorcinol, it is known also as 1, 2-benzenediol. The oral LD₅₀ for rats is reported as 3890 mg/kg of body weight (364).

According to Sollman (1474) the approximate 48-hour TL_m for goldfish is 14 mg/l. For perch, the lethal concentration has been reported as 5 to 10 mg/l (2977). Another authority (3405) gives the lower toxic limit for perch at 12 mg/l, while 27.5 mg/l was toxic in 20 minutes. In Lake Huron water at 12°C, the sea lamprey was not affected during a 24-hour exposure to 5.0 mg/l (2976). For minnows, 20 mg/l was toxic in 51.9 minutes (3405). Bandt (2904) reports the thresholds of toxic effect at 10 mg/l for bleak and 15 mg/l for carp. The taste of the flesh of carp is influenced by 2.5 mg/l of pyrocatechol.

Toward lower aquatic life, Bringmann and Kuhn (2158) found that the toxic threshold for Daphnia occurred at 4 mg/l during a 48-hour exposure at 23°C. For the diatom Scenedesmus, the threshold was 6 mg/l during a 96-hour exposure at 24°C. The beginning of a poisoning effect toward Escherichia coli at 27°C occurred at 90 mg/l. Toward protozoa, the toxic effect of pyrocatechol occurs at about 860 mg/l (2904).

#### **PYROGALLOL**

 $C_6H_3(OH)_3$ 

(see also Benzene Derivatives)

This white, odorless, crystalline substance is highly soluble in water. It is used in the dyeing of woolens and furs, for staining leather, and as a developer in photography (364). The oral  $LD_{50}$  for dogs is 25 mg/kg of body weight.

Toward goldfish in tap water at room temperature, Sollman (1474) found the approximate 48-hour  $TL_m$  for pyrogallol to be 18 mg/l.

The threshold concentration for toxic action has been reported at 20 mg/l for bleak and 50 mg/l for carp (2904). The taste of the flesh of bleak and carp is influenced at 20-30 mg/l (2904). For the sea lamprey in Lake Huron water at 12°C, 5 mg/l caused no deleterious effect in 24 hours (2976).

Bringmann and Kuhn (2158, 3343) reported the threshold of toxicity toward *Daphnia* held for 2 days at 23°C to be 18 mg/l; toward *Scenedesmus* during 4 days at 24°C to be 8 mg/l; toward *Microregma* 50 mg/l; and toward *E. coli* for 1-2 days at 27°C to be 30 mg/l. For protozoa, a toxic effect has also been reported at 375 mg/l (2904).

#### **PYROPHOSPHATES**

(see Phosphates and Phosphoric Acids)

## QUATERNARY AMMONIUM COMPOUNDS

(see Chapter X)

### QUINACRINE HYDROCHLORIDE

 $C_{23}H_{30}CIN_3O\cdot 2HCl\cdot 2H_2O$ 

Known commonly as atabrine, this soluble crystalline solid is used in the prevention and treatment of malaria. The oral LD₅₀ for roosters is reported as 714 mg/kg of body weight (364). Using fingerling channel catfish, Clemens and Sneed (2981) found this compound to be highly toxic. At 25°C, the 24-, 48-, and 120-hour TL_m concentrations were 0.93, 0.89, and 0.80 mg/l respectively. At 120 hours, all fish survived 0.5 mg/l but all died at 1.3 mg/l.

## QUINALDINE

C10H9N

(see also Quinoline)

This colorless, oily liquid, insoluble in water, is known also as 2-methylquinoline. The oral  $LD_{50}$  in rats is given as 1230 mg/kg of body weight (364). Toward fingerling trout at 12-13°C, a concentration of 5.0 mg/l was toxic in 60 minutes (3245).

## QUINHYDRONE

 $C_{12}H_{10}O_4$ 

Slightly soluble in cold water, this green crystalline substance is used as an electrode in pH determinations. The oral LD₅₀ for rats is given as 225 mg/kg of body weight (364). In Lake Huron water at 12-13°C, rainbow trout, bluegill sunfish, and sea lamprey were killed by the following concentrations at the designated times (2976):

(2510):	Time in Hours Until Death at		
Type of Fish	$5.0 \ mg/l$	1.0 mg/l	0.1 mg/l
Rainbow trout	1	14	No effect
Bluegill sunfish	3	4	14
Sea Jamprey	· 9	14	No effect

In River Havel water, Bringmann and Kuhn (2158, 3343) found the threshold of toxic effect to occur at 0.4 mg/l for Daphnia; 0.7 mg/l for Microregma, a protozoan; 4.0 mg/l for the alga Scenedesmus, and 5 mg/l for Escherichia coli.

#### QUININE

 $C_{20}H_{24}N_2O_2$ 

In the form of quinine dihydrochloride, this alkaloid of cinchona bark is used in drugs, especially to suppress malarial attacks. It has been reported to impart a taste to water at a concentration of 0.5 mg/l (759) and at 4.0 mg/l (1578).

Hora and Nair (758) reported that pollution of water by the effluent from a quinine factory had very little injurious effect on fish. According to Clemens and Sneed (2981), the 24-, 48-, and 96-hour TL_m concentrations for quinine sulfate toward fingerling channel catfish at 23°C were 42.0, 38.6, and 34.0 mg/l respectively.

#### QUINIZARIN

 $C_{14}H_8O_4$ 

This orange crystalline substance is highly soluble in water. In Lake Huron water at 12-13°C, a concentration of 5.0 mg/l had no effect on rainbow trout, bluegill sunfish, or sea lamprey during a 24-hour exposure (2976).

#### QUINOLINE

 $C_9H_7N$ 

(see also Coal Tar)

Quinoline occurs in coal tar in small amounts. It is an extremely hygroscopic liquid, absorbing up to 22 percent water, but it is difficultly soluble in cold water. The commercial applications of quinoline include the manufacture of dyes and drugs, and use as a solvent for resins and terpenes. It may occur in coal-tar and gasplant wastes.

Toward fish and other aquatic life, the following effects of quinoline have been reported:

Concentrat	ion Type of		,
$in \ mg/l$	Organism	$E \it ff e c t$	Reference
5.0	Rainbow trout	Lethal in 14 hours at 13°C	s 2976
5.0	Bluegill sunfish	Lethal in 4 hours at 13°C	2976
5.0	Sea lamprey	Caused illness in 4 hours at 13°C	2976
7.5	Fish	Lethal	2961, 2977
7.5–10	Yearling trout	Lethal in 60 min- utes at 13°C	3245
10	Bleak, bream, carp	Toxic threshold	2904
<30	Perch	Lethal	2920
50	Perch, sunfish	Lethal	313, 363, 365, 463
50	Microregma	Toxic threshold	3343
52	Daphnia	Toxic threshold at 23°C	2158
140	Scenedesmus	Toxic threshold at 24°C	2158
600	E. Coli	Toxic threshold at 27°C	2158
750	Ciliates	Toxic	2904

According to Cole (311) quinoline paralyzes the respiratory muscles. It is reported (2904) to influence the taste of the flesh of carp at concentrations of 0.5 to 1.0 mg/l.

## QUINONE $C_6H_4O_2$

With a penetrating chlorine-like odor, quinone is only slightly soluble in water. It is used in photography, dye manufacture, tanning, and as an oxidizing agent. The oral  $LD_{50}$  in rats is given as 130 mg/kg of body weight (364).

According to Hiatt et al. (3350), a concentration of 1.0 mg/l caused a slight irritant activity in marine fish, while 10 mg/l caused moderate activity from irritation. The lethal concentration for perch has been reported as 5 to 10 mg/l (2977). For p-quinone the threshold concentration for toxic effect has been reported (2904) as 0.1 mg/l for bleak, 0.2 mg/l for bream and 1.0 mg/l for carp and tench. It begins to influence the taste of flesh of tench and carp at 0.5 mg/l.

Quinone compounds are selectively toxic toward blue algae at 1.0 mg/l but not toward green algae or most higher plants (2977). In River Havel water, Bringmann and Kuhn (2158, 3343) found that the thresholds of toxicity occurred at 0.4 mg/l for Daphnia (23°C), 2.0 mg/l for Microregma, 6 mg/l for Scenedesmus (24°C) and 50-60 mg/l for E. coli (27°C). Toxic effects have also been reported for ciliates and rotatoria at 1.0 mg/l (2904).

#### RADIUM

(see also Chapter VIII)

A product of the distintegration of uranium, natural radium has long been used in physical research, radiotherapy, and the manufacture of luminous paints. With the increasing availability of other radioisotopes, however, the need for and use of radium has decreased. Radium undergoes spontaneous disintegration with the formation of radon, one gram of radium producing about 10⁻⁴ ml of radon per day (364). This property is utilized in measuring radium in natural waters (3641, 3642).

Hursh (3641) measured the radium content of the raw water and tap water of 42 sources of supply, serving approximately one-fifth of the population of the U.S. The radium in raw water ranged from 0.002 to  $6.54 \times 10^{-9}$ mg/l with a median of  $0.049 \times 10^{-9}$  mg/l, whereas in tap water the range was 0.00 to  $5.79 \times 10^{-9}$  mg/l with a median of  $0.028 \times 10^{-9}$  mg/l. In general, ground-water sources contained a higher concentration of radium than surface water supplies. Hursh also measured the radium content of 25 deceased persons at Rochester, N.Y. where the radium content of tap water is close to the median of the 42 other sources of supply. The average wholebody content of radium was found to be  $120 \times 10^{-9}$  mg. approximately three orders of magnitude lower than the level judged safe for workers in the radium industry. Hursh (3641) concluded that the accumulation of naturally occurring radium from water and food does not constitute a health hazard for the population as a whole.

Lucas (3643) reported that the Ra-226 content of certain midwest water supplies ranged from less than 0.03 to  $37 \times 10^{-9}$  mg/l. Surface supplies and wells in glacial deposits or limestone formations were with rare exception found to contain less than  $1.0 \times 10^{-9}$  mg/l whereas wells penetrating deep sandstones had Ra-226 contents of 1.0 to  $37 \times 10^{-9}$  mg/l. A population of 1,000,-000 was identified as consuming water in excess of 1.0  $\times$ 10-9 mg/l of Ra-226. Smith et al. (3642) measured the natural radioactivity of ground-water supplies in Maine and New Hampshire, finding the average Ra-226 activity of drilled and dug wells in Maine to be 66 and 73 pc/l respectively and in New Hampshire 6.9 and 4.1 pc/l respectively. Since one gram of radium emanates one curie, these activities correspond to 4.1 to  $73 \times 10^{-9}$  mg/l of radium, or somewhat higher than the results of Hursh (3641) or Lucas (3643). A tabulation of natural radioactivities of natural waters, presented by Smith et al. (3642) shows a variation from as low as  $0.01 \times 10^{-9}$  mg/l in the River Thames to as high as  $7.1 \times 10^{-4}$  mg/l for spring waters in Japan. The average for all river waters was given as  $0.07 \times 10^{-9}$  mg/l and for all sea waters as  $0.08 \times 10^{-9} \text{ mg/l}$ .

The 1962 Drinking Water Standards of the U.S.P.H.S. (2036) limit the radioactivity from Ra-226 to 3 picocuries/l, corresponding to  $3 \times 10^{-9}$  mg/l of radium; but the WHO International and European Drinking Water Standards (2328, 2329) both limit total alpha emitters, including Ra-226, to 1.0 pc/l, or  $1.0 \times 10^{-9}$  mg/l. On the basis of the foregoing resume of the Ra-226 content of water supplies in the U.S., it is apparent that many of them do not meet the U.S. standards.

Tsivoglou et al. (3644, 3645, 3646, 3647, 3648) have reported on problems of radioactive waste disposal to surface waters, especially along the Animas River which receives wastes from uranium processing. Uranium is the parent of a series of 14 radioactive isotopes that occur in nature. Inasmuch as the uranium only is desired, all of the daughter elements are discarded as wastes. Radium is the most hazardous radioelement in these wastes. The bulk of the radium, perhaps 98 to 99 percent, is generally retained undissolved in tailings ponds; but the remaining dissolved portion can constitute a significant stream pollution problem, affecting domestic and industrial water supply, irrigation, stock watering, and aquatic life. Indeed, a portion of the undissolved radium also escapes to the stream and constitutes a hazard as it builds up in bottom muds.

#### REOVIRUSES

(see Chapter VII-Enteroviruses)

#### RESINS

The term "resin" is applied here to the mixture of various solid or semi-solid organic substances derived from the residue of wood pulping or the distillation of turpentine. Ellis (611), investigating a plant in Mississippi using pine for the production of turpentine, pine oil, and resin, found in the wastes some turpentine, pinene ( $C_{10}H_{16}$ ), and turpene. In a dilution of 1:1000, this waste was rapidly lethal to fish, and few survived a 1:10,000 dilution. Lethality was attributed to certain organic acids and turpene derivatives.

Waste liquors from a synthetic resin plant had a strong odor of phenol and formaldehyde, according to Schaut (362) and produced a medicinal taste, when chlorinated, at a dilution of 1:25,000,000. At a dilution of 1:2400 in stabilized tap water, minnows became distressed in five minutes.

Resin acids, which occur in Kraft mill wastes, are toxic to fish in concentrations reported at 1.0 mg/l to 5.0 mg/l by several references (311, 344, 658, 766, 1687, 3649). The sodium salts of such resin acids are toxic to fish at concentrations of about 1.0 mg/l (190, 344, 658, 3500, 3523, 3553, 3632). Daphnia magna is slightly more resistant, succumbing at about 3.0 mg/l of the sodium salts of resin acids while for Chironomous larvae the minimum lethal concentration is about 50 mg/l (190, 574, 690, 3500, 3523, 3553).

#### RESORCINOL

 $C_6H_4(OH)_2$ 

(see also Pyrocatechol)

This crystalline solid is distinguished structurally from pyrocatechol in that the hydroxyl groups are in the 1, 3 positions. It is known also as 1, 3-benzenediol. Highly soluble in water, it is used in explosives, dyes, resins, and tanning operations (364). It is also used as an antiseptic agent, especially for skin diseases.

Nesmeyanova (3402) reported that the odor threshold for resorcinol was 40 mg/l in unchlorinated water, but no lower with chlorination. The threshold of toxic action toward fish was given (2904) as 35 mg/l for bleak and carp. A concentration of 30 mg/l gave the first indication of taste in the flesh of carp (2904).

According to Bringmann and Kuhn (2158) the threshold of toxic effect toward *Daphnia* occurred at 0.8 mg/l during a 48-hour exposure at 23°C; but toward the diatom *Scenedesmus* the toxic threshold was 60 mg/l at 24°C for 96 hours. Resorcinol at concentrations up to 1000 mg/l had no effect on *E. coli* at 27°C. For the protozoan *Microregma*, the threshold of toxic effect occurred at 40 mg/l (3343).

#### RICIN

This white powder is a highly toxic albumin that is obtained from castor seed. According to Schaut (362) 17.1 mg/l in stabilized tap water produced a 75 percent mortality among minnows in 20 hours of exposure. At 6.0 mg/l, the mortality was 50 percent after 48 hours. Chlorination appeared to have destroyed the toxicity.

#### ROAD DRAINAGE

(see Tars)

#### ROCCAL

(See Chapter X)

#### ROTENONE

(see Chapter IX)

#### RUBBER PLANT WASTES

In waste water from synthetic-rubber plants in Germany, according to Bandt (616), the substances that impart taste to the flesh of fish are the higher, partially unsaturated aldehydes and hydrocarbons. Styrol, in spite of its low solubility, imparts taste to fish. Rubber waste products are attacked and decomposed by a wide variety of bacteria and fungi, with a resulting B.O.D. and the production of CO₂ (666). Waste liquors from rubber-reelaiming plants at a dilution of 1:2400 in stabilized tap water, gave a dirty yellow color and a distinct odor, according to Schaut (362). At this dilution, minnows would not eat but they recovered their appetite when transferred to clear water. At a dilution of 1:2400 they were normal.

## RUBIDIUM Rb

Occurring widely in nature in small concentrations, this alkali metal is highly reactive; hence it is found only in the combined or ionized state and never as the pure metal. Rubidium salts are very soluble in water. They occur in some mineral springs. They are used in making zeolite catalysts and also in photoelectric cells (364, 2121). Rubidium is fairly abundant in food elements, especially beans and barley, and it occurs in concentrations of 20-40 mg/kg in animal tissues (2121). There is no evidence that it serves any essential metabolic function, but it can be substituted for potassium in some physiological processes (2121). High concentrations of rubidium in a low-potassium diet for animals causes irritation of muscular nerves. There is no evidence of rubidium toxicity toward human beings (2121)

Using water from the River Havel, Bringmann and Kuhn (2158, 3343) found that the toxic threshold of rubidium, added as rubidium chloride, was 14 mg/l for the alga Scenedesmus and the protozoan Microregma.

Toward Daphnia and Escherichia coli concentrations up to 1000 mg/l had no apparent effect.

#### RUTHENIUM

This gray, lustrous, hard metal occurs in the ores from which platinum, nickel, and copper are extracted. It also occurs in the combined form in the minerals osmiridium and laurite. Some of its salts are soluble in water. Until the advent of nuclear fission, little attention was paid to ruthenium. It was used in platinum and palladium alloys as a hardener, and for colors in ceramics (364, 2121). There is no evidence that ruthenium is highly toxic, nor does it appear to be essential for animal or plant nutrition.

As fission products of uranium, ruthenium-103 and ruthenium-106 occur in fallout from nuclear explosions. Morgan (3386) reports the following concentration factors for ruthenium-103.

Organism Concentration Factor
Ochromonas (a flagellate) 4000-6500
Navicula (diatom) 7900

Since ruthenium-106 does not become adsorbed on rocks or soil, it may be expected to travel great distances in ground water (1976).

# SALICYLIC ACID AND SALICYLATES

C6H4OHCOOH

Salicylic acid is a crystalline substance, soluble in water to the extent of about 2000 mg/l. It is used in the manufacture of salicylates, acetylsalicylic acid (aspirin), and dyes. It is also used as a food preservative, but such use is forbidden in some countries (364).

Ruchhoft (459, 946) quotes references to the effect that, in chlorinated water, the minimum concentrations of salicylates usually giving tastes are as follows:

 Substance
 Concentration in mg/l

 Salicylic acid
 0.01

 Sodium salicylate
 0.10

 Ammonium-salicylate
 0.10

 Salicylaldehyde
 less than 0.001

In Lake Erie water at 25°C, the threshold concentration of sodium salicylate for immobilization of *Daphnia magna* with 48 hours of exposure was 1450 mg/l, according to Anderson (352). Toxicity was attributed to factors other than osmotic pressure. Hermann (2923) reported that 110 mg/l inhibited the 5-day BOD of synthetic sewage by 50 percent.

#### SALINITY

(see Dissolved Solids, Specific Electrical Conductance)

#### SALT WORKS WASTES

Ellis (1327) studied the pollutional effects of various wastes from salt works on fish and Daphnia magna. The wastes included bittern liquor (the supernatant fluid after natural brine has lost most of its sodium chloride), bromine-still waste and neutralized bromine-still wastes, and a concentrated solution of calcium chloride. In dilutions of 1:50, all of these effluents were dangerous to goldfish and Daphnia magna. The bittern liquor was harmless when diluted 1:100 and well-neutralized bro-

mine still waste was not injurious in dilutions of 1:500. If not properly neutralized, however, it was dangerous up to dilutions of 1:1000. Fresh bromine-still waste was harmful up to 1:10,000 dilution.

#### SANTOBRITE

(see Chapter IX, Pentachlorophenol and Pentachlorophenates; also Chapter X)

#### SANTOMERSE

(see Chapter X)

#### SAPONINS

C₃₂H₅₄O₁₈

Saponins are glycosides that are used in medicine and industry as foam producers. They are found in nature in many plants, and in horse-chestnut seed (777), and they occur in wastes from potato-starch and sugar-beet factories. In addition to foaming, they produce an aromatic woody odor in water in a concentration of 17.1 mg/l, and when such water is chlorinated the taste becomes medicinal (362).

The toxic limit to most fish for beet saponin or acid saponin appears to be about 5.0 mg/l (311, 458, 778). A concentration of 17.1 mg/l, however, did not affect minnows during 24 hours of exposure (362). Ellis (313) found that 10 mg/l in hard water produced marked distress in goldfish in five hours and 100 mg/l killed them in 7 to 24 hours.

#### SAPROPHYTIC BACTERIA

(see Chapter VII)

#### SARIN

(see Chapter IX)

#### SAWDUST

There appears to be a difference of opinion among the authors of the references dealing with sawdust in water. Ellis (779) reports that extract leached from one gram of pine sawdust in 24 hours killed fish when diluted with 20,000 parts of fresh stream water. Extracts from old sawdust piles after a slow, drizzly rain were also highly toxic to fish. Knight (540) on the other hand, claims that trout lived for two weeks in water heavily polluted with sawdust, with no trace of injury. He states, however, that sawdust in millstreams can interfere with the breeding of fish, especially those that require sandy or gravelly bottoms. Also, sawdust may destroy insect life, reduce fish-food organisms, and harm the development of young fish.

Ward (560) avers that it is incorrect to assume that pulp and sawdust from lumber and paper mills kill fish by clogging their gills, inasmuch as wastes are now known to be dangerous because of toxic substances or oxygen depletion. Healthy fish are not suffocated by solid particles and their gills become choked with debris only when the fish are weakened by other causes and are already dying.

#### **SCHISTOSOMES**

(see Chapter VII)

#### SCHRADAN

(see Chapter IX)

## SECONDARY SODIUM ALKYL SULFATE (Teepol)

(see Chapter X)

#### SELENIOUS ACID

 $H_2SeO_3$ 

(see also Selenium)

When selenium dioxide, SeO₂, is dissolved in water, selenious acid is formed. At normal pH values, i.e. 5 to 8, this acid is only partially dissociated in water, with most of the molecules occurring as HSeO₃⁻ (911). In stabilized tap water, minnows were not harmed during a one-hour exposure to 17.1 mg/l of selenious acid (362).

#### **SELENIUM** Se

- 1. General. Analogous to sulfur in many of its chemical combinations, selenium is used in its elemental form and as several salts in a variety of industrial applications, such as pigmentation in paints, dyes, and glass production; as a component of rectifiers, semiconductors, photo-electric cells, and other electrical apparatus; as a supplement to sulfur in the rubber industry; as a component of alloys; and for insecticide sprays (364, 2121, 2129). Selenium occurs in some soils as basic ferric selenite, as calcium selenate, as elemental selenium, and in organic compounds derived from decayed plant tissue. In some areas of South Dakota and Wyoming, soils may contain up to 30 mg/kg of selenium (2121). Selenium may be expected in trace quantities in the municipal sewage from industrial communities. Although selenium is found in some natural waters, food appears to be a more likely source for human ingestion (1049, 1328, 1329).
- 2. Cross References. Arsenic, Selenious Acid, Sodium Selenite.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Proof of human injury by selenium is scanty and definite symptoms of selenium poisoning have not been identified; but it is widely believed that selenium is highly toxic to man (353, 997, 1329, 1330). It has been stated that the symptoms of selenium poisoning are similar to those of arsenic poisoning (555).

In areas where selenium poisoning of livestock is common, the toxic effects appear to be associated with the consumption of high concentrations of selenium in food rather than in the water (152, 1331). In food stuffs 4.0 mg/kg is considered an extreme tolerance limit; and 3 mg/kg is regarded as a safer limit (353).

Mild chronic selenium poisoning has been observed in humans living in areas where the soil and produce are rich in selenium. In addition, there have been cases of selenosis at industrial establishments that use or produce selenium compounds. Hydrogen selenide (H₂Se) in the air in concentrations as low as 0.2 parts per million by volume produces definite toxic symptoms (2129).

Selenium in trace amounts appears to be essential for the nutrition of animals, including man, although very little is known about the mechanism of its action (3217). Arsenic and selenium are apparently antagonistic in their toxicity, tending to counteract each other. Selenium salts are rapidly and efficiently absorbed from the gastro-intestinal tract and excreted largely through the urine. Retention is highest in the liver and kidney (2121, 2129).

Surveys have shown that dental caries rates of permanent teeth were significantly higher in seleniferous areas than in non-seliniferous areas (2253). There is also a tendency for increased malocclusion and gingivitis in seleniferous areas (2253).

The U.S. Food and Drug Administration placed a "zero tolerance" on selenium and seleniferous materials with respect to permissible residue on fruits and other edible crops (3651).

The USPHS Drinking Water Standards (2036) have restricted selenium to 0.05 mg/l on a mandatory basis for many years (See Table 5-1). In 1962, however, the new standards lowered the mandatory limit to 0.01 mg/l. The WHO International (2328) and European (2329) Drinking Water Standards prescribe a mandatory limit of 0.05 mg/l. These strict standards were undoubtedly set because of the similarity between arsenic and selenium poisoning, the dental effect, and the known toxicity to livestock, as described below.

b. Irrigation. In general, the soil in parts of the world where selenium poisoning occurs naturally contains 1 to 6 mg/kg of selenium in the top eight inches. However, plants vary in their ability to absorb selenium; the final selenium concentration in the plant will be determined by many factors, including the species and age of the plant, season of the year, and the concentration of soluble selenium compounds in the root zone (1049).

Plants can absorb relatively large amounts of selenium from irrigation water or soil without apparent injury to themselves. Certain weeds, such as Astragulus, may contain as much as 4500 mg/kg of selenium (1049). Other plants grown on seleniferous soil have been found to contain as much as, or more than, 1610 mg/kg of selenium (dry weight) (1003, 1328). Byers believes that any vegetation containing 5.0 mg/kg of selenium is potentially dangerous for livestock; and that any soil containing more than 0.5 mg/kg is also hazardous (1329). Russell has pointed out that fodder containing as little as one mg/kg of selenium has caused poisoning, and states that 4.0 mg/kg is the tolerance limit of livestock (1049).

Cereals and grains concentrate selenium from the soil, the amount depending on the chemical condition of the selenium, the type of crop, and the sulfate content of the soil. High sulfates diminish the uptake of selenium. Up to 63 mg/kg of selenium have been found in wheat and up to 17.8 mg/kg in onions (2121).

Plants have been injured by selenium in the soil; wheat plants have been severely damaged by 30 mg/kg of sodium selenate in the soil (1328). However, injury to plants can be reduced or prevented by sulfate ion, when it is present in a concentration about 12 times as high as that of selenium (1328). Klintworth (1493) believes that selenium is harmful to plants at all concentrations. Walker and Rigdon (1688) have prepared an extensive bibliography of papers on selenium toxicity to plants and animals.

The USDA Regional Salinity Laboratory at Riverside, California, has not established limits on selenium, but Dr. Beath of the Research Chemistry Department, University of Wyoming, suggests the following tentative limits of selenium in water for irrigation (3652):

Irrigation Class	Selenium in mg/l	Remarks
1-low	0.00 - 0.10	No plant toxicity anticipated
2-medium	0.11-0.20	Usable, but with possible long-term accumulations under particular conditions should be watched
3-high	0.21-0.50	Doubtful-probable toxic accumula- tion in plants except under espe- cially favorable conditions
4-very high	over 0.50	Non-usable under any conditions

c. Stock and Wildlife Watering. Selenium poisoning ("alkali disease" or "blind staggers") occurs frequently among livestock in the Great Plains regions of the United States and Canada, and also in Mexico. It can be produced in laboratory rats, as well as livestock, by feeding abnormal amounts of inorganic selenium compounds or seliniferous feed. In general, the soil in affected areas contains 1 to 6 mg/kg of selenium in the top eight inches, but higher values have also been found. Not all such soils give rise to toxic vegetation, partly because of differences in the solubility of the selenium compounds present and their availability to plants. Where poisoning is prevalent, samples of vegetation have been found to contain as little as one mg/kg of selenium. About four mg/kg appears to be the tolerance limit for livestock. Acute poisoning is caused by ingesting large amounts.

Selenium poisoning occurs naturally among cattle, sheep, horses, pigs, and even poultry, in both chronic and acute forms. It is characterized by loss of hair from mane and tail and soreness of the feet, as well as by deformity, loss of condition, and emaciation. Among poultry, the eggs give rise to abnormal or weak chicks

(1049, 1328).

Impairment of vision, weakness of limbs, and respiratory death have resulted from livestock feeding on plants containing 100 to 1000 mg/kg of selenium. At lower concentrations in vegetation, up to 24 mg/kg, livestock is subject to "alkali disease" involving lack of vitality, loss of hair, sterility, lameness, and possibly death from anemia and malnutrition (2129).

Rats show toxic effects from diets containing 3 to 40 mg/kg of selenium. A dose of 4 grams of powdered selenium introduced into a dog's stomach appeared to be harmless; but 4 mg of soluble selenate per kilogram of

body weight was quickly fatal (353).

The lethal dose of selenium salts for cattle is believed to be 2 mg per animal pound (1003). As sodium selenite administered by mouth, the minimum lethal dose of selenium for horses is about 1.5 mg per kilogram of body weight; for cows and calves, 4.5 to 5.0 mg per kg; and for pigs, 6 to 8 mg per kg. Chronic poisoning of cattle has been caused by as little as 1 to 4 mg/kg of selenium in fodder (1049). Milk from cows in poisoning areas contains 0.3 to 1.2 mg/l of selenium (1049).

In water, 0.4 to 0.5 mg/l of selenium is believed to be non-toxic to cattle. Such water may contribute to selenium poisoning, but the selenium content of the feed is

a more critical factor (997, 1003).

The toxicity of 9 to 18 mg/kg of selenium in the dry ration of rats, pigs, and dogs has been counteracted by various arsenic compounds administered in the drinking water (see also Arsenic) (921, 1005).

Selenium in the dry ration at a concentration of 0, 2, or 4 mg/kg did not affect the health of poultry or the hatchability of eggs. Chicks fed 5-8 mg/kg of selenium showed no harmful effects. A concentration of 5 mg/kg (dry ration) should be considered the toxic threshold for poultry (1551).

Kohlmeyer and Moxan found that 5 mg/kg of selenium (dry ration) did not affect the hatchability of turkey eggs, but 9 mg/kg caused abnormalities in young

turkeys (1551).

An increase in mortality among rats fed a ration containing 11 mg/kg of Se has been caused by the presence in drinking water at concentrations of 5 mg/l of various chemicals. The presence of 5 mg/l of soluble tungsten in the drinking water reduced the mortality slightly. For a comprehensive presentation of the selenium problem, particularly in feeds, the reader is referred to the paper by Moxan and Rhian (1481).

d. Fish and Other Aquatic Infe. Added as sodium selenite, 2.0 mg/l of selenium has been toxic to goldfish in eight days, and lethal in 18 to 46 days (353). Minute concentrations of selenium appear not to be harmful to fish during an exposure period of several days; however, constant exposure to traces of selenium has caused disturbances of appetite and equilibrium, pathological changes, and even deaths of fish after several weeks. Concentrations considered safe for human beings over a period of weeks have been toxic to fish (770, 3203).

Barnhart (3653) describes a reservoir in Colorado that has been stocked repeatedly with a variety of game fishes, but the fish die in a few weeks. Bottom deposits in the reservoir contain high concentrations of selenium. It is believed that selenium is passed up through the food chain to the fish which accumulate this element in the liver in lethal concentrations.

Using water from the River Havel, from which the test organisms had been recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effect of selenium added as sodium selenite. For Daphnia the median threshold effect for a 48-hour exposure at 23°C occurred at 2.5 mg/l of selenium; for Scenedesmus exposed at 24°C for 4 days, the median threshold level was also 2.5 mg/l as selenium; but for Escherichia coli at 27°C it was 90 mg/l of selenium, and for a protozoan (Microregma) it was 183 mg/l.

#### SESONE

(see Chapter IX)

### SETTLEABLE SOLIDS

(see also Suspended Solids, Silt)

Settleable solids may consist of sewage and industrial sludges, including many kinds of suspended solids that tend to settle out slowly on the stream bottom, thereby smothering bottom organisms, covering and destroying spawning beds, blanketing bacteria, fungi, and decomposing organic wastes, and in general trapping and maintaining offensive and deleterious stream conditions. Deposits of solids interfere with recreation, navigation, fish and shellfish production, and destroy esthetic values

of water. They may decompose to produce putrefactive odors and they may exude products of decomposition to overlying waters (611, 664, 673, 684, 780, 781, 782, 783, 2407, 3654, 3655).

Ellis has recommended that the stream bottom should not be blanketed to a depth of more than one-quarter of an inch by sedimentary deposits in order to prevent destruction of bottom fauna and shellfish (347).

According to many authorities, settleable solids should be removed from sewage and effluents before discharge into streams or ocean, or on land for irrigation purposes (784, 785, 786, 787, 788). Several alternative recommendations or practices have been mentioned in the literature, and most standards or criteria for streams include a provision that wastes discharged thereto should not form sludge banks or deposits. In this connection it is significant to recognize that dissolved or colloidal solids may be synthesized by bacteria in a stream to form suspended and settleable sludge consisting primarily of bacterial and biological slimes. Sulfite waste liquors, for example, contain little or no settleable solids but they can result in sizeable sludge deposits as a result of biological action in the stream (7).

Specific limiting or threshold concentrations of settleable solids permitted in natural waters are not to be found in the literature. Instead, it is generally required that settleable solids be removed from sewage or industrial wastes.

#### SEVIN

(see Chapter IX)

## SILICA AND SILICATES

SiO₂, SiO₃--

- 1. General. The element silicon is not found free in nature but it occurs as silica in sand or quartz and as silicates in feldspar, kaolinite, and other minerals. Silicon dioxide, or silica, is insoluble in water or acids, except hydrofluoric, but it may occur in natural waters as finely divided or colloidal suspended matter, in concentrations of one to 40 mg/l (32, 2342). Silicon is used in metallurgy and silica is widely employed in industry for making glass, silicates, ceramics, abrasives, enamels, petroleum products, etc. (364). Silicates have been used in water treatment as coagulants and corrosion inhibitors while sodium silicofluoride has been used as a fluoridating agent.
- 2. Cross Reference. Turbidity, Suspended Solids, Silt.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Sodium silicates have been used as coagulants for the removal of turbidity and iron (1332) and dosages of 4.0 to 8.0 mg/l have been used to form protective coatings on pipes to inhibit corrosion of iron (206, 1333, 1334, 3305, 3656) or lead (1335). In concentrations found in natural or treated waters, silica or silicates appear to have caused no adverse physiological effects (36). According to Raux (178), silica in a concentration greater than 50 mg/l may cause difficulties arising from turbidity. When municipal water is used for boiler feed water, however, the presence of silicates may be detrimental (see below).

b. Industrial Water Supplies. A summary of the recommended limits of silica in water for various industrial processes, as discussed in Chapter V, is presented below:

Industrial Use	Recommended Limit in mg/l
Brewing	50
Boiler feed water, 0-150 psi	40
150-250 psi	20
250-400 psi	5
400 psi and over	1
Pulp and paper mills:	
Groundwood pulp	50
Soda and sulfate pulp	20
Kraft pulp, bleached	50
Kraft pulp, unbleached	100
Fine paper	20
Rayon pulp production	25

Silica appears to be particularly undesirable in boiler feed waters (212, 1336, 1337, 1338) because it passes over in the steam and deposits in the tubes of heaters and on steam-turbine blades. Silica appears to have a volatility or solubility in steam (3657), for as much as 0.4 mg/l of silica per ml of steam has been found leaving the boilers, according to Schwartz (1339), who found that silica in boiler feed water gave the following concentrations in condensate:

Silica in	Silica in
Feedwater, mg/l	Condensate, mg/l
25	0.43
100	0.07 to 0.90
200	1.8

For the maximum concentration of silica in boiler feed water, Reichelt (1689) recommended 0.5 mg/l while Stassart (1690) preferred a limit of 0.3 mg/l for high-pressure boilers. Imhoff (1340) suggested that the silica content of steam be kept below 0.1 mg/l to control turbine-blade deposits at operating pressures of 350 psi.

c. Irrigation. Silica, per se, is generally considered to be of little importance in irrigation practice (268). Limits for several constituents suggested for irrigation water by the U.S. Department of Agriculture include silica at 10 to 50 mg/l.

d. Fish and Other Aquatic Life. An abundance of silica in water, along with other necessary nutrients, favors the growth of diatoms (36, 1287) (see also Silt, Turbidity, and Suspended Solids). Indeed, blooms of diatoms synthesize silica into the tests of the organisms and thereby lower the content in the water. The diatom Asterionella, and possibly other algae, require silica in concentrations above 0.5 mg/l for growth in ponds, and cannot utilize silica when present at lower concentrations (1453). For factors by which silicon (radioactive or otherwise) is concentrated from water into biological forms, see Chapter VIII.

#### SILICON

(see Silica and Silicates)

#### SILT

1. General. By the term "silt" is meant loose sedimentary material, rock particles, mud, or clay that settle readily and may be transported by bed-load movement. Silt results from erosion, logging, mining, dredging, or irrigation operations, steel mills, gravel washing, the

precipitation of certain industrial dusts, such as those from limestone saw-mills, and also from operations in cotton and wool-cleansing plants (779, 2194, 2879, 3655, 3658, 3659). Fine silt may stay in suspension and be classified as "suspended solids", while the larger particles settle to the bottom of the water course. Like other suspended solids in streams, silt may have far-reaching effects on the nature and biota of the stream by reducing the amount of light transmitted by the water, by altering the rate of temperature change in water strata, by adsorbing organic matter and other substances that create unfavorable conditions on the bottom, and by blanketing the stream bottom (2183). Although a moderate amount of silt may have a beneficial effect on aquatic life by increasing the amount of mineral nutrients available (789), excessive quantities have been reported to affect deleteriously all of the desirable uses of water (346, 780, 781, 790, 2879, 2895, 3654, 3660, 3661).

- 2. Cross References. Suspended Solids, Settleable Solids, Turbidity.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Silt and mud are undesirable in domestic and industrial water supplies, and the cost of removing mud from water may exceed all other costs in making water suitable for use (780).
- b. Irrigation. Mud constituents of water can fertilize the soil and may also be valuable for closing up cracks in the earth channels of water. However, grit and sand may injure crops (791). Silt from fertile land is beneficial, but silt from the subsoil of eroded areas deposited on the surface of productive soils can markedly decrease their productivity (246). Silt consisting of clay-like matter can result in the packing of sediment on soil to form an impervious blanket, keeping air and water out of the soil (792). Over a three-year period of observation, silty water did not affect the yields of corn as compared with the yields from plots irrigated with clear water; however, oat fields were reduced when sediment was deposited in sufficient quantities before germination to prevent the emergence of the seedlings; and heavy silting killed bean plants grown in furrows, but not those grown on ridges (793).
- c. Aquatic Life. Silt in water reduces light penetration, alters the rate of temperature change in different water levels, and carries organic wastes to the bottom where processes of decay may continue to operate over a long period, leading to oxygen depletion, changes in pH, and other unfavorable conditions. Erosion and silting hinder fish production, smother food organisms, destroy spawning grounds, and fill pools (308, 611, 781, 790, 794, 795, 796, 797). Smith has reported that silting has reduced the bottom fauna of the Rogue River by 25 to 50 percent (798). According to Ellis, hard particles cause abrasive injuries to the delicate external organs, such as gills, spiracles, and fins, of miscellaneous aquatic animals, and fine particles tend to coat and destroy fish eggs (347, 799, 800). Ellis has recommended, therefore, that suspensoids of a hardness of one or more should be so finely divided as to pass through a 1000-mesh screen, and that the stream bottom should not be blanketed to more than one-quarter of an inch (see also Turbidity) (313, 347, 801).

Salmon and trout can withstand a heavy load of silt for several weeks; nevertheless, by limiting successful reproduction and the food supply, silting is harmful to fish (800). Ward (560, 882) agrees that silt deposits may smother spawning beds and nests, but believes that natural and mining silts are not always inimical to fish life; they may possibly be beneficial because of the food organisms and particles they carry and because muddy waters afford protection to fish against predatory animals and anglers. Ward cites experiments in which young salmon were maintained for three to four weeks without harm in circulating water containing a suspension of mud in a concentration above 1000 mg/l. Griffin (802) has reported experiments of three to four weeks' duration in which trout and salmon fingerlings fed and grew apparently well in muddy water carrying a constant silt load of 300 to 750 mg/l, and for short intervals daily during stirring, a load as high as 2300 to 6500 mg/l (For comparison, the Willamette River in heavy flood, when it appeared muddy, carried a silt concentration of only 42 mg/l).

Ziebell (2687) and Wagner (3662) measured the productivity in terms of aquatic insect populations upstream and downstream from a gravel dragline operation. He found a productivity decline of 85 percent as a result of the gravel operation. Turbidities were increased from zero to 91 mg/l and suspended solids from 2 mg/l upstream to 103 mg/l downstream. Tarzwell (2407) cites an instance where bottom samples from a silted area averaged only 36 organisms per sq ft whereas in a clean

stream bottom the average was 249 per sq ft.

d. Shellfish Culture. Most fresh-water mussels have been unable to maintain themselves in either sand or gravel bottoms when a layer of silt one-quarter to one inch deep was allowed to accumulate on the surface (790). Silt deposits can smother both mussels (331, 795, 798) and oysters (332, 790). Silt in suspension chokes the respiratory and intestinal passages of young shell-fish (314, 332, 803). Silt concentrations from 1000 to 4000 mg/l have depressed the pumping and feeding rate of oysters as much as 94 percent; and in heavy suspensions oysters have been stopped feeding entirely (804). On the other hand, some species of oysters thrive in silt-laden water (315, 804), and silt from dredging operations in the Susquehanna River did not cause oyster deaths (795).

As little as 100 mg/l of silt or other turbidity-producing substance seriously reduces the pumping rate of oysters to as low as 40 percent; 1000 mg/l caused a drop to 20 percent of the normal rate; and 3000-4000 mg/l resulted in a reduction to 4 percent. Silt, kaolin, and chalk all gave comparable results. When the oysters were returned to clear water, however, they resumed their

normal pumping (1448).
e. Recreation and Navigation. Silt

e. Recreation and Navigation. Silt and mud destroy esthetic values and produce deposits in harbors that cause significant economic losses (780, 781, 1033).

Ag

#### SILVER

1. General. In nature, silver is found in the elemental state and combined in ores such as argentite, Ag₂S, horn silver, AgCl, proustite, Ag₃AsS₃, and pyrargyrite, Ag₃SbS₃. From these ores, silver ions may be leached into

ground waters and surface waters, but since many silver salts such as the chloride, sulfide, phosphate, and arsenate are insoluble, silver ions cannot be expected to occur in significant concentration in natural waters. Nine municipal water supplies in the U.S. have shown the presence of 0.05 mg/l of silver ion and at Denver the concentration is reported as 0.2 mg/l (152). Silver nitrate is highly soluble and silver sulfate moderately so (1224).

Silver metal is used in jewelry and silverware, in alloys, for electroplating, and in the processing of food and beverages. Silver nitrate is used in photography, ink manufacture, electroplating, coloring porcelain, and as an antiseptic (364, 2121). From such sources, traces of

silver can be expected to reach natural waters.

2. Cross References. Nitrates.

3. Effects on Beneficial Uses.

a. Domestic Water Supplies. Silver oxide has been used for water purification at Warsaw, Poland, and other cities. There is abundant literature on the oligodynamic action of silver and its bactericidal power, but a review of such literature is beyond the scope of this report. Dosages of 0.000001 to 0.5 mg/l of silver have been reported as sufficient to sterilize water (577, 1341, 1342, 1343, 3408, 3663, 3664, 3665). At such dosage rates, silver is not an irritant, has no toxic action toward humans, and does not interfere with the taste (1344). The fatal dose of silver nitrate for humans has been reported as 10 grams (2129).

Silver occurs in soil humus up to 5 mg/kg, in grain and cereals up to 0.9 mg/kg, and in mushrooms up to several hundred mg/kg (2121). Silver nitrate solution has been used as an antiseptic, especially in the upper

respiratory system.

Prior to 1962, no restriction was placed on silver in the USPHS Drinking Water Standards (2036), nor does any limitation presently appear in the WHO International or European standards (2328, 2329). The 1962 edition of the USPHS Standards (2036) sets a mandatory limit of 0.05 mg/l of silver. Presumably, this restriction was set not because of the danger of silver in natural sources of water supply but to prevent its intentional addition to water, in excessive amounts, for disinfection. The limit was based on cosmetic considerations rather than public-health effects.

The chronic administration of silver salts, not uncommon in the early part of the 20th century, led to a bluish permanent darkening of the skin called "argyria". With prolonged administration of silver salts, a small proportion is absorbed and deposited in the skin where it is reduced by light to metallic silver (2129). This impregnation of the tissues with silver causes no recognizable disturbance to health (3704), but is obviously undesirable from an esthetic viewpoint. Although the total dosage of ingested silver required to produce argyria is not known, the intravenous injection of 1 gram will cause this effect. Based on the USPHS limit of 0.05 mg/l of silver and two liters per day of water consumption, it would take over 27 years to ingest one gram of silver, a large part of which would pass through the intestinal tract without assimilation (2121). This calculation ignores the daily intake of silver from food, which might be appreciable for mushroom lovers.

b. Fish and Other Aquatic Life. Using silver nitrate, Marsh and Robertson (1459) found that 0.04 mg/l killed some (but not all) test salmon fry in tap water within 48 hours; 0.44 mg/l of silver nitrate proved decidedly toxic. A concentration of 0.033 mg/l of silver nitrate did not prove fatal in 48 hours. The highest concentration of silver nitrate tolerated by young eels for more than 24 hours was reported to be about 0.2 mg/l. Toward guppies, the LD₅₀ value was found to be 0.0043 mg/l, as silver (2921).

Jones (1460) found that the lethal concentration limit of silver applied as silver nitrate, for sticklebacks at 15-18°C was 0.003 mg/l. In different concentrations of silver the average survival times of the fish were as follows: one week at 0.004 mg/l, four days at 0.01 mg/l and only one day at 0.1 mg/l, as silver. Anderson (598) reported that the toxic threshold of silver nitrate for

sticklebacks was 0.0048 mg/l.

The level of toxicity of silver toward lower organisms has been reported by several observers. Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of silver, added as silver nitrate, on various species during a 4-day exposure, at 23-27°C. For Daphnia and for Microregma the median threshold effect occurred at 0.03 mg/l of silver, for E. coli at 0.04 mg/l, and for Scenedesmus at 0.05 mg/l. Jones (608) tested the toxicity of silver nitrate toward Polycelis nigra, a flatworm, and found the threshold concentration to be 0.15 mg/l of silver. Toward Daphnia magna in Lake Erie water at 25°C, the threshold for immobilization was reported (598) to be 0.0051 mg/l of silver nitrate. Hodgson (2956) studied the stimulating effects of several substances on the water beetle, Laccophilus maculosus. He found that 580 mg/l of silver nitrate stimulated 50 percent of the beetles into movement, but no lethal dose was reported.

The Severn and Mersey River Boards in England (2950) have set working standards of 1.0 mg/l on the

total of all heavy metals, including silver.

#### SILVEX

(see Chapter IX)

#### SIMAZINE

(see Chapter IX)

## SINOX

(see Chapter IX)

#### SKATOLE

 $C_9H_9N$ 

This constituent of coal tar, feces, and some plants is soluble in hot water, giving a fecal odor (364). The odor is detectable at a concentration of 0.0012 mg/l (1756).

### SLAKED LIME

(see Calcium Hydroxide)

#### SOAPS

(see also Chapter X)

Soaps are salts of fatty acids, usually made by the saponification of a vegetable oil with sodium hydroxide.

They may be formed also by resinous acids in the Kraft

process at paper mills.

Toward fish, crude sulfate soap from Kraft mill wastes had a minimum lethal concentration of 5.0 mg/l toward minnows and shiners, according to research by the National Council for Stream Improvement (190, 344, 574, 658, 690, 3500, 3523). LeClerc and Devlaminck (3666) report that for minnows the minimum lethal concentration of sodium palmitate and sodium oleate was 10-12 mg/l in distilled water and 900-1000 mg/l in hard water. For sodium stearate it was 10-12 mg/l in distilled water and 250-300 mg/l in hard water. The effect of water hardness was confirmed by Henderson et al. (1910) who found that the 96-hour TLm values for three packaged soaps ranged from 29 to 42 mg/l in soft water but averaged 1470 mg/l in hard water. Soaps form insoluble complexes or precipitates in hard water which are apparently non-toxic to fish. The pure compound, sodium stearate, was somewhat less toxic than the packaged soap products

Cole (311) claims that dairy wastes contain soaps that are toxic to fish at 600 mg/l and Schaut (362) reports that soapy waste waters at a dilution of 1:240 had no effect on minnows. Turnbull et al. (2093) reported that the 48-hour TL_m of truck-washing soap solution toward bluegill sunfish at 20°C occurred at dilutions of 1:357 to 1:416.

Toward other aquatic organisms, crude sulfate soap from Kraft mills had a  $TL_m$  of 50 mg/l for Chironomus larvae, 10 mg/l for mayfly larvae, and 5.0 mg/l for Daphnia magna (190, 574, 690, 3500, 3523). Soaps in concentrations of 1000 to 2500 mg/l were lethal to mosquito pupae by reducing the surface tension of the water so that the pupae were unable to maintain their position and suffocated (805). Solutions containing 5,000 to 10,000 mg/l were directly toxic to the pupae. In another instance (756) soap in a concentration of 2000 mg/l completely destroyed mosquito larvae and pupae.

## SODA PULP MILL WASTE

(see Kraft Pulp Mill Wastes)

#### SODIUM

N

1. General. This very active metal does not occur free in nature, but sodium compounds constitute 2.83 percent of the crust of the earth (364). Owing to the fact that most sodium salts are extremely soluble in water, any sodium that is leached from soil or discharged to streams by industrial wastes will remain in solution. Some sodium may be removed by ion-exchange phenomena in the passage of ground waters through certain soils. For other effects of sodium on soils, see Chapter V—Agricultural Supply.

Sodium is the cation of many salts used in industry and as such is one of the most common ions in process wastes. The information presented below pertains to literature in which the sodium ion, per se, was mentioned without reference to the sodium salt. Where concentrations were given in terms of the salt, the literature has been abstracted under the appropriate sodium com-

pound.

2. Cross References. Sodium Salts, Potassium, Dissolved Solids, Chapter IV, Chapter V.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Sodium in drinking water may be harmful to persons suffering from cardiac, renal, and circulatory diseases (1242, 3667), and as much as 200 mg of sodium from drinking water may be injurious (152). Although it has been reported (627) that drinking water of good quality may contain up to 115 mg/l of sodium, Hibbard (250) recommends a limit of 10 mg/l as desirable. According to Lockhart et al. (3241) the taste threshold of sodium in distilled water varies with the sodium salt used, as follows:

Salt Tested	Taste Threshold of Sodium in mg/l
Sodium acetate	140
Sodium carbonate	34
Sodium bicarbonate	290
Sodium chloride	135
Trisodium phosphate	75

b. Industrial Water Supplies. More than 50 mg/l of sodium plus potassium in boiler waters may cause foaming (1214). Other limitations for sodium, as given in Chapter V, are expressed in terms of the sodium salts (see Sodium Chloride, Carbonate, and Sulfate).

c. Irrigation. Sodium is required in very limited amounts for most plant growth (3634). An exception is the desert plant, halogeton, which apparently needs sodium for optimum growth (3668). In high concentrations sodium is not only toxic to plants but deleterious to soil conditions (268, 635, 1322) (see also Chapter V—Irrigation). Sodium carbonate and bicarbonate are more harmful than other sodium salts to plants (273). On a weight basis, chlorides are generally more toxic to plants than sulfates, but at equal osmotic pressures, sodium sulfate appeared to be more injurious to flax than sodium chloride (1093).

High concentrations of sodium (e.g. 106-212 mg/l) in water used for sprinkler irrigation can, under certain conditions and with a few plants, cause deleterious accumulations of sodium in the foliage (3669, 3670). Sufficient sodium has been absorbed by citrus leaves from a single sprinkling with water containing 69 to 190 mg/l of sodium to cause serious leaf burn and defoliation (3670).

Sodium-saturated soils are greasy to feel. Sodium soil colloids swell, closing the pores of the soil, reducing soil permeability to water and air, and increasing the pH of the soil solution to dangerous levels. The deterioration of soil quality because of sodium in the irrigation water is a steadily cumulative process, with impaired drainage resulting in even more highly concentrated soil solutions (280).

Kelley reported that an average concentration of 82 mg/l of sodium in water from the Colorado River was not expected to affect seriously either the growth of citrus trees or soil conditions in the South Coastal Basin of California (1060). For an instance where sodium figured prominently in a court case, see Barakis vs American Cyanamid Co. in Chapter IV.

d. Stock and Wildlife Watering. Excess concentrations of various sodium salts in the drinking water are deleterious to various animals. Well waters containing 7000 mg/l of sodium were toxic to chicks (1551). A threshold limit of 2000 mg/l of sodium for livestock has been suggested by Stander (3373). For further details,

see Sodium Salts, Dissolved Solids, Chapter V. Sodium bicarbonate is less injurious than sodium carbonate (640).

e. Fish and Other Aquatic Life. Of the United States waters supporting a good fish fauna, ordinarily the concentration of sodium plus potassium is less than 6 mg/l in about 5 percent; less than 10 mg/l in about 50 percent; and less than 85 mg/l in about 95 percent (310).

The toxicity threshold of sodium for Polycelis nigra is 4370 mg/l from sodium ehloride, and 1000 mg/l from sodium nitrate (353, 608). A sodium concentration of 500 mg/l is lethal to stickleback (353). On the other hand, moderate amounts of sodium in water may reduce the toxicity of potassium and ammonium salts toward fish (306).

The possible accumulation of radioactive sodium (Na-24) in aquatic life, fish, or oysters is not considered to be hazardous owing to the short half life (about 15 hours) of radiosodium (2442).

Several investigators have reported independently that 500-1000 mg/l of sodium was toxic to fish in distilled and soft waters when sodium chloride or nitrate was tested 1450, 2941). However, Gueylard reported as harmless to sticklebacks concentrations up to 4720 mg/l of sodium in distilled water and up to 7870 mg/l in tap water when sodium chloride was added (1459).

Freeman and Fowler (1691), using a standardized double-distilled water, studied the toxicity of five inorganic sodium salts to Daphnia magna at 23°C. The 100-hour toxicity thresholds were determined for each salt alone, in combinations of two, and in combinations of three. The 100-hour toxicity threshold was defined as the concentration that will immobilize 50 percent of the organisms in 100 hours. Rather than list their results separately under the specific sodium salts involved, all of their data are presented under this heading in order that the magnitudes can be compared. For each of the five salts tested singly, the 100-hour toxicity thresholds and the resulting pH values are shown in the following tabulation:

Compound Tested	100-Hour Toxicity Threshold in mg/l	pH at $Threshold$
Sodium bisulfite	102	7.3.
Sodium carbonate	524	9.5
Sodium chromate	0.42	7.8
Sodium silicate	247	9.1
Sodium sulfate	4547	7.7

When these salts were tested in combinations of two, the results were as follows:

results were as	TOHOWS.	
Compounds $Tested$	100-Hour Toxicity Thresholds in mg/l	pH at $Threshold$
Sodium bisulfite Sodium carbonate	85 <b>43</b> 6	9.2
Sodium bisulfite Sodium chromate	70 0.286	7.3
Sodium bisulfite Sodium silicate	177 427	7.5
Sodium bisulfite Sodium sulfate	82 3642	7.5
Sodium carbonate Sodium chromate	$\begin{array}{c} 408 \\ 0.33 \end{array}$	9.3
Sodium carbonate Sodium silicate	180 85	9.3

Compounds Tested	100-Hour Toxicity Thresholds in mg/l	pH at Threshold
Sodium carbonate Sodium sulfate	221 1918	9.2
Sodium chromate Sodium silicate	0.159 93	8.7
Sodium chromate Sodium sulfate	0.276 $2984$	7.9
Sodium silicate Sodium sulfate	158 2899	9.0

In combinations of three, the toxicities of the sodium salts were as follows:

Compounds Tested	100-Hour Toxicity Thresholds in mg/l	pH at $Threshold$
Sodium bisulfite Sodium carbonate Sodium chromate	87 440 0.35	9.3
Sodium bisulfite Sodium carbonate Sodium silicate	38 194 92	8.8
Sodium bisulfite Sodium carbonate Sodium sulfate	58 295 2562	9.0
Sodium bisulfite Sodium chromate Sodium silicate	144 0.861 506	6.9
Sodium bisulfite Sodium chromate Sodium sulfate	75 0.306 8312	6.9
Sodium bisulfite Sodium silicate Sodium sulfate	52 126 2308	8.5
Sodium carbonate Sodium chromate Sodium silicate	182 0.146 86	9.1
Sodium carbonate Sodium chromate Sodium sulfate	$240 \\ 0.192 \\ 2079$	9.3
Sodium carbonate Sodium silicate Sodium sulfate	155 73 1343	8.8
Sodium chromate Sodium silicate Sodium sulfate	0.201 119 2180	8.5

From the foregoing tabulations it is noted that the toxicity of sodium salts depends largely on the anion involved, the chromate being exceedingly toxic and the sulfate least so. Moreover, there appears to be no correlation between the toxicity displayed and the pH value, but since Daphnia magna is known to live within the pH range 6.2-9.5, which embraces all of the foregoing results, pH was apparently not the sole cause of mortality. It is also noted that the thresholds for specific compounds are lower when tested in combinations of two or three with the exception of sodium bisulfite with sodium silicate, or with sodium silicate and sodium chromate. This latter variation may be attributable to the possible oxidizing action of the chromate on the bisulfite (1691).

## SODIUM ACETATE NaC₂H₃O₂·3H₂O

Highly soluble in water, this compound is used as a mordant in textile dyeing, as a buffering agent in chemical production, in photography, and in medicine as a diuretic, expectorant, or alkalizer (364). According to Lockhart et al. (3241), the taste threshold of the anhydrous salt is 500 mg/l, or for the crystalline form 830 mg/l. Hodgson (2956) studied the stimulating effects of

sodium acetate on the water beetle (Laccophilus maculosis) and found that a concentration of 32,600 mg/l was required to stimulate the movement of 50 percent of the beetles.

## SODIUM ACID PYROPHOSPHATE Na₂H₂P₂O₇

Soluble in water with an acid reaction, this white fused substance is used chiefly in baking powder (364). A concentration of 400 mg/l in sea water caused a decrease in irritability of oysters, but 500 mg/l caused oyster deaths within 44 hours (1448, 1467).

#### SODIUM ALKYL ARYL SULFONATE

#### SODIUM ALKYL BENZENE SULFONATE

#### SODIUM ALKYL SULFATE

(see Chapter X)

#### SODIUM ALUMINATE

NaAlO₂

This highly soluble salt is used in water treatment, for sizing in paper mills, and for printing in textile plants (364). Wallen et al. (2940) tested its toxicity toward mosquito-fish (Gambusia affinis) in turbid water at 17-19°C. They found 24-, 48-, and 96-hour TL_m values of 199, 126, and 111 mg/l respectively. This salt coagulated the water and reduced turbidity.

#### SODIUM ANTHRAQUINONE-α-SULFONATE

# SODIUM ARYL ALKYL POLYETHER SULFONATE

(see Chapter X)

#### SODIUM ARSENATE

Na₂HAsO₄

(see also Arsenic, Arsenic Trioxide, Sodium Arsenite)

This colorless, odorless salt, readily soluble in water, is used in dyeing and printing fabrics and in various fungicides and insecticides.

It is not highly toxic to fish or other aquatic life. According to Jones (2120) the lethal concentration of sodium arsenate toward minnows at 16-20°C is 234 mg/l, as arsenic. It has also been reported (617) that minnows survived for 16 hours in a solution of sodium arsenite equivalent to 250 mg/l of arsenic.

Toward lower forms of aquatic life, the toxicity of sodium arsenate is variable. The threshold concentration for immobilization of *Daphnia magna* in Lake Erie water has varied from 18 to 31 mg/l as sodium arsenate, or 4.3 to 7.5 mg/l as arsenic (352, 353, 358). The toxic threshold for the flatworm *Polycelis nigra*, is reported to be 670 mg/l as AsO₄, or 361 mg/l as arsenic (354).

#### SODIUM ARSENITE

 $NaAsO_2$ 

(see also Arsenic, Arsenic Trioxide, Sodium Arsenite)

Freely soluble in water, sodium arsenite is used in dyeing, in arsenical soap making, in termite extermination, and in weed-killers. As a commercial preparation it is often a mixture of several sodium and arsenic compounds. Therefore, references to sodium arsenite solutions are often reported in terms of arsenic concentration or as arsenic trioxide equivalents.

Sodium arsenite has been used extensively as a herbicide for the control of mixed submerged vegetation in static water. Commercial sodium arsenite contains varying amounts of other arsenic compounds and impurities; hence it is labeled in terms of equivalent arsenic trioxide (As₂O₃). For the control of submerged vegetation in ponds and lakes, applications of 2 to 5 mg/l as arsenic trioxide (1.5 to 3.8 mg/l as As) have been found effective. Although these concentrations are generally considered to be safe for fish and other aquatic animals, it is advisable to spray only a part of the pond or lake at one time so that fish may avoid the sprayed area. Fish are reported to be sensitive to sub-lethal doses of sodium arsenite and will generally swim away into fresh water (890, 2861, 3671). Commercial sodium arsenite in concentrations up to 10 mg/l (arsenic content not stated) have been used for weed control in Wisconsin lakes without harm to the fish population (1006).

The following concentrations of sodium arsenite, expressed as arsenic, have been reported as lethal, toxic, or otherwise deleterious to aquatic organisms:

	1		
Concentration,	,		,
as Arsenic,	Time of		
mg/l	Exposure	Organism	Reference
1.0-2.0		Fish	1692
1.4-2.3		Fish food organisms	574, 1007
1.9-3.0		Midges, mayflies,	514, 1007
		amphipods	3009
4.6	48 hours	Daphnia	2158
5.0	10 days	Pink salmon	2091
5.0	48 hours	Microregma	
		(protozoan)	33 <b>4</b> 3
5.2	<del></del> -	Daphnia magna	352
8.4	48-hour $\mathbf{TL}_{\mathbf{m}}$	Chum salmon frv	2900
15	48 & 72-hour TLm	Fingerling channel	-000
450		catfish	2981
17.8		Minnow	2920
20	36 hours	Rainbow trout,	
20	00.	minnows	3005
	36 hours	Minnows	617
27	72-hour TLm	Minnows	3672
27.6	$24$ -hour $\mathrm{TL}_{\mathrm{m}}$	Fingerling channel	
29	40:	catfis <u>h</u>	2981
	48-hour TLm	Minnows	3672
35-46	48 hours	Scenedesmus	2158
45	24-hour TL _m	Minnows	3672
290	48 hours	Escherichia coli	2158

The literature on weed control contains statements that applications of sodium arsenite up to 10 mg/l as  $As_2O_3$  (7.6 mg/l as As) are not harmful to fish, but the foregoing table would indicate that the threshold level is somewhat lower than expected. Furthermore, fish-food organisms are susceptible at concentrations as low as 1.0 mg/l.

On the other hand, the following concentrations of sodium arsenite, expressed as arsenic, have been reported to have no harmful effects on the organism noted:

Concentration, as Arsenic, mg/l	Time of Exposure	Organism Re	ference
1.3		Fish or fish-food organis	
1.3-1.5		Fish-food organisms	1007, 1008
1.4-2.9		Fish	416
2.9		Chironomus larvae	574
5.0	24 hours	Trout, bluegills, sea	0,1
		lamprey	2976
8-16		Damselflies, dragonflies,	
		sowbugs, water mites	3009
15	96 hours	Minnows	3672

Lawrence (3673, 3674) reports that two applications of 4 mg/l of sodium arsenite applied one month apart in experimental ponds reduced the number of bottom organisms an average of 34 percent and reduced bluegill production an average of 42 percent as compared with control ponds. Two applications of 8 mg/l of sodium arsenite applied one month apart reduced the number of bottom organisms an average of 45 percent and bluegills 65 percent as compared with control ponds. An application of 4 mg/l killed all microcrustacea and greatly reduced the population of rotifers.

#### SODIUM AZIDE

 $NaN_3$ 

Highly soluble in water, this crystalline solid is used in chemical manufacturing and in medicine as a hypotensive agent (364). Using water of the River Havel, Bringmann and Kuhn (2158, 3343) determined the thresholds of toxicity to be 0.3 mg/l for Daphnia, 3 mg/l for Microregma (a protozoan), 4 mg/l for Scenedesmus (an alga), and 19 mg/l for Escherichia coli. Toward trout, bluegills, and sea lamprey in Lake Huron water at 12°C, 5 mg/l of sodium azide had no apparent effect during a 24-hour exposure (2976).

#### SODIUM BENZENE SULFONATE

(see Chapter X)

#### SODIUM BENZOATE

C₆H₅COONa

(see also Benzoic Acid)

This highly soluble salt is used as a preservative in food products with concentrations up to 1000 mg/kg being permitted. The oral LD₅₀ for rats is given as 4100 mg/kg of body weight (364).

In Lake Erie water at 25°C, the threshold concentration of sodium benzoate for immobilization of *Daphnia* magna with 48 hours of exposure was less than 650 mg/l, and Anderson (352) estimated the true threshold concentration to be about 585 mg/l. Toxicity was due to factors other than osmotic pressure.

#### SODIUM BICARBONATE

NaHCO₃

1. General. This freely soluble salt dissociates completely in water into sodium and bicarbonate ions. The concentration of bicarbonate ions, in turn, depends upon the resulting pH value (see Bicarbonates, Carbonates). The bicarbonate acts as a powerful buffering agent. Sodium bicarbonate is used in the manufacture of many sodium salts, as a source of carbon dioxide, in fire extinguishers, in effervescent salts and baking powder, in cleaning compounds, and in many industrial processes.

Goudey (992) suggested classification of ground waters and included the following recommendations as to sodium bicarbonate limits: Class AA (domestic), 0 mg/l; Class A (irrigation), 0 to 50 mg/l; Class B (irrigation), 50 to 100 mg/l; and Class C (irrigation and industry), more than 100 mg/l.

- 2. Cross References. Sodium Carbonate, Bicarbonates. Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of sodium bicarbonate in water is reported (3241) to be 1060 mg/l.

- b. Industrial Water Supplies. It has been recommended (173) that the sodium bicarbonate concentration of raw water to be used for making ice not exceed 35 mg/l.
- c. Irrigation. Water containing sodium carbonate or bicarbonate as the predominant salts may be more harmful to plants than water with other sodium salts (273). Sodium bicarbonate, although it is an important buffer in water, may be directly or indirectly harmful to plants. It may be toxic, it tends to increase soil alkalinity, and in addition, by precipitating calcium carbonate out of solution, it reduces calcium concentration of the soil and soil permeability (264, 268). A concentration of 1500 to 2000 mg/l of sodium bicarbonate in the water has caused a 50-percent reduction in the dry weight of tomatoes grown in liquid culture (1345). In irrigation water 4000 mg/l has rendered soils alkaline and impaired their fertility (921).
- d. Stock and Wildlife Watering. The following concentrations of sodium bicarbonate in drinking water have been reported as injurious to animals by causing thirst, diarrhea, and impaired growth:

Concentration in mg/l	Animal	Reference
6000	Chicks	287, 284, 2980
15000	Rats	287, 284
20000	Rats	287, 284

Concentrations from 12,000 to 24,000 mg/l have caused

deaths among chicks (284).

e. Fish and Other Aquatic Life. The toxic threshold concentration of sodium bicarbonate for *Polycelis nigra*, a flatworm, was found to be 7140 mg/l (354). The threshold concentration of sodium bicarbonate for immobilization of *Daphnia magna* in Lake Erie water was reported to be 2350 mg/l (352) and 4200 mg/l (358). Cairns et al. (2933, 2934, 2935) found the 96-hour TL_m values for bluegill sunfish in standard dilution water at 20°C to be 8250 to 9000 mg/l depending on the size of the fish. Using highly turbid water at 20-22°C and the mosquito-fish as the test organism, Wallen et al. (2940) found the 96-hour TL_m to be 7550 mg/l. The 24-hour TL_m was 7700 mg/l.

#### SODIUM BIFLUORIDE

NaF·HF

(see also Sodium Fluoride)

This highly soluble powder produces an acid reaction in solution; hence it is used as a "sour" in laundrying (364). According to Simonin (3271) the fish *Tinca vulgaris* is killed by 100 mg/l of this compound.

#### SODIUM BISULFATE

NaHSO₄

(see also Sulfates, Sulfuric Acid)

Known also as sodium acid sulfate, this compound is freely soluble in water and dissociates into Na^{*} and HSO₄ ions. The concentration of the bisulfate ion in solution depends upon the resulting pH value and above pH4 almost all bisulfate will be converted to sulfate ion.

For immobilization of Daphnia magna, the threshold concentration of sodium bisulfate in Lake Erie water was found to be less than 145 mg/l (352). Later work by Fairchild (2946) showed that the threshold toxicity value is dependent on dissolved oxygen. For Daphnia

exposed 100 hours at 23°C, the threshold concentrations were as follows:

Dissolved Oxygen, mg/l	Threshold Level of Toxicity, mg/l
6.5	153
8.9	145
1.55	106

#### SODIUM BISULFITE

NaHSO₃

Used as a disinfectant and bleach in textile, laundering, paper, and fermentation industries, this compound is freely soluble in water, dissociating into Na⁺ and HSO₃⁻ ions. The concentration of the undissociated bisulfite ion depends upon the resulting pH value; furthermore, it is readily oxidized to sulfate (364).

The toxicity threshold (100-hours at 23°C) to Daphnia magna has been reported at 102 mg/l (1691), but in the presence of other sodium salts, this threshold may be somewhat lower (see Sodium). Fairchild (2946) also studied the toxicity of sodium bisulfite toward Daphnia at various concentrations of dissolved oxygen at 23°C, with the following results:

Dissolved Oxygen, mg/l	Threshold Level of Toxicity, mg/l
9.3	109
6.5	61
3.2	77
1.6	70

Le Clerc et al. (2942, 2943, 2944) exposed minnows for 6 hours to solutions of sodium bisulfite in distilled and hard water. The minimum lethal dose in distilled water at 19°C was 60-65 mg/l and in hard water at 18°C it was 80-85 mg/l. Using turbid water at 17-22°C and the mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values to be 240 mg/l. This concentration greatly reduced the turbidity.

### SODIUM BORATE

 $Na_2B_4O_7 \cdot 10 H_2O$ 

(see also Boron, Sodium Perborate)

Commonly known as borax, this compound is used extensively as a cleaning agent in homes and industry. It is also employed as a wood preservative, as a treatment against wood fungus, in tanning operation, and for the control of aquatic weeds (898). Certain other borates, such as phenyl mercury borate in a concentration of 10 mg/l, have been used effectively against the growth of slimes in pipes in paper mills (1346).

According to Le Clerc and Devlaminck (2942, 2943, 2944), the minimum lethal dose of sodium borate (Na₂B₄O₇·10H₂O) toward minnows was 3000 to 3300 mg/l at 19°C in distilled water and 7000 to 7500 mg/l at 17°C in hard water. Toward mosquito fish (Gambusia affinis) in turbid water, Wallen et al. (2940) found the 96-hour  $TL_m$  at 22-26°C to be 3600 mg/l.

With respect to lower aquatic life, sodium borate appears to be more toxic than towards fish. The threshold concentration for immobilization of Daphnia magna was reported (352) as being much less than 240 mg/l and was estimated at 120 mg/l (353). The toxic threshold concentration of sodium borate for Polycelis nigra, a planarian worm, was found to be 1530 mg/l as borate (354).

#### SODIUM BROMATE

NaBrO₃

(see also Bromine, Sodium Bromide)

Highly soluble in water, this crystalline salt is used in ore processing and for promoting the growth of yeast cells. The oral MLD for rabbits is given at 580 mg/kg of body weight (364).

## SODIUM BROMIDE

NaBr

(see also Bromine)

Used primarily in photographic work, this salt of bromine is highly soluble in water. In water supplies used for preparing photographic solutions, bromides slow up the rate of the chemical reactions (242). The toxicity threshold concentrations of sodium bromide reported for Daphnia magna in Lake Erie water at 25°C range from 4100 to 8200 mg/l (352, 353). The toxic threshold concentration of sodium bromide for Polycelis nigra, a flatworm, was found to be 14,400 mg/l (354). To stimulate the movement of water beetles (Laccophilus maculosis), a sodium bromide concentration of 14,400 mg/l was required (2956).

## SODIUM p- BROMOBENZENESULFONATE SODIUM BUTYL MERCAPTIDE C₄H₉SNa

This soluble compound ionizes in water to form sodium and mercaptide ions. In normal pH ranges, the mercaptide ion reacts with hydrogen ion to form butyl mercaptan. In testing the toxicity of various refinery materials toward bluegill sunfish, Turnbull et al. (2093) determined  $TL_m$  values as follows:

	$TL_m Values in mg/l$				
	$as SH$ $as C_4H_9SNa$		$\widetilde{I_{s}}SNa$		
	24-hour	48-hour	24-hour	48-hour	
Without reoxygenation	7.4	5.5	25.1	18.7	
With reoxygenation	4.1	3.5	13.9	11.9	

## SODIUM n. BUTYL SULFONATE

(see Chapter X)

#### SODIUM CARBONATE

Na₂CO₃

- 1. General. Sources of sodium carbonate in water include natural minerals, and effluents from chemical plants and paper mills. Known also as "soda ash", this salt is highly soluble in water and dissociates into sodium and carbonate ions, with a resulting increase in alkalinity and a tendency to raise the pH value. The carbonate ions will react with hydrogen ions until an equilibrium is established (see Carbonates, Bicarbonates, and Alkalinity). Sodium carbonate is used in the manufacture of glass, soap, and other sodium salts, in textile scouring, in water treatment and in numerous other processes (364).
- 2. Cross References. Dissolved Solids, Carbonates, Bicarbonates, Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of sodium carbonate in water is reported as 15 to 75 mg/l (621) and as 78 mg/l (3241). Waters containing 360, 430, and 500 mg/l of sodium carbonate have been considered wholesome and safe (32, 36).

- b. Industrial Water Supplies. Sodium carbonate in water for making ice is about 1.25 times as objectionable as sulfates and chlorides (231). Sodium carbonate in water for preparing developer solutions for use in photography may speed up the action of weakly alkaline solutions (242). For brewing, a limit of 100 mg/l has been recommended (see Chapter V).
- c. Irrigation. Sodium carbonate is extremely toxic to plants (264, 268). Sodium carbonate in irrigation water hardens soil and reduces its permeability (348) (see also Chapter V). On the other hand, it has been reported that 100 to 400 mg/l of sodium carbonate in the water was not injurious to various greenhouse plants over a period of six months of use (1205).
- d. Stock and Wildlife Watering. Waters containing high concentrations of sodium carbonate cause diarrhea, symptoms of malnutrition, unsatisfactory growth, and may also interfere with reproduction of livestock. The following concentrations of sodium carbonate have been reported as injurious to animals:

Concentration in $mg/l$	Animal	Effect	Reference
1.025	General livestock	Diarrhea	2394
7.500	Poultry	Lethal in 7 days	2980
10,000-15,000	Rats	Lethal to young	287
10,000-19,000	Rats	Inhibited growth	2980
10,000-20,000	Rats	Lethal to young	284
20,000	Rats	Lethal to young	640

e. Fish and Other Aquatic Life. The threshold concentration of sodium carbonate for immobilization of Daphnia magna in Lake Erie water at 25°C was reported to be 424 mg/l (358); less than 424 mg/l (352); and 300 mg/l (574). The minimum lethal concentration for Daphnia was also shown to be 300 mg/l at 17°C and at 800 mg/l all animals were killed (3523). The 100-hour toxicity threshold at 23°C in double-distilled water for Daphnia magna has also been reported at 524 mg/l with a resulting pH value of 9.5. According to Fairchild (2946), the threshold of toxicity toward Daphnia depends on the dissolved oxygen content of the test water. At 23°C for a 100-hour exposure he found the threshold toxicity level to be 552 mg/l at a dissolved oxygen tension of 6.5 mg/l; but only 267 mg/l when the DO dropped to 1.53 mg/l.

The following concentrations of sodium carbonate have been reported to kill fish:

oncentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
68	Тар	120 hours	King salmon	3501
70	Тар	120 hours	Silver salmon	3501
80	Тар	120 hours	Cutthroat trou	t 3501
200		4.5 hours	Bass	1030
250		120 hours	Shiners	190
250-300	Tap	Tew hours	Shiners, sucker	s,
	-		carp	313
300	Standard	96-hour TLm	Sunfish	2933
500		4.5-11 hours	Sunfish	1030
500	- <b></b>	7-9 hours	Bass	1030
500		½-3 days	Bass	1030
530	Tap	3 days	Bluegills	313
740	Turbid	24-hour TLm	Mosquito-fish	2940
840	Turbid	48-hour TL	Mosquito-fish	2940
1200	Turbid	96-hour TLm	Mosquito-fish	2940

The following concentrations of sodium carbonate have not been harmful within the time specified:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
33	5 days	Cutthroat trout	3501
44	5 days	Silver salmon	$3501 \\ 3501$
58	5 days	King salmon Bass	1030
100 200	7 days 7 days	Sunfish	1030
200-500	7 days	Goldfish	1030
500	7 days	Some goldfish	1030

## SODIUM CARBOXYMETHYL CELLULOSE

(see Chapter X)

#### SODIUM CHLORATE

NaClO_a

(see also Chlorine)

This strong oxidizing compound dissolves readily in water and ionizes to Na⁺ and ClO₈⁻; but the anion is unstable in aqueous solution, releasing oxygen and forming OCl⁻. (see Chlorine). Sodium chlorate is used for weed control, as well as in the manufacturing of matches and explosives, dyeing and printing of fabrics, and tanning and finishing of leather. It is also found in some effluents from chlorine and bromine works. Concentrations from 20,000 to 40,000 mg/l, as used for weed control, are considered non-toxic for man and animals, but create a fire hazard as the water evaporates (897). The oral LD₅₀ in rats is given as 12,000 mg/kg of body weight (3009).

The threshold of toxicity for perch is given as 11,000 mg/l and for bleak as 13,000 mg/l in tap water (2977). A concentration of 1000 mg/l in hard water was not harmful to goldfish during a 5-day exposure (313).

With respect to lower organisms, the literature is not consistent. The toxic threshold of sodium chlorate toward Polycelis nigra, a flatworm, was found to be 16,000 mg/l (354) and toward Daphnia magna 4240 mg/l (352). Bringmann and Kuhn (2158) report the threshold concentration toward Daphnia to be greater than 1000 mg/l; but toward the alga Scenedesmus the threshold level was only 3 mg/l as chlorate (about 3.8 mg/l as sodium chlorate) and toward E. coli only 4 mg/l as chlorate (5.1 mg/l as sodium chlorate).

### SODIUM CHLORIDE

NaCl

- 1. General. Sodium chloride in water may be of natural origin, or it may be introduced as a component of sewage or industrial wastes, including effluents from salt and brine works, oil wells, dairies, spent irrigation waters, etc. The sodium and chloride ions in natural waters are frequently the most prevalent, and they constitute the bulk of the ions in sea water.
- 2. Cross References. Tastes, Chlorides, Dissolved Solids, Specific Conductance, Mercuric Chloride, Distilled Water, Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Sodium chloride can be tasted in water by most people at a concentration of 550 mg/l (947); however, taste threshold values from 200 to 900 mg/l have also been reported (621, 3241, 3391,

3392). Water containing more than 500 mg/l of sodium chloride may be unpalatable and cause appetite disturbances (284, 948). Although an excess of sodium chloride induces thirst or can act as a diuretic (623), water containing up to 1410 mg/l has been used by some communities for many years without appreciable harm; however, 1000 to 1500 mg/l of sodium chloride generally renders water unpalatable (32, 36, 621). It has also been reported that 7500 mg/l of salt is harmless and that 10,000 mg/l causes vomiting (621, 579) (see also Sodium, Dissolved Salts, Chapter III, Chapter V).

b. Industrial Water Supplies. For ice making, as much as 342 mg/l of sodium chloride would probably not be detrimental, if it were the only salt present in the water (229). A concentration of 1000 to 1500 mg/l of sodium chloride in the process water causes tastes in canned foods, but does not affect the quality in other ways (224). For brewing, some sodium chloride is desirable and necessary in the water (171). It has been reported that 75 to 150 mg/l of sodium chloride is desirable in brewing water, but more than 500 mg/l is deleterious (170). It has also been recommended that for brewing waters the salt concentration should not exceed 200 mg/l (173); or 275 mg/l (152, 168). Other salt recommendations for brewing waters include the following values: pale ales I, 30 mg/1; pale ales II, 30 to 60 mg/1; mild ales, 60 to 120 mg/1; and stout, 120 to 175 mg/l (170). Good ale has been brewed, however, with water containing as much as 715 mg/l of sodium chloride (32). See Chapter V.

Larson and King (3675) conclude that the rates of corrosion of iron and steel in water are a function of the specific mineral quality as well as the alkalinity and pH values. They indict NaCl and other sodium salts as strong contributors to the rate of corrosion. For example, in a water with 400 mg/l of alkalinity (as CaCO₃) and pH 7, the corrosion rate will be zero at 100 mg/l of NaCl, but when the NaCl concentration is 400 mg/l, the corrosion rate will be about 100 mg per sq cm per day (3675).

c. Irrigation (see also Chapter V; Dissolved Solids). The effects of sodium chloride in irrigation water vary with the individual plants, the species, and environmental and climatic conditions. The presence of 10 milliequivalents or more of sodium chloride in nutrient solutions depressed root growth and water absorption by corn and tomato plants (1348). In irrigation water 100 to 200 mg/l of sodium chloride has caused injury to avocado trees in some soils, and also to some flowers, but many other plants are not sensitive to such concentrations (921). Water used for irrigation should not contain more than 700 mg/l of dissolved minerals in which sodium chloride predominates (638). Tomatoes have been killed by water containing 2000 mg/l of sodium chloride, but chrysanthemums have been resistant to as much as 3000 mg/l (921). To peas in liquid culture 4000mg/l or more of sodium chloride was toxic and 9000 mg/l permitted almost no growth. The growth of wheat and barley plants in liquid culture was depressed by 8000 mg/l of sodium chloride; 10,500 mg/l appeared to be lethal over a long period, although some plants could tolerate this concentration for a limited period of a few weeks. In general, no plants grew to any appreciable

extent when irrigated with water containing 15,000 mg/l of sodium chloride (1349).

Young rice is sensitive to the presence of chlorides in water, but develops resistance as the plant matures. According to Shutts (1693), the commonly accepted tolerances of rice to salt water are as follows:

Concentrations of Salts	• •
as $NaCl, mg/l$	Tolerances
600	Tolerable at all stages
1300	Rarely harmful, and only to seedlings in dry, hard soil
1700	Harmful before tillering; tolerable from jointing to heading
3400	Harmful before booting; tolerable from booting to heading
5100	Harmful at all stages

Chlorides tended to accumulate in plants and soil when wheat was grown 2 and 10 meters away from a ditch carrying water containing 103,000 mg/l sodium chloride. Increasing concentrations of salt caused progressively greater reductions in height, weight, leaf growth and seed number of affected plants (1694).

The effect of NaCl on plant growth has been demonstrated by culture in sand to which various concentrations of salt have been added to the normal nutrient solution. With sand culture, the effect of sodium on the soil structure is avoided as a contributing factor. Results are shown below:

NaCl Added		Crop	Relative	
Atmospheres	mg/l	Designation .	Dry Weight	Reference
Control	<del></del>	All	100	200,010,000
1.0	1400	Rice straw	89.7	3379
		Rice grain	74.5	3379
1.5	07.00	Rice roots	90.9	3379
7.0	2100	Bean plant	89.0	3376
•		Bean leaves	87.3	3376
2.0	0000	Bean roots	93.3	3376
2.0	2800	Rice straw	46.1	3379
		Rice grain	12.0	3379
2.5		Rice roots	49.6	3379
2.0	3500	Bean plant	73.8	3376
		Bean leaves	70.5	3376
		Bean roots	80.1	3376

This table demonstrates that NaCl affects the growth of plants and that rice is more sensitive than beans.

d. Stock and Wildlife Watering (see also Chapter V; Dissolved Solids). Salt poisoning has been reported among a great variety of livestock; its symptoms include malnutrition, wasting diseases, diarrhea, nervous disturbances, decreased milk or egg production, reduced reproduction, and sometimes death. The minimum lethal dose of sodium chloride for poultry has been reported as about 2 grams per pound (1350). The following doses of sodium chloride have been reported to be toxic to various animals: pheasants and rabbits, 3 grams (3676); ducks, 6 grams; dogs, 30 to 60 grams; sheep and pigs, 120 to 140 grams; cows, 2 to 3 kilograms; and horses, 1 to 2 kilograms (284).

The following concentrations of NaCl in drinking water have been reported to have caused the indicated effects on animals:

Reactions	Reference	Concentration of NaCl, $mg/l$	Animal
4000 5000	Laying hens Young chicks	Watery droppings Nervousness, in-	2398
		ability to stand	1351, 1551

Concentration			D. (
of $NaCl$ , $mg/l$	Animal	Reactions	Reference
7000	Swine	Slight scouring	2398
7000	Cattle	Reduction in weight	2398
7200	Sheep	Lethal to some	642, 1352
9000	Chicks	Lethal to two- thirds	2980
10000	Rats	Decreased reproduction	284, 287, 295
10000	Cattle, swine,	Toxic effect	2398
10000	Laying hens	Loss of weight and egg production	l 2398
15000	Rats	Retarded growth, some deaths	284, 287, 295
15000	Cattle	Reduced water intake	3392
15000-17600	Cattle	Sickened or killed	293, 294, 1350
15000-25000	Cattle, hens, pigs, rabbits	Injurious or fatal	284
17500	Cattle	Lost weight	2396
20000	Young chicks	Death in three days	1551

On the other hand, the following concentrations of NaCl in drinking water have been reported to cause no apparent adverse effect on the designated animals:

of NaCl, in mg/l	Animal	Reference
1025	General livestock	2394
2000	Young chicks	1551
2450	Cattle, sheep, swine, poultry	3391
3000	Chicks	2980
4000	Cattle, swine, poultry	2398
5000	Rats	284, 287, 295
5720	Sheep, horses	642, 1352
9000-10000	Dairy cows	292, 293
9123	Horses, without working	642
11440	Cattle and sheep	642
11690	Rats	2398
12500	Cattle	2396
20000	Cattle not in milk production	288
25000	Sheep	288

e. Fish and Other Aquatic Life. (see Dissolved Solids; Chapter V). The following concentrations of sodium chloride have immobilized or killed fresh-water fish:

Concentration of NaCl, mg/l	$Type\ of\ Water$	Time of Exposure	Type of Fish	Reference
1270- 2540	Soft, distilled		Fish	1459
2500 2500		120 hours	Shiners Fish	190 3 <del>44</del>
2500	Distilled	9-24 days	Minnows	313
3820- 5100	Hard, alkaline		Fresh-water fish	1459
3850 5000	Natural		Whitefish, pickerel Newly hatched tro	
5000	Distilled	148 hours	Shiners	313, 645
5000	Distilled	200-250 hours	Bass	313, 645
8500	Distilled	4-8 days	Minnows, perch	1459 645
10000		97-148 hours	Shiners, bass	1459
10000	Tap	4-8 days	Minnows, perch	313
10000	River	4-10 days	Goldfish	2942.
10000	Distilled	6 hours	Minnows	2943, 2944
10000			Fish	603, 1070
11500-12000 .	Hard	6 hours	Minnows	2942, 2943, 2944

Concentration of NaCl, mg/l		$Time\ of \ Exposure$	Type of Fish	Reference
11680-14600 11700 11765 12946 14000 15000 15000-30000 16500 17550 20000 50000	Tap Distilled Aerated Synthetic Natural Turbid	17 hours 96-hour TLm 24 hours 4.7 hours 24 hours 96-hour TLm 1.3 hours 15 minutes	Stickleback Salmon eggs and fr Goldfish Bluegills Goldfish Bass Fresh-water fish Whitefish Mosquito-fish Shiners Trout	353 1459 313 3381 1459 2920 645 1459 598 2940 645 441

On the other hand, the following concentrations of NaCl have been reported as harmless in the time specified:

Concentration of NaCl, mg/l 5000 5850	Type of Water River Tap	Survival Time 25 days	Type of Fish Goldfish Salmon eggs and	
9100-17500 11700 12000	 Distilled	30 days 50 hours	larvae and youn stickleback Perch Young eels Stickleback Stickleback	g 1459 644 1459 1459 1459
20000 25000-30000 30000	Tap 	30-60 minutes	Older trout Brook trout	1459 441

The threshold concentrations of sodium chloride in natural waters reported for immobilization of Daphnia and other fish-food organisms range from 2100 to 6143 mg/l (352, 353, 358, 598, 2946, 2955). Yet in distilled water, one mg/l of NaCl killed Daphnia magna in three hours (313). The resistance of Daphnia magna to NaCl appears to vary with the oxygen tension (2946). At 6.4 mg/l of dissolved oxygen the threshold toxicity level of NaCl was 5093 mg/l, but at 1.48 mg/l of DO, the threshold for NaCl was only 3170 mg/l (2946). Many small crustacea and fish fry are immobilized by concentrations above 3100 mg/l (598). The toxic threshold for a flatworm, Polycelis nigra, was found to be 11,200 mg/l (354).

In Lake Eric water at 20-25°C, threshold limits for several fish-food organisms were reported (2955) as follows:

Organism tr Daphnia magna, young Daphnia magna, adult Leptodora kindtii	shold Concen- ation, mg/l-
Daphnia magna, adult	3700
Leptodora kindtii	4600
	3700
Cuclops vernalis	6100
Diaptomus oregonensis	3030

A Russian article (3677) indicates the following maximum NaCl tolerances for fresh-water organisms at two temperatures:

r.Poztavaz da i	NaCl Tolerance in mg/		
Organism	20°C	3°C	
Stictochironomus	788	1000	
An oligochaete	1576	2000	
Daphnia magna	200	800	
Cuclous serrulatus	394		
Leucaspisis delineatus	1970		

Anderson considers sodium chloride concentrations above 3000 mg/l deleterious to both fish-food organisms and fish fry and recommends a permissible limit of 2000 mg/l in fresh waters (598). On the other hand, higher

concentrations of sodium chloride have been found to decrease somewhat the toxicity of some metallic compounds toward fish (1265) (see also Mercuric Chloride). Sodium chloride is the least toxic to fish of the chlorides of potassium, magnesium, calcium and sodium. Sodium chloride is antagonistic to the toxicity of calcium and potassium chlorides (353, 307). A concentration of 50 mg/l of sodium chloride has greatly increased the antagonistic effect of sodium nitrate toward copper sulfate poisoning of fish (311). The toxicity of sodium chloride toward fish is decreased by calcium chloride (307).

f. Shellfish Culture. The most favorable salt content of water for oyster growth is about 30,800 mg/l of salinity of which about 80 percent is sodium chloride (314).

## SODIUM p-CHLOROBENZENE SULFONATE

(see Chapter X)

## SODIUM CHROMATE

(see Chromium)

## SODIUM CITRATE

C₃H₄OH(COONa)₃·2H₂O

(see also Citric Acid)

This highly soluble salt has many uses in medicine, especially as an anticoagulant. It is also used in photography and as a sequestering agent to remove trace metals (364).

Anderson (352) reports that the threshold concentration for immobilization of *Daphnia magna* in Lake Erie water at 25°C was 825 mg/l. For *Polycelis nigra*, a flatworm, the threshold for toxicity at 15 to 18°C was a 0.015 molar concentration, or 4420 mg/l of sodium citrate (354).

## SODIUM CYANATE

NaOCN

(see also Cyanides, Hydrogen Cyanide)

Cyanates are formed when cyanides in waste waters are treated by alkaline chlorination. According to Resnick et al. (2974), cyanates are stable in aerobic water at pH 7 and 20°C for at least 10 days. Eventually, cyanates undergo hydrolysis to yield ammonium carbonate. In anaerobic solutions cyanates are reduced not to cyanide but to a mixture of ammonia and formic acid.

According to Washburn (1070) the maximum tolerance limit of creek chub to sodium cyanate is 75 mg/l.

#### SODIUM CYANIDE

NaCN

- 1. General. This highly soluble salt is used in electroplating baths, for extracting gold and silver from ores, and for generating HCN gas in fumigating operations (364). Upon solution in water, the cyanide ion combines with hydrogen ions in the water to form weakly dissociated hydrogen cyanide, thereby tending to raise the pH of the solution. For further explanation of the cyanides, see Hydrogen Cyanide.
- 2. Cross References. Cyanides, Cyanogen Chloride, Hydrogen Cyanide, Nitriles, and other cyanide salts.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The fatal dose of NaCN for man by ingestion is reported to be about 0.2 grams

(353), but since the fatal dose of HCN has been given as 50 to 60 mg (364), the former figure may be high. See also Cyanides and Hydrogen Cyanide.

b. Stock and Wildlife Watering. The approximate minimum toxic dose of NaCN for sheep is given as 4.15 mg per kg of body weight, and a dose of 5.22 mg per kg

is lethal (353).

c. Fish and Other Aquatic Life. The following concentrations of sodium cyanide have been shown to be harmful or toxic to fish:

Concentrate				
of $NaCN$	. Time of	Tupe of		
$in\ mg/l$		Fish	Remarks	Reference
0.05	124 hours	Treut	100 percent mortality	1115
0.28	96 hours	Bluegills	TLm in soft water	2958
0.33 - 0.35	2.5 hours	Minpows	Lethal	1468
0.4	I hour	Minnows	Stopped eating	362
0.43	96 hours		TLm in soft water	2958
0.44	48 hours	Fathead Minnow	TI.m	3335
0.5	4 to 6 hours	Goldfish and	25	9999
		green sunfish	Lethal, 25°C	3678
0.5 to 0.7	24 hours	Minnows	25 percent mortality	362
0.66	96 hours	Fathead minnow	TLm in hard water	2958
0.75	24 hours	Minnows	50 percent mortality	362
0.8	24 hours	Minnows	100 percent mortality	362
1.0	0.7 to 10 hours		Lethal at 25°C	
1	20 minutes	Trout	100 percent mortality	3678
1.5	0.6 to 24 hours	Goldfish and	100 percent mortanty	1115
		green sunfish	Lethal	3678
2	47 minutes	Trout	Lethal	
2.0		Sticklebacks	Lethal at 17°C	1116
3.1	90 minutes	Fish	Depressed respiration	2920
4.3		Hardy carp	Paralyzed	468
5 5	12 minutes	Shiner	Killed	362
5	2 hours	Trout, bluegill	Killed	1115
10	4 minutes	Shiner	Killed	2976
-		PHATEI	WILLIAM .	1115

Non-toxic or non-harmful concentrations have been reported as follows:

Concentrat of NaCN in mg/I		Type of Fish	Remarks	Reference
0.02 0.08		Trout fingerlings		1115
0.3	24 hours	Trout	Non-toxic	1109
2.3	155 minutes	Minnows	No effect	362
5.0		Fish	Survived	468
U.U	2 hours	Sea lamprev	III but enreised	9076

According to Anderson (365), the threshold concentration for immobilization of *Daphnia magna* in Lake Erie water at 25°C was found to be less than 3.4 mg/l of sodium cyanide and Jones (354) reports that the threshold concentration for *Polycelis nigra*, a flatworm, is 16 mg/l as cyanide (30 mg/l as NaCN). A concentration of 3.6 mg/l of NaCN inhibited BOD by 50 percent (2949).

## SODIUM DECYLBENZENE SULFONATE

SODIUM n-DECYL SULFATE

SODIUM 2, 5-DICHLOROBENZENE SULFONATE (see Chapter X)

## SODIUM DICHROMATE

(see Chromium)

## SODIUM DIHYDROGEN PHOSPHATE

(see Sodium Phosphates)

#### SODIUM DI (2-ETHYLHEXYL) SULFOSUCCINATE

#### SODIUM DIOCTYL SULFOSUCCINATE

## SODIUM DODECYLBENZENE SULFONATE

## SODIUM DODECYL SULFATE

## SODIUM 2-ETHYLHEXYL SULFATE

(see Chapter X)

## SODIUM FERROCYANIDE

Na₄Fe(CN)₆

(see also Cyanides, Hydrogen Cyanide, Potassium Ferro- and Ferricyanide)

This compound, containing reduced iron, is highly soluble in water. It is used for blueprinting, in photography, pigments, dyes, and metallurgy (364). In aqueous solution it decomposes under the action of sunlight

to release cyanide ion and HCN.

For Daphnia magna in Lake Erie water at 25°C, the toxic concentration was reported by Anderson (352) to be less than 600 mg/l, or about 540 mg/l (353). For Polycelis nigra, a planarium, Jones (354) found the toxic threshold to be 170 mg/l. It should be recognized, however, that under the action of sunlight with the resultant decomposition to cyanides, this compound may be much more lethal. For further details, see Potassium ferrocyanide.

## SODIUM FLUORIDE

NaF

(see also Fluorides)

Highly soluble in water, this crystalline solid is used as a pesticide, as a fluoridating agent in municipal water, and in many industrial processes. The LD50 for hamsters was found to be 70-80 mg/kg of body weight (3705). Much of the information described under "Fluorides" was derived from the use of sodium fluoride and will not be repeated here.

Bringmann and Kuhn (2158, 3343) found the threshold of NaF for Daphnia at 23°C to be 270 mg/l during a 2-day exposure. For Scenedesmus the threshold of toxic effect was 95 mg/l during 4 days at 24°C, for Microregma 226 mg/l, and for Escherichia coli at 27°C it was 180 mg/l. According to Wantland (3705), freeliving protozoa and freshwater rotifers survived and reproduced in water containing 1000 mg/l of NaF, but were killed at 1700 mg/l.

# SODIUM FORMATE

(see Formic Acid and Formates)

## SODIUM HYDROCARBON SULFONATE

(see Chapter X)

## SODIUM HYDROSULFIDE

(see Sodium Sulfhydrate)

## SODIUM HYDROXIDE

NaOH

1. General. This common caustic compound is highly soluble in water with dissociation to sodium and hydroxide ions, with a consequent effect upon alkalinity and pH. Sodium hydroxide may occur in wastes from the following industries: soap manufacture; cleaning compounds; pulp and paper; petroleum, mineral and vegetable oils; leather; reclaimed rubber; ink; dyes and textile dyeing; cotton; perfumes; water glass; coal distillation, etc.

2. Cross References. Sodium, Alkalinity, Hydroxides.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The taste threshold of sodium hydroxide in water is reported to be 1 to 50 mg/l (621). A dose of 1.95 grams of sodium hydroxide may cause death in man (353).

b. Stock and Wildlife Watering. Sodium hydroxide, in a concentration of 5000 mg/l, was almost harmless for rats; 10,000 mg/l caused nervousness, sore eyes, diar-

rhea, and retarded growth (284, 287).

e. Fish and Other Aquatic Life. The toxicity threshold concentration of sodium hydroxide for Daphnia magna has been reported to range from 40 to 240 mg/l (190, 352, 353, 358, 574, 690, 1466, 3500, 3523). Concentrations of sodium hydroxide from 125 to 1000 mg/l have been lethal to various insect larvae (190, 574, 690, 3500). A concentration of 100 mg/l has not been harmful to mayflies, and 700 mg/l has not been harmful to Chironomous larvae (690).

The following concentrations of sodium hydroxide have been reported to have killed fish:

	- <b>A</b> .			
Concentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
20 25 35 40 48 70 71.5 96 99 100 100 100 125 180 (pH 12)	Fresh Stagnant Circulating Tap Tap Turbid Circulating	24 hours 24 hours 5 hours 4.5 hours 2-10 minutes 48-hour TLm 120 hours 3-20 hours 95-hour TLm 23 hours	Silver salmon Brook trout Cutthroat trout Creek chub King salmon Fish, crabs Carp, shiners, suckers Fish, oysters Carp, shiners, suckers Bluegill sunfish Minnows Fish Shiners Goldfish, bass Mosquito-flish Fish, oysters	\$502, \$501 \$59 \$502, \$501 1442 \$502, \$501 823 \$59 \$23 \$18 \$29 \$690, 190, \$500 658, \$44 190 1030 2940 823

The following concentrations of sodium hydroxide have not harmed fish within the time specified:

			_	
Concentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
10 11			Cutthroat trout Silver salmon	3502, 3501 3502, 3501
20	Fresh	24 hours	Creek chub King salmon	1442 3502, 3501
27 50	Distilled	2 hours	Perch, roach Goldfish, bass	313 1030
50		7 days	Carp, shiners, suckers	
55.5		5 hours	Some fish	823
200		e none	D0120	

For roach and perch in sodium hydroxide solutions of 1:5000 strength, the time until loss of equilibrium was found to be about 30 minutes. In 1:10,000 dilutions, both kinds of fish survived for 40 minutes (1357).

According to Murdock (1460) sodium hydroxide has not been shown to be lethal to fully developed fish in natural fresh waters unless the pH value is well over 9. The lethal pH for goldfish is given by Jones (2920) as 10.9, and by Cairns and Scheier (2933, 2934) for bluegill sunfish as 10.5.

To stimulate the movement of water beetles (Laccophilus maculosus), Hodgson (2956) found that a concentration of 400 mg/l of NaOH was required.

## SODIUM IODATE

NaIO₃

(see also Iodine)

The threshold concentration of sodium iodate for the immobilization of Daphnia magna in Lake Erie water was found to be less than 158 mg/l (352). The toxic threshold concentration of sodium iodate for the flatworm Polycelis nigra was found to be 230 mg/l, as iodate (354).

#### SODIUM IODIDE

NaI

(see also Iodine)

The taste threshold of sodium iodide in chlorinated water is reported to be about 0.005 mg/l (459). The threshold concentration of sodium iodide for the immobilization of Daphnia magna in Lake Erie water was found to be 3.3 mg/l (352). A concentration of 5 mg/l had no effect on the sea lamprey during a 24-hour exposure in Lake Huron water at 12°C (2976). The toxic threshold concentration of sodium iodide for Polycelis nigra a flatworm, was found to be 6600 mg/l (354). To stimulate movement of the water beetle (Laccophilus maculosis) a sodium iodide concentration of 14,700 mg/l was required (2956).

# SODIUM ISOPROPYL NAPHTHALENE SULFONATE

## SODIUM KERYLBENZENE SULFONATE

# SODIUM LAURYL AND MYRISTYL COLLAMIDE SULFONATE

## SODIUM LAURYL SULFATE

(see Chapter X)

## SODIUM METABISULFITE

Na₂S₂O₅

This highly soluble solid is used in medicine as an antioxidant (364). According to Le Clerc (2942) the minimum lethal dose to minnows during a 6-hour exposure was 60-65 mg/l in distilled water at 18°C and 75-80 mg/l in hard water at 17°C.

## SODIUM MOLYBDATE

(see Molybdenum)

# SODIUM MONOBUTYL PHENYLPHENOL MONOSULFONATE

# SODIUM MONOETHYL PHENYLPHENOL MONOSULFONATE

# SODIUM NAPHTHALENE - $\beta$ - SULFATE

(see Chapter X)

## SODIUM NITRATE

NaNO₃

- 1. General. Known commonly as "Chile saltpeter", this compound was formerly used extensively for the manufacture of nitric acid. It is also used in making glass, enamels, matches, and cigarettes, and in pickling meats. The technical grade is employed in fertilizers as a source of nitrate. The compound is readily soluble in water, releasing sodium and nitrate ions.
  - 2. Cross References. Sodium Nitrates.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of sodium nitrate in water is reported to be about 450 to

- 800 mg/l (621). Sodium nitrate acts as a diurectic (364, 623).
- b. Industrial Water Supplies. Sodium nitrate in water interferes with fermentation processes and causes disagreeable tastes in beer (165).
- c. Stock and Wildlife Watering. A dose of 240 grams of sodium nitrate has been fatal to cows; 20 grams, to sheep; and 6 grams to dogs (284). A concentration of 6200 mg/l of sodium nitrate in water has caused frenzy, paralysis, diuresis, cyanosis, and deaths among cows (284). Pigs fed with soup prepared with well water containing 1740-2970 mg/l of sodium nitrate died from methemoglobinemia. A total dose of 90 mg of sodium nitrate per kg of body weight is fatal to pigs (1695).
- d. Fish and Other Aquatic Life. The toxicity threshold concentration of sodium nitrate for *Daphnia magna* has been reported to be 5000 mg/l and 8500 mg/l (352, 353, 358).

The following concentrations of sodium nitrate have been reported as toxic to fish:

Concentration in mg/l	r Type of Water	Time of Exposure	Type of Fish	Reference
1,282	Distilled	14 hours	Goldfish	313
1,845	Tap		Stickleback	598, 1460
2,000		4 days	Goldfish	1035
2,000-4,000			Some sunfish	1035
2,210	Тар	7 days	Stickleback	1460
2,950	Тар	4 days	Stickleback	1460
4,000	Hard	80 hours	Goldfish	313
	Tap	48 hours	Stickleback	1460
6,650	Turbid	96-hour TLm	Mosquito-fish	2940
10,000	Standard	96-hour TLm	Bluegill sunfish	2933, 2934
11,060	Tap	24 hours	Stickleback	1460
12,000	Aerated :	96-hour TLm	Bluegill sunfish	3381
13,600			Stickleback	2920

The following concentrations of sodium nitrate have not been harmful to fish within the time specified:

Concentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
1,000	Hard		Goldfish	313, 1035
2,000-4,000	Hard		Some sunfish	1035
3,000	Hard	100 hours	Goldfish	313
4,000	Hard		Bass	1035

#### SODIUM NITRATE

NaNO₂

(see also Nitrates, Nitrites, Sodium)

This soluble salt is used in the manufacture of dyes and other chemicals, in textile processes, and in photography. In water it dissociates completely and under aerobic conditions the nitrite ions are oxidized to nitrates. The oral MLD for dogs is given as 330 mg/kg of body weight (364).

A concentration of 17.1 mg/l of NaNO₂ was apparently harmless to minnows during a 24-hour exposure (362); but 50 mg/l can be fatal in 14 days (3577). A massive dose of 10,000 mg/l is lethal to minnows in 1.5 hours (3577). Testing mosquito-fish (Gambusia affinis) in highly turbid water at 21-24°C, Wallen et al. (2940) found the 24-hour TL_m to be 8.1 mg/l while the 48- and 96-hour TL_m values were 7.5 mg/l. There was no decrease in turbidity by this dosage. Sodium nitrite has an antagonostic effect upon the toxicity of copper sulfate to goldfish. In cencentrations up to 5000 mg/l, sodium nitrite has decreased the toxic effect of 10 mg/l of copper sulfate toward goldfish (311).

The toxic threshold concentration of sodium nitrite for the flatworm *Polycelis nigra* was found to be 42 mg/l (354). Toward *Daphnia magna* in Lake Erie water, the threshold concentration for immobilization was reported as less than 28 mg/l (352); but in River Havel water at 23°C it was given (2158) as 99 mg/l of NaNO₂. Also in River Havel water, the toxic threshold for *E. coli* was found to be 195 mg/l but for *Scenedesmus* concentrations up to 1500 mg/l of NaNO₂ were harmless.

## SODIUM m-NITROBENZENE SULFONATE

## SODIUM 4-NITROCHLOROBENZENE -2-SULFONATE

(see Chapter X)

# **SODIUM NITROFERRICYANIDE** Na₂Fe(CN)₅NO (see also Cyanides, Sodium Ferricyanide)

This substance is used primarily in chemical laboratories for the detection of many organic compounds (364). According to Schaut (362), minnows exposed for one hour to 17.1 mg/l of sodium nitroferricyanide in stabilized tap water showed no effects. Toward *Polycelis nigra*, a flatworm, the toxic concentration was found to be 190 mg/l, as nitroferricyanide (354). Like the ferricyanides, this substance tends to decompose slowly in aqueous solution, but faster in sunlight, to release cyanide ions (see Cyanides).

#### SODIUM OLEATE

(see Fatty Acids, also Chapter X)

## SODIUM OXALATE

(see Oxalic Acid, Oxalates)

## SODIUM PALMITATE

## SODIUM PENTACHLOROPHENATE

(see Chapter X)

## SODIUM PERBORATE

NaBO₃·4H₂O

(see also Boron, Sodium Borate, Chapter X)

Relatively soluble in water, this white crystalline salt is used in bleaching operations, in soaps, and in dentifrices. When mixed with warm water it decomposes to liberate pascent oxygen.

The threshold concentration of sodium perborate for immobilization of Daphnia magna in Lake Erie water at 25°C was found to be very much less than 5.2 mg/l (352) and was estimated at 2.6 mg/l (353). Fingerling trout survived a sodium perborate concentration of 160 mg/l for 24 hours but 80 percent were killed by 320 mg/l.

## SODIUM p-PHENOL SULFONATE

(see Chapter X)

#### SODIUM PHOSPHATES

(see also Phosphates, Phosphoric Acid)

Under this designation, six sodium phosphates are considered:

(a) Sodium phosphate, monobasic, NaH₂PO₄·H₂O also known as sodium dehydrogen phosphate. Highly soluble in water, it is used in baking powders and treatment of boiler water. The aqueous solution is acid.

(b) Sodium phosphate, dibasic, Na₂HPO₄·7H₂, or disodium hydrogen phosphate. It is highly soluble in water and gives an alkaline solution. It is used in human and

veterinary medicine as a laxative.

(c) Sodium phosphate, tribasic, Na₃PO₄·12H₂O, or trisodium phosphate. Also highly soluble in water, it is used in photographic developers, treatment of municipal and boiler water, in detergent compounds, and in tanneries, paper mills, and laundering plants.

(d) Tetrosodium pyrophosphate,  $\tilde{N}a_4P_2O_7$ , or sodium pyrophosphate. It is used as a sequestering agent in water treatment, cleaning compounds, oil well drilling,

and other processes.

(e) Sodium hexametaphosphates are mixtures of (NaPO₃)₆ that occur in commercial detergents such as Calgon, Micromet and Quadrafos.

(f) Sodium tripolyphosphate, Na₅P₃O₁₀, used as a

sequestering agent and meat preservative.

Campbell et al. (2059) indicate that the taste threshold for trisodium phosphate is 225 mg/l and for Calgon 200 mg/l. According to Lockhart et al. (3241) the taste threshold of trisodium phosphate in water is 180 mg/l. Cohen et al. (2049) found that as little as 0.1 mg/l of sodium tripolyphosphate inhibited the coagulation of turbid water by ferric sulfate.

For Polycelis nigra, a flatworm, the toxic threshold concentration of trisodium phosphate (Na₃PO₄·12H₂O) was found to be 9860 mg/l (354). The threshold concentrations for immobilization of Daphnia magna in Lake Erie water at 25°C were found to be lower than the fol-

lowing values:

Compound	$Concentration\ in\ mg/l$
Sodium dehydrogen phosphate	1560
Disodium hydrogen phosphate	59 59
Trisodium phosphate	52

To stimulate the movement of water beetles (Laccophilus maculosis) in water, Hodgson (2956) found that a trisodium phosphate concentration of 179,000 mg/l was

required.

Toward fish, sodium phosphates are not strongly toxic, the principal effect being a change in pH value. Using turbid water and the mosquito-fish (Gambusia affinis) as the test animal, Wallen et al. (2940) report the following results:

To.	mperatur	e vH		$TL_m$ in $mg/l$	
Compound	•C	Range 2	4-hour	48-hour	96-hour
NaH ₂ PO ₄	19-23	7.6-11.0	720	720	720
Na,P2O7 10H2O	19-24	8.2-9.8	1380	1380	1380
Na _s PO ₄	17-22	7.4–10.3	467	467	151

The Water Pollution Research Board of England (2907) tested a mixture of sodium tripolyphosphates and tetrasodium pyrophosphate on rainbow trout. It was found that 560 mg/l as phosphate caused no deaths in 24 hours but 1120 mg/l as phosphate killed all of the fish.

Quadrafos, a sodium hexametaphosphate, was tolerated by fish in concentrations up to 3,500 mg/l, but this concentration killed oysters (3005).

## SODIUM PYROPHOSPHATE

(see Sodium Phosphates)

#### SODIUM SALICYLATE

(see Salicylic Acids and Salicylates)

#### SODIUM SELENITE

Na₂SeO₃, Na₂SeO₃ · 5H₂O

- 1. General. Sodium selenite is found in some types of soil and in wastes from pottery works. It is freely soluble in water.
  - 2. Cross References. Selenium, Selenious Acid.
  - 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. For most mammals the fatal dose of sodium selenite is about 4 to 6 mg per kilogram of body weight. Sodium selenate is about half as toxic as sodium selenite. The minimum lethal dose of sodium selenite for rabbits is about 1.5 mg per kg of body weight (353).

As sodium selenite, administered orally or as a drench, the minimum lethal single dose of selenium for horses is about 1.5 mg per kg of body weight; for cows and calves, 4.5 to 5.0 mg per kg of body weight; and for pigs, 6 to 8 mg per kg (1049).

b. Fish and Other Aquatic Life. The following concentrations of sodium selenite have been reported as toxic to fish.

Concentration	Type of	$Time\ of$		
in $mg/l$	Water	Exposure	Type of Fish	Reference
10	Hard	98-144 hours	Goldfish	353, 313
100	Very soft	1-4 days	Goldfish	353
100	Hard	8-19.5 hours	Goldfish	353: 313

Bringmann and Kuhn (2158, 3343) investigated the toxicity of sodium selenite in River Havel water. They found the following thresholds of toxicity:

Organism	$Temperature \ ^{\circ}C$	Time of Exposure	Threshold  Concentrations  in mg/l
	24	2 days 4 days	2.5 2.5
Escherichia co Microregma _			90
m icroreyma _			183

## SODIUM SILICATE

Na₂SiO₃

This colorless crystalline salt is only slightly soluble in water, but in combination with other sodium silicates such as Na₂Si₃O₇ it is marketed as a solution known as "water glass," which has numerous commercial applications (34).

The 100-hour toxicity threshold of sodium silicate in double-distilled water at 23°C to Daphnia magna has been reported (1691) at 247 mg/l with a resulting pH value of 9.1, but in the presence of other sodium salts this threshold may be somewhat lower (see Sodium).

The Water Pollution Research Board of England determined that sodium silicate was not lethal to fingerling rainbow trout at a concentration of 256 mg/l. Using turbid water at 21-22°C, Wallen et al. (2940) found that the 96-hour  $TL_m$  for the mosquito-fish (Gambusia affinis) was 2320 mg/l.

## SODIUM SILICOFLUORIDE

Na₂SiF₆

(see also Fluorides)

This white granular powder, highly soluble in water, has been used extensively in the fluoridation of drinking water. The oral LD50 in rats has been reported (364) as 125 mg/kg of body weight. For guinea pigs, the oral  $\mathrm{LD}_{50}$  is given as 250 mg/kg of body weight (3271). Toward the fish, Tinca vulgaris, Simonin (3271) reports the lethal dose to be 50 mg/l.

## SODIUM STEARATE

(see Chapter X)

## SODIUM SULFATE

Na₂SO₄ and Na₂SO₄·10H₂O

- 1. General. Sodium and sulfate ions may occur naturally in water, or they may be derived from various industrial wastes, such as those from paper mills. Sodium sulfate is used in manufacturing dyes, glass, soaps, freezing mixtures, and paper; and in dyeing and printing of textiles. It is readily soluble in water.
  - 2. Cross References. Sulfates, Sodium.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of sodium sulfate in water is 250 to 500 mg/l (621). In high concentrations, sodium sulfate has a purgative effeet (623). Water containing 500 mg/l of sodium sulfate and 1200 mg/l of magnesium sulfate occasionally has caused diarrhea among human beings; under ordinary conditions such water would be regarded as unsuitable for domestic use (36).
- b. Industrial Water Supplies. For boiler waters, the ratio between the concentration of sodium sulfate and that of sodium sulfite is significant. The following ratios as given in Chapter V, are specified as limits:

Boiler Pressure	Ratio
in psi	NasSO::NasSO
0-150	1:1
150-250	2:1
More than 250	3:1

For brewing, waters should not contain more than about 100 mg/l of sodium sulfate, and for ice making, not more than 300 mg/l (see Chapter V).

Larson and King (3675) conclude that the rates of corrosion of iron and steel in water are a function of the specific mineral quality as well as the alkalinity and pH values. They indict sodium sulfate and other sodium salts as strong contributors to the rate of corrosion. For example, in a water with 400 mg/l of alkalinity (as CaCO₃) and pH 7, the corrosion rate will be zero at 200 mg/l of Na₂SO₄, but when the concentration of sodium sulfate is 400 mg/l, the corrosion rate will be about 100 mg per sq cm per day (3675).

c. Irrigation. A concentration of 4000 mg/l of sodium sulfate in the soil is injurious to plants (246). At 710 mg/l, sodium sulfate has depressed root growth and water absorption of plants grown in liquid culture

The effect of Na₂SO₄ on plant growth has been demonstrated by culture in sand to which various concentrations of this salt have been added to the normal nutrient solution. With sand culture, any alteration of the soil structure is avoided as a factor contributing to sodium effects. Results are shown below:

Na ₂ SO ₄ Added in mg/l	Portion of Crop	Relative Dry Weight	Reference
Control		100	
2560	Rice straw	91.9	3379
2000	Rice grain	79.8	3379
	Rice roots	95.4	3379
2840	Tomato vine	88.2	3679
2010	Tomato root	85.0	3679
3840	Bean plant	87.5	3376
3030	Bean roots	90.2	3376
	Bean leaves	86.3	3376
5120	Rice straw	55.6	3379
0120	Rice grain	15.6	3379
	Rice roots	58.2	3379

d. Stock and Wildlife Watering. Water containing 4546 to 7369 mg/l of salts, mostly sodium sulfate, was not harmful to two cows over a two-year period; however, a sudden change from normal water to this water caused diarrhea (291). At a level of 7000 mg/l there was some evidence of weight reduction in cattle and at 10,000 mg/l weight losses were severe (2398). Rats were not harmed by water containing 15,000 mg/l of sodium sulfate (284). Poultry, however, experienced a 33 percent mortality after drinking for 15 days water containing 7500 mg/l of sodium sulfate. Ballantyne (2394) sets the threshold limit of Na₂SO₄ for all livestock at 2050 mg/l.

e. Fish and Other Aquatic Life. The following concentrations of sodium sulfate were reported to be toxic or lethal to fish and other aquatic life:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
100	120 hours	Shiners	190
100		Fish	344
1000	7 days	hydra	1696
4547	100 hours	$Daphnia\ magna$	1691
5000	7-28 days	Water snails	1696
5000	6-30 hours	Microcrustacea	1467
5000	1-6 days	Fingerling trout	1696
5000-7105		Daphnia magna	352, 358, 574
5200	48 hours	Daphnia	3523
6700		Cutthreat trout	3502
6820		Polycelis nigra	354
7000	1-2 days	Rainbow trout	1696
11,200-12,000	6 hours	Minnows, distilled water	2942
12.750	96-hour TL	Bluegill sunfish	2933
13,400-184,000	7-69 days	Perch	<del>644</del>
13,500	96-hour TLm	Bluegill sunfish	2936, 3381
16,500		Silver salmon	3502
16,500	96-hour TLm	Mosquito-fish	2940
16,700-17,600	6 hours	Minnows, hard water	2942
24,000	24-hour TLm	Mosquito-fish	2940

The following concentrations of sodium sulfate were not harmful to aquatic life in the indicated time:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
100		Minnows	3523
500	24 hours	Goldfish	313
705	24 hours	Rainbow trout	2907
1000	5 days	Fish	609
2500		Cutthroat trout	3502
5000	6-16 days	Dace	1696
5000		Daphnia	3523
5000-10,000		Water plants	1696
7500	24 days	Perch	1696
10,000		Silver salmon	3502
15,000	24 days	Carp	1696

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
15,000 Up to 15,000 15,000-20,000	7 days 28 days	Roach Algae Protozoa	1696 1696 1696

To stimulate the movement of water beetles, Laccophilus maculosis, Hodgson (2956) found that 35,600 mg/l of sodium sulfate was required. Fairchild (2946) reported that the threshold toxicity value of sodium sulfate toward Daphnia depended on the dissolved oxygen concentration. At a DO value of 6.6 mg/l, the toxicity threshold of Na₂SO₄ was 5514 mg/l; but at a DO value of 1.46 mg/l, the toxicity threshold of Na₂SO₄ dropped to 2752 mg/l.

#### SODIUM SULFIDE

Na₂S

- 1. General. Sodium sulfide is used in tanneries and may also be a constituent of Kraft mill wastes, and beetsugar-factory effluents. It has a high chlorine demand and a high oxygen demand; a small continuous dose of sodium sulfide can result in oxygen depletion and fish deaths (313, 362). It is highly soluble in water, the sulfide ions tending to react with hydrogen ion to form HS or H₂S, depending on the pH value of the solution.
- 2. Cross References. Sulfide, Distilled Water, Hydrogen Sulfide.

3. Effects Upon Beneficial Uses.

a. Industrial Water Supplies. Even when present in very low concentrations, sodium or potassium sulfide in the water used for mixing developers for photographic use can result in chemical fogging of emulsions on the films (242).

b. Fish and Other Aquatic Life. The following concentrations of sodium sulfide have been reported as toxic or lethal to fish:

Concentration in mg/l		Time of Exposure	Type of Fish	Reference
0.55	pH 5.2		Young carp	1698
1.0 (threshold)	Aerated		Salmonoid fish	1582
1.8 (lethal)	Aerated		Salmoneid fish	1582
2.0	Distilled		Minnows	361
2.4			Brown trout	2920
3.0	<u></u>		Minnows	690
3.0	12°C		Cutthroat trout	3502
3.0			Shiners, minnows	344, 658, <b>690</b>
3.1	15°C		Silver salmon	3502
3.2	10 0	48-hour TLm	Fathead minnows	3335
3.3	pH 7.4		Young carp	1698
3.5 3.5	17.5°C		King salmon	3502
7.8	11.0 0	90 minutes	Minnows	468
	Hard, 15°C	6 hours	Minnows	2942
10-11	main, 10 C	O DOME	Stickleback	2920
11	Distilled, 25°C	6 hours	Minnows	2942
12-13	Distinct, 25 C	6 minutes	Minnews	468
39	Hard	0 militares	Minnows	361
50	Standard	48-hour TLm	Bluegill spofish	2093
61 750	Turbid	96-hour TLm	Mosquito-fish	2940

The maximum concentration of sodium sulfide that produced no mortality has been given (3502) as 1.8 mg/l for king salmon at 17.5°C, 1.3 mg/l for silver salmon at 15°C, and 1.0 mg/l for cutthroat trout at 12°C. Fish tried to avoid solutions of sodium sulfide in concentrations of 3.1 to 39.0 mg/l (1046).

Fish removed from toxic concentrations of sodium sulfide before they stopped breathing recovered and survived (468). Minnows exposed to 17.1 mg/l of sodium sulfide in tap water have been disturbed for as long as five hours; within 24 hours, however, the sulfide had disappeared and the fish recovered (362). On the other hand, Ellis quotes a reference to the effect that exposure

for one hour to 1150 mg/l of sodium sulfide in tap water has resulted in the death of tench six days later (313).

When Na₂S is added to water it dissociates to release sulfide ions which then react with hydrogen ions to form HS or H₂S, depending on the pH value of the solution (see Hydrogen Sulfide). For that reason, the toxicity of sodium sulfide tends to increase as the pH of the water decreases from 9 to 6 (1046). This relationship has been shown by Tomiyama and Yamagawa (1698) for young carp as follows:

pH Value	Critical Lethal Concentration, mg/l
5.2	0.55
6.1	0.95
7.4	3.3
8.2	8.0

Other aquatic life have responded to sodium sulfide as shown below:

a	once	an for	a ti	~~
u	$v \sim c$	TILLT	ult	on

Mayfly larvae Insect larvae	Killed	eference 690
Bivalve larvae Mesocyclops leuckarti	Killed Lethal Toxic threshold	690 2989 2955
Daphnia magna Daphnia magna		690, 2955
Polycelis nigra Daphnia Scenedesmus E. coli	Toxic threshold Toxic threshold Toxic threshold Toxic threshold	354 2158 2158 2158 2158 690
	Mesocyclops leuckarti Daphnia magna Daphnia magna Polycelis nigra Daphnia Scenedesmus	Mesocyclops leuckarti Daphnia magna  Daphnia magna  Polycelis nigra Daphnia Becenedesmus  Toxic threshold

#### SODIUM SULFHYDRATE

NaHS

Completely and rapidly soluble in water, with an H₂S odor, this crystalline substance is used in tanneries for dehairing hides, in the manufacture of sulfur dyes, and for desulfurizing viscous rayon (364). It may also be found in Kraft mill wastes.

Using turbid water at 21-33°C, Wallen et al. (2940) studied the toxicity of NaHS toward the mosquito-fish, Gambusia affinis. They found the 24-, 48-, and 96-hour TL_m values to be 206 mg/l. The 144-hour TL_m was lowered to 138 mg/l. Haydu et al. (3501, 3502) report the minimum lethal concentrations of NaHS to be 3.3 mg/l for king salmon, 3.5 mg/l for silver salmon, 1.8 mg/l for cutthroat trout, and 0.5 mg/l for Wisconsin minnows. The maximum concentrations of sodium sulfhydrate tolerated by king salmon, silver salmon, and cutthroat trout are 2.1, 2.5, and 0.3 mg/l respectively (3501, 3502).

Gillette et al. (1442) tested the toxicity of this substance to creek chub, a fish considered to be average in tolerance. They found that the concentration below which all four test fish survived for 24 hours was 4 mg/l, while above 10 mg/l all fish died. The critical concentration of NaHS to salmonoid fish in water containing over 5 mg/l of dissolved oxygen ranged from 0.3 mg/l for threshold damage to 2.5 mg/l for lethality (1582).

#### SODIUM SULFITE

Na₂SO₃

1. General. This soluble salt is used chiefly in photographic developers and fixing operations. It is also employed in bleaching operations and as a reducing agent in the manufacture of dyes (364). Sodium and sulfite

ions may occur in various paper mill and beet-sugar-factory effluents (313).

- 2. Cross References. Sulfites, Sulfite Waste Liquor.
- 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. A concentration of 15,000 mg/l of sodium sulfite in the drinking water of rats caused no apparent injury (287).
- b. Fish and Other Aquatic Life. The lethal concentration of sodium sulfite to goldfish in 96 hours at 18-23°C has been reported (2920) as 100 mg/l; but on the other hand, concentrations up to 260 mg/l at pH 5 to 9 have been observed to be harmless to young earp (1698). Using turbid water at 18-26°C, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m for mosquito-fish to be 2600 mg/l.

The toxic threshold concentration of sodium sulfite for the flatworm, *Polycelis nigra*, was found to be 7580 mg/l (354). The minimum lethal concentration for *Daphnia* has been reported to be 300 mg/l (574, 3523). For the immobilization of *Daphnia magna* in Lake Erie water at 25°C, the threshold concentration of sodium sulfite has been reported to be 440 mg/l (352) and 3784 mg/l (358).

## SODIUM SULFONATES

(see Chapter X)

# SODIUM TETRAPROPYLENE BENZENE SULFONATE

(see Chapter X)

## SODIUM THIOCYANATE

NaSCN

(see also Cyanides, Hydrogen Cyanide, Potassium Thiocyanate)

This highly soluble salt is used in the manufacture of other thiocyanates, especially the organic compounds, and in many of the same processes as potassium thiocyanate (364). When chlorinated, it breaks down to release cyanide ions (see KSCN).

According to Schaut (362), fish were killed in two hours by 3240 mg/l of sodium thiocyanate. For Daphnia magna in Lake Erie water at 25°C, however, the threshold concentration was found by Anderson (352) to be less than 11.3 mg/l or about 10.2 mg/l (353). The threshold concentration for Polycelis nigra, a planarian, was reported by Jones (354) at 700 mg/l as SCN-.

Thiocyanate compounds have been used for the treatment of hypertension in human patients. The daily ingestion of less than approximately 120 mg of SCN has not given rise to reports of harmful effects in patients treated for 10 years (2963).

#### SODIUM THIOSULFATE

 $Na_2S_2O_3 \cdot 5H_2O$ 

Sodium and thiosulfate ions may occur as constituents of Kraft mill wastes. The toxic threshold concentration of sodium thiosulfate for the flatworm Polycelis nigra was found to be 8400 mg/l (354). The threshold concentration of sodium thiosulfate for the immobilization of Daphnia magna in Lake Erie water was found to be much less than 520 mg/l (352). The minimum lethal concentration of sodium thiosulfate for minnows has been reported to be 5.0 mg/l, for a 120-hour period (190, 344). Using highly turbid water at 22-24°C, Wallen et

#### SCHRADAN

(see Chapter IX)

## SECONDARY SODIUM ALKYL SULFATE (Teepol)

(see Chapter X)

#### SELENIOUS ACID

 $H_2SeO_3$ 

(see also Selenium)

When selenium dioxide, SeO₂, is dissolved in water, selenious acid is formed. At normal pH values, i.e. 5 to 8, this acid is only partially dissociated in water, with most of the molecules occurring as HSeO₃⁻ (911). In stabilized tap water, minnows were not harmed during a one-hour exposure to 17.1 mg/l of selenious acid (362).

#### SELENIUM

Se

- 1. General. Analogous to sulfur in many of its chemical combinations, selenium is used in its elemental form and as several salts in a variety of industrial applications, such as pigmentation in paints, dyes, and glass production; as a component of rectifiers, semiconductors, photo-electric cells, and other electrical apparatus; as a supplement to sulfur in the rubber industry; as a component of alloys; and for insecticide sprays (364, 2121, 2129). Selenium occurs in some soils as basic ferric selenite, as calcium selenate, as elemental selenium, and in organic compounds derived from decayed plant tissue. In some areas of South Dakota and Wyoming, soils may contain up to 30 mg/kg of selenium (2121). Selenium may be expected in trace quantities in the municipal sewage from industrial communities. Although selenium is found in some natural waters, food appears to be a more likely source for human ingestion (1049, 1328, 1329).
- 2. Cross References. Arsenic, Selenious Acid, Sodium Selenite.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Proof of human injury by selenium is scanty and definite symptoms of selenium poisoning have not been identified; but it is widely believed that selenium is highly toxic to man (353, 997, 1329, 1330). It has been stated that the symptoms of selenium poisoning are similar to those of arsenic poisoning (555).

In areas where selenium poisoning of livestock is common, the toxic effects appear to be associated with the consumption of high concentrations of selenium in food rather than in the water (152, 1331). In food stuffs 4.0 mg/kg is considered an extreme tolerance limit; and 3 mg/kg is regarded as a safer limit (353).

Mild chronic selenium poisoning has been observed in humans living in areas where the soil and produce are rich in selenium. In addition, there have been cases of selenosis at industrial establishments that use or produce selenium compounds. Hydrogen selenide (H₂Se) in the air in concentrations as low as 0.2 parts per million by volume produces definite toxic symptoms (2129).

Selenium in trace amounts appears to be essential for the nutrition of animals, including man, although very little is known about the mechanism of its action (3217). Arsenic and selenium are apparently antagonistic in their toxicity, tending to counteract each other. Selenium salts are rapidly and efficiently absorbed from the gastro-intestinal tract and excreted largely through the urine. Retention is highest in the liver and kidney (2121, 2129).

Surveys have shown that dental caries rates of permanent teeth were significantly higher in seleniferous areas than in non-seliniferous areas (2253). There is also a tendency for increased malocclusion and gingivitis in seleniferous areas (2253).

The U.S. Food and Drug Administration placed a "zero tolerance" on selenium and seleniferous materials with respect to permissible residue on fruits and other edible crops (3651).

The USPHS Drinking Water Standards (2036) have restricted selenium to 0.05 mg/l on a mandatory basis for many years (See Table 5-1). In 1962, however, the new standards lowered the mandatory limit to 0.01 mg/l. The WHO International (2328) and European (2329) Drinking Water Standards prescribe a mandatory limit of 0.05 mg/l. These strict standards were undoubtedly set because of the similarity between arsenic and selenium poisoning, the dental effect, and the known toxicity to livestock, as described below.

b. Irrigation. In general, the soil in parts of the world where selenium poisoning occurs naturally contains 1 to 6 mg/kg of selenium in the top eight inches. However, plants vary in their ability to absorb selenium; the final selenium concentration in the plant will be determined by many factors, including the species and age of the plant, season of the year, and the concentration of soluble selenium compounds in the root zone (1049).

Plants can absorb relatively large amounts of selenium from irrigation water or soil without apparent injury to themselves. Certain weeds, such as Astragulus, may contain as much as 4500 mg/kg of selenium (1049). Other plants grown on seleniferous soil have been found to contain as much as, or more than, 1610 mg/kg of selenium (dry weight) (1003, 1328). Byers believes that any vegetation containing 5.0 mg/kg of selenium is potentially dangerous for livestock; and that any soil containing more than 0.5 mg/kg is also hazardous (1329). Russell has pointed out that fodder containing as little as one mg/kg of selenium has caused poisoning, and states that 4.0 mg/kg is the tolerance limit of livestock (1049).

Cereals and grains concentrate selenium from the soil, the amount depending on the chemical condition of the selenium, the type of crop, and the sulfate content of the soil. High sulfates diminish the uptake of selenium. Up to 63 mg/kg of selenium have been found in wheat and up to 17.8 mg/kg in onions (2121).

Plants have been injured by selenium in the soil; wheat plants have been severely damaged by 30 mg/kg of sodium selenate in the soil (1328). However, injury to plants can be reduced or prevented by sulfate ion, when it is present in a concentration about 12 times as high as that of selenium (1328). Klintworth (1493) believes that selenium is harmful to plants at all concentrations. Walker and Rigdon (1688) have prepared an extensive bibliography of papers on selenium toxicity to plants and animals.

The USDA Regional Salinity Laboratory at Riverside, California, has not established limits on selenium, but Dr. Beath of the Research Chemistry Department, University of Wyoming, suggests the following tentative limits of selenium in water for irrigation (3652):

Irrigation Class	Selenium in mg/l	Remarks
1-low	0.00 - 0.10	No plant toxicity anticipated
2-medium	0.11-0.20	Usable, but with possible long-term accumulations under particular conditions should be watched
3-high	0.21-0.50	Doubtful-probable toxic accumula- tion in plants except under espe- cially favorable conditions
4-very high	over $0.50$	Non-usable under any conditions

c. Stock and Wildlife Watering. Selenium poisoning ("alkali disease" or "blind staggers") occurs frequently among livestock in the Great Plains regions of the United States and Canada, and also in Mexico. It can be produced in laboratory rats, as well as livestock, by feeding abnormal amounts of inorganic selenium compounds or seliniferous feed. In general, the soil in affected areas contains 1 to 6 mg/kg of selenium in the top eight inches, but higher values have also been found. Not all such soils give rise to toxic vegetation, partly because of differences in the solubility of the selenium compounds present and their availability to plants. Where poisoning is prevalent, samples of vegetation have been found to contain as little as one mg/kg of selenium. About four mg/kg appears to be the tolerance limit for livestock. Acute poisoning is caused by ingesting large amounts.

Selenium poisoning occurs naturally among cattle, sheep, horses, pigs, and even poultry, in both chronic and acute forms. It is characterized by loss of hair from mane and tail and soreness of the feet, as well as by deformity, loss of condition, and emaciation. Among poultry, the eggs give rise to abnormal or weak chicks (1049, 1328).

Impairment of vision, weakness of limbs, and respiratory death have resulted from livestock feeding on plants containing 100 to 1000 mg/kg of selenium. At lower concentrations in vegetation, up to 24 mg/kg, livestock is subject to "alkali disease" involving lack of vitality, loss of hair, sterility, lameness, and possibly death from anemia and malnutrition (2129).

Rats show toxic effects from diets containing 3 to 40 mg/kg of selenium. A dose of 4 grams of powdered selenium introduced into a dog's stomach appeared to be harmless; but 4 mg of soluble selenate per kilogram of body weight was quickly fatal (353).

The lethal dose of selenium salts for cattle is believed to be 2 mg per animal pound (1003). As sodium selenite administered by mouth, the minimum lethal dose of selenium for horses is about 1.5 mg per kilogram of body weight; for cows and calves, 4.5 to 5.0 mg per kg; and for pigs, 6 to 8 mg per kg. Chronic poisoning of cattle has been caused by as little as 1 to 4 mg/kg of selenium in fodder (1049). Milk from cows in poisoning areas contains 0.3 to 1.2 mg/l of selenium (1049).

In water, 0.4 to 0.5 mg/l of selenium is believed to be non-toxic to cattle. Such water may contribute to selenium poisoning, but the selenium content of the feed is a more critical factor (997, 1003).

The toxicity of 9 to 18 mg/kg of selenium in the dry ration of rats, pigs, and dogs has been counteracted by

various arsenic compounds administered in the drinking water (see also Arsenic) (921, 1005).

Selenium in the dry ration at a concentration of 0, 2, or 4 mg/kg did not affect the health of poultry or the hatchability of eggs. Chicks fed 5-8 mg/kg of selenium showed no harmful effects. A concentration of 5 mg/kg (dry ration) should be considered the toxic threshold for poultry (1551).

Kohlmeyer and Moxan found that 5 mg/kg of selenium (dry ration) did not affect the hatchability of turkey eggs, but 9 mg/kg caused abnormalities in young turkeys (1551).

An increase in mortality among rats fed a ration containing 11 mg/kg of Se has been caused by the presence in drinking water at concentrations of 5 mg/l of various chemicals. The presence of 5 mg/l of soluble tungsten in the drinking water reduced the mortality slightly. For a comprehensive presentation of the selenium problem, particularly in feeds, the reader is referred to the paper by Moxan and Rhian (1481).

d. Fish and Other Aquatic Life. Added as sodium selenite, 2.0 mg/l of selenium has been toxic to goldfish in eight days, and lethal in 18 to 46 days (353). Minute concentrations of selenium appear not to be harmful to fish during an exposure period of several days; however, constant exposure to traces of selenium has caused disturbances of appetite and equilibrium, pathological changes, and even deaths of fish after several weeks. Concentrations considered safe for human beings over a period of weeks have been toxic to fish (770, 3203).

Barnhart (3653) describes a reservoir in Colorado that has been stocked repeatedly with a variety of game fishes, but the fish die in a few weeks. Bottom deposits in the reservoir contain high concentrations of selenium. It is believed that selenium is passed up through the food chain to the fish which accumulate this element in the liver in lethal concentrations.

Using water from the River Havel, from which the test organisms had been recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effect of selenium added as sodium selenite. For Daphnia the median threshold effect for a 48-hour exposure at 23°C occurred at 2.5 mg/l of selenium; for Scenedesmus exposed at 24°C for 4 days, the median threshold level was also 2.5 mg/l as selenium; but for Escherichia coli at 27°C it was 90 mg/l of selenium, and for a protozoan (Microregma) it was 183 mg/l.

### SESONE

(see Chapter IX)

#### SETTLEABLE SOLIDS

(see also Suspended Solids, Silt)

Settleable solids may consist of sewage and industrial sludges, including many kinds of suspended solids that tend to settle out slowly on the stream bottom, thereby smothering bottom organisms, covering and destroying spawning beds, blanketing bacteria, fungi, and decomposing organic wastes, and in general trapping and maintaining offensive and deleterious stream conditions. Deposits of solids interfere with recreation, navigation, fish and shellfish production, and destroy esthetic values

of water. They may decompose to produce putrefactive odors and they may exude products of decomposition to overlying waters (611, 664, 673, 684, 780, 781, 782, 783, 2407, 3654, 3655).

Ellis has recommended that the stream bottom should not be blanketed to a depth of more than one-quarter of an inch by sedimentary deposits in order to prevent destruction of bottom fauna and shellfish (347).

According to many authorities, settleable solids should be removed from sewage and effluents before discharge into streams or ocean, or on land for irrigation purposes (784, 785, 786, 787, 788). Several alternative recommendations or practices have been mentioned in the literature, and most standards or criteria for streams include a provision that wastes discharged thereto should not form sludge banks or deposits. In this connection it is significant to recognize that dissolved or colloidal solids may be synthesized by bacteria in a stream to form suspended and settleable sludge consisting primarily of bacterial and biological slimes. Sulfite waste liquors, for example, contain little or no settleable solids but they can result in sizeable sludge deposits as a result of biological action in the stream (7).

Specific limiting or threshold concentrations of settleable solids permitted in natural waters are not to be found in the literature. Instead, it is generally required that settleable solids be removed from sewage or industrial wastes.

#### SEVIN

(see Chapter IX)

#### SILICA AND SILICATES

SiO₂, SiO₃--

- 1. General. The element silicon is not found free in nature but it occurs as silica in sand or quartz and as silicates in feldspar, kaolinite, and other minerals. Silicon dioxide, or silica, is insoluble in water or acids, except hydrofluoric, but it may occur in natural waters as finely divided or colloidal suspended matter, in concentrations of one to 40 mg/l (32, 2342). Silicon is used in metallurgy and silica is widely employed in industry for making glass, silicates, ceramics, abrasives, enamels, petroleum products, etc. (364). Silicates have been used in water treatment as coagulants and corrosion inhibitors while sodium silicofluoride has been used as a fluoridating agent.
- 2. Cross Reference. Turbidity, Suspended Solids, Silt.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Sodium silicates have been used as coagulants for the removal of turbidity and iron (1332) and dosages of 4.0 to 8.0 mg/l have been used to form protective coatings on pipes to inhibit corrosion of iron (206, 1333, 1334, 3305, 3656) or lead (1335). In concentrations found in natural or treated waters, silica or silicates appear to have caused no adverse physiological effects (36). According to Raux (178), silica in a concentration greater than 50 mg/l may cause difficulties arising from turbidity. When municipal water is used for boiler feed water, however, the presence of silicates may be detrimental (see below).

b. Industrial Water Supplies. A summary of the recommended limits of silica in water for various industrial processes, as discussed in Chapter V, is presented below:

Industrial Use	Recommended Limit in mg/l
Brewing Boiler feed water, 0-150 psi 150-250 psi 250-400 psi	50 40 20 5
400 psi and over Pulp and paper mills: Groundwood pulp Soda and sulfate pulp Kraft pulp, bleached Kraft pulp, unbleached Fine paper Rayon pulp production	50 20 50 100 20 25

Silica appears to be particularly undesirable in boiler feed waters (212, 1336, 1337, 1338) because it passes over in the steam and deposits in the tubes of heaters and on steam-turbine blades. Silica appears to have a volatility or solubility in steam (3657), for as much as 0.4 mg/l of silica per ml of steam has been found leaving the boilers, according to Schwartz (1339), who found that silica in boiler feed water gave the following concentrations in condensate:

Silica in	Silica in
Feedwater, mg/l	Condensate, mg/l
25	0.43
100	0.07 to 0.90
200	1.8

For the maximum concentration of silica in boiler feed water, Reichelt (1689) recommended 0.5 mg/l while Stassart (1690) preferred a limit of 0.3 mg/l for high-pressure boilers. Imhoff (1340) suggested that the silica content of steam be kept below 0.1 mg/l to control turbine-blade deposits at operating pressures of 350 psi.

c. Irrigation. Silica, per se, is generally considered to be of little importance in irrigation practice (268). Limits for several constituents suggested for irrigation water by the U. S. Department of Agriculture include silica at 10 to 50 mg/l.

d. Fish and Other Aquatic Life. An abundance of silica in water, along with other necessary nutrients, favors the growth of diatoms (36, 1287) (see also Silt, Turbidity, and Suspended Solids). Indeed, blooms of diatoms synthesize silica into the tests of the organisms and thereby lower the content in the water. The diatom Asterionella, and possibly other algae, require silica in concentrations above 0.5 mg/l for growth in ponds, and cannot utilize silica when present at lower concentrations (1453). For factors by which silicon (radioactive or otherwise) is concentrated from water into biological forms, see Chapter VIII.

#### SILICON

(see Silica and Silicates)

### SILT

1. General. By the term "silt" is meant loose sedimentary material, rock particles, mud, or clay that settle readily and may be transported by bed-load movement. Silt results from erosion, logging, mining, dredging, or irrigation operations, steel mills, gravel washing, the

precipitation of certain industrial dusts, such as those from limestone saw-mills, and also from operations in cotton and wool-cleansing plants (779, 2194, 2879, 3655, 3658, 3659). Fine silt may stay in suspension and be classified as "suspended solids", while the larger particles settle to the bottom of the water course. Like other suspended solids in streams, silt may have far-reaching effects on the nature and biota of the stream by reducing the amount of light transmitted by the water, by altering the rate of temperature change in water strata, by adsorbing organic matter and other substances that create unfavorable conditions on the bottom, and by blanketing the stream bottom (2183). Although a moderate amount of silt may have a beneficial effect on aquatic life by increasing the amount of mineral nutrients available (789), excessive quantities have been reported to affect deleteriously all of the desirable uses of water (346, 780, 781, 790, 2879, 2895, 3654, 3660, 3661).

- 2. Cross References. Suspended Solids, Settleable Solids, Turbidity.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Silt and mud are undesirable in domestic and industrial water supplies, and the cost of removing mud from water may exceed all other costs in making water suitable for use (780).
- b. Irrigation. Mud constituents of water can fertilize the soil and may also be valuable for closing up cracks in the earth channels of water. However, grit and sand may injure crops (791). Silt from fertile land is beneficial, but silt from the subsoil of eroded areas deposited on the surface of productive soils can markedly decrease their productivity (246). Silt consisting of clay-like matter can result in the packing of sediment on soil to form an impervious blanket, keeping air and water out of the soil (792). Over a three-year period of observation, silty water did not affect the yields of corn as compared with the yields from plots irrigated with clear water; however, oat fields were reduced when sediment was deposited in sufficient quantities before germination to prevent the emergence of the seedlings; and heavy silting killed bean plants grown in furrows, but not those grown on ridges (793).
- c. Aquatic Life. Silt in water reduces light penetration, alters the rate of temperature change in different water levels, and carries organic wastes to the bottom where processes of decay may continue to operate over a long period, leading to oxygen depletion, changes in pH, and other unfavorable conditions. Erosion and silting hinder fish production, smother food organisms, destroy spawning grounds, and fill pools (308, 611, 781, 790, 794, 795, 796, 797). Smith has reported that silting has reduced the bottom fauna of the Rogue River by 25 to 50 percent (798). According to Ellis, hard particles cause abrasive injuries to the delicate external organs, such as gills, spiracles, and fins, of miscellaneous aquatic animals, and fine particles tend to coat and destroy fish eggs (347, 799, 800). Ellis has recommended, therefore, that suspensoids of a hardness of one or more should be so finely divided as to pass through a 1000-mesh screen, and that the stream bottom should not be blanketed to more than one-quarter of an inch (see also Turbidity) (313, 347, 801).

Salmon and trout can withstand a heavy load of silt for several weeks; nevertheless, by limiting successful reproduction and the food supply, silting is harmful to fish (800). Ward (560, 882) agrees that silt deposits may smother spawning beds and nests, but believes that natural and mining silts are not always inimical to fish life; they may possibly be beneficial because of the food organisms and particles they carry and because muddy waters afford protection to fish against predatory animals and anglers. Ward cites experiments in which young salmon were maintained for three to four weeks without harm in circulating water containing a suspension of mud in a concentration above 1000 mg/l. Griffin (802) has reported experiments of three to four weeks' duration in which trout and salmon fingerlings fed and grew apparently well in muddy water carrying a constant silt load of 300 to 750 mg/l, and for short intervals daily during stirring, a load as high as 2300 to 6500 mg/l (For comparison, the Willamette River in heavy flood, when it appeared muddy, carried a silt concentration of only 42 mg/l).

Ziebell (2687) and Wagner (3662) measured the productivity in terms of aquatic insect populations upstream and downstream from a gravel dragline operation. He found a productivity decline of 85 percent as a result of the gravel operation. Turbidities were increased from zero to 91 mg/l and suspended solids from 2 mg/l upstream to 103 mg/l downstream. Tarzwell (2407) cites an instance where bottom samples from a silted area averaged only 36 organisms per sq ft whereas in a clean

stream bottom the average was 249 per sq ft.

d. Shellfish Culture. Most fresh-water mussels have been unable to maintain themselves in either sand or gravel bottoms when a layer of silt one-quarter to one inch deep was allowed to accumulate on the surface (790). Silt deposits can smother both mussels (331, 795, 798) and oysters (332, 790). Silt in suspension chokes the respiratory and intestinal passages of young shell-fish (314, 332, 803). Silt concentrations from 1000 to 4000 mg/l have depressed the pumping and feeding rate of oysters as much as 94 percent; and in heavy suspensions oysters have been stopped feeding entirely (804). On the other hand, some species of oysters thrive in silt-laden water (315, 804), and silt from dredging operations in the Susquehanna River did not cause oyster deaths (795).

As little as 100 mg/l of silt or other turbidity-producing substance seriously reduces the pumping rate of oysters to as low as 40 percent; 1000 mg/l caused a drop to 20 percent of the normal rate; and 3000-4000 mg/l resulted in a reduction to 4 percent. Silt, kaolin, and chalk all gave comparable results. When the oysters were returned to clear water, however, they resumed their

normal pumping (1448).

e. Recreation and Navigation. Silt and mud destroy esthetic values and produce deposits in harbors that cause significant economic losses (780, 781, 1033).

## SILVER

Ag

1. General. In nature, silver is found in the elemental state and combined in ores such as argentite, Ag₂S, horn silver, AgCl, proustite, Ag₃AsS₃, and pyrargyrite, Ag₃SbS₃. From these ores, silver ions may be leached into

ground waters and surface waters, but since many silver salts such as the chloride, sulfide, phosphate, and arsenate are insoluble, silver ions cannot be expected to occur in significant concentration in natural waters. Nine municipal water supplies in the U.S. have shown the presence of 0.05 mg/l of silver ion and at Denver the concentration is reported as 0.2 mg/l (152). Silver nitrate is highly soluble and silver sulfate moderately so (1224).

Silver metal is used in jewelry and silverware, in alloys, for electroplating, and in the processing of food and beverages. Silver nitrate is used in photography, ink manufacture, electroplating, coloring porcelain, and as an antiseptic (364, 2121). From such sources, traces of

silver can be expected to reach natural waters.

2. Cross References. Nitrates.

3. Effects on Beneficial Uses.

a. Domestic Water Supplies. Silver oxide has been used for water purification at Warsaw, Poland, and other cities. There is abundant literature on the oligodynamic action of silver and its bactericidal power, but a review of such literature is beyond the scope of this report. Dosages of 0.000001 to 0.5 mg/l of silver have been reported as sufficient to sterilize water (577, 1341, 1342, 1343, 3408, 3663, 3664, 3665). At such dosage rates, silver is not an irritant, has no toxic action toward humans, and does not interfere with the taste (1344). The fatal dose of silver nitrate for humans has been reported as 10 grams (2129).

Silver occurs in soil humus up to 5 mg/kg, in grain and cereals up to 0.9 mg/kg, and in mushrooms up to several hundred mg/kg (2121). Silver nitrate solution has been used as an antiseptic, especially in the upper

respiratory system.

Prior to 1962, no restriction was placed on silver in the USPHS Drinking Water Standards (2036), nor does any limitation presently appear in the WHO International or European standards (2328, 2329). The 1962 edition of the USPHS Standards (2036) sets a mandatory limit of 0.05 mg/l of silver. Presumably, this restriction was set not because of the danger of silver in natural sources of water supply but to prevent its intentional addition to water, in excessive amounts, for disinfection. The limit was based on cosmetic considerations rather than public-health effects.

The chronic administration of silver salts, not uncommon in the early part of the 20th century, led to a bluish permanent darkening of the skin called "argyria". With prolonged administration of silver salts, a small proportion is absorbed and deposited in the skin where it is reduced by light to metallic silver (2129). This impregnation of the tissues with silver causes no recognizable disturbance to health (3704), but is obviously undesirable from an esthetic viewpoint. Although the total dosage of ingested silver required to produce argyria is not known, the intravenous injection of 1 gram will cause this effect. Based on the USPHS limit of 0.05 mg/l of silver and two liters per day of water consumption, it would take over 27 years to ingest one gram of silver, a large part of which would pass through the intestinal tract without assimilation (2121). This calculation ignores the daily intake of silver from food, which might be appreciable for mushroom lovers.

b. Fish and Other Aquatic Life. Using silver nitrate, Marsh and Robertson (1459) found that 0.04 mg/l killed some (but not all) test salmon fry in tap water within 48 hours; 0.44 mg/l of silver nitrate proved decidedly toxic. A concentration of 0.033 mg/l of silver nitrate did not prove fatal in 48 hours. The highest concentration of silver nitrate tolerated by young eels for more than 24 hours was reported to be about 0.2 mg/l. Toward guppies, the LD₅₀ value was found to be 0.0043 mg/l, as silver (2921).

Jones (1460) found that the lethal concentration limit of silver applied as silver nitrate, for sticklebacks at 15-18°C was 0.003 mg/l. In different concentrations of silver the average survival times of the fish were as follows: one week at 0.004 mg/l, four days at 0.01 mg/l and only one day at 0.1 mg/l, as silver. Anderson (598) reported that the toxic threshold of silver nitrate for

sticklebacks was 0.0048 mg/l.

The level of toxicity of silver toward lower organisms has been reported by several observers. Using water from the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of silver, added as silver nitrate, on various species during a 4-day exposure, at 23-27°C. For Daphnia and for Microregma the median threshold effect occurred at 0.03 mg/l of silver, for E. coli at 0.04 mg/l, and for Scenedesmus at 0.05 mg/l. Jones (608) tested the toxicity of silver nitrate toward Polycelis nigra, a flatworm, and found the threshold concentration to be 0.15 mg/l of silver. Toward Daphnia magna in Lake Erie water at 25°C, the threshold for immobilization was reported (598) to be 0.0051 mg/l of silver nitrate. Hodgson (2956) studied the stimulating effects of several substances on the water beetle, Laccophilus maculosus. He found that 580 mg/l of silver nitrate stimulated 50 percent of the beetles into movement, but no lethal dose was reported.

The Severn and Mersey River Boards in England (2950) have set working standards of 1.0 mg/l on the

total of all heavy metals, including silver.

#### SILVEX

(see Chapter IX)

#### SIMAZINE

(see Chapter IX)

### SINOX

(see Chapter IX)

## SKATOLE

 $C_9H_9N$ 

This constituent of coal tar, feces, and some plants is soluble in hot water, giving a fecal odor (364). The odor is detectable at a concentration of 0.0012 mg/l (1756).

#### SLAKED LIME

(see Calcium Hydroxide)

#### SOAPS

(see also Chapter X)

Soaps are salts of fatty acids, usually made by the saponification of a vegetable oil with sodium hydroxide.

They may be formed also by resinous acids in the Kraft

process at paper mills.

Toward fish, crude sulfate soap from Kraft mill wastes had a minimum lethal concentration of 5.0 mg/l toward minnows and shiners, according to research by the National Council for Stream Improvement (190, 344, 574, 658, 690, 3500, 3523). LeClerc and Devlaminck (3666) report that for minnows the minimum lethal concentration of sodium palmitate and sodium oleate was 10-12 mg/l in distilled water and 900-1000 mg/l in hard water. For sodium stearate it was 10-12 mg/l in distilled water and 250-300 mg/l in hard water. The effect of water hardness was confirmed by Henderson et al. (1910) who found that the 96-hour TLm values for three packaged soaps ranged from 29 to 42 mg/l in soft water but averaged 1470 mg/l in hard water. Soaps form insoluble complexes or precipitates in hard water which are apparently non-toxic to fish. The pure compound, sodium stearate, was somewhat less toxic than the packaged soap products

Cole (311) claims that dairy wastes contain soaps that are toxic to fish at 600 mg/l and Schaut (362) reports that soapy waste waters at a dilution of 1:240 had no effect on minnows. Turnbull et al. (2093) reported that the 48-hour TL_m of truck-washing soap solution toward bluegill sunfish at 20°C occurred at dilutions of 1:357 to 1:416.

Toward other aquatic organisms, crude sulfate soap from Kraft mills had a TL_m of 50 mg/l for *Chironomus* larvae, 10 mg/l for mayfly larvae, and 5.0 mg/l for *Daphnia magna* (190, 574, 690, 3500, 3523). Soaps in concentrations of 1000 to 2500 mg/l were lethal to mosquito pupae by reducing the surface tension of the water so that the pupae were unable to maintain their position and suffocated (805). Solutions containing 5,000 to 10,000 mg/l were directly toxic to the pupae. In another instance (756) soap in a concentration of 2000 mg/l completely destroyed mosquito larvae and pupae.

### SODA PULP MILL WASTE

(see Kraft Pulp Mill Wastes)

#### SODIUM

Na

1. General. This very active metal does not occur free in nature, but sodium compounds constitute 2.83 percent of the crust of the earth (364). Owing to the fact that most sodium salts are extremely soluble in water, any sodium that is leached from soil or discharged to streams by industrial wastes will remain in solution. Some sodium may be removed by ion-exchange phenomena in the passage of ground waters through certain soils. For other effects of sodium on soils, see Chapter V—Agricultural Supply.

Sodium is the cation of many salts used in industry and as such is one of the most common ions in process wastes. The information presented below pertains to literature in which the sodium ion, per se, was mentioned without reference to the sodium salt. Where concentrations were given in terms of the salt, the literature has been abstracted under the appropriate sodium com-

pound.

2. Cross References. Sodium Salts, Potassium, Dissolved Solids, Chapter IV, Chapter V.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Sodium in drinking water may be harmful to persons suffering from cardiac, renal, and circulatory diseases (1242, 3667), and as much as 200 mg of sodium from drinking water may be injurious (152). Although it has been reported (627) that drinking water of good quality may contain up to 115 mg/l of sodium, Hibbard (250) recommends a limit of 10 mg/l as desirable. According to Lockhart et al. (3241) the taste threshold of sodium in distilled water varies with the sodium salt used, as follows:

Salt Tested	Taste Threshold of Sodium in mg/l
Sodium acetate	140
Sodium carbonate	3 <del>4</del>
Sodium bicarbonate	290
Sodium chloride	135
Trisodium phosphate	· 75

b. Industrial Water Supplies. More than 50 mg/l of sodium plus potassium in boiler waters may cause foaming (1214). Other limitations for sodium, as given in Chapter V, are expressed in terms of the sodium salts (see Sodium Chloride, Carbonate, and Sulfate).

c. Irrigation. Sodium is required in very limited amounts for most plant growth (3634). An exception is the desert plant, halogeton, which apparently needs sodium for optimum growth (3668). In high concentrations sodium is not only toxic to plants but deleterious to soil conditions (268, 635, 1322) (see also Chapter V—Irrigation). Sodium carbonate and bicarbonate are more harmful than other sodium salts to plants (273). On a weight basis, chlorides are generally more toxic to plants than sulfates, but at equal osmotic pressures, sodium sulfate appeared to be more injurious to flax than sodium chloride (1093).

High concentrations of sodium (e.g. 106-212 mg/l) in water used for sprinkler irrigation can, under certain conditions and with a few plants, cause deleterious accumulations of sodium in the foliage (3669, 3670). Sufficient sodium has been absorbed by citrus leaves from a single sprinkling with water containing 69 to 190 mg/l of sodium to cause serious leaf burn and defoliation (3670).

Sodium-saturated soils are greasy to feel. Sodium soil colloids swell, closing the pores of the soil, reducing soil permeability to water and air, and increasing the pH of the soil solution to dangerous levels. The deterioration of soil quality because of sodium in the irrigation water is a steadily cumulative process, with impaired drainage resulting in even more highly concentrated soil solutions (280).

Kelley reported that an average concentration of 82 mg/l of sodium in water from the Colorado River was not expected to affect seriously either the growth of citrus trees or soil conditions in the South Coastal Basin of California (1060). For an instance where sodium figured prominently in a court case, see Barakis vs American Cyanamid Co. in Chapter IV.

d. Stock and Wildlife Watering. Excess concentrations of various sodium salts in the drinking water are deleterious to various animals. Well waters containing 7000 mg/l of sodium were toxic to chicks (1551). A threshold limit of 2000 mg/l of sodium for livestock has been suggested by Stander (3373). For further details,

see Sodium Salts, Dissolved Solids, Chapter V. Sodium bicarbonate is less injurious than sodium carbonate (640).

e. Fish and Other Aquatic Life. Of the United States waters supporting a good fish fauna, ordinarily the concentration of sodium plus potassium is less than 6 mg/l in about 5 percent; less than 10 mg/l in about 50 percent; and less than 85 mg/l in about 95 percent (310).

The toxicity threshold of sodium for *Polycelis nigra* is 4370 mg/l from sodium chloride, and 1000 mg/l from sodium nitrate (353, 608). A sodium concentration of 500 mg/l is lethal to stickleback (353). On the other hand, moderate amounts of sodium in water may reduce the toxicity of potassium and ammonium salts toward fish (306).

The possible accumulation of radioactive sodium (Na-24) in aquatic life, fish, or oysters is not considered to be hazardous owing to the short half life (about 15 hours) of radiosodium (2442).

Several investigators have reported independently that 500-1000 mg/l of sodium was toxic to fish in distilled and soft waters when sodium chloride or nitrate was tested 1450, 2941). However, Gueylard reported as harmless to sticklebacks concentrations up to 4720 mg/l of sodium in distilled water and up to 7870 mg/l in tap water when sodium chloride was added (1459).

Freeman and Fowler (1691), using a standardized double-distilled water, studied the toxicity of five inorganic sodium salts to Daphnia magna at 23°C. The 100-hour toxicity thresholds were determined for each salt alone, in combinations of two, and in combinations of three. The 100-hour toxicity threshold was defined as the concentration that will immobilize 50 percent of the organisms in 100 hours. Rather than list their results separately under the specific sodium salts involved, all of their data are presented under this heading in order that the magnitudes can be compared. For each of the five salts tested singly, the 100-hour toxicity thresholds and the resulting pH values are shown in the following tabulation:

Compound	100-Hour Toxicity	pH at
Tested	Threshold in $mg/l$	Threshold
Sodium bisulfite	102	7.3
Sodium carbonate	524	9.5
Sodium chromate	0.42	7.8
Sodium silicate	2 <del>4</del> 7	9.1
Sodium sulfate	4547	7.7

When these salts were tested in combinations of two, the results were as follows:

20 (10 1	
100-Hour Toxicity Thresholds in mg/l	pH at $Threshold$
85 436	9.2
70 0.286	7.3
177 427	7.5
82 3642	7.5
408 0.33	9.3
180 85	9.3
	Thresholds in mg/l  85 436 70 0.286 177 427 82 3642 408 0.33

Compounds Tested	100-Hour Toxicity Thresholds in mg/l	pH at $Threshold$
Sodium carbonate Sodium sulfate	221 1918	9.2
Sodium chromate Sodium silicate	$\begin{array}{c} \textbf{0.159} \\ \textbf{93} \end{array}$	8.7
Sodium chromate Sodium sulfate	0.276 2984	7.9
Sodium silicate Sodium sulfate	158 2899	9.0

In combinations of three, the toxicities of the sodium salts were as follows:

Compounds Tested	100-Hour Toxicity Thresholds in mg/l	$pH\ at$ $Threshold$
Sodium bisulfite Sodium carbonate Sodium chromate	87 440 0.35	9.3
Sodium bisulfite Sodium carbonate Sodium silicate	38 194 92	8.8
Sodium bisulfite Sodium carbonate Sodium sulfate	58 295 2562	9.0
Sodium bisulfite Sodium chromate Sodium silicate	144 0.861 506	6.9
Sodium bisulfite Sodium chromate Sodium sulfate	75 0.306 3312	6.9
Sodium bisulfite Sodium silicate Sodium sulfate	52 126 2308	8.5
Sodium carbonate Sodium chromate Sodium silicate	182 0.146 86	9.1
Sodium carbonate Sodium chromate Sodium sulfate	$240 \\ 0.192 \\ 2079$	9.3
Sodium carbonate Sodium silicate Sodium sulfate	155 73 1343	8.8
Sodium chromate Sodium silicate Sodium sulfate	0.201 119 2180	8.5

From the foregoing tabulations it is noted that the toxicity of sodium salts depends largely on the anion involved, the chromate being exceedingly toxic and the sulfate least so. Moreover, there appears to be no correlation between the toxicity displayed and the pH value, but since Daphnia magna is known to live within the pH range 6.2-9.5, which embraces all of the foregoing results, pH was apparently not the sole cause of mortality. It is also noted that the thresholds for specific compounds are lower when tested in combinations of two or three with the exception of sodium bisulfite with sodium silicate, or with sodium silicate and sodium chromate. This latter variation may be attributable to the possible oxidizing action of the chromate on the bisulfite (1691).

#### SODIUM ACETATE

 $NaC_2H_3O_2 \cdot 3H_2O$ 

Highly soluble in water, this compound is used as a mordant in textile dyeing, as a buffering agent in chemical production, in photography, and in medicine as a diuretic, expectorant, or alkalizer (364). According to Lockhart et al. (3241), the taste threshold of the anhydrous salt is 500 mg/l, or for the crystalline form 830 mg/l. Hodgson (2956) studied the stimulating effects of

sodium acetate on the water beetle (*Laccophilus maculosis*) and found that a concentration of 32,600 mg/l was required to stimulate the movement of 50 percent of the beetles.

## **SODIUM ACID PYROPHOSPHATE** Na₂H₂P₂O₇

Soluble in water with an acid reaction, this white fused substance is used chiefly in baking powder (364). A concentration of 400 mg/l in sea water caused a decrease in irritability of oysters, but 500 mg/l caused oyster deaths within 44 hours (1448, 1467).

#### SODIUM ALKYL ARYL SULFONATE

## SODIUM ALKYL BENZENE SULFONATE

#### SODIUM ALKYL SULFATE

(see Chapter X)

#### SODIUM ALUMINATE

NaAlO₂

This highly soluble salt is used in water treatment, for sizing in paper mills, and for printing in textile plants (364). Wallen et al. (2940) tested its toxicity toward mosquito-fish (Gambusia affinis) in turbid water at 17-19°C. They found 24-, 48-, and 96-hour TL_m values of 199, 126, and 111 mg/l respectively. This salt coagulated the water and reduced turbidity.

## SODIUM ANTHRAQUINONE-α-SULFONATE

# SODIUM ARYL ALKYL POLYETHER SULFONATE

(see Chapter X)

## SODIUM ARSENATE

Na₂HAsO₄

(see also Arsenic, Arsenic Trioxide, Sodium Arsenite)

This colorless, odorless salt, readily soluble in water, is used in dyeing and printing fabrics and in various fungicides and insecticides.

It is not highly toxic to fish or other aquatic life. According to Jones (2120) the lethal concentration of sodium arsenate toward minnows at 16-20°C is 234 mg/l, as arsenic. It has also been reported (617) that minnows survived for 16 hours in a solution of sodium arsenite equivalent to 250 mg/l of arsenic.

Toward lower forms of aquatic life, the toxicity of sodium arsenate is variable. The threshold concentration for immobilization of *Daphnia magna* in Lake Erie water has varied from 18 to 31 mg/l as sodium arsenate, or 4.3 to 7.5 mg/l as arsenic (352, 353, 358). The toxic threshold for the flatworm *Polycelis nigra*, is reported to be 670 mg/l as AsO₄, or 361 mg/l as arsenic (354).

### SODIUM ARSENITE

NaAsO₂

(see also Arsenic, Arsenic Trioxide, Sodium Arsenite)

Freely soluble in water, sodium arsenite is used in dyeing, in arsenical soap making, in termite extermination, and in weed-killers. As a commercial preparation it is often a mixture of several sodium and arsenic compounds. Therefore, references to sodium arsenite solutions are often reported in terms of arsenic concentration or as arsenic trioxide equivalents.

Sodium arsenite has been used extensively as a herbicide for the control of mixed submerged vegetation in static water. Commercial sodium arsenite contains varying amounts of other arsenic compounds and impurities; hence it is labeled in terms of equivalent arsenic trioxide (As₂O₃). For the control of submerged vegetation in ponds and lakes, applications of 2 to 5 mg/l as arsenic trioxide (1.5 to 3.8 mg/l as As) have been found effective. Although these concentrations are generally considered to be safe for fish and other aquatic animals, it is advisable to spray only a part of the pond or lake at one time so that fish may avoid the sprayed area. Fish are reported to be sensitive to sub-lethal doses of sodium arsenite and will generally swim away into fresh water (890, 2861, 3671). Commercial sodium arsenite in concentrations up to 10 mg/l (arsenic content not stated) have been used for weed control in Wisconsin lakes without harm to the fish population (1006).

The following concentrations of sodium arsenite, expressed as arsenic, have been reported as lethal, toxic, or otherwise deleterious to aquatic organisms:

Concentration,	. •		
as Arsenic,	Time of		
mg/l	Exposure	Organism	Reference
1.0-2.0		Fish	1692
1.4-2.3		Fish food organisms	
1.9-3.0	· <del></del>	Midges, mayflies,	,
4.6	48 hours	amphipods Daphnia	3009
5.0	10 days		2158
5.0	48 hours	Pink salmon	2091
0.0	40 HOURS	Microregma	
5.2		(protozoan)	3343
	40 5	Daphnia magna	352
8.4	48-hour TLm	Chum salmon fry	2900
15	48 & 72-hour TLm	Fingerling channel	
		eatfish	2981
17.8		Minnow	2920
20	36 hours	Rainbow trout,	
		minnows	3005
20	36 hours	Minnows	617
27	72-hour TLm	Minnows	3672
27.6	24-hour TLm	Fingerling channel	0012
	27 Hour Tabe	catfish	2981
29	48-hour TLm	Minnows	
35-46			3672
45	48 hours	Scenedesmus	2158
	24-hour TL _m	Minnows	3672
.290	48 hours	Escherichia coli	2158

The literature on weed control contains statements that applications of sodium arsenite up to 10 mg/l as  $\text{As}_2\text{O}_3$  (7.6 mg/l as As) are not harmful to fish, but the foregoing table would indicate that the threshold level is somewhat lower than expected. Furthermore, fish-food organisms are susceptible at concentrations as low as 1.0 mg/l.

On the other hand, the following concentrations of sodium arsenite, expressed as arsenic, have been reported to have no harmful effects on the organism noted:

Uoncentration, as Arsenic, mg/l	Time of Exposure	Organism Refe	erence
1.3		Fish or fish-food organism	1007
1.3-1.5	·	Fish-food organisms	1007, 1008
1.4-2.9		Fish	416
2.9		Chironomus larvae	574
5.0	24 hours	Trout, bluegills, sea lamprey	2976
8-16	•	Damselflies, dragonflies, sowbugs, water mites	3009
15	96 hours	Minnows	3672

Lawrence (3673, 3674) reports that two applications of 4 mg/l of sodium arsenite applied one month apart in experimental ponds reduced the number of bottom organisms an average of 34 percent and reduced bluegill production an average of 42 percent as compared with control ponds. Two applications of 8 mg/l of sodium arsenite applied one month apart reduced the number of bottom organisms an average of 45 percent and bluegills 65 percent as compared with control ponds. An application of 4 mg/l killed all microcrustacea and greatly reduced the population of rotifers.

#### SODIUM AZIDE

 $NaN_3$ 

Highly soluble in water, this crystalline solid is used in chemical manufacturing and in medicine as a hypotensive agent (364). Using water of the River Havel, Bringmann and Kuhn (2158, 3343) determined the thresholds of toxicity to be 0.3 mg/l for Daphnia, 3 mg/l for Microregma (a protozoan), 4 mg/l for Scenedesmus (an alga), and 19 mg/l for Escherichia coli. Toward trout, bluegills, and sea lamprey in Lake Huron water at 12°C, 5 mg/l of sodium azide had no apparent effect during a 24-hour exposure (2976).

## SODIUM BENZENE SULFONATE

(see Chapter X)

#### SODIUM BENZOATE

CeH5COONa

(see also Benzoic Acid)

This highly soluble salt is used as a preservative in food products with concentrations up to 1000 mg/kg being permitted. The oral LD₅₀ for rats is given as 4100 mg/kg of body weight (364).

In Lake Erie water at 25 °C, the threshold concentration of sodium benzoate for immobilization of *Daphnia* magna with 48 hours of exposure was less than 650 mg/l, and Anderson (352) estimated the true threshold concentration to be about 585 mg/l. Toxicity was due to factors other than osmotic pressure.

#### SODIUM BICARBONATE

NaHCO₃

1. General. This freely soluble salt dissociates completely in water into sodium and bicarbonate ions. The concentration of bicarbonate ions, in turn, depends upon the resulting pH value (see Bicarbonates, Carbonates). The bicarbonate acts as a powerful buffering agent. Sodium bicarbonate is used in the manufacture of many sodium salts, as a source of carbon dioxide, in fire extinguishers, in effervescent salts and baking powder, in cleaning compounds, and in many industrial processes.

Goudey (992) suggested classification of ground waters and included the following recommendations as to sodium bicarbonate limits: Class AA (domestic), 0 mg/l; Class A (irrigation), 0 to 50 mg/l; Class B (irrigation), 50 to 100 mg/l; and Class C (irrigation and industry), more than 100 mg/l.

2. Cross References. Sodium Carbonate, Bicarbonates, Chapter V.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The taste threshold of sodium bicarbonate in water is reported (3241) to be 1060 mg/l.

- b. Industrial Water Supplies. It has been recommended (173) that the sodium bicarbonate concentration of raw water to be used for making ice not exceed 35 mg/l.
- c. Irrigation. Water containing sodium carbonate or bicarbonate as the predominant salts may be more harmful to plants than water with other sodium salts (273). Sodium bicarbonate, although it is an important buffer in water, may be directly or indirectly harmful to plants. It may be toxic, it tends to increase soil alkalinity, and in addition, by precipitating calcium carbonate out of solution, it reduces calcium concentration of the soil and soil permeability (264, 268). A concentration of 1500 to 2000 mg/l of sodium bicarbonate in the water has caused a 50-percent reduction in the dry weight of tomatoes grown in liquid culture (1345). In irrigation water 4000 mg/l has rendered soils alkaline and impaired their fertility (921).
- d. Stock and Wildlife Watering. The following concentrations of sodium bicarbonate in drinking water have been reported as injurious to animals by causing thirst, diarrhea, and impaired growth:

Concentration in mg/l	Animal	Reference
6000	Chicks	287, 284, 2980
15000	Rats	287, 284
20000	Rats	287, 28 <del>4</del>

Concentrations from 12,000 to 24,000 mg/l have caused

deaths among chicks (284).

e. Fish and Other Aquatic Life. The toxic threshold concentration of sodium bicarbonate for *Polycelis nigra*, a flatworm, was found to be 7140 mg/l (354). The threshold concentration of sodium bicarbonate for immobilization of *Daphnia magna* in Lake Erie water was reported to be 2350 mg/l (352) and 4200 mg/l (358). Cairns et al. (2933, 2934, 2935) found the 96-hour TL_m values for bluegill sunfish in standard dilution water at 20°C to be 8250 to 9000 mg/l depending on the size of the fish. Using highly turbid water at 20-22°C and the mosquito-fish as the test organism, Wallen et al. (2940) found the 96-hour TL_m to be 7550 mg/l. The 24-hour TL_m was 7700 mg/l.

#### SODIUM BIFLUORIDE

NaF·HF

(see also Sodium Fluoride)

This highly soluble powder produces an acid reaction in solution; hence it is used as a "sour" in laundrying (364). According to Simonin (3271) the fish *Tinca vulgaris* is killed by 100 mg/l of this compound.

## SODIUM BISULFATE

NaHSO₄

(see also Sulfates, Sulfuric Acid)

Known also as sodium acid sulfate, this compound is freely soluble in water and dissociates into Na⁺ and HSO₄ ions. The concentration of the bisulfate ion in solution depends upon the resulting pH value and above pH4 almost all bisulfate will be converted to sulfate ion.

For immobilization of Daphnia magna, the threshold concentration of sodium bisulfate in Lake Erie water was found to be less than 145 mg/l (352). Later work by Fairchild (2946) showed that the threshold toxicity value is dependent on dissolved oxygen. For Daphnia

exposed 100 hours at 23°C, the threshold concentrations were as follows:

Dissolved Oxygen, mg/l	Threshold Level of Toxicity, mg/l
6.5	153
8.9	145
1.55	106

#### SODIUM BISULFITE

NaHSO₃

Used as a disinfectant and bleach in textile, laundering, paper, and fermentation industries, this compound is freely soluble in water, dissociating into Na⁺ and HSO₃⁻ ions. The concentration of the undissociated bisulfite ion depends upon the resulting pH value; furthermore, it is readily oxidized to sulfate (364).

The toxicity threshold (100-hours at 23°C) to Daphnia magna has been reported at 102 mg/l (1691), but in the presence of other sodium salts, this threshold may be somewhat lower (see Sodium). Fairchild (2946) also studied the toxicity of sodium bisulfite toward Daphnia at various concentrations of dissolved oxygen at 23°C, with the following results:

Dissolved Oxygen, mg/l	Threshold Level of Toxicity, mg/l
9.3	109
6.5	61
3.2	77
1.6	70

Le Clerc et al. (2942, 2943, 2944) exposed minnows for 6 hours to solutions of sodium bisulfite in distilled and hard water. The minimum lethal dose in distilled water at 19°C was 60-65 mg/l and in hard water at 18°C it was 80-85 mg/l. Using turbid water at 17-22°C and the mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24-, 48-, and 96-hour  $TL_m$  values to be 240 mg/l. This concentration greatly reduced the turbidity.

#### SODIUM BORATE

 $Na_2B_4O_7 \cdot 10 H_2O$ 

(see also Boron, Sodium Perborate)

Commonly known as borax, this compound is used extensively as a cleaning agent in homes and industry. It is also employed as a wood preservative, as a treatment against wood fungus, in tanning operation, and for the control of aquatic weeds (898). Certain other borates, such as phenyl mercury borate in a concentration of 10 mg/l, have been used effectively against the growth of slimes in pipes in paper mills (1346).

According to Le Clerc and Devlaminck (2942, 2943, 2944), the minimum lethal dose of sodium borate (Na₂B₄O₇·10H₂O) toward minnows was 3000 to 3300 mg/l at 19°C in distilled water and 7000 to 7500 mg/l at 17°C in hard water. Toward mosquito fish (Gambusia affinis) in turbid water, Wallen et al. (2940) found the 96-hour  $TL_m$  at 22-26°C to be 3600 mg/l.

With respect to lower aquatic life, sodium borate appears to be more toxic than towards fish. The threshold concentration for immobilization of Daphnia magna was reported (352) as being much less than 240 mg/l and was estimated at 120 mg/l (353). The toxic threshold concentration of sodium borate for Polycelis nigra, a planarian worm, was found to be 1530 mg/l as borate (354).

## SODIUM BROMATE

NaBrO_a

(see also Bromine, Sodium Bromide)

Highly soluble in water, this crystalline salt is used in ore processing and for promoting the growth of yeast cells. The oral MLD for rabbits is given at 580 mg/kg of body weight (364).

## SODIUM BROMIDE

NaBr

(see also Bromine)

Used primarily in photographic work, this salt of bromine is highly soluble in water. In water supplies used for preparing photographic solutions, bromides slow up the rate of the chemical reactions (242). The toxicity threshold concentrations of sodium bromide reported for Daphnia magna in Lake Erie water at 25°C range from 4100 to 8200 mg/l (352, 353). The toxic threshold concentration of sodium bromide for Polycelis nigra, a flatworm, was found to be 14,400 mg/l (354). To stimulate the movement of water beetles (Laccophilus maculosis), a sodium bromide concentration of 14,400 mg/l was required (2956).

## SODIUM p- BROMOBENZENESULFONATE SODIUM BUTYL MERCAPTIDE C4H9SNa

This soluble compound ionizes in water to form sodium and mercaptide ions. In normal pH ranges, the mercaptide ion reacts with hydrogen ion to form butyl mercaptan. In testing the toxicity of various refinery materials toward bluegill sunfish, Turnbull et al. (2093) determined  $TL_m$  values as follows:

	$TL_m \ Values \ in \ mg/l$			
	as SH		as C ₄ H ₈ SNa	
	24-hour	48-hour	24-hour	48-hour
Without reoxygenation	7.4	5.5	25.1	18.7
With reoxygenation	4.1	3.5	13.9	11.9

#### SODIUM n - BUTYL SULFONATE

(see Chapter X)

## SODIUM CARBONATE

Na₂CO₃

- 1. General. Sources of sodium carbonate in water include natural minerals, and effluents from chemical plants and paper mills. Known also as "soda ash", this salt is highly soluble in water and dissociates into sodium and carbonate ions, with a resulting increase in alkalinity and a tendency to raise the pH value. The carbonate ions will react with hydrogen ions until an equilibrium is established (see Carbonates, Bicarbonates, and Alkalinity). Sodium carbonate is used in the manufacture of glass, soap, and other sodium salts, in textile scouring, in water treatment and in numerous other processes (364).
- 2. Cross References. Dissolved Solids, Carbonates, Bicarbonates, Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of sodium carbonate in water is reported as 15 to 75 mg/l (621) and as 78 mg/l (3241). Waters containing 360, 430, and 500 mg/l of sodium carbonate have been considered wholesome and safe (32, 36).

- b. Industrial Water Supplies. Sodium carbonate in water for making ice is about 1.25 times as objectionable as sulfates and chlorides (231). Sodium carbonate in water for preparing developer solutions for use in photography may speed up the action of weakly alkaline solutions (242). For brewing, a limit of 100 mg/l has been recommended (see Chapter V).
- c. Irrigation. Sodium carbonate is extremely toxic to plants (264, 268). Sodium carbonate in irrigation water hardens soil and reduces its permeability (348) (see also Chapter V). On the other hand, it has been reported that 100 to 400 mg/l of sodium carbonate in the water was not injurious to various greenhouse plants over a period of six months of use (1205).
- d. Stock and Wildlife Watering. Waters containing high concentrations of sodium carbonate cause diarrhea, symptoms of malnutrition, unsatisfactory growth, and may also interfere with reproduction of livestock. The following concentrations of sodium carbonate have been reported as injurious to animals:

Concentration in mg/l	Animal	Effect	Reference
1.025	General livestock	Diarrhea	2394
7,500	Poultry	Lethal in 7 days	2980
10,000-15,000	Rats	Lethal to young	287
10,000-19,000	Rats	Inhibited growth	2980
10,000-20,000	Rats	Lethal to young	284
20,000	Rats	Lethal to young	640

e. Fish and Other Aquatic Life. The threshold concentration of sodium carbonate for immobilization of Daphnia magna in Lake Erie water at 25°C was reported to be 424 mg/l (358); less than 424 mg/l (352); and 300 mg/l (574). The minimum lethal concentration for Daphnia was also shown to be 300 mg/l at 17°C and at 800 mg/l all animals were killed (3523). The 100-hour toxicity threshold at 23°C in double-distilled water for Daphnia magna has also been reported at 524 mg/l with a resulting pH value of 9.5. According to Fairchild (2946), the threshold of toxicity toward Daphnia depends on the dissolved oxygen content of the test water. At 23°C for a 100-hour exposure he found the threshold toxicity level to be 552 mg/l at a dissolved oxygen tension of 6.5 mg/l; but only 267 mg/l when the DO dropped to 1.53 mg/l.

The following concentrations of sodium carbonate have been reported to kill fish:

een reported	LEUMIN			
Joncentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
68	Tap	120 hours	King salmon	3501
70	Тар	120 hours	Silver salmon	3501
80	Tap	120 hours	Cutthroat trou	t 3501
200		4.5 hours	Bass	1030
250		120 hours	Shiners	190
250-300	Tap	Tew hours	Shiners, suckers,	
			carp	313
300	Standard	96-hour TLm	Sunfish	2933
500		4.5-11 hours	Sunfish	1030
500		7-9 hours	Bass	1030
500		½-3 days	Bass	1030
530	Тар	3 days	Bluegills	313
740	Turbid	24-hour TLm	Mosquito-fish	2940
840	Turbid	48-hour TLm	Mosquito-fish	2940
1200	Turbid	96-hour TLm	Mosquito-fish	2940

The following concentrations of sodium carbonate have not been harmful within the time specified:

Concentration in mg/l	$Time\ of\ Exposure$	Type of Fish	Reference
33	5 days	Cutthroat trout	3501
44	5 days	Silver salmon	3501
58	5 days	King salmon	3501
100	7 days	Bass	1030
200	7 days	Sunfish	1030
200-500	7 days	Goldfish	1030
500	7 days	Some goldfish	1030

## SODIUM CARBOXYMETHYL CELLULOSE

(see Chapter X)

### SODIUM CHLORATE

NaClO₃

(see also Chlorine)

This strong oxidizing compound dissolves readily in water and ionizes to Na⁺ and  $ClO_3^-$ ; but the anion is unstable in aqueous solution, releasing oxygen and forming OCl⁻. (see Chlorine). Sodium chlorate is used for weed control, as well as in the manufacturing of matches and explosives, dyeing and printing of fabrics, and tanning and finishing of leather. It is also found in some effluents from chlorine and bromine works. Concentrations from 20,000 to 40,000 mg/l, as used for weed control, are considered non-toxic for man and animals, but create a fire hazard as the water evaporates (897). The oral  $LD_{50}$  in rats is given as 12,000 mg/kg of body weight (3009).

The threshold of toxicity for perch is given as 11,000 mg/l and for bleak as 13,000 mg/l in tap water (2977). A concentration of 1000 mg/l in hard water was not harmful to goldfish during a 5-day exposure (313).

With respect to lower organisms, the literature is not consistent. The toxic threshold of sodium chlorate toward Polycelis nigra, a flatworm, was found to be 16,000 mg/l (354) and toward Daphnia magna 4240 mg/l (352). Bringmann and Kuhn (2158) report the threshold concentration toward Daphnia to be greater than 1000 mg/l; but toward the alga Scenedesmus the threshold level was only 3 mg/l as chlorate (about 3.8 mg/l as sodium chlorate) and toward E. coli only 4 mg/l as chlorate (5.1 mg/l as sodium chlorate).

## SODIUM CHLORIDE

NaCl

- 1. General. Sodium chloride in water may be of natural origin, or it may be introduced as a component of sewage or industrial wastes, including effluents from salt and brine works, oil wells, dairies, spent irrigation waters, etc. The sodium and chloride ions in natural waters are frequently the most prevalent, and they constitute the bulk of the ions in sea water.
- 2. Cross References. Tastes, Chlorides, Dissolved Solids, Specific Conductance, Mercuric Chloride, Distilled Water, Chapter V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Sodium chloride can be tasted in water by most people at a concentration of 550 mg/l (947); however, taste threshold values from 200 to 900 mg/l have also been reported (621, 3241, 3391,

3392). Water containing more than 500 mg/l of sodium chloride may be unpalatable and cause appetite disturbances (284, 948). Although an excess of sodium chloride induces thirst or can act as a diuretic (623), water containing up to 1410 mg/l has been used by some communities for many years without appreciable harm; however, 1000 to 1500 mg/l of sodium chloride generally renders water unpalatable (32, 36, 621). It has also been reported that 7500 mg/l of salt is harmless and that 10,000 mg/l causes vomiting (621, 579) (see also Sodium, Dissolved Salts, Chapter III, Chapter V).

b. Industrial Water Supplies. For ice making, as much as 342 mg/l of sodium chloride would probably not be detrimental, if it were the only salt present in the water (229). A concentration of 1000 to 1500 mg/l of sodium chloride in the process water causes tastes in canned foods, but does not affect the quality in other ways (224). For brewing, some sodium chloride is desirable and necessary in the water (171). It has been reported that 75 to 150 mg/l of sodium chloride is desirable in brewing water, but more than 500 mg/l is deleterious (170). It has also been recommended that for brewing waters the salt concentration should not exceed 200 mg/l (173); or 275 mg/l (152, 168). Other salt recommendations for brewing waters include the following values: pale ales I, 30 mg/l; pale ales II, 30 to 60 mg/l; mild ales, 60 to 120 mg/l; and stout, 120 to 175 mg/l (170). Good ale has been brewed, however, with water containing as much as 715 mg/l of sodium chloride (32). See Chapter V.

Larson and King (3675) conclude that the rates of corrosion of iron and steel in water are a function of the specific mineral quality as well as the alkalinity and pH values. They indict NaCl and other sodium salts as strong contributors to the rate of corrosion. For example, in a water with 400 mg/l of alkalinity (as CaCO₃) and pH 7, the corrosion rate will be zero at 100 mg/l of NaCl, but when the NaCl concentration is 400 mg/l, the corrosion rate will be about 100 mg per sq cm per day (3675).

c. Irrigation (see also Chapter V; Dissolved Solids). The effects of sodium chloride in irrigation water vary with the individual plants, the species, and environmental and climatic conditions. The presence of 10 milliequivalents or more of sodium chloride in nutrient solutions depressed root growth and water absorption by corn and tomato plants (1348). In irrigation water 100 to 200 mg/l of sodium chloride has caused injury to avocado trees in some soils, and also to some flowers, but many other plants are not sensitive to such concentrations (921). Water used for irrigation should not contain more than 700 mg/l of dissolved minerals in which sodium chloride predominates (638). Tomatoes have been killed by water containing 2000 mg/l of sodium chloride, but chrysanthemums have been resistant to as much as 3000 mg/l (921). To peas in liquid culture 4000 mg/l or more of sodium chloride was toxic and 9000 mg/l permitted almost no growth. The growth of wheat and barley plants in liquid culture was depressed by 8000 mg/l of sodium chloride; 10,500 mg/l appeared to be lethal over a long period, although some plants could tolerate this concentration for a limited period of a few weeks. In general, no plants grew to any appreciable

extent when irrigated with water containing 15,000 mg/l of sodium chloride (1349).

Young rice is sensitive to the presence of chlorides in water, but develops resistance as the plant matures. According to Shutts (1693), the commonly accepted tolerances of rice to salt water are as follows:

Concentrations of Salts	
$as\ NaCl,\ mg/l$	Tolerances
600	Tolerable at all stages
1300	Rarely harmful, and only to seedlings in dry, hard soil
1700	Harmful before tillering; tolerable from jointing to heading
3400	Harmful before booting; tolerable from booting to heading
5100	Harmful at all stages

Chlorides tended to accumulate in plants and soil when wheat was grown 2 and 10 meters away from a ditch carrying water containing 103,000 mg/l sodium chloride. Increasing concentrations of salt caused progressively greater reductions in height, weight, leaf growth and seed number of affected plants (1694).

The effect of NaCl on plant growth has been demonstrated by culture in sand to which various concentrations of salt have been added to the normal nutrient solution. With sand culture, the effect of sodium on the soil structure is avoided as a contributing factor. Results are shown below:

NaCl Added		Crop	Relative		
Atmospheres	mg/l	Designation	Dry Weight	Reference	
Control		All	100	200,010,000	
1.0	1400	Rice straw	89.7	3379	
		Rice grain	74.5	3379	
		Rice roots	90.9	3379	
1.5	2100	Bean plant	89.0	3376	
		Bean leaves	87.3	3376	
0.0		Bean roots	93.3	3376	
2.0	2800	Rice straw	46.1	3379	
		Rice grain	12.0	3379	
		Rice roots	49.6	3379	
2.5	3500	Bean plant	73.8	3376	
		Bean leaves	70.5	3376	
		Bean roots	80.1	3376	

This table demonstrates that NaCl affects the growth of plants and that rice is more sensitive than beans.

d. Stock and Wildlife Watering (see also Chapter V; Dissolved Solids). Salt poisoning has been reported among a great variety of livestock; its symptoms include malnutrition, wasting diseases, diarrhea, nervous disturbances, decreased milk or egg production, reduced reproduction, and sometimes death. The minimum lethal dose of sodium chloride for poultry has been reported as about 2 grams per pound (1350). The following doses of sodium chloride have been reported to be toxic to various animals: pheasants and rabbits, 3 grams (3676); ducks, 6 grams; dogs, 30 to 60 grams; sheep and pigs, 120 to 140 grams; cows, 2 to 3 kilograms; and horses, 1 to 2 kilograms (284).

The following concentrations of NaCl in drinking water have been reported to have caused the indicated effects on animals:

Reactions	Reference	Concentration of NaCl, mg/l	Animal
4000 5000	Laying hens Young chicks	Watery droppings Nervousness, in-	2398
	a cang chicag	ability to stand	1351, 1551

Concentration	4: 1::-1	Reactions	Reference
of $NaCl, mg/l$	Animal		<u>*</u>
7000	Swine	Slight scouring	2398
7000	Cattle	Reduction in weight	2398
7200	Sheep	Lethal to some	642, 1352
9000	Chicks	Lethal to two- thirds	2980
10000	Rats	Decreased reproduction	284, 287, 295
10000	Cattle, swine,		
	poultry	Toxic effect	2398
10000	Laying bens	Loss of weight and egg production	2398
15000	Rats	Retarded growth, some deaths	284, 287, 295
15000	Cattle	Reduced water intake	3392
15000-17600	Cattle	Sickened or killed	293, 294, 1350
15000-25000	Cattle, hens, pigs, rabbits	Injurious or fatal	284
17500	Cattle	Lost weight	2396
20000	Young chicks	Death in three days	1551

On the other hand, the following concentrations of NaCl in drinking water have been reported to cause no apparent adverse effect on the designated animals:

Concentration of NaCl, in mg/l	Animal	Reference
1025	General livestock	2394 1551
2000	Young chicks Cattle, sheep, swine, poultry	3391
2450 3000	Chicks	2980
4000	Cattle, swine, poultry	2398
5000	Rats	284, 287, 295 642, 1352
5720 9000-10000	Sheep, horses Dairy cows	292, 293
9123	Horses, without working	642
11440	Cattle and sheep	642
11690	Rats	2398 2396
12500 20000	Cattle Cattle not in milk production	288
25000	Sheep	288

e. Fish and Other Aquatic Life. (see Dissolved Solids; Chapter V). The following concentrations of sodium chloride have immobilized or killed fresh-water fish:

Concentration of NaCl, mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
1270- 2540	Soft,		Fish	1459
	distilled	400.1		190
2500		120 hours	Shiners	344
2500		. == -	Fish	
2500	Distilled	9-24 days	Minnows	313
3820- 5100	Hard,			1450
	alkaline		Fresh-water fish	1459
3850	Natural		Whitefish, pickerel	
5000		,	Newly hatched tro	
5000	Distilled	148 hours	Shiners	313,
***				645
5000	Distilled	200-250 hours	Bass	313,
0000				<b>64</b> 5
8500	Distilled	4-8 days	Minnows, perch	1459
10000		97-148 hours	Shiners, bass	645
10000	Тар	4-8 days	Minnows, perch	1459
10000	River	4-10 days	Goldfish	313
10000	Distilled	6 hours	Minnows	2942,
10000	Distinca	0.10412		2943,
		•		2944
10000			Fish	603.
10000			- AUA	1070
11500-12000	Hard	6 hours	Minnows	2942.
11300-12000	LINEU	OHORIZ	WITH TO U.D.	2943.
				2944

14000 14000 15000 15000-30000 16500 17550	-	Time of Exposure  17 hours 96-hour TL _m 24 hours  4.7 hours 24 hours 96-hour TL _m	Stickleback Salmon eggs and f Goldfish Bluegills Bluegills Goldfish Bass Fresh-water fish Whitefish Mosquito-fish	313 3381 1459 2920 645 1459 598 2940
		96-hour TL _m 1.3 hours 15 minutes	Mosquito-fish Shiners Trout	2940 645 441

On the other hand, the following concentrations of NaCl have been reported as harmless in the time specified:

Concentration of NaCl, mg/l	$Type\ of\ Water$	Survival Time	Type of Fish	Reference
5000 5850	River Tap	25 days 	Goldfish Salmon eggs and larvae and youn stickleback	g 1459
9100-17500 11700 12000 20000 25000-30000 30000	Distilled Tap	30 days 50 hours  30-60 minutes	Perch Young eels Stickleback Stickleback Older trout Brook trout	644 1459 1459 1459 1459 441

The threshold concentrations of sodium chloride in natural waters reported for immobilization of Daphnia and other fish-food organisms range from 2100 to 6143 mg/l (352, 353, 358, 598, 2946, 2955). Yet in distilled water, one mg/l of NaCl killed Daphnia magna in three hours (313). The resistance of Daphnia magna to NaCl appears to vary with the oxygen tension (2946). At 6.4 mg/l of dissolved oxygen the threshold toxicity level of NaCl was 5093 mg/l, but at 1.48 mg/l of DO, the threshold for NaCl was only 3170 mg/l (2946). Many small crustacea and fish fry are immobilized by concentrations above 3100 mg/l (598). The toxic threshold for a flatworm, Polycelis nigra, was found to be 11,200 mg/l (354).

In Lake Erie water at 20-25°C, threshold limits for several fish-food organisms were reported (2955) as follows:

	Threshold Concen tration, mg/l
Organism	
Daphnia magna, young	3700
Daphnia magna, adult	4600
Leptodora kindtii	3700
Cyclops vernalis	
Diaptomus oregonensis	3030

A Russian article (3677) indicates the following maximum NaCl tolerances for fresh-water organisms at two temperatures:

NaCl Tolerance in mg/l

— <b></b>	NaCl Tolerance in mg/	
Organism	20°C	3°C
Stictochironomus	₋ 788	1000
An oligochaete	1576	2000
Daphnia magna		800
Cuclons serrulatus	_ 394	
Leucaspisis delineatus	1970	

Anderson considers sodium chloride concentrations above 3000 mg/l deleterious to both fish-food organisms and fish fry and recommends a permissible limit of 2000 mg/l in fresh waters (598). On the other hand, higher

concentrations of sodium chloride have been found to decrease somewhat the toxicity of some metallic compounds toward fish (1265) (see also Mercuric Chloride). Sodium chloride is the least toxic to fish of the chlorides of potassium, magnesium, calcium and sodium. Sodium chloride is antagonistic to the toxicity of calcium and potassium chlorides (353, 307). A concentration of 50 mg/l of sodium chloride has greatly increased the antagonistic effect of sodium nitrate toward copper sulfate poisoning of fish (311). The toxicity of sodium chloride toward fish is decreased by calcium chloride (307).

f. Shellfish Culture. The most favorable salt content of water for oyster growth is about 30,800 mg/l of salinity of which about 80 percent is sodium chloride

(314).

# SODIUM p-CHLOROBENZENE SULFONATE

(see Chapter X)

## SODIUM CHROMATE

(see Chromium)

## SODIUM CITRATE

C₃H₄OH(COONa)₃·2H₂O

(see also Citric Acid)

This highly soluble salt has many uses in medicine, especially as an anticoagulant. It is also used in photography and as a sequestering agent to remove trace metals (364).

Anderson (352) reports that the threshold concentration for immobilization of *Daphnia magna* in Lake Erie water at 25°C was 825 mg/l. For *Polycelis nigra*, a flatworm, the threshold for toxicity at 15 to 18°C was a 0.015 molar concentration, or 4420 mg/l of sodium citrate (354).

### SODIUM CYANATE

NaOCN

(see also Cyanides, Hydrogen Cyanide)

Cyanates are formed when cyanides in waste waters are treated by alkaline chlorination. According to Resnick et al. (2974), cyanates are stable in aerobic water at pH 7 and 20°C for at least 10 days. Eventually, cyanates undergo hydrolysis to yield ammonium carbonate. In anaerobic solutions cyanates are reduced not to cyanide but to a mixture of ammonia and formic acid.

According to Washburn (1070) the maximum tolerance limit of creek chub to sodium cyanate is 75 mg/l.

## SODIUM CYANIDE

NaCN

- 1. General. This highly soluble salt is used in electroplating baths, for extracting gold and silver from ores, and for generating HCN gas in fumigating operations (364). Upon solution in water, the cyanide ion combines with hydrogen ions in the water to form weakly dissociated hydrogen cyanide, thereby tending to raise the pH of the solution. For further explanation of the cyanides, see Hydrogen Cyanide.
- 2. Cross References. Cyanides, Cyanogen Chloride, Hydrogen Cyanide, Nitriles, and other cyanide salts.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The fatal dose of NaCN for man by ingestion is reported to be about 0.2 grams

(353), but since the fatal dose of HCN has been given as 50 to 60 mg (364), the former figure may be high. See also Cyanides and Hydrogen Cyanide.

b. Stock and Wildlife Watering. The approximate minimum toxic dose of NaCN for sheep is given as 4.15 mg per kg of body weight, and a dose of 5.22 mg per kg

is lethal (353).

c. Fish and Other Aquatic Life. The following concentrations of sodium cyanide have been shown to be harmful or toxic to fish:

C	oncentrati				
	of NaCN,		Type of		
		Exposure	Fish	Remarks	Reference
	0.05	124 hours	Trout	100 percent mortality	1115
	0.28	96 hours	Bluegills	TLm in soft water	2958
	0.33 - 0.35	2.5 hours	Minnows	Lethal	1468
	0.4	1 hour	Minnows	Stopped eating	362
	0.43	96 hours	Fathead Minnow	TLm in soft water	
	0.44	48 hours	Fathead Minnow	mt_	2958
	0.5	4 to 6 hours	Goldfish and	11m	3335
		2 20 0 100.0	green sunfish	Lothel Ot 20	
	0.5 to 0.7	24 hours	Minnows	Lethal, 25°C	3678
	0.66	96 hours		25 percent mortality	362
	0.75	24 hours	Fathead minnow		2958
	0.8	24 hours	Minnows	50 percent mortality	362
	1.0		Minnows	100 percent mortality	362
	1	0.7 to 10 hours	Mixed fish	Lethal at 25°C	3678
		20 minutes	Trout	100 percent mortality	1115
	1.5	0.6 to 24 hours	Goldfish and		
			green sunfish	Lethal	3678
	2	47 minutes	Trout	Lethal	1116
	2.0		Sticklebacks	Lethal at 17°C	2920
	3.1	90 minutes	Fish	Depressed respiration	468
	4.8		Hardy carp	Paralyzed	362
	5 5	12 minutes	Shiner	Killed	1115
	5	2 hours		Killed	2976
1	0	4 minutes	Shiner	Killed	1115
					1119

Non-toxic or non-harmful concentrations have been reported as follows:

Concentrat	ion			
of NaCN in mg/l	, Time of Exposure	Type of Fish	Remarks	Reference
0.02 0.08		Trout fingerlings	No effect	1115
0.03	24 hours	Trout Minnows	Non-toxic	1109
2.3	155 minutes	Fish	No effect Survived	362 468
5.0	2 hours	Sea lamprey	Ill, but survived	2976

According to Anderson (365), the threshold concentration for immobilization of Daphnia magna in Lake Erie water at 25°C was found to be less than 3.4 mg/l of sodium cyanide and Jones (354) reports that the threshold concentration for Polycelis nigra, a flatworm, is 16 mg/l as cyanide (30 mg/l as NaCN). A concentration of 3.6 mg/l of NaCN inhibited BOD by 50 percent (2949).

## SODIUM DECYLBENZENE SULFONATE

## SODIUM n-DECYL SULFATE

SODIUM 2, 5-DICHLOROBENZENE SULFONATE (see Chapter X)

## SODIUM DICHROMATE

(see Chromium)

## SODIUM DIHYDROGEN PHOSPHATE

(see Sodium Phosphates)

## SODIUM DI (2-ETHYLHEXYL) SULFOSUCCINATE

## SODIUM DIOCTYL SULFOSUCCINATE

## SODIUM DODECYLBENZENE SULFONATE

## SODIUM DODECYL SULFATE

## SODIUM 2-ETHYLHEXYL SULFATE

(see Chapter X)

## SODIUM FERROCYANIDE

Na₄Fe(CN)₆

(see also Cyanides, Hydrogen Cyanide, Potassium Ferro- and Ferricyanide)

This compound, containing reduced iron, is highly soluble in water. It is used for blueprinting, in photography, pigments, dyes, and metallurgy (364). In aqueous solution it decomposes under the action of sunlight

to release cyanide ion and HCN.

For Daphnia magna in Lake Erie water at 25°C, the toxic concentration was reported by Anderson (352) to be less than 600 mg/l, or about 540 mg/l (353). For Polycelis nigra, a planarium, Jones (354) found the toxic threshold to be 170 mg/l. It should be recognized, however, that under the action of sunlight with the resultant decomposition to cyanides, this compound may be much more lethal. For further details, see Potassium ferrocyanide.

## SODIUM FLUORIDE

NaF

(see also Fluorides)

Highly soluble in water, this crystalline solid is used as a pesticide, as a fluoridating agent in municipal water, and in many industrial processes. The  $LD_{50}$  for hamsters was found to be 70-80 mg/kg of body weight (3705). Much of the information described under "Fluorides" was derived from the use of sodium fluoride and will not be repeated here.

Bringmann and Kuhn (2158, 3343) found the threshold of NaF for Daphnia at 23°C to be 270 mg/l during a 2-day exposure. For Scenedesmus the threshold of toxic effect was 95 mg/l during 4 days at 24°C, for Microregma 226 mg/l, and for Escherichia coli at 27°C it was 180 mg/l. According to Wantland (3705), freeliving protozoa and freshwater rotifers survived and reproduced in water containing 1000 mg/l of NaF, but were killed at 1700 mg/l.

# SODIUM FORMATE

(see Formic Acid and Formates)

# SODIUM HYDROCARBON SULFONATE

(see Chapter X)

## SODIUM HYDROSULFIDE

(see Sodium Sulfhydrate)

## SODIUM HYDROXIDE

NaOH

1. General. This common caustic compound is highly soluble in water with dissociation to sodium and hydroxide ions, with a consequent effect upon alkalinity and pH. Sodium hydroxide may occur in wastes from the following industries: soap manufacture; cleaning compounds; pulp and paper; petroleum, mineral and vegetable oils; leather; reclaimed rubber; ink; dyes and textile dyeing; cotton; perfumes; water glass; coal distillation, etc.

2. Cross References. Sodium, Alkalinity, Hydroxides.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The taste threshold of sodium hydroxide in water is reported to be 1 to 50 mg/l (621). A dose of 1.95 grams of sodium hydroxide may cause death in man (353).

b. Stock and Wildlife Watering. Sodium hydroxide, in a concentration of 5000 mg/l, was almost harmless for rats; 10,000 mg/l caused nervousness, sore eyes, diar-

rhea, and retarded growth (284, 287).

c. Fish and Other Aquatic Life. The toxicity threshold concentration of sodium hydroxide for Daphnia magna has been reported to range from 40 to 240 mg/l (190, 352, 353, 358, 574, 690, 1466, 3500, 3523). Concentrations of sodium hydroxide from 125 to 1000 mg/l have been lethal to various insect larvae (190, 574, 690, 3500). A concentration of 100 mg/l has not been harmful to mayflies, and 700 mg/l has not been harmful to Chironomous larvae (690).

The following concentrations of sodium hydroxide

have been reported to have killed fish:

Concentration in mg/l	Type of Water	Time of Exposure	$Type\ of \ Fish$	Reference
20 25 35 40 48 70 71.5 96 99	Fresh Stagnant Circulating Tap Tap	24 hours 24 hours 5 hours 4.5 hours 2-10 minutes 48-hour TLm	Silver salmon Brook trout Cutthroat trout Creek chub King salmon Fish, crabs Carp, shiners, suckers Fish, oysters Carp, shiners, suckers Bluegill sundish Minnows	3502, 3501 359 3502, 3501 1442 3502, 3501 823 359 823 313 2093 690, 190, 3500 658, 344
100 100 100 125 180 (pH 12)	Turbid Circulating	120 hours 3-20 hours 96-hour TLm 23 hours	Fish Shiners Goldfish, bass Mosquito-fish Fish, oysters	190 1030 2940 823

The following concentrations of sodium hydroxide have not harmed fish within the time specified:

Concentration in mg/l 10 11 20 27 50	Type of Water Fresh Distilled	Time of Exposure  24 hours 2 hours 7 days	Type of Fish Cutthroat trout Silver salmon Creek chub King salmon Perch, roach Goldfish, bass Carn, shiners, suckers	Reference 3502, 3501 3502, 3501 1442 3502, 3501 313 1030 359
50 55.5 200	·	7 days 5 hours	Carp, shiners, suckers Some fish	

For roach and perch in sodium hydroxide solutions of 1:5000 strength, the time until loss of equilibrium was found to be about 30 minutes. In 1:10,000 dilutions, both kinds of fish survived for 40 minutes (1357).

According to Murdock (1460) sodium hydroxide has not been shown to be lethal to fully developed fish in natural fresh waters unless the pH value is well over 9. The lethal pH for goldfish is given by Jones (2920) as 10.9, and by Cairns and Scheier (2933, 2934) for bluegill sunfish as 10.5.

To stimulate the movement of water beetles (Laccophilus maculosus), Hodgson (2956) found that a concentration of 400 mg/l of NaOH was required.

### SODIUM IODATE

NaIO₃

(see also Iodine)

The threshold concentration of sodium iodate for the immobilization of *Daphnia magna* in Lake Erie water was found to be less than 158 mg/l (352). The toxic threshold concentration of sodium iodate for the flat-

worm Polycelis nigra was found to be 230 mg/l, as iodate (354).

#### SODIUM IODIDE

NaI

(see also Iodine)

The taste threshold of sodium iodide in chlorinated water is reported to be about 0.005 mg/l (459). The threshold concentration of sodium iodide for the immobilization of Daphnia magna in Lake Erie water was found to be 3.3 mg/l (352). A concentration of 5 mg/l had no effect on the sea lamprey during a 24-hour exposure in Lake Huron water at 12°C (2976). The toxic threshold concentration of sodium iodide for Polycelis nigra a flatworm, was found to be 6600 mg/l (354). To stimulate movement of the water beetle (Laccophilus maculosis) a sodium iodide concentration of 14,700 mg/l was required (2956).

# SODIUM ISOPROPYL NAPHTHALENE SULFONATE

## SODIUM KERYLBENZENE SULFONATE

# SODIUM LAURYL AND MYRISTYL COLLAMIDE SULFONATE

## SODIUM LAURYL SULFATE

(see Chapter X)

## SODIUM METABISULFITE

Na₂S₂O₅

This highly soluble solid is used in medicine as an antioxidant (364). According to Le Clerc (2942) the minimum lethal dose to minnows during a 6-hour exposure was 60-65 mg/l in distilled water at 18°C and 75-80 mg/l in hard water at 17°C.

## SODIUM MOLYBDATE

(see Molybdenum)

# SODIUM MONOBUTYL PHENYLPHENOL MONOSULFONATE

# SODIUM MONOETHYL PHENYLPHENOL MONOSULFONATE

## SODIUM NAPHTHALENE - \( \beta \) - SULFATE

(see Chapter X)

#### SODIUM NITRATE

NaNO_a

- 1. General. Known commonly as "Chile saltpeter", this compound was formerly used extensively for the manufacture of nitric acid. It is also used in making glass, enamels, matches, and cigarettes, and in pickling meats. The technical grade is employed in fertilizers as a source of nitrate. The compound is readily soluble in water, releasing sodium and nitrate ions.
  - 2. Cross References. Sodium Nitrates.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The taste threshold of sodium nitrate in water is reported to be about 450 to

- 800 mg/l (621). Sodium nitrate acts as a diurectic (364, 623).
- b. Industrial Water Supplies. Sodium nitrate in water interferes with fermentation processes and causes disagreeable tastes in beer (165).
- c. Stock and Wildlife Watering. A dose of 240 grams of sodium nitrate has been fatal to cows; 20 grams, to sheep; and 6 grams to dogs (284). A concentration of 6200 mg/l of sodium nitrate in water has caused frenzy, paralysis, diuresis, cyanosis, and deaths among cows (284). Pigs fed with soup prepared with well water containing 1740-2970 mg/l of sodium nitrate died from methemoglobinemia. A total dose of 90 mg of sodium nitrate per kg of body weight is fatal to pigs (1695).
- d. Fish and Other Aquatic Life. The toxicity threshold concentration of sodium nitrate for *Daphnia magna* has been reported to be 5000 mg/l and 8500 mg/l (352, 353) 358)

The following concentrations of sodium nitrate have been reported as toxic to fish:

Concentration in mg/l	r Type of Water	Time of Exposure	Type of Fish	Reference
1,282	Distilled	14 hours	Goldfish	313
1,845	Тар		Stickleback	598, 14 <b>6</b> 0
2,000		4 days	Goldfish	1035
2,000-4,000			Some sunfish	1035
2,210	Тар	7 days	Stickleback	1460
2,950	Тар	4 days	Stickleback	1460
4,000	Hard	80 hours	Goldfish	313
5,530	Тар	48 hours	Stickleback	1460
6,650	Turbid	96-hour TLm	Mosquito-fish	2940
10,000	Standard	96-hour TLm	Bluegill sunfish	2933, 2934
11,060	Тар	24 hours	Stickleback	1460
12,000	Aerated	96-hour TLm	Bluegill sunfish	3381
13,600			Stickleback	2920

The following concentrations of sodium nitrate have not been harmful to fish within the time specified:

Concentration in mg/l	Type of Water	Time of Exposure	Type of Fish	Reference
1,000	Hard		Goldfish	313, 1035
2,000-4,000	Hard		Some sunfish	1035
3,000	Hard	100 hours	Goldfish	313
4,000	Hard		Bass	1035

#### SODIUM NITRATE

NaNO₂

(see also Nitrates, Nitrites, Sodium)

This soluble salt is used in the manufacture of dyes and other chemicals, in textile processes, and in photography. In water it dissociates completely and under aerobic conditions the nitrite ions are oxidized to nitrates. The oral MLD for dogs is given as 330 mg/kg of body weight (364).

A concentration of 17.1 mg/l of NaNO₂ was apparently harmless to minnows during a 24-hour exposure (362); but 50 mg/l can be fatal in 14 days (3577). A massive dose of 10,000 mg/l is lethal to minnows in 1.5 hours (3577). Testing mosquito-fish (Gambusia affinis) in highly turbid water at 21-24°C, Wallen et al. (2940) found the 24-hour TL_m to be 8.1 mg/l while the 48- and 96-hour TL_m values were 7.5 mg/l. There was no decrease in turbidity by this dosage. Sodium nitrite has an antagonostic effect upon the toxicity of copper sulfate to goldfish. In cencentrations up to 5000 mg/l, sodium nitrite has decreased the toxic effect of 10 mg/l of copper sulfate toward goldfish (311).

The toxic threshold concentration of sodium nitrite for the flatworm Polycelis nigra was found to be 42 mg/l (354). Toward Daphnia magna in Lake Erie water, the threshold concentration for immobilization was reported as less than 28 mg/l (352); but in River Havel water at 23°C it was given (2158) as 99 mg/l of NaNO2. Also in River Havel water, the toxic threshold for E. coli was found to be 195 mg/l but for Scenedesmus concentrations up to 1500 mg/l of NaNO2 were harmless.

# SODIUM m-NITROBENZENE SULFONATE

## SODIUM 4-NITROCHLOROBENZENE -2-SULFONATE

(see Chapter X)

#### SODIUM NITROFERRICYANIDE Na₂Fe(CN)₅NO

(see also Cyanides, Sodium Ferrieyanide)

This substance is used primarily in chemical laboratories for the detection of many organic compounds (364). According to Schaut (362), minnows exposed for one hour to 17.1 mg/l of sodium nitroferricyanide in stabilized tap water showed no effects. Toward Polycelis nigra, a flatworm, the toxic concentration was found to be 190 mg/l, as nitroferricyanide (354). Like the ferricyanides, this substance tends to decompose slowly in aqueous solution, but faster in sunlight, to release cyanide ions (see Cyanides).

## SODIUM OLEATE

(see Fatty Acids, also Chapter X)

## SODIUM OXALATE

(see Oxalic Acid, Oxalates)

### SODIUM PALMITATE

## SODIUM PENTACHLOROPHENATE

(see Chapter X)

## SODIUM PERBORATE

 $NaBO_3 \cdot 4H_2O$ 

(see also Boron, Sodium Borate, Chapter X)

Relatively soluble in water, this white crystalline salt is used in bleaching operations, in soaps, and in dentifrices. When mixed with warm water it decomposes to liberate nascent oxygen.

The threshold concentration of sodium perborate for immobilization of Daphnia magna in Lake Erie water at 25°C was found to be very much less than 5.2 mg/l (352) and was estimated at 2.6 mg/l (353). Fingerling trout survived a sodium perborate concentration of 160 mg/l for 24 hours but 80 percent were killed by 320 mg/l.

## SODIUM p-PHENOL SULFONATE

(see Chapter X)

#### SODIUM PHOSPHATES

(see also Phosphates, Phosphoric Acid)

Under this designation, six sodium phosphates are considered:

(a) Sodium phosphate, monobasic, NaH₂PO₄·H₂O also known as sodium dehydrogen phosphate. Highly soluble in water, it is used in baking powders and treatment of boiler water. The aqueous solution is acid.

(b) Sodium phosphate, dibasic, Na₂HPO₄·7H₂, or disodium hydrogen phosphate. It is highly soluble in water and gives an alkaline solution. It is used in human and

veterinary medicine as a laxative.

(c) Sodium phosphate, tribasic, Na₃PO₄·12H₂O, or trisodium phosphate. Also highly soluble in water, it is used in photographic developers, treatment of municipal and boiler water, in detergent compounds, and in tanneries, paper mills, and laundering plants.

(d) Tetrosodium pyrophosphate, Na₄P₂O₇, or sodium pyrophosphate. It is used as a sequestering agent in water treatment, cleaning compounds, oil well drilling,

and other processes.

(e) Sodium hexametaphosphates are mixtures of (NaPO₃)₆ that occur in commercial detergents such as Calgon, Micromet and Quadrafos.

(f) Sodium tripolyphosphate, Na₅P₃O₁₀, used as a

sequestering agent and meat preservative.

Campbell et al. (2059) indicate that the taste threshold for trisodium phosphate is 225 mg/l and for Calgon 200 mg/l. According to Lockhart et al. (3241) the taste threshold of trisodium phosphate in water is 180 mg/l. Cohen et al. (2049) found that as little as 0.1 mg/l of sodium tripolyphosphate inhibited the coagulation of turbid water by ferric sulfate.

For Polycelis nigra, a flatworm, the toxic threshold concentration of trisodium phosphate (Na₃PO₄·12H₂O) was found to be 9860 mg/l (354). The threshold concentrations for immobilization of Daphnia magna in Lake Erie water at 25°C were found to be lower than the fol-

lowing values:

Compound	Concentration in mg/l
Sodium dehydrogen phosphate	1560
Disodium hydrogen phosphate	59
Trisodium phosphate	52

To stimulate the movement of water beetles (Laccophilus maculosis) in water, Hodgson (2956) found that a trisodium phosphate concentration of 179,000 mg/l was

required.

Toward fish, sodium phosphates are not strongly toxic, the principal effect being a change in pH value. Using turbid water and the mosquito-fish (Gambusia affinis) as the test animal, Wallen et al. (2940) report the following results:

T.	mperatur	e vH		$TL_m$ in $mg/l$	
Compound	°C	Range 2	24-hour	48-hour	96-hour
NaH ₂ PO ₄	19–23	7.6-11.0		720	720
Na ₄ P ₂ O ₇ ·10H ₂ O	19-24	8.2 - 9.8	1380	1380	1380 151
Na ₂ PO ₄	17 - 22	7.4-10.3	467	467	191

The Water Pollution Research Board of England (2907) tested a mixture of sodium tripolyphosphates and tetrasodium pyrophosphate on rainbow trout. It was found that 560 mg/l as phosphate caused no deaths in 24 hours but 1120 mg/l as phosphate killed all of the

Quadrafos, a sodium hexametaphosphate, was tolerated by fish in concentrations up to 3,500 mg/l, but this

concentration killed oysters (3005).

## SODIUM SILICOFLUORIDE

(see also Fluorides)

Na₂SiF₆

# SODIUM PYROPHOSPHATE

(see Sodium Phosphates)

## SODIUM SALICYLATE

(see Salicylic Acids and Salicylates)

### SODIUM SELENITE

 $Na_2SeO_3$ ,  $Na_2SeO_3 \cdot 5H_2O$ 

- 1. General. Sodium selenite is found in some types of soil and in wastes from pottery works. It is freely soluble in water.
  - 2. Cross References. Selenium, Selenious Acid.
  - 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. For most mammals the fatal dose of sodium selenite is about 4 to 6 mg per kilogram of body weight. Sodium selenate is about half as toxic as sodium selenite. The minimum lethal dose of sodium selenite for rabbits is about 1.5 mg per kg of body weight (353).

As sodium selenite, administered orally or as a drench, the minimum lethal single dose of selenium for horses is about 1.5 mg per kg of body weight; for cows and calves, 4.5 to 5.0 mg per kg of body weight; and for pigs, 6 to 8 mg per kg (1049).

b. Fish and Other Aquatic Life. The following concentrations of sodium selenite have been reported as toxic to fish.

Concentration in mg/l	$Type\ of\ Water$	Time of Exposure	Type of Fish	Reference
10	Hard	98-144 hours	Goldfish	353. 313
100	Very soft	1-4 days	Goldfish	353
100	Hard	8-19.5 hours	Goldfish	353, 313

Bringmann and Kuhn (2158, 3343) investigated the toxicity of sodium selenite in River Havel water. They found the following thresholds of toxicity:

	Threshold		
Organism	$Temperature \ ^{\circ}C$	$Time\ of\ Exposure$	Concentrations in mg/l
Daphnia	23	2 days	2.5
Scenedesmus _	24	4 days	2.5
Escherichia col Microregma			90
Material Control of the Control of t			183

## SODIUM SILICATE

Na₂SiO₃

This colorless crystalline salt is only slightly soluble in water, but in combination with other sodium silicates such as Na₂Si₃O₇ it is marketed as a solution known as "water glass," which has numerous commercial applications (3 4).

The 100-hour toxicity threshold of sodium silicate in double-distilled water at 23°C to *Daphnia magna* has been reported (1691) at 247 mg/l with a resulting pH value of 9.1, but in the presence of other sodium salts this threshold may be somewhat lower (see Sodium).

The Water Pollution Research Board of England determined that sodium silicate was not lethal to fingerling rainbow trout at a concentration of 256 mg/l. Using turbid water at 21-22°C, Wallen et al. (2940) found that the 96-hour TL_m for the mosquito-fish (Gambusia affinis) was 2320 mg/l.

This white granular powder, highly soluble in water, has been used extensively in the fluoridation of drinking water. The oral  $LD_{50}$  in rats has been reported (364) as 125 mg/kg of body weight. For guinea pigs, the oral  $LD_{50}$  is given as 250 mg/kg of body weight (3271). Toward the fish, *Tinca vulgaris*, Simonin (3271) reports the lethal dose to be 50 mg/l.

## SODIUM STEARATE

(see Chapter X)

## SODIUM SULFATE Na₂SO₄

Na₂SO₄ and Na₂SO₄·10H₂O

- 1. General. Sodium and sulfate ions may occur naturally in water, or they may be derived from various industrial wastes, such as those from paper mills. Sodium sulfate is used in manufacturing dyes, glass, soaps, freezing mixtures, and paper; and in dyeing and printing of textiles. It is readily soluble in water.
  - 2. Cross References. Sulfates, Sodium.

3. Effects Upon Beneficial Uses.

- a. Domestic Water Supplies. The taste threshold of sodium sulfate in water is 250 to 500 mg/l (621). In high concentrations, sodium sulfate has a purgative effect (623). Water containing 500 mg/l of sodium sulfate and 1200 mg/l of magnesium sulfate occasionally has caused diarrhea among human beings; under ordinary conditions such water would be regarded as unsuitable for domestic use (36).
- b. Industrial Water Supplies. For boiler waters, the ratio between the concentration of sodium sulfate and that of sodium sulfite is significant. The following ratios as given in Chapter V, are specified as limits:

Boiler Pressure	Ratio
in psi	NasSO,:NasSO
0-150	1:1
150-250	2:1
More than 250	3:1

For brewing, waters should not contain more than about 100 mg/l of sodium sulfate, and for ice making, not more than 300 mg/l (see Chapter V).

Larson and King (3675) conclude that the rates of corrosion of iron and steel in water are a function of the specific mineral quality as well as the alkalinity and pH values. They indict sodium sulfate and other sodium salts as strong contributors to the rate of corrosion. For example, in a water with 400 mg/l of alkalinity (as CaCO₃) and pH 7, the corrosion rate will be zero at 200 mg/l of Na₂SO₄, but when the concentration of sodium sulfate is 400 mg/l, the corrosion rate will be about 100 mg per sq cm per day (3675).

c. Irrigation. A concentration of 4000 mg/l of sodium sulfate in the soil is injurious to plants (246). At 710 mg/l, sodium sulfate has depressed root growth and water absorption of plants grown in liquid culture (1348).

The effect of Na₂SO₄ on plant growth has been demonstrated by culture in sand to which various concentrations of this salt have been added to the normal nutrient solution. With sand culture, any alteration of the soil

structure is avoided as a factor contributing to sodium effects. Results are shown below:

$Na_sSO_s$ $Added$ in $mg/l$	Portion of Crop	Relative Dry Weight	Reference
Control		100	3379
2560	Rice straw	91.9	
	Rice grain	79.8	3379
	Rice roots	95. <b>4</b>	3379
2840	Tomato vine	88.2	3679
2010	Tomato root	85.0	3679
3840	Bean plant	87.5	3376 ·
0010	Bean roots	90.2	3376
	Bean leaves	86.3	3376
5120	Rice straw	55.6	3379
0120	Rice grain	15.6	3379
	Rice roots	58.2	3379

d. Stock and Wildlife Watering. Water containing 4546 to 7369 mg/l of salts, mostly sodium sulfate, was not harmful to two cows over a two-year period; however, a sudden change from normal water to this water caused diarrhea (291). At a level of 7000 mg/l there was some evidence of weight reduction in cattle and at 10,000 mg/l weight losses were severe (2398). Rats were not harmed by water containing 15,000 mg/l of sodium sulfate (284). Poultry, however, experienced a 33 percent mortality after drinking for 15 days water containing 7500 mg/l of sodium sulfate. Ballantyne (2394) sets the threshold limit of Na₂SO₄ for all livestock at 2050 mg/l.

e. Fish and Other Aquatic Life. The following concentrations of sodium sulfate were reported to be toxic

or lethal to fish and other aquatic life:

Concentration in mg/l	Time of Exposure	Type of Fish	Reference
100	120 hours	Shiners	190
100	_	Fish	3 <del>44</del>
1000	7 days	hydra	1696
4547	100 hours	Daphnia magna	1691
5000	7-28 days	Water snails	1696
5000	6-30 hours	Microcrustacea	1467
5000	1-6 days	Fingerling trout	1696
5000-7105		Daphnia magna	352, 358, 574
5200	48 hours	Daphnia	3523
6700		Cutthroat trout	3502
6820		Polycelis nigra	35 <b>4</b>
7000	1-2 days	Rainbow trout	1696
11,200-12,000	6 hours	Minnows, distilled	2942
,,,		water	
12,750	96-hour TLm	Bluegill sunfish	2933
13,400-184,000	7-69 days	Perch	644
13.500	96-hour TLm	Bluegill sunfish	2936, 3381
16,500		Silver salmon	3502
16,500	96-hour TLm	Mosquito-fish	2940
16,700-17,600	6 hours	Minnows, hard	2942
10,100 11,000		water	
24,000	24-hour TLm	Mosquito-fish	2940
•			

The following concentrations of sodium sulfate were not harmful to aquatic life in the indicated time:

Time of Exposure	Type of Fish	Reference
	Minnows	3523
24 hours	Goldfish	313
24 hours	Rainbow trout	2907
5 days	Fish	609
	Cutthroat trout	3502
6-16 days	Dace	1696
	Daphnia	3523
	Water plants	1696
24 days	Perch	1696
	Silver salmon	3502
24 days	Carp	1696
	Time of Exposure  24 hours 24 hours 5 days 6-16 days 24 days	Time of Exposure

Concentration in ma/l	Time of Exposure	$Type\ of \ Fish$	Reference
15,000	7 days	Roach Algae	1696 1696
Up to 15,000 15,000-20,000	28 days	Protozoa	1696

To stimulate the movement of water beetles, Laccophilus maculosis, Hodgson (2956) found that 35,600 mg/l of sodium sulfate was required. Fairchild (2946) reported that the threshold toxicity value of sodium sulfate toward Daphnia depended on the dissolved oxygen concentration. At a DO value of 6.6 mg/l, the toxicity threshold of Na₂SO₄ was 5514 mg/l; but at a DO value of 1.46 mg/l, the toxicity threshold of Na₂SO₄ dropped to 2752 mg/l.

## SODIUM SULFIDE

 $Na_2S$ 

- 1. General. Sodium sulfide is used in tanneries and may also be a constituent of Kraft mill wastes, and beetsugar-factory effluents. It has a high chlorine demand and a high oxygen demand; a small continuous dose of sodium sulfide can result in oxygen depletion and fish deaths (313, 362). It is highly soluble in water, the sulfide ions tending to react with hydrogen ion to form HS-or H₂S, depending on the pH value of the solution.
- 2. Cross References. Sulfide, Distilled Water, Hydrogen Sulfide.

3. Effects Upon Beneficial Uses.

a. Industrial Water Supplies. Even when present in very low concentrations, sodium or potassium sulfide in the water used for mixing developers for photographic use can result in chemical fogging of emulsions on the films (242).

b. Fish and Other Aquatic Life. The following concentrations of sodium sulfide have been reported as toxic

or lethal to fish:

Concentration in mg/l		Time of Exposure	Type of Fish	Reference
0.55	pH 5.2		Young carp	1698
1.0 (threshold)	Aerated		Salmonoid fish	1582
1.8 (lethal)	Aerated		Salmoneid fish	1582
2.0	Distilled		Minnows	361
2.4	Distinct		Brown trout	2920
3.0			Minnows	690
3.0	12°C		Cutthroat trout	3502
3.0	12 0		Shiners, minnows	344, 658, 690
3.1	15°C		Silver salmon	3502
3.2	10 0	48-hour TLm	Fathead minnows	3335
3.2 3.3	pH 7.4	10 202- 0	Young carp	1698
3.5	17.5°C		King salmon	3502
3.3 7.8	11.0 0	90 minutes	Minnows	468
	Hard, 15°C	6 hours	Minnows	2942
10-11	Haid, 15 C	d Hours	Stickleback	2920
11	Distilled, 25°C	6 hours	Minnows	2942
12-13	Distilled, 20 G	6 minutes	Minnows	468
39	Hard	о пиничен	Minnows	361
50	Standard	48-hour TLm	Bluegill sunfish	2093
61 750	Turbid	96-hour TLm	Mosquite-fish	2940

The maximum concentration of sodium sulfide that produced no mortality has been given (3502) as 1.8 mg/l for king salmon at 17.5°C, 1.3 mg/l for silver salmon at 15°C, and 1.0 mg/l for cutthroat trout at 12°C. Fish tried to avoid solutions of sodium sulfide in concentrations of 3.1 to 39.0 mg/l (1046).

Fish removed from toxic concentrations of sodium sulfide before they stopped breathing recovered and survived (468). Minnows exposed to 17.1 mg/l of sodium sulfide in tap water have been disturbed for as long as five hours; within 24 hours, however, the sulfide had disappeared and the fish recovered (362). On the other hand, Ellis quotes a reference to the effect that exposure

for one hour to 1150 mg/l of sodium sulfide in tap water has resulted in the death of tench six days later (313).

When Na₂S is added to water it dissociates to release sulfide ions which then react with hydrogen ions to form HS⁻ or H₂S, depending on the pH value of the solution (see Hydrogen Sulfide). For that reason, the toxicity of sodium sulfide tends to increase as the pH of the water decreases from 9 to 6 (1046). This relationship has been shown by Tomiyama and Yamagawa (1698) for young carp as follows:

$pH\ Value$	Critical Lethal Concentration, mg/l
5.2	0.55
6.1 7.4	0.95 3.3
8.2	8.0

Other aquatic life have responded to sodium sulfide as shown below:

#### Concentration

$in\ mg/l$	Organism	Remarks	Reference
1-2 2-1000 2.44 3.2 9.4-10	Mayfiy larvae Insect larvae Bivalve larvae Mesocyclops leuckarti Daphnia magna	Killed Killed Lethal Toxic threshold Killed or immobilize	690 690 2989 2955 ed 352,
10 34 63 97 226 1000	Daphnia magna Polycelis nigra Daphnia Scenedesmus E. coli Chironomus larvae	48-hour MLD at 17° Toxic threshold Toxic threshold Toxic threshold Toxic threshold Resisted	690, 2955 C 3523 354 2158 2158 2158 690

## SODIUM SULFHYDRATE

NaHS

Completely and rapidly soluble in water, with an H₂S odor, this crystalline substance is used in tanneries for dehairing hides, in the manufacture of sulfur dyes, and for desulfurizing viscous rayon (364). It may also be found in Kraft mill wastes.

Using turbid water at 21-33°C, Wallen et al. (2940) studied the toxicity of NaHS toward the mosquito-fish, Gambusia affinis. They found the 24-, 48-, and 96-hour TL_m values to be 206 mg/l. The 144-hour TL_m was lowered to 138 mg/l. Haydu et al. (3501, 3502) report the minimum lethal concentrations of NaHS to be 3.3 mg/l for king salmon, 3.5 mg/l for silver salmon, 1.8 mg/l for cutthroat trout, and 0.5 mg/l for Wisconsin minnows. The maximum concentrations of sodium sulfhydrate tolerated by king salmon, silver salmon, and cutthroat trout are 2.1, 2.5, and 0.3 mg/l respectively (3501, 3502).

Gillette et al. (1442) tested the toxicity of this substance to creek chub, a fish considered to be average in tolerance. They found that the concentration below which all four test fish survived for 24 hours was 4 mg/l, while above 10 mg/l all fish died. The critical concentration of NaHS to salmonoid fish in water containing over 5 mg/l of dissolved oxygen ranged from 0.3 mg/l for threshold damage to 2.5 mg/l for lethality (1582).

#### SODIUM SULFITE

 $Na_2SO_3$ 

1. General. This soluble salt is used chiefly in photographic developers and fixing operations. It is also employed in bleaching operations and as a reducing agent in the manufacture of dyes (364). Sodium and sulfite

ions may occur in various paper mill and beet-sugar-factory effluents (313).

- 2. Cross References. Sulfites, Sulfite Waste Liquor.
- 3. Effects Upon Beneficial Uses.

a. Stock and Wildlife Watering. A concentration of 15,000 mg/l of sodium sulfite in the drinking water of

rats caused no apparent injury (287).

b. Fish and Other Aquatic Life. The lethal concentration of sodium sulfite to goldfish in 96 hours at 18-23°C has been reported (2920) as 100 mg/l; but on the other hand, concentrations up to 260 mg/l at pH 5 to 9 have been observed to be harmless to young carp (1698). Using turbid water at 18-26°C, Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m for mosquito-fish to be 2600 mg/l.

The toxic threshold concentration of sodium sulfite for the flatworm, Polycelis nigra, was found to be 7580 mg/l (354). The minimum lethal concentration for Daphnia has been reported to be 300 mg/l (574, 3523). For the immobilization of Daphnia magna in Lake Erie water at 25°C, the threshold concentration of sodium sulfite has been reported to be 440 mg/l (352) and 3784 mg/l (358).

## SODIUM SULFONATES

(see Chapter X)

# SODIUM TETRAPROPYLENE BENZENE SULFONATE

(see Chapter X)

## SODIUM THIOCYANATE

NaSCN

(see also Cyanides, Hydrogen Cyanide, Potassium Thiocyanate)

This highly soluble salt is used in the manufacture of other thiocyanates, especially the organic compounds, and in many of the same processes as potassium thiocyanate (364). When chlorinated, it breaks down to release cyanide ions (see KSCN).

According to Schaut (362), fish were killed in two hours by 3240 mg/l of sodium thiocyanate. For Daphnia magna in Lake Erie water at 25°C, however, the threshold concentration was found by Anderson (352) to be less than 11.3 mg/l or about 10.2 mg/l (353). The threshold concentration for Polycelis nigra, a planarian, was reported by Jones (354) at 700 mg/l as SCN-.

Thiocyanate compounds have been used for the treatment of hypertension in human patients. The daily ingestion of less than approximately 120 mg of SCN has not given rise to reports of harmful effects in patients treated for 10 years (2963).

#### SODIUM THIOSULFATE

 $Na_2S_2O_3 \cdot 5H_2O$ 

Sodium and thiosulfate ions may occur as constituents of Kraft mill wastes. The toxic threshold concentration of sodium thiosulfate for the flatworm Polycelis nigra was found to be 8400 mg/l (354). The threshold concentration of sodium thiosulfate for the immobilization of Daphnia magna in Lake Erie water was found to be much less than 520 mg/l (352). The minimum lethal concentration of sodium thiosulfate for minnows has been reported to be 5.0 mg/l, for a 120-hour period (190, 344). Using highly turbid water at 22-24°C, Wallen et

al. (2940) found the 96-hour TL_m toward the mosquito-fish (Gambusia affinis) to be 24,000 mg/l.

## SODIUM TRIPOLYPHOSPHATE

(see Sodium Phosphates)

#### SODIUM TUNGSTATE

(see Tungsten)

### SOLIDS

(see also Dissolved Solids, Specific Electrical Conductance, Suspended Solids, Silt, Settleable Solids, Tur-

bidity, and Distilled Water)

Solids in water are classified as either "dissolved", i.e., capable of passing a fine mat of asbestos fiber in a Gooch crucible, or "suspended", i.e., retained on the asbestos mat. Both dissolved and suspended solids may be differentiated further as "fixed", i.e., inorganic, and "volatile", i.e., organic material or volatile matter driven off by ignition at about 600°C. In this report, no attempt is made to segregate fixed and volatile solids (469).

Another test for solids, readily conducted by means of the Imhoff cone, is the determination of "settleable" solids, i.e., the volume in ml per liter that will settle in one hour. The total effect of dissolved solids is also measured by the effect of the dissociated ions on the conductivity of the solution. This test for total dissolved solids is known as the "specific electrical conductance".

In this report each of the aforementioned categories of solids is considered separately and the reader is referred, therefore, to each type as itemized above.

## SORBITAN MONOLAURATE

(see Chapter X)

## SORBITAN MONOSTEARATE

(see Chapter X)

## SPECIFIC ELECTRICAL CONDUCTANCE

1. General. Natural inland waters usually contain in solution relatively small quantities of mineral salts, but in waters polluted by brines and various chemical wastes the salt concentration may rise to levels harmful to living organisms because of the increase in osmotic pressure. In studies of waters for use in irrigation and fish production, the salinity is often expressed as specific electrical conductance. The determination of conductivity is a quick method for measuring the ion concentration of water. Procedures and equipment are described by Standard Methods for the Examination of Water and Waste Water (469), by Ellis and coworkers (247), and by Wilcox (635). Conductivity is reported as specific electrical conductance, the reciprocal of the resistance in ohms of a column of solution one centimeter long and with a cross section of one square centimeter, at a specified temperature, usually 25°C.

In fish studies, specific electrical conductance is reported directly as reciprocal ohms (mhos) at 25°C. Thus, a 0.005N solution of NaCl, containing 292.2 mg/l, has a specific electrical conductance, K, of 0.000604 mhos or  $604 \times 10^{-6}$  mhos at 25°C. In irrigation studies, however,

it is customary to report specific electrical conductance as  $K\times 10^5$  or as EC  $\times 10^6$  at 25°C. For the 0.005N solution of NaCl, irrigation literature would report the conductance as  $K\times 10^5=60.4$  or as EC  $\times 10^6=604$ . Considering the combined effects of all of the dissolved salts, it has been found that  $K\times 10^5$  values times 6.5, and EC  $\times 10^6$  values times 0.65, are approximately equal to the concentrations of dissolved salts in mg/l. Values of  $K\times 10^5$  divided by 10 are approximately equal to the concentration of cations or anions in equivalents per million (269). Where NaCl is the only salt,  $K\times 10^5$  values should be multiplied by 4.7 to 5.7 to give concentrations in mg/l, depending on the concentration.

- 2. Cross References, Dissolved Solids.
- 3. Effects Upon Beneficial Uses.
  - a. Domestic Water Supply. See Dissolved Solids.
- b. Irrigation Waters. Conductance is one of the most important criteria for the classification of irrigation waters (see Chapter V—Irrigation). The limits suggested by various authorities (246, 263, 269, 273, 274) are summarized in the following table:

# SPECIFIC ELECTRICAL CONDUCTANCE OF IRRIGATION WATERS

Designation	EC × 10° at 25°C in Micromhos per cm	Reference
Class I, suitable under most conditions	<1000 < 750	246, 273, 274, 1912 267, 1733
Class II, suitability on crop, climate, etc.	1000–3000 750–3000	246, 273, 274, 1912 267, 1733
Class III, unsuitable und most conditions	er >3000	246, 267, 274, 273 1733, 1912
Excellent	< 250	269, 263
Good	250- 750	269, 263
Permissible	750-2000	269, 263
Doubtful	2000-3000	269, 263
Unsuitable	>3000	269, 263

b. Fish and Other Aquatic Life. All substances in solution in the water collectively exert osmotic pressure on the organisms living in it, and the aquatic life is adapted to the conditions imposed upon the water by its dissolved constituents. Most species can tolerate some changes in the relative amounts of salts normally present if the total concentration is not exceeded. However, wide variations in the total salinity or in the concentrations of individual salts can have far-reaching effects upon stream fauna, resulting even in the elimination of species.

When the osmotic pressure is sufficiently high, owing to salts in solution, water may be drawn from gills and other delicate external organs, with considerable damage to cells, or even death. High concentrations of many kinds of pollutants present this danger apart from any other toxic or corrosive effects they may have.

Ellis' studies of inland fresh waters indicated that the specific conductance of streams and rivers supporting a good mixed fish fauna lay, in general, between 150 and 500 mhos  $\times$  10⁻⁶ at 25°C, except in streams of the western plains and desert areas, particularly those carrying the more alkaline natural waters. Such waters, draining land rich in soluble alkalis, were found to have a conductance as high as 5000 mhos  $\times$  10⁻⁶ at 25°C. However, good mixed fish fauna were usually not found in waters with

a specific conductance greater than 2000 mhos  $\times$  10⁻⁶ at 25°C. On the basis of his studies Ellis had concluded that conductances in excess of 1000 mhos  $\times$  10⁻⁶ at 25°C in most types of stream, or in excess of 2000 mhos in the alkaline western streams are probably indicative of the presence of acid or salt pollution of various kinds (247, 313, 345, 347, 801).

Using Ellis' data, Hart et al. (310) have reported that among United States waters supporting a good fish fauna about 5 percent have a specific conductivity under 50  $\times$  10⁻⁶ mhos at 25°C; about 50 percent under 270  $\times$  10⁻⁶ mhos; and about 95 percent under 1100  $\times$  10⁻⁶ mhos.

Ellis (611) has also found that a specific conductance of  $4000 \times 10^{-6}$  mhos at 25°C is approximately the upper limit of ionizable salts tolerated by fish in mixtures of sodium, magnesium, and calcium compounds in gas-well waters.

## STANNIC AND STANNOUS SALTS

(see Tin)

#### STRONTIUM

Sr

(see also Chapter VIII)

Related to calcium, magnesium, and barium, this element is not found free in nature. It occurs largely with calcium or barium minerals, in the form of the sulfate (celestite) or the carbonate (strontianite). The carbonate is soluble only to the extent of about 10 mg/l and the sulfate to about 114 mg/l (364). Hence, strontium ions are not likely to occur in high concentrations in surface waters. The concentration in sea water has been given as 10 mg/l (2121) and 8.5 mg/l (3345). It is not adsorbed readily by soils and hence strontium may be expected to travel readily along with ground waters (1976). Strontium metal is used in some alloys of tin and lead. The salts are used in pyrotechnics, in refining beet sugar, in manufacturing glass and paints, in ceramics, and in some medicines (364, 2121).

Strontium is present in plant and animal tissues in trace concentrations, but it occurs in much higher concentrations in bone structures. There is no evidence that strontium is essential for plant nutrition, but there are indications that it is necessary for the growth of animals and especially for calcification of bones and teeth. In humans, the strontium content of bones has been given as 120 to 234 mg/kg, in contrast with a tissue concentration of less than 0.1 mg/kg. Toxicologically, no evidence was uncovered to show that non-radioactive strontium salts taken or ally by man or animals produces deleterious action. Its toxicity is probably on the same order of magnitude as calcium (2121). Indeed, strontium bromide has been used medicinally as a sedative and antiepileptic; strontium iodide has been used in iodine therapy; and strontium lactate for osteoporosis (364).

With the advent of nuclear fission and weapons testing, strontium came to the forefront of publicity as one of the inevitable constituents of fall-out. Owing to its long half-life and its tendency to accumulate in bone structure, Sr-90 is ranked second only to Ra-226 as a hazard to human health. The 1962 Drinking Water Standards of the USPHS (2036) limit the Sr-90 content to 10 pc/l. The WHO Standards, both European

and International (2328, 2329) limit the total betaemitters, including Sr-90, to 10 pc/l. As a result of nuclear testing, rain water has been reported to contain from 2 to 8 pc/l (3680, 3681). In lake waters, the Sr-90 activity has reached 0.45 pc/l, in river waters 0.24 pc/l, but in ground waters less than 0.01 pc/l (3680). Food, however, and not water is considered to be the major vehicle by which radiostrontium reaches humans. It is estimated that less than 10 percent of the Sr-90 ingestion comes from consumption of water (3682).

Crop plants tend to accumulate radiostrontium from soils and water contaminated with fallout from nuclear explosions or waste products from nuclear reactors (3683). Plants do not appear to discriminate between calcium and strontium in soil moisture and hence the ratio of these two elements in plant tissue tends to be the same as their ratio in the soil solution. The uptake of strontium by plants can be reduced by adding calcium to the soil or applied water (3683, 3684, 3685, 3686).

Owens et al. (3689) measured the uptake of radiostrontium by aquatic macrophytes during 7 days exposure in hard river water containing Sr-89 with an activity of about  $0.01 \times 10^{-3}$  c/l. Concentration factors for 6 species varied from 30 to 74. In soft water, however, watercress had a concentration factor of 200 after 28 days in contrast to 55 in hard water. Other experiments (1816) showed concentration factors for watercress in the order of 600 to 800 in soft water (20 mg/l of CaCO₃) and less than 100 in hard water (300 mg/l CaCO₃). Again, the increase in calcium and magnesium ions appears to militate against the uptake of strontium. For *Porphyra*, an edible seaweed in South Wales (2435) the concentration factor was only 0.05-0.3.

Planktonic algae have also been shown to concentrate radiostrontium. The greatest part of the radioactivity in the cells appears to be due to Y-90, the radioactive daughter of Sr-90 (3690). Concentration factors for algae have been reported at values ranging from 8 to 3060 (2442, 3385, 3386, 3690). For marine bacteria, a concentration factor of about 100 has been given (3386).

For fish, Foreman and Bidwell (3691) observed that Sr-90 concentrated in the flesh, bones, and scales of rudd by factors of 2.6, 71, and 209 respectively. For lobsters, Templeton (2435) reported a concentration factor for non-radioactive strontium of 300 in the shell and 2.0 in the flesh. He indicated a probable accumulation factor of 150 for goldfish (the whole fish). Krumholz (3692) found that fish in a lake that received radioactive waste effluents at Oak Ridge concentrated radiostrontium by factors of 20,000 to 30,000 in hard tissues.

It is evident that the major hazard to humans of radiostrontium in water lies not in direct consumption but in plants and fish that accumulate this element.

### STRONTIUM CHLORIDE

 $SrCl_2 \cdot 6H_2O$ 

(see also Strontium)

This highly soluble salt is used in pyrotechnics, in the manufacture of other strontium salts, and in freezing mixtures for refrigerators (364, 2121). Toward fish, strontium chloride has a low order of toxicity. Ellis (313) reported that 15,384 mg/l in distilled water killed goldfish in 17 to 31 hours. According to Jones (2920)

is the lethal concentration of SrCl₂ at 20°C was 18,000 mg/l for goldfish. Toward a small fresh-water fish (*Orizias*), the lethal concentration was given (1459) as about 20,000 mg/l for a 24-hour exposure.

Toward smaller aquatic life, the lethal dose may be somewhat lower. According to Anderson (598), the threshold concentration for immobilization of Daphnia magna in Lake Erie water at 25°C was found to be 114 mg/l in 64 hours. Bringmann and Kuhn (2158, 3343) found the threshold concentration for Daphnia at 23°C to be 210 mg/l of strontium; and for the protozoan, Microregma, it was 329 mg/l as strontium. Jones (608) reported that the threshold for Polycelis nigra, a flatworm, during a 48-hour exposure was 6600 mg/l. Toward the alga, Scenedesmus, and the bacterium, E. coli, 1000 mg/l as strontium had no noticeable effect (2158).

## STRONTIUM FLUORIDE

 $SrF_2$ 

This salt is soluble in water to the extent of only 117 mg/l at 18°C (364). Yet, Simonin (3271) reports that the lethal dose for tench is 30,000 mg/l.

#### STRONTIUM NITRATE

 $Sr(NO_3)_2$ 

(see also Strontium)

This highly soluble salt is used for pyrotechnics, signal lights, flares, and matches. At a concentration of 9615 mg/l in distilled water, it was reported (313) to kill goldfish in 32 to 146 hours. For sticklebacks, the lethal dose was found to be 1200 mg/l during prolonged exposure. The average survival times at other concentrations were as follows: one week at 1500 mg/l, four days at 3000 mg/l, two days at 7000 mg/l, and one day at 10,000 mg/l, all expressed as strontium (1460). Goldfish were reported (1459) to have survived exposure for four days to strontium nitrate at concentrations of 3200 mg/l as strontium. According to Jones (608) the threshold concentration for *Polycelis nigra*, a flatworm, was 3500 mg/l as strontium.

## STRYCHNINE

 $C_{21}H_{22}N_2O_2$ 

Strychnine and its salts are used for destroying rodents and predatory animals, and for trapping fur-bearing animals (364). The likelihood that it will reach natural waters in significant concentrations is small, Smith (922) reports that adults may safely drink daily 0.078 to 0.25 gallons of water containing 10 mg/l of strychnine (i.e., 2.94 to 9.45 mg per day) and a fatal dose of such water would be 1.5 to 3.0 gallons (56.7 to 113.4 mg). Carson (1483) states that strychnine in water is detectable because of its bitter taste in concentrations of more than 2 or 3 mg/l.

## SUCROSE

 $C_{12}H_{22}O_{11}$ 

(see also Sugars)

Sucrose, obtained from sugar cane and sugar beet, is used as a sweetening agent and food, for fermentation, in pharmacy, and in many industrial processes. Rohlich and Sarles (759) report that the threshold concentration for tasting sucrose in water is about 5000 mg/l.

For fish and other aquatic life, the primary detrimental effect of sucrose arises from its high BOD. Ellis

(313) reports that concentrations of 34 to 218 mg/l in distilled water caused the death of minnows in 24 to 48 hours. This effect, however, may have been due more to the distilled water than to the sucrose. Garrey (307) writes that cane-sugar solutions can be directly toxic to fish, being least toxic when the osmotic pressure of the water equals that of the blood. He reports that 137,000 mg/l of cane sugar in solution killed fish in 12 hours and 85,000 to 100,000 mg/l killed in three days.

#### SUGARS

(see also Beet-Sugar Wastes, Dextrose, Sucrose)

In addition to the possible harmful effects in streams, arising from deoxygenation and osmotic action, sugars are sometimes detrimental in industrial process waters. Hewlett (806) states that boiler feed water should contain not more than 5.0 mg/l of sugar, inasmuch as sugar causes foaming and the deposition of a film of decomposition products on the walls.

Sugar is one of the most detrimental substances that can be introduced in a mixture containing portland cement. Very small quantities in the mixing water may prevent portland cement mixtures from attaining their potential strength, but dry sugar has no effect on the hardened concrete. At 0.05 percent by weight of the sand (or 3400 mg/l in a 1:3 mix) sugar caused nearly all specimens to disintegrate in water (193, 360).

Oysters were harmed and even killed by feeding on sugar, oatmeal, or flour, according to Boyce and Herdman (807). Oysters thrive best on living plankton and live well in sewage-polluted water; but they appear unable to feed on carbohydrates and sugars.

Sugars in water can be tasted in a concentration of 2000 mg/l (1578).

## SULFATED AMINE

(see Chapter X)

## SULFATED FATTY ESTER

(see Chapter X)

### SULFATED ESTERS

(see Chapter X)

### SULFATED MONOGLYCERIDES

(see Chapter X)

#### SULFATE PULP MILL WASTES

(see Kraft Pulp Mill Wastes)

#### SULFATES

 $SO_4^{--}$ 

1. General. Sulfates occur naturally in waters, particularly in the western United States, as a result of leachings from gypsum and other common minerals. They may also occur as the final oxidized stage of sulfides, sulfites, and thiosulfates: e.g., iron pyrite FeS may be leached from abandoned coal mines and the sulfide ions converted in surface streams to sulfates (1358). Sulfates may also occur as the oxidized state of organic matter in the sulfur cycle, but they, in turn, may serve as sources of energy for sulfate-splitting bacteria (see

Sulfur Bacteria). Finally, sulfates may be discharged in numerous industrial wastes, such as those from tanneries, sulfate-pulp mills, textile mills, and other plants that use sulfates or sulfuric acid.

The sulfates of lead, barium strontium and calcium are relatively insoluble (1224), but sodium, potassium, and ammonium sulfate are highly soluble.

- 2. Cross References. Sulfur, Sulfides, Sulfur Dioxide, Various sulfate salts, Chapter V, Chapter VII—Sulfur Bacteria.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The 1962 Drinking Water Standards of the USPHS (2036) recommend that sulfates do not exceed 250 mg/l, except where a more suitable supply is not available. This limit does not appear to be based on taste or physiological effects other than a laxative action toward new users. Public water supplies with sulfate contents above this limit are commonly and constantly used without adverse effects (152). The 1958 WHO International Standards (2328) established a "permissible limit" of 200 mg/l and an "excessive limit" of 400 mg/l, but set no maximum allowable limit. The 1961 WHO European Standards (2329) include a recommended limit of 250 mg/l for sulfates.

Korotchenok (622) reported on heavily mineralized drinking waters in western Turkmenia (USSR), noting that no outbreaks of disease have been ascribed to waters in which the content of sulfate did not exceed 1295 mg/l. In British Somaliland well waters used for human consumption contain very high sulfates, many having 2000-3000 mg/l. One village is using water of 4400 mg/l sulfates (1546). A survey in North Dakota (1628a) indicated that water containing less than 600 mg/l of sulfates is usually safe. In reviewing the literature, Moore (621) quotes Sollman to the effect that concentration of 1000 mg/l of sulfates in water is harmless. A cathartic dose is 1.0 to 2.0 grams, or a liter of water containing 1000 to 2000 mg/l of sulfates.

Sulfates appear to have no detrimental effect on the corrosion of brass fittings in domestic water systems (1359), nor do concentrations less than 200 mg/l increase plumbo-solvency (1073). However, for the effects of higher concentrations, see Sodium Sulfate. Whipple is quoted by Moore (621) to the effect that the taste thresholds of sulfate salts were as follows:

Sodium sulfate	200-500  mg/l
Calcium sulfate	250-900  mg/l
Magnesium sulfate	400-600 mg/

b. Industrial Water Supplies. Limiting or threshold concentrations, or optimum ranges, as described in Chapter V for sulfates are assembled below:

	Limits of Recommended Values, mg/l			
Industrial Process	80,	CaSO,	MgSO,	Na ₂ SO ₄
Brewing		100-500	100-200	100
Carbonated beverages Concrete corrosion	250 25			
Ice making Milk industry		300	130-300	300
Photographic processes	60	100		
Sugar making	20	100		
Textiles	100	_ <del></del>		

Ice appears to be particularly susceptible to excessive sulfates, since they become trapped in the entire block

instead of migrating toward the core where they can be removed (534). A widely quoted formula is used by some ice makers in which the sulfates are weighted as 1.00, the chlorides as 0.75, and sodium carbonate as 1.25. When the sum of these weighted concentrations is less than 171 mg/l, first quality ice can be made readily; at higher values added precautions are needed and if the total is more than 684 mg/l merchantable ice cannot be expected (164, 168, 228, 231). In concentrations of 257 mg/l or less, sodium sulfate is reported to cause a white shell in ice (229).

Sulfates appear to increase the corrosiveness of water toward concrete (see Chapter V-Concrete Mixing and Concrete Corrosion). Kellam (196) states, "If the SO3 is less than 25 mg/l, injury from this source will be mild and inconsequential. When the SO3 is in the hundreds of mg/l, it is a possible source of great harm and protection must be provided". Hammerton (360) claims that there will be little attack if the sulfate concentration is less than 300 mg/l (as SO₃), but if the sulfate is greater than 1000 mg/l attack will be rapid (855). As pointed out hereinbefore, the disintegration of concrete is a function of several factors, including pH, carbonic acid, sulfates, and biological action (2355). According to Szigligeti (1699) sulfates in excess of 300 mg/l in soil and water are detrimental to asbestos-cement and asbestosconcrete pipes.

c. Irrigation. Sulfates are somewhat less toxic than chlorides in irrigation waters (275). In high concentrations, sulfate ions may cause the precipitation of calcium and may in themselves be toxic to plants (281). Scofield (263) gave examples of permissible limits of sulfates for a definite region of irrigation waters as follows:

Excellent	less than 102 mg/
Good	100 to 200 - 7
Permissible	192 to 550 mg/l
Doubtful	550 to 576 mg/l
Unsuitable	576 to 960 mg/l
O manifemate	over 960 mg/l

Eaton, McGallum and Mayhugh (264) condensed these same values into three classifications: less than 192 mg/l, from 192 to 576 mg/l, and over 576 mg/l. Hinman (219) points out that concentrations over 500 mg/l are generally hazardous. The 10-year weighted average sulfate concentration of Colorado River water is 230 mg/l and Kelley (1060) did not feel that this concentration will be deleterious to underground waters or eitrus trees in southern California.

- d. Stock and Wildlife Watering. In Minnesota, cattle that drank water containing 3590 mg/l and 2104 mg/l of sulfate developed run-down, ragged appearances and eventually weakened and died (643). However, sulfate seems to offset in part the toxicity of selenium toward cattle (1328). At concentrations of 2500 mg/l, sulfates caused diarrhea in dogs (3693). A threshold limit of 1000 mg/l has been suggested by Stander (3373).
- e. Fish and Other Aquatic Life. In U.S. waters that support good game fish, 5 percent of the waters contain less than 11 mg/l of sulfates, 50 percent less than 32 mg/l, and 95 percent less than 90 mg/l (310). Experiments indicate that water containing less than 0.5 mg/l of sulfate will not support growth of algae (2203). For further data on specific sulfates, see sodium sulfate, copper sulfate, potassium sulfate, etc.

4. Summary. On the basis of the information gleaned from literature, it appears that the following concentrations of sulfate will not be detrimental for the indicated beneficial use:

a. Domestic water supply	500	mg/l
b. Irrigation	260	mg/l
c. Stock watering	500	mg/l

## SULFATE SUBSTITUTED AMIDE

(see Chapter X)

SULFIDES S

(see also Hydrogen Sulfide, Sulfur, Salts of Sulfides and Chapter VII—Sulfur Bacteria)

Sulfides are constitutents of many industrial wastes such as those from tanneries, paper mills, chemical plants, and gas works; but they are also generated in sewage and some natural waters by the anaerobic decomposition of organic matter. When added to water, soluble sulfide salts such as Na₂S dissociate into sulfide ions which in turn react with the hydrogen ions in the water to form HS- or H₂S, the proportion of each depending upon the resulting pH value (see Hydrogen sulfide). Thus, when reference is made to sulfides in water, the reader should bear in mind that the sulfide is probably in the form of HS- or H₂S.

Owing to the unpleasant taste and odor which result when sulfides occur in water, it is unlikely that any person or animals will consume a harmful dose (1077). The thresholds of taste and smell were reported (686) to be 0.2 mg/l of sulfides in pulp-mill wastes. For industrial uses, however, even small traces of sulfides are often detrimental (see Hydrogen sulfide). Sulfides are of little importance in irrigation waters (268).

The toxicity of solutions of sulfides toward fish increases as the pH value is lowered, i.e., the H₂S or HS-, rather than the sulfide ion, appears to be the toxicity principle (346). In water containing 3.2 mg/l of sodium sulfide, trout overturned in two hours at pH 9.0, in 10 minutes at pH 7.8, and in four minutes at pH 6.0, as reported by Southgate (346). According to Doudoroff (2409) inorganic sulfides have proved fatal to sensitive fishes such as trout at concentrations between 0.5 and 1.0 mg/l as sulfide, even in neutral and somewhat alkaline solutions.

#### SULFITES

(see Sulfur Dioxide)

## SULFITE WASTE LIQUORS

1. General. The waste water resulting from the pulping of wood with calcium on magnesium bisulfite liquor with steam under pressure are known as sulfite waste liquors (SWL) or spent sulfite liquors (SSL). They contain in dissolved or very finely divided suspension approximately half of the weight of the wood used for pulping, and comprise fiber-binding substances such as lignin and pectin, hemicelluloses, sulfur dioxide, sulfites, polythionates, organic acids, calcium or magnesium, and numerous other organic and inorganic substances. Acid

in reaction, they are high in BOD and dissolved organic matter, with a persistent pungent odor and a tendency

to foam in receiving streams. Gunter and McKee (2415) have summarized the chemical and physical characteristics of SWL. They point out that most SWL contains 10 to 14 percent total solids, with 5-day BOD values of about 30,000 mg/l. The lignin component of SWL comprises a great variety of highmolecular-weight compounds that include benzene or phenol complexes to which sulfonate has been added for pulping purposes. SWL can be detected in dilute concentrations in receiving waters by the Pearl-Benson test, which is precise and reproducible but not specific. Many natural phenolic substances will produce positive tests. The Pearl-Benson test is calibrated in terms of SWL having 10 percent solids. In effect, then, it expresses the dilution of 10 percent SWL expressed in parts per million by volume. Hence, a P-B reading of 15 ppm represents only 1.5 mg/l of total solids in the original SWL. For this reason, Gunter and McKee (2415) proposed the term "Pearl-Benson Index" or "PBI" to describe the concentrations measured by this

- 2. Cross References. Sulfur and Sulfur Compounds.
- 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The controlling factor for SWL in streams that may be used for domestic water supply appears to be taste and odor. To eliminate the taste of SWL, a dilution of 1:25,000 appears to be necessary (7). At such dilutions, the concentrations of other potential pollutants from SWL are insignificant.

b. Fish and Other Aquatic Life. The principal deleterious effect of SWL towards fish appears to be its high BOD, with resultant oxygen depletion. Dilutions of 1:200 or better are required to prevent serious oxygen depletion. (673). Compared with Kraft mill effluents, SWL is relatively non-toxic (683). A second deleterious effect arises from the fact that the sugars in SWL stimulate the growth of Sphaerotilus in streams (2500, 2642).

Most of the references dealing with the effect of SWL on fish express their findings in terms of dilution. Since the strength of the SWL is seldom given, results cannot be compared exactly; but it is logical to assume that the SWL was approximately 10 percent solids. The following table summarizes the observed effects of SWL on fish:

IISII:			
Given Dilution	r Type of		
(ppm by volum	e) Fish	Observed Effect	Reference
50-75		No effect	3503
500-600		Threshold of lethal-	
		ity, 30 days	2642
530-1550	Pink salmon	5 percent kill	3695
560-1175	Chinook salmon	5 percent kill	3695
599-1022	Young herring	Tolerance level	3694
805	Chinook salmon	TL _m for 30 days	3524
880	Chum salmon	Toxic threshold	2091
1000	Trout	Lethal in a few days	673
1015-1230	Silver salmon	5 percent kill	3695
1330-2000	Trout	Lethal	359
1700	Coho salmon	TL _m for 30 days	3524
2000	Salmon	Avoidance reaction	3524
2000-5000	Warm-water fish	Survived 10-20 days	673
5000	Mixed	No deaths in 28 days	311, 688
5000	Fish	Toxic	687
8330-20,000	Trout fry, perch,		
	and bass	Killed in 29-113 bour	
·	•	in non-aerated wate:	r 808

Given Dilut (ppm by volu		Observed Effect	Reference
10,000	Bass	Not killed in 17 days	•
20,000 100,000 100,000	Salmon fry Fish Rock bass	in aerated water Killed in 28 hours Lethal Lethal	808 311, 688 540 359

Long exposures to SWL affect the internal organs of fish, with definite damage at dilutions of 1:100,000. Moreover, SWL gives a taste to fish flesh (7).

Very little quantitative information is available upon which to assess the effects of SWL on fish-food organisms. In general, it appears that SWL exerts no direct toxic action except at concentrations in excess of 1000 ppm by volume of 10 percent SWL. The sparse literature in this subject has been reviewed and summarized by Gunter and McKee (2415). Lasater (3694) found that some copepods could not tolerate SWL, with significant mortalities being reported at 50-157 ppm of 10 percent SWL in 2 to 14 days.

c. Shellfish Culture. On the basis of a comprehensive literature review, Gunter and McKee (2415) recommended that the Pearl-Benson index attributable to SWL in waters overlying beds for the growing of Olympia oysters should not exceed 10 during the months of April through October and 20 during the months of November through March. In waters overlying beds of the Pacific oyster, the PBI should not exceed 40 during April through October nor 80 during November through March. There appears to be some evidence that PBI concentrations of 8 to 16 are inimical to the adult Olympia oyster and perhaps the threshold concentration for adverse effects is even lower. Adult-Pacific oysters appear to be far more tolerant of SWL than Olympias. It is apparent that Pacifics can withstand PBI concentrations of 50 to 100, or perhaps even more, over long periods of time without mortality.

Toward oyster larvae, on the other hand, SWL may be more adverse toward Pacifics than towards Olympia. owing to the difference in spawning mechanisms. For Pacific larvae, PBI values of 8 to 16 represent a tentative threshold of toxicity. In recent work, Lindsay, Westley, and Woelke (3696) point out that the reproductive eycle of Olympia oysters was affected by fresh ammoniabase SWL at PBI values of 2, 4, and 8; but these effects were not demonstrated as being necessarily adverse. The development of Pacific larvae was affected at PBI values of 2 and greater, and at 18 almost 100 percent of the larvae were abnormal. These authors also point out that SWL is lethal to Monas sp, an important oyster food organism at P-B indices of 1,000 to 10,000. Over several months, SWL appears to have a depressing effect on this food organism at PBI values as low as 2.5.

## SULFOETHYL METHYL OLYAMIDE

(see Chapter X)

## SULFONATED AMIDE

(see Chapter X)

#### SULFONATED ESTERS

(see Chapter X)

## SULFONATED CASTOR OIL

(see Chapter X)

#### SULFOXIDE

(see Chapter IX)

#### SULFUR

?

(see also Hydrogen Sulfide, the various sulfur compounds, Chapter VII—Sulfur Bacteria)

Elemental sulfur occurs in a free state in nature and it may also result in water from the oxidation of sulfides (see Chapter VII—Sulfur Bacteria). It is insoluble in water but it may be present in suspension in the colloidal state. It is used in the manufacture of sulfur compounds, insecticides, fungicides, matches, plastics, and enamels, in the vulcanizing of rubber, and in the synthesis of dyes (364, 1224). Pharmaceutical sulfur has been used internally as a laxative and parasiticide in doses of 1 to 4 gms (364).

Traces of sulfur in water used for plating baths will affect the smoothness or brightness of the deposits (214), and in photographic developers colloidal sulfur will react and cause fog (242). References are quoted by Ellis (313) to the effect that 1600 mg/l of colloidal sulfur in tap water was fatal to goldfish in 3.5 to 5.25 hours and 2100 mg/l in 48 to 71 minutes. According to Harukawa (1360), 16,000 mg/l of colloidal sulfur killed goldfish in five hours and 200,000 mg/l in less than one hour, but the author points out that the theoretical threshold concentration for goldfish is probably about 10 to 80 mg/l (time is not specified). In highly turbid water, Wallen et al. (2940) found the 96-hour TL_m for the mosquito-fish to be over 10,000 mg/l.

Radioactive sulfur, S-35, is reported to concentrate by a factor of 5 in the soft tissues of vertebrates and invertebrates (3375). For more detail on concentration factor, see Chapter VIII.

#### SULFUR DIOXIDE

 $SO_2$ 

(see also Sulfur, Sulfates)

A colorless, nonflammable gas with a suffocating odor, sulfur dioxide is soluble in water to the extent of over 100,000 mg/l at 20°C. The dissolved gas combines with water to form sulfurous acid, thus  $SO_2 + H_2O \rightleftharpoons H_2SO_3$  and the sulfurous acid dissociates according to the equations:

Equations	$K~{ m at}~25^{\circ}{ m C}$
$\mathrm{H_2SO_3} \rightleftharpoons \mathrm{H^+ + HSO_3^-}$	$1.7 \times 10^{-2}$
and $HSO_3^- \rightleftharpoons H^+ + SO_3^-$	$5 \times 10^{-6}$

The percentages of undissociated sulfurous acid, HSO₃, and sulfite ion at various pH values are shown by the following tabulation:

Percent as

llowing ta	bulation:	Percent as	
pH	$H_2SO_3$	HSOs	$SOs^{}$
4	0.56	94.7	4.74
5	0.04	66.5	33. <b>46</b>
6		16.7	83.3
7		2.0	98.0
8		0.2	99.8
9	·	0.02	99.98
~			

Very little of the sulfurous acid remains undissociated in the normal pH ranges; at pH 5 and below, HSO₃-predominates and above 5 the bivalent sulfite ion prevails (911).

In the presence of oxidizing agents such as dissolved oxygen and chlorine, the sulfite ion is gradually oxidized to sulfate, the sulfur changing from a+4 valence to +6 (364).

In domestic water, sulfur dioxide and sulfites are deleterious primarily in that they lower the pH value and increase corrosivity. By being oxidized and utilizing dissolved oxygen, on the other hand, sulfites may retard corrosion. Konrich and Haase (1312) fear that a high concentration of sulfite ion in water may cause exzema.

In 1917, Shelford (363) reported that 16 to 19 mg/l of sulfur dioxide killed orange-spotted sunfish in one hour. Ellis (313) quotes references to the effect that concentrations of SO₂ of 10 mg/l in tap water caused trout to float helplessly within 10 minutes, and Ellis (609) also reported that 5.0 mg/l of SO₂ kills trout in one hour. According to Bandt (656), 0.5 mg/l of sulfurous acid is toxic to fish. Sulfurous acid is lethal to tench at a concentration of 1.0 mg/l for two hours (2977).

## SULFURIC ACID $H_2SO_4$

1. General. Like hydrochloric, nitric, and other strong acids, sulfuric acid dissociates almost completely in water to release sulfate ions and hydrogen ions, thereby tending to lower the pH value. At very low pH values (3 and lower), some of the sulfate ion will remain as acid sulfate, HSO₄-, but at higher pH values dissociation to sulfate ions is practically complete (911). In considering the effects of sulfuric acid upon the beneficial uses of water, therefore, it must be recognized that an increase in sulfate ions and a lowering of pH are involved.

Sulfuric acid is the most important and widely used acid. It is employed in nearly all chemical processes and in many other industries, e.g., the production of fertilizers, other acids, explosives, and dyestuffs, for the purification of oils, and for pickling of metals (364, 1224). As a result of its wide use, increased sulfate ions and lowered pH values are likely to result in many types of industrial wastes.

- 2. Cross References. Acidity, pH, Sulfates.
- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. (see Sulfates, Acidity, and pH)
- b. Fish and Other Aquatic Life. The following concentrations of sulfuric acid in water have been reported as lethal or toxic toward fish:

Concentra- tion of H ₂ SO ₄ in mg/l	Time of exposure	Type of water  Distilled, 20°C	Species of fish Sunfish Minnows Trout	Reference 359 2942 359
6. 25. 7. 36. 10. 0. 24. 5. 26. 0. 42. 49. 59. 0. 71. 2. 80. 1. 110-120. 138. 0. 167.	15 minutes	Distilled	Bluegills Gamefish Bluegills Minnows Mosquito-fish Bluegill sunfish Goldfish Pickerel Whitefish Minnows Goldfish Fish	313 1010, 541 359 362 2940 2093 313

Non-toxic or harmless concentrations of sulfuric acid have been reported as follows:

3.68.     1 month     Distilled     Bluegills     313       17.0.     Over 4 days     Soft     Goldfish     353       20.0     24 hours     Minnows     359       100.0     100 hours     Hard     Goldfish     313	have been reported	as lunuws.		D. 0
	3.68   1 month   17.0   Over 4 days   20.0   24 hours   100.0   100 hours   10	Distilled	Bluegills Goldfish Minnows, Goldfish	313 353 359 313

Toward other aquatic life, the following concentrations of sulfuric acid were harmful:

29 24-72 bours 23 .11 24-72 bours 24-72 bo	Soft, pH 5	Daphnia magna Bivalve larvae All aquatic life Daphnia magna Daphnia magna	313 2989 541 358 353
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The foregoing tabulations illustrate the fact that the toxicity of sulfuric acid toward aquatic life is a function of the resulting pH, i.e., a dose that would be lethal in distilled water or soft water might be harmless in a highly buffered water. Doudoroff and Katz (361) report that strong mineral acids such as sulfuric can be directly lethal to fully developed fish in most natural waters only when the pH is reduced to 5.0 or lower. Ellis (611) confirms this observation by stating that sulfuric acid must be diluted so as to give a pH of 4.5 or higher in order for fish to survive, and to pH 5.5 to make it possible for other aquatic organisms to thrive and provide food for fish. Death of trout has been reported (2920) at pH 3.9, while for sunfish, bass, and carp (3697) a pH of 3.5 caused death and 4.0 gave pronounced gill irritation. For Polycelis nigra, the toxic threshold of sulfuric acid has been reported (353) as 0.63 mg/l of hydrogen ion, or at pH 3.2 in distilled water. When sulfuric acid in streams depresses the pH below 5.0, specialized flora and fauna develop (3608).

c. Shellfish Culture. Oysters are sensitive to changes in pH. A dose of 100 mg/l of sulfuric acid killed 18 percent of oyster spat in five days (317, 523).

## SULFUROUS ACID

(see Sulfur Dioxide)

## SURFACE ACTIVE AGENTS

(see Chapter X)

#### SUSPENDED SOLIDS

1. General. In natural waters, suspended solids consist normally of erosion silt, organic detritus, and plankton. The impact of man's activities, however, alter and augment the suspended solids in surface waters by the

discharge of liquid wastes from communities and industries, by increased erosion from deforested and cultivated areas, by gravel washings and mine tailings, by steel mill wastes, and by dusts that are blown into streams (308, 347, 473, 540, 541, 611, 664, 673, 684, 701, 779, 780, 799, 814, 1552, 1700, 3655, 3658).

To differentiate between suspended solids and settleable solids is often difficult, because these two terms are often confused in the literature, although the method of determination of each is clearly described in Standard Methods for the Examination of Water and Wastewater (469). Strictly speaking, until they have settled to the bottom of a water course (or a laboratory sample bottle), all settleable solids are suspended solids. On the other hand, only a fraction of the suspended solids are settleable and this fraction is dependent upon quiescence, temperature, density, flocculation, and many other factors. In this section of the report only those references that deal strictly with the term "suspended solids" are considered.

Where stream classifications and standards have been promulgated, or where effluent standards are used, the test for suspended solids is generally employed as a significant criterion. For details of standards used by state and interstate agencies, see Chapter III.

- 2. Cross References. Turbidity, Silt, Settleable Solids, and Chapters III and V.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The 1962 USPHS Drinking Water Standards (2036) do not specify limiting concentrations for suspended solids, but such concentrations are indirectly controlled by the limits on turbidity (5 units) and total solids (500 mg/l). Bean (1745) has proposed that, for drinking water of ideal quality, suspended matter by limited to 0.1 mg/l or less. In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be in sufficient concentration to be objectionable or to interfere with normal treatment processes (see Chapter III for details). Those agencies that employ effluent standards, however, are more specific in delineating concentrations (or percentage removals) of suspended solids in effluents.
- b. Industrial Water Supplies. Suspended solids in water interfere with many industrial processes, and cause foaming in boilers (815), or incrustations on equipment exposed to water, especially as the temperature rises (1361, 3698). Water for steel manufacturing should contain not over 25 mg/l of suspended solids (249). Suspended solids are undesirable in water for textile industries (185, 212, 258, 2377); paper and pulp (212, 402); beverages (180, 181); dairy products (816); butadience (251); laundries, dyeing, photography, cooling systems, and power plants (369). For further details, see specific industries as listed in Chapter V.
- c. Irrigation Water. Paperboard mill waste waters containing 240 mg/l of suspended solids have been successfully used for spray irrigation of alfalfa. There was no problem from suspended paper fibers (3699).
- d. Fish and Other Aquatic Life. Disregarding any possible toxic effects attributable to substances leached out by water, suspended solids may kill fish and shellfish

by causing abrasive injuries; by clogging the gills and respiratory passages of various aquatic fauna; and by blanketing the stream bottom, killing eggs, young, and food organisms, and destroying spawning beds (3660). Indirectly, suspended solids are inimical to aquatic life because they screen out light (see Turbidity) and because, by earrying down and trapping bacteria and decomposing organic wastes on the bottom, they promote and maintain the development of noxious conditions and oxygen depletion, killing fish, shellfish and fish food organisms, and reducing the recreational value of the water.

While it appears to be debatable whether wood fibers (673, 688, 3675) and other suspended solids cause the death of healthy fish by clogging their gills, nevertheless, there is agreement that they are harmful to the extent that they blanket the stream bed, prevent normal growth of food organisms and contribute to conditions of decay. It has been pointed out that healthy fish may swim through heavy suspensions of solids without significant injury (2546); yet, in the presence of even low concentrations of toxic substances, fish may be so weakened that the abrasive and clogging actions of suspended solids become more effective and dangerous, and even lethal (313).

Ellis (313, 347, 801) has recommended that all cellulose pulps and sawdust be excluded from streams; that suspended solids of a hardness of one or more (mineralogical scale) be so finely divided as to pass through a 1000-mesh screen; and that the stream bottom not be blanketed to a depth of more than one-quarter inch.

Tests on the survival of rainbow trout in suspensions of inert solids (kaolin and diatomaceous earth) showed that concentrations of 30 mg/l had no observable effect, a few fish died at 90 mg/l, while at 270 mg/l more than half of the fish died in 2 to 12 weeks. No difference could be detected between the lethal effects of kaolin and diatomaceous earth, although the particle size of the former lay mostly in the range of 0.13 to 5.0 microns, and of the latter in the range of 1 to 6 microns (88, 3321). In concurrent field tests in England, it was found that a stream containing 60 mg/l of suspended solids had just as many trout and invertebrates as a clear control stream; but in the River Fal, with 1000 mg/l of suspended matter, trout were only one-seventh and invertebrates only onethird of the densities in control streams. In the polluted . River Par, with about 6000 mg/l of suspended solids, trout were one-seventh and invertebrates one-nineteenth of the densities in the control streams (88). Based on the laboratory phase of the investigation, it seems unlikely that reductions in trout populations were caused solely by reductions in food supply.

Waste fibers from a wood grinding mill, built in 1915, have covered and destroyed certain spawning grounds of whitefish in a Swedish river. Since 1923 the total annual catch of fish from this river has been reduced to about 1 pound per acre. Laboratory experiments showed that fish eggs in aquaria whose bottoms were covered with this material had a 36-75 percent mortality rate, whereas in the control aquaria the mortality rate was 3-15 percent (1701).

Destruction of fish and plankton in a long stretch of river polluted by mine wastes was attributed not to the

effects of any toxic chemicals, but to the deposition on skin and gills of particles of iron hydroxide (1702).

According to Robinson (2614) concentrations of some suspended materials as high as 1458 mg/l were filtered and passed through the gut of Daphnia magna with no apparent harm; but charcoal and montmorillonite were toxic at 100 mg/l, ground glass at 98 mg/l, chlorite at 120 mg/l, and illite at 264 mg/l.

e. Shellfish Culture. In concentrations of suspended matter and silt higher than 750 mg/l, the development of eggs and larvae of the venus clam was decreased (3700).

## SYNTHETIC DETERGENTS

(see Chapter X)

#### SYSTOX

(see Chapter IX)

## TANNIC ACID

 $C_{76}H_{52}O_{46}$ 

- 1. General. Tannic acid occurs naturally in the bark and fruit of many plants. In the pure state it is a yellowish brown powder with a faint characteristic odor and an astringent taste. Highly soluble in water and alcohol, it is used as a mordant in dyeing, in the manufacture of ink, for sizing paper and silk, in tanning, for clarifying beer and wine, and for many other commercial purposes.
  - 2. Cross References. Acids, Organic, General.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Tannic acid has a high chlorine demand and when chlorinated a concentration of 17.1 mg/l gave a sweetish odor (362). Concentrations of 2.0 to 4.0 mg/l give water a woody taste and odor (701).
- b. Industrial Water Supplies. To prevent the formation of scale in boilers, 3.0 to 5.0 mg/l of tannic acid have been added to boiler feed waters (1363) and tannins such as quebracho have proved satisfactory for prevention of embrittlement of locomotive boilers (824).
- c. Fish and Other Aquatic Life. The lethal doses reported for fish vary widely, depending on the species tested and the conditions of the experiment. At least 0.4 mg/l is required to affect most fish and some species can survive 10 mg/l or more, according to Westfall and Ellis (701); yet Ellis (313) reports that 10 mg/l in hard water was not injurious in 100 hours to goldfish, but that 100 mg/l killed in 9 to 20 hours. Belding (359) quotes references to the effect that the lethal doses to kill in 24 hours were 6.25 mg/l for trout, 71 mg/l for minnows and 142 mg/l for goldfish. Schaut (362) found that minnows lost their appetite in 17.1 mg/l of tannic acid but did not die.

Using highly turbid water and the mosquito-fish (Gambusia affinis) as the test organism, Wallen et al. (2940) found the 24- and 48-hour TLm for tannic acid to be 41 mg/l while the 96-hour  $TL_m$  was 37 mg/l. The addition of tannic acid increased the turbidity from an initial 135 mg/l to 170 mg/l, but lowered the pH only from 7.3 to 6.7. The State of Washington Department of Fisheries (2091) found the critical level for young chinook salmon to be 1.73 to 2.85 mg/l for a 72-hour exposure in flowing fresh water and below 1.70 mg/l in flowing sea water.

According to Doudoroff and Katz (361), tannic acid can be toxic to fish without lowering the pH to 5.0. Toxicity is then attributable chiefly to the undissociated acid in solution and hence pH is not a reliable index of dangerous pollution.

In Lake Erie water, according to Anderson (358) the threshold concentration for immobilization of Daphnia magna after prolonged exposure at 25°C was 26 mg/l, but it may be as low as 3.0 mg/l.

## TARTARIC ACID AND TARTRATES

COOH(CHOH)₂COOH

Tartaric acid occurs in many fruits, generally in the form of calcium, magnesium, or potassium tartrate. It is produced commercially from argols or wine-lees that are formed in the production of wine. Highly soluble in water, it is used in baking powders, dyeing and printing fabrics, tanning, and many other commercial processes.

The toxicity of tartaric acid to fish and aquatic life depends on the hardness and buffering action of the water. Doudoroff and Katz (361) maintain that tartaric acid can be directly toxic to fully developed fish only when it lowers the pH value to 5.0 or lower and Cambosu (833) points out that the disinfecting action of tartaric acid is lowest in hard water owing to the precipitation of insoluble calcium tartrate.

In hard water, 200 mg/l of tartaric acid was not lethal to goldfish after 100 hours of exposure but in soft water 100 mg/l killed them in three hours. In hard water, 1000 mg/l killed in three to four hours, according to Ellis (313).

In Lake Erie water at 25°C, Anderson (358) shows that the threshold concentration of tartaric acid for immobilization of Daphnia magna after prolonged exposure was 135 mg/l. For sodium tartrate, the threshold concentration was 3150 mg/l (352), and the toxicity was attributed to factors other than osmotic pressure. Because tartrates are salts of a weak acid, their addition to water would be expected to raise rather than lower the pH value.

The threshold of toxicity of sodium tartrate to the flatworm Polycelis nigra at 15 to 18°C was about 9600 mg/l of tartrate, according to Jones (354).

## TARS

- 1. General. The references abstracted herein deal primarily with tar on tarred roads and the effects of such tar upon nearby streams as a result of rainfall, leaching action, and drainage. For a more thorough treatment of coal tar and its constituents, see the cross references, especially Oil-Petroleum.
- 2. Cross References. Acridine, Cresols, Cresylic Acid, Hydrocarbons, Naphthalene, Oil-Petroleum, Phenanthrene, Phenol, Pyridine, Quinoline, Thiophene, Xylene, and similar compounds.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Test sections of tarred roads were washed with distilled water equal to one inch of rainfall and the chlorinated run-off waters were tested for tastes and odors, according to Carpenter and

Klinger (825). They concluded that chlorophenolic tastes were liable to appear in water supplies if heavy rain fell within two hours after surfacing a road with primer coat, but the danger was less pronounced with aging or with resurfacing.

b. Fish and Other Aquatic Life. The death of fish in the Tees estuary was attributed in part to tar acids which were present in concentrations of 0.1 to 0.3 mg/l (826). Commercial tar products, especially the less-viscous types, contain large amounts of water-soluble poisons (827). Undiluted samples of drainage from tarred roads caused a loss of equilibrium in perch after 10 minutes but they recovered later in fresh water. Drainage after the first rainfall on a newly tarred road killed all six test perch in 13 minutes (365). One such lethal effluent contained 18.5 mg/l of tar acids and 2.0 mg/l of tar bases. In other tests, saturated extracts of coal-tar pitch killed trout within one hour.

Shelford (363) reported that sunfish were killed in one hour by liquid tar acids at a concentration of 70 mg/l, while Gutsell (463) found that 66 mg/l was fatal in one hour and 13 to 33 mg/l in one to three days. One liquid tar paste killed sunfish in one day at a concentration of only 2.0 mg/l. Yearling trout were susceptible to aqueous extracts of tar, with 20 mg/l proving lethal in one hour (828).

Two independent investigators, Schuman (829) and Herrman (830) contend that the amounts of phenols, cresols, and xylenols that could possibly be leached from tar-surfaced roads would not injure fish and other aquatic life. Another anonymous article (831) points out that young perch and roach showed no ill effects after three hours with an extract from bituminous road material and young brown trout were unharmed after 19 weeks in a pond receiving actual drainage from a bituminous road.

From the differences in results and conclusions presented above, it is probable that the lethality of washings from tarred roads depends on the type and composition of tar employed, its age, the action of soil and material processes on the waters as they flow from the road to the stream, the temperature, and numerous other variables that cannot be evaluated readily.

A study was made of the toxic limit toward yearling trout (3245) of the acidic, basic, and neutral fractions of tar. The toxic limit was defined as the concentration resulting in a loss of fish equilibrium in 60 minutes at 12°C. Toxicity in relation to boiling point and solubility is shown in the following tabulation:

Tar Fraction	$Boiling \ Point, {}^{\circ}C$	Toxic Limit, mg/l	Solubility mg/l	Effective Toxicity*
Tar acids	197-210	6.0	16,500	27.5
ρ.	240-270	3.0	4.125	13.8
	270-300	2.0	1,375	6.88
	300-325	1.5	825	5.50
Tar bases	205-235	7.5	1.274	1.70
· ·	230-250	7.5	951	1.27
	275-305	3.0	438	1.46
	320-3 <del>4</del> 5	1.0	238	2.38
Neutral oils	200-240	3.75	35	0.935
	240-280	3.75	25.3	0.675
·	290-344	3.75	14.1	0.376

*Effective toxicity is given as solubility  $imes 10^{-2}$  divided by toxic limit.

The toxic limit alone is not definitive of the hazard of tar fractions for all of the substances would not necessarily be abstracted from the tar by water to the same extent. The "effectivity toxicity" takes into account the fact that the hazard rises with the solubility and is inversely related to the toxic limit, i.e. the lower the toxic limit, the more toxic is the substance.

The tabulation shows that the toxicity of tar acids and tar bases increases with the boiling point, while the toxicity of neutral oils is relatively independent of the boiling point. The variations in solubility are much greater than the variations in toxic limits; hence solubility must be considered as a major factor in determining the harmfulness to fish. It is significant to note in all cases, however, that the solubilities far exceed the toxic limits; hence all of these tar ingredients are potentially harmful to fish.

Albersmeyer and Erichsen (3404) studied the effects of tar constituents in waste waters, but they used pure phenolic compounds. Their results are included under cresols, phenols, and xylenols.

c. Shellfish. According to Mitchell (832) there was no noticeable effect of water-gas tar on oysters in constantly renewed sea water; but large amounts of tar in stagnant sea water causes serious or fatal effects. The danger of tar depends on the ability of the oyster to rid itself of such foreign matter.

#### TASTES

(see also Odors, Chapters III, VII, IX, and X)

While taste responses are often difficult to differentiate from odor responses because the senses of taste and smell are closely inter-related, certain non-volatile substances dissolved in water can cause tastes without causing odors. To some extent, therefore, the subject of taste-producing substances in water may be discussed independently. Although no procedures for taste determinations are recommended by Standard Methods for the Examination of Water and Wastewater (469), threshold taste tests are made using techniques similar to those used for odor tests (459).

It is not practicable to retabulate here the taste thresholds of all of the potential pollutants covered in this chapter and in Chapters VII, IX, and X. Where taste thresholds of specific substances were revealed in the literature, they are included in the description of the designated pollutant. Taste thresholds for several compounds have been tabulated by Lockhart et al. (3241), Baker (2058), Filicky et al. (2040), Cohen et al. (3301), and Campbell et al. (2059).

Rohlich and Sarles (759) have stated that volatile substances can generally be detected by smell in much lower concentrations than by taste. However, it has been reported that the extremely disagreeable tastes imparted to chlorinated water by phenol, cresol hydrocarbons of the benzene series, anthracene, and naphthalene can be detected at concentrations far below the odor threshold; possibly from one-fiftieth to one-hundredth of the quantity tetected by odor can be distinguished by taste. The taste characteristics have been described as (a) very similar to iodoform as typified by chlorinated phenol; (b) intermediate between that given by o-cresol and p-cresol

on chlorination; and (c) similar to that given by p-cresol which more nearly resembles p-cresol itself than a chlorinated product. This subject is covered in some detail by Ruchoft and Ettinger (459), who have assembled from various sources the taste thresholds for phenolic compounds when chlorinated in very dilute solution. Their studies indicate that this taste problem is by no means a simple one, and that usually the effect of chlorine on phenols and cresols is first to increase the taste, and then to reduce it to zero as further chlorine is added.

Dissolved gases and minerals make water palatable and distilled water has a flat taste. The tolerance of salts in water, according to their taste, is partly a matter of individual reaction, and taste tolerances can be developed, when it becomes necessary to use a comparatively

unsatisfactory water supply.

The flesh of fish can acquire a taste from organic compounds in the water. This subject has been studied by Albersmeyer and Erichsen (3404), Boetius (3492), Bandt (2827), Hendersen et al. (2958) and Viehl (3707). For details and concentrations, see the specific potential pollutants, but especially phenol, cresol, xylenol, oils, nitriles, and similar compounds.

### TBA

TDE

#### TEDION

(see Chapter IX)

# TEEPOL (Secondary Sodium Alkyl Sulfate)

(see Chapter X)

## TEMPERATURE

1. General. Temperature changes in bodies or streams of water may result from natural climatic phenomena or from the introduction of industrial wastes, such as distillery effluents or discharges of cooling waters used by many industries. The temperature is important, and sometimes critical, for many uses of water. It affects the palatability of water, treatment processes, the value of water for many industrial uses, including cooling processes and its suitability as a habitat for aquatic life (199, 834, 835, 836).

Many state and interstate water-pollution-control agencies place restrictions on temperatures or allowable temperature increases. For a description of such standards or criteria, see Chapter III and its appendices.

The elevation of stream temperatures, especially as the result of spent cooling waters, may become a serious pollution problem. Additional heat may contribute to undesirable stream conditions such as decreased oxygen capacity, increased oxygen demand, anaerobic zones, putrefication of sludge deposits, and the growth of sewage fungus (1464, 1652, 1714, 1715, 1716, 3708, 3709, 3710). Stream temperatures may also be increased by irrigation practices and the return of agricultural drainage. Temperature rises of 10 to 20°C have been reported (2032, 2340). The return of cooling waters to underground aquifers has also been known to increase groundwater temperatures by 20°C (3711, 3712).

- 2. Cross References. Oxygen and other specific substances in Chapter VI, also Chapter III for state and interstate criteria, and Chapter VII for effects on biological pollutants.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. For drinking purposes, water with a temperature of 10°C is usually satisfactory. Temperatures of 15°C or higher are usually objectionable. Whipple is reported to have found that temperatures above 19°C cause complaints from most consumers (837).

Increased temperatures may stimulate growth of tasteand odor-producing organisms in lakes and impoundments (379, 388, 422, 537, 663, 838). Sometimes a drop in temperature has stimulated growth of some organisms (207).

In general, the survival time of infectious bacteria, cysts of *E. histolytica*, and ova of parasitic worms is reduced as temperature of the contaminated water increases. Cultures of *Leptospira* in river water have survived for 9 days at 5-6°C, but for only 4 days at 31°C (710). *E. Typhosa* and coliform organisms survive for longer periods at lower temperatures (302, 488, 715, 716), and pathogenic organisms have survived for a year under ice (718). *Schistosoma* ova die in 9 days at 29-32°C, in three weeks at 15-24°C, and in three months or longer at 7°C (840).

The efficiency of water purification and treatment methods may be markedly affected by the water temperature. It has been found that filtration is more effective in winter than in summer (841) and that chlorination is more effective in summer (841). It has also been reported that filtration is more effective at summer temperatures than at winter temperatures (837). The alum dose required to reduce the color of raw water was observed to be as much as 2.2 times greater at 14°-24°C than at 8-14°C (842); on the other hand, less alum has been found necessary at higher temperatures (837). Flocculation and sedimentation rates are increased as the temperature is increased. It was found that at 2°C the settling period was 73 percent longer than at 20°C (843). The exchange capacity of baseexchange materials used in water-softening processes varies with temperature, but not in a uniform direction; for some substances rising temperatures increase the exchange capacity, for others they reduce it (844).

The bactericidal effects of disinfectants are generally increased by an increase in the temperature of the water. For example, for a given dose of free chlorine the period required to disinfect water at 8°C is more than nine times as great as at 40°C (845) (also see 490, 493, 846, 847, 848). However, a Russian investigator has reported that temperature changes from 1° to 20°C have had no effect on the bactericidal efficiency of chlorine (849) and the killing effect of ozone upon cysts of *E. histolytica* was not changed by temperature variations from 10° to 27°C (850).

b. Industrial Water Supplies. For various industrial uses of water, the water temperature may be highly significant, possibly the factor of greatest importance, for example, in the pulp and paper industry (851). Water for barley malting purposes should have a uniform tem-

perature of about 12°C (240). For use on farms and in dairy factories the temperature should be 16°C or less (549). For use in steel mills, water must have a temperature below 24°C (249). For use in rayon manufacturing the water must be cool (852). Streams have lost their value for cooling purposes as the water temperature has risen as much as 27°C during the course of discharge and reuse of the water by many industries in succession (1652, 1714).

Warm water accelerates corrosion in pipe lines and cooling systems.

- c. Irrigation Water. Below 10°C water weeds grow very sparsely, between 10-15°C growth is prolific, reaching a maximum above 15°C (858). One report indicates that rice irrigation was not harmed by cooling water that raised the temperature by 11°C (1717), but another article (3713) indicates that water of 32°C virtually destroyed rice plants.
- d. Fish and Other Aquatic Life. Changes in water temperature as a result of human activity are generally upward. An exception is the release of cold bottom water from stratified artificial impoundments, which may alter the flora and fauna for many miles downstream from the dam. Other activities of man such as the discharge of cooling waters, warm industrial wastes, and return irrigation water generally raise the temperature of receiving waters, with the following concomitant effects: (a) higher temperatures diminish the solubility of dissolved oxygen and thus decrease the availability of this essential gas, (b) elevated temperatures increase the metabolism, respiration, and oxygen demand of fish and other aquatic life, approximately doubling the respiration for a 10°C rise in temperature; hence the demand for exygen is increased under conditions where the supply is lowered, (e) the toxicity of many substances is intensified as the temperature rises, (d) higher temperatures militate against desirable fish life by favoring the growth of sewage fungus and the putrefaction of sludge deposits, and finally (e) even with adequate dissolved oxygen and the absence of any toxic substances, there is a maximum temperature that each species of fish or other organism can tolerate; higher temperatures produce death in 24 hours or less.

The maximum temperatures that adult fish can tolerate vary with the species of fish, prior acclimatization, oxygen availability, and the synergistic effects of other pollutants. Median tolerance limits (TL_m) have been reported by several authors, as shown in the following tabulation. Species have been arranged in order of heat tolerance.

## LETHAL TEMPERATURES FOR FISH

		Exposure	?	
Common Name	Scientific Name	$Time, \\ Hours$	${^{\circ}C}$	Refer- ence
Goldfish	Carassius auratus		38.6	3714
Mosquito-fish Gizzard shad	Gambusia affinis		37.3	3715
Largemouth bass	Dorosoma cepedianum _ Micropterus salmoides _		36.5 36.4	3715
		24	$\frac{30.4}{28.9}$	3715 3716
Carp Roach	Cyprinus carpio		35.7	3716
Troach	Rutilus rutilus		35.3	3720

		_		
		Exposu		
Common Nam	e Scientific Name	Time,	$TL_m$	Refer
Brown bullhead	Ameiurus nebulosis	Hours		ence
	Imetalus negulosis		35.1	3717
Northern black bullhead	4		34.5	3715
	Ameiurus melas melas_	24	35.0	3716
Golden shiner	Notomigonus crysoleuca	8	34.7	3715
Bluegill sunfish	Lepomis machrochirus		35.0	3719
_	•		33.8	3715
Pumpkinseed	Lepomis gibbosus	12	34.5	3717
		24	30.2	3716
Bluntnose minno	w Hyborhynchus notatus_		34.0	
•			33.3	3715
Fathead minnow	Pimephales promelas		_	3714
Northern channe	l		33.8	3717
catfish	Ictalurus lacustris		33.5	9715
Northern redbelly	7		0.00	3715
dace	Chrosomus eos	70	99.4	
Common shiner	Notropis cornutus		33.1	3717
	1. ott opis cornutus		33.0	3715
		12	32.0	3717
Creek chub	Sametitus -1		31.0	3714
Oloca chap	Semotilus atromaculatus	_ 12 .	32.6	3717
•			31.5	3715
Finescale dace	D.C		30.3	3714
Yellow perch	Pfrille neogaea	_ 12	32.3	3717
renow perch	Perca flavescens		32.3	3715
		12	30.9	3717
		<del></del>	29.7	3714
Saltwater perch		12	29.2	3716
Guppy			32.2	3719
	Lebistes reticulatus		32.0	3721
Common white				
sucker	Catostomus commersonni_	. 12	31.2	3717
			29.3	3714
Pearl dace	Margariscus margarita	12	31.1	3717
Lake emerald			01.1	01,21
shiner	Notropis atherinoides		30.7	3714.
			50.1	3715,
Brook stickleback	Eucalia inconstans	19	30.6	
Blacknose dace	Rhinichthys atratulus	12		3717
	arranas		29.5 29.3	3715
Squaw fish	Ptychocheilus oregonensis			3714
Common brook	1 vychochettus oregonensis	24	29.3	3716
trout	Salvalinas Lautini			
	Salvelinus fontinalus	12	26.1	3717
			25.3	3714
Salmon (spring,			25.0	2623
pink, sockeye,				
chum, coho)	Oncorhychus sp	68	25.1	9710
Lake trout	Lalvelinus namaycush	wo		3718
	nomengeusn		23.5	3722

As shown by this table, goldfish, bass, and carp are relatively tolerant of high temperatures whereas trout and salmon are sensitive. These temperatures, however, apply to adult fish.

For spawning and hatching of eggs, much lower temperatures are required. Trout eggs will not hatch over 14.4°C (2650); Chinook salmon eggs fare well at 16°C but suffer mortalities at 18°C (3723); Rocky Mountain whitefish eggs are affected at 20-21°C (3724); and the TL_m for herring larvae varies from 22 to 24°C (3725). It is apparent, therefore, that many fish are unable to complete their life cycles unless the temperatures at the time of spawning and hatching are 10 to 15°C below the median tolerance limits (2414).

Fish have optimum temperatures for rate of growth and reproduction. Given a choice, they also show a preference for water of a definite temperature range. The following optimum or preferendum temperatures have been reported:

Common Name of Fish	Optimum or Preferred Temperature, °C	Reference
Rainbow trout Chum salmon Sockeye salmon Lake trout Coho salmon Greenthroat darter Largemouth bass Roach Guppy Carp	13 13.5 15 15-17 20 20-23 22-25 23-24 23-25 32	3726 3726 3729 3722 3729 3730 3731 3728 3727 3732

If the temperature of a reach of stream is raised by 5-10°C, it is probable that cold-water game fish will avoid this reach and that they will be replaced by course warm-water fish. Thus, without any direct mortality, the character of the fish life will change. It will also change because of effects upon spawning and hatching of eggs.

Sudden changes in temperature are believed to be deleterious to fish life, with abrupt changes of 5°C or greater likely to be harmful (2414). Rainbow trout could not stand a temperature shock of 11°C above an acclimatization temperature of 12°C, but could tolerate a shock of 8°C above an acclimatization at 10°C (3733).

The Aquatic Life Advisory Committee of ORSANCO (see Chapter III) has recommended (2414) that waste discharges be so controlled that the temperature of the receiving water: (a) shall not be raised above 34°C at any place or at any time, (b) shall not be raised above 23°C at any place or at any time during the months of December through April, and (c) shall not be raised whatsoever in streams suitable for trout propagation.

Increased temperature is also an important consideration when toxic substances are present in a stream. Many substances (e.g. cyanides, phenol, xylene, zinc) exhibit increased toxicity at elevated temperatures. For details, see the specific pollutants in Chapters VI, IX, and X. This synergistic effect is aggravated at low tensions of dissolved oxygen. See "Dissolved Oxygen" for its relationship with temperature.

Changes in temperature also affect lower aquatic and marine life. For each organism there is a thermal death point and also a range of temperature of optimum growth. Temperature is one of the environmental factors that determines which organisms will thrive and which will diminish in numbers and size. There is relatively little information in the literature about optimum temperatures for aquatic flora and fauna. Diatoms apyear to grow best at 15-25°C, green algae at 25-35°C, and blue-green algae at 30-40°C (2190, 2621, 3734).

e. Shellfish Culture. Among oysters, the genus Crassostrea will survive temperatures of -5°C to 35°C; but the genus Ostrea will survive only from -1°C to 30°C. The Olympia oyster (O. lurida) will spawn at 15-16°C but the Pacific oyster (C. gigas) regires a temperature of about 20°C for successful spawning (315, 317, 2415). Temperature has an important influence on the pumping rate of oysters. Below 3°C only insignificant quantities of water are pumped, for the oyster is almost dormant; from 8° to 16°C, the pumping rate increases rapidly; above 20°C the metabolism consumes protoplasm faster than it can be synthesized from food; and at 30°-35°C, the oyster is in distress (1448). The low rate of pumping in cold water enables an oyster to avoid bacterial contamination from overlying waters so that the bacterial quality of the oyster is generally better than that of the water. In some states, therefore, the harvesting of oysters from moderately polluted areas is permitted when the temperature of the water is consistently below 5°C (317, 523, 869).

Scallops accustomed to water between 5 and 20°C may be killed by sudden changes to temperatures of 21 to 23°C (3735). The rate of growth of the clam, Venus mercenaria, is negligible below 10°C but reaches its optimum at 23°C, probably because higher pumping rates at that temperature are combined with increased productivity of phytoplankton (2416). The fresh-water mussel, Dreissenia polymorpha, is destroyed in 15 minutes by a tem-

perature of 40°C (2426).

f. Swimming and Other Recreational Uses. Rising temperatures stimulate the decomposition of sludge, formation of sludge gas, multiplication of saprophytic bacteria and fungi (particularly in the presence of organic wastes), and the consumption of oxygen by putrefactive processes, thus affecting the esthetic value of a water course (835). On the other hand, increased temperatures may be beneficial to recreation by lengthening the swimming season (3736).

## TEPP

(see Chapter IX)

## TETRACHLOROPHENOL

(see Halogenated Phenols)

# TETRASODIUM PYROPHOSPHATE

(see Sodium Phosphates)

#### TETRYL

 $(NO_2)_3C_6H_2N(CH_3)NO_2$ 

This yellow crystalline substance, known also as Nitramine, is insoluble in water. It is used primarily as an indicator but it may also occur in wastes from munitions works. Such wastes were found to kill minnows in 25 to 40 minutes when diluted 1:1.5 with tap water, according to Degani (544).

## TEXTILE WASTES

(see Dyes)

## TRIBROMOPHENOL

(see Halogenated Phenols)

## TETRAETHYL LEAD

(see Lead Tetraethyl)

## TETROSAN

(see Chapter X)

#### THALLIUM

Pure thallium is a bluish-white, soft, inelastic, heavy metal which oxidizes readily in air to thallium oxide. Its salts are used as poisons for rats and other rodents (364), and as ant bait. Thallium salts are also used in dyes and pigments in fireworks, in optical glass, and as a depilatory. It is a cumulative poison, four times as toxic as arsenious oxide, and it affects the sympathetic nervous system, causes muscular pains, endocrine disturbances, and loss of hair (677). It does not occur normally in animal tissues, but when taken into animal bodies it is cumulative (2121). Thallium salts, for the most part, are highly soluble in water and consequently any industrial discharges of this element are not likely to form precipitates as carbonates, hydroxides, or other common compounds.

Landauer (933) tested the effects of thallium salts on fowl and their molting mechanism. Of several thallium salts tested, the acetate was more toxic than the fluoride, sulfate, or carbonate. A daily dose of 50 ml of a 400 mg/l solution (20 mg) of thallium acetate caused death of test birds in 11 days and daily doses of 10 mg in water killed birds in 19 days. Chicks died in 11 weeks of chronic poisoning as a result of doses varying from 0.05 mg at two days old to 6 mg at seven weeks of age. The  $LD_{50}$  concentration for thallous acetate administered orally to rats, rabbits and dogs was found to be 32 mg/kg as thallium and for thallie oxide it was 39 mg/kg (3737).

A nutrient solution containing 102 mg/l of thallium was slightly injurious to sugar beets in sand culture (1473), and 341-2730 mg/l completely inhibited the germination of cress and mustard seeds during an 18-day exposure period (1479).

## THIOCRESOL

(see Mercaptan, General)

## THIOCYANATES

(see Ammonium, Potassium and sodium Thiocyanates)

## THIOPHENE

 $C_4H_4S$ 

(see also Coal Tar)

Thiophene is found in coal-tar and gas-plant wastes. It is a liquid with a slight aromatic odor resembling that of benzene. Insoluble in water, it is in itself a solvent and is used in the manufacture of resins, dyes, and pharmaceuticals. According to Shelford (313, 363, 463), 27 mg/l of thiophene in tap water killed orange-spotted sunfish in one hour.

### THIOPHENOL

(see Mercaptan, General)

#### THIRAM

(see Chapter IX)

## THORIUM

 $\mathbf{T}$ 

This grayish-white lustrous metal is used in the manufacture of incandescent mantles and filaments for lamps (364). It is also used in nuclear reactors in conjuction with U-235. It occurs naturally in several minerals, such as the silicate and oxide, with a valence of 4. A concentration of 775 mg/l of thorium completely inhibited the germination of cress and mustard seeds during an 18-day exposure, and 97-388 mg/l considerably delayed germination and retarded growth (1479).

The lethal concentration of thorium chloride for three mature small fresh-water fish (Orizias), exposed for 24 hours to only 20 ml of test solution, was reported (1459) to be about 18 mg/l. Using water from the River Havel from which the test organism were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of thorium nitrate on four organisms. For Scenedesmus the median threshold effect for a 4-day exposure at 24°C occurred at 0.4-0.8 mg/l as thorium; for E. coli at 27°C, the median toxic level was at 0.8 mg/l as Th; for a protozoan (Microregma), 25 mg/l was deleterious, but for Daphnia at 23°C for 48 hours, 1000 mg/l of thorium was not toxic.

#### THURICIDE

(see Chapter IX)

TIN

- Sn 1. General. Tin is not present in natural waters, but it may occur in industrial wastes or in trace amounts when water is stored for any length of time in tin-coated metal containers (152). Stannic and stannous chloride are used as mordants for reviving colors, and dyeing of fabrics, weighting of silk, and tinning of vessels. Stannic chromate is used in decorating porcelain, and stannic oxide is used in glass works, dye houses, and for fingernail polishes. Stannic sulfide is used in some lacquers and varnishes (364). Tin compounds are also used in fungicides, insecticides, and antihelminthics (2121). From many of these processes, tin salts may reach surface waters or ground water; but because many of the salts are insoluble in water, it is unlikely that much of the tin will remain in solution or suspension.
  - 2. Cross References. Fluorides
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. No reports have been uncovered to indicate that tin can be detrimental in domestic water supplies. Traces of tin occur in the human diet from canned foods and it has been estimated that the average diet contains 17.14 mg of tin per day. Man can apparently tolerate 850 to 1000 mg per day of free tin in the diet (353). There is no definite evidence that tin plays any essential biological role in human nutrition (2121).
- b. Irrigation. In nutrient solution at a concentration of about 40 mg/l, stannous ions were not harmful to sugar beets in sand culture (1473).
- c. Stock and Wildlife Watering. Rats have tolerated 25 mg or more of sodium stannous tartrate in the diet over a period of 4 to 12 months without ill effects (2121). Cats fed 20 mg of tin, as stannous tartrate or stannous chloride, per kg of body weight, showed no effect over a 3-month period but dosages of 30 and 50 mg per kg apparently caused some loss of body weight (3738). Guinea pigs survived on a diet containing 770 mg/kg of tin salts (2121). On the basis of these feeding experiments it is unlikely that any concentration of tin that would occur in water could be detrimental to livestock.
- d. Fish and Other Aquatic Life. It is apparent that trace concentrations of tin are beneficial to fish. Stannous ions at a concentration of about 0.6 mg/l accelerated the growth of goldfish (3770). It has been re-

ported that goldfish survived 1000 mg/l of SnCl₂ (626 mg/l of tin) in very soft water at pH 3.5 for 1.0 to 1.5 hours and in hard water at pH 3.8 for 4 to 5 hours (598, 1459, 1466). Young eels have survived stannous chloride at a concentration of 1.2 mg/l of tin for over 50 hours, but succumbed to 6.0 mg/l in 2.8 hours (1459).

Threshold concentrations for the immobilization of crustacea in Lake Erie water to which stannic chloride (SnCl₄) was added were reported (2955) as follows:

Test Organism	Threshold Concentration of SnCl, in mg.
Leptodora kindtii	114
Cyclops vernalis	125
Daphnia magna (young)	146

In contrast, the toxicity threshold of stannous chloride (SnCl₂) toward *Daphnia* in Lake Erie water was given as 25 mg/l (598).

# TITANIUM Ti

Abundantly distributed in the earth's crust, titanium ores and salts constitute 0.5 to as much as 10 percent of soils. It serves as an inert element, similar to silicon in chemical and biological behavior. It is present in plants chiefly in the leaves and trace amounts are found in most animal tissues and organs (364, 2121).

Titanium metal is used as a constituent of several alloys. Titanium salts, primarily the oxide, are used as pigments in the paint industry, as filler in paper making, as mordants in the dyeing industry, in the manufacture of electronic apparatus, and in the glass and ceramics industry. Although several of the salts, e.g. the ammonium oxalate, nitrate, sulfate, and trichloride, are highly soluble, titanium dioxide is insoluble and tends to precipitate as a granular material (364, 2121, 2972).

There is no evidence that titanium is essential for plant or animal nutrition. It is not absorbed to any measurable degree by the human intestine, but appears to be almost completely inert and innocuous in the human alimentary system (2121). In nutrient solution, about 12 mg/l of titanium was reported to be slightly injurious to sugar beets in sand culture (1473).

When dense blooms of Gymnodinium occurred off the Florida west coast, spectrographic analyses of the water showed 3.37-33.7 mg/l of titanium. The role and origin of the titanium were not discovered (1720, 2722). Tarzwell and Henderson (2154) conducted exploratory tests to find the 96-hour TLm of titanium sulfate toward the fathead minnow. In soft water, they found 8.2 mg/l as titanium while in hard water the TLm value was 120 mg/l. Using water of the River Havel from which the test organisms had been recovered, Bringmann and Kuhn (2158, 3343) found the median threshold effect of titanium chloride toward Scenedesmus exposed at 24°C for 4 days occurred at 2.0 mg/l of titanium. For Daphnia held for 48 hours at 23°C, the median threshold level was 4.6 mg/l of titanium and for a protozoan (Microregma) it was 4.0 mg/l.

Titanium is accumulated in aquatic organisms from the surrounding water. Lackey (2442) reported concentration factors of 200 to 10,000 for six species of brown algae. For further details about concentration factors, see Chapter VII—Radioactivity.

#### TOLUENE

 $C_6H_5CH_3$ 

This flammable liquid with an odor of benzene is a constituent of coal tar. It is used in the manufacture of organic substances and as a solvent in the extractions of various principles from plants. The oral  $LD_{50}$  for white rats was reported as 7000 mg/kg of body weight (3348).

The concentrations of toluene that proved lethal to fish in clear water have been reported from 10 to over 90 mg/l, depending on the temperature and the species of fish (363, 461, 463, 544, 2977). Using highly turbid water, and the mosquito-fish (Gambusia affinis) Wallen et al. (2940) found the 24-, 48-, and 96-hour TL_m values at 17-22°C to be 1340, 1260, and 1180 mg/l respectively. The toluene had little effect on the turbidity of the water.

Toward lower organisms, Bringmann and Kuhn (2158) found that the threshold of toxicity for Daphnia occurred at 60 mg/l, for the diatom Scenedesmus at 120 mg/l, and for E. coli at 200 mg/l. North et al. (2108) reported that 10 mg/l of toluene gave a large reduction in the photosynthetic activity of the giant kelp (Macrocytsis pyrifera) in a 96-hour exposure.

#### TOLUIDINE

 $C_6H_4CH_3NH_2$ 

This aminotoluene occurs in three forms: m-toluidine, a colorless liquid slightly soluble in water, o-toluidine, a light yellow liquid slightly soluble in water, and p-toluidine, a white solid highly soluble in water. All three isomers are used in the manufacture of dyes and dye products (364).

The lethal level for fish (isomer not specified) is reported as 100 mg/l (2977). Concentrations of 1000 mg/l of o-, m-, and p-toluidine have no apparent effect on Escherichia coli at 27°C. For the diatom Scenedesmus, the threshold of toxicity at 24°C of o- and p-toluidine lies at 10 mg/l and for m-toluidine at 8 mg/l. For Daphnia at 23°C, the toxic threshold is reported at 8 mg/l with o-toluidine but for m- and p-toluidine it is only 0.6 mg/l (2158).

### TOLYL MERCAPTAN

(see Mercaptan, General)

#### TOTAL SOLIDS

(see Solids)

### TOXAPHENE

(see Chapter IX)

### TOXIC SUBSTANCES

The terms "toxic substance" or "toxic minerals" occur in standards of criteria that have proposed or promulgated by state and interstate water-pollution-control agencies, but unfortunately the terms are not well defined. Furthermore, where either term is used, qualitative rather than quantitative limits are set. The New England Interstate Water Pollution Control Commission, for example, specified that "substances potentially toxic" shall be "none" in Classes A and B, and "not in toxic concentrations or combinations" in Classes C and D (see Chapter III).

Goudey (992) suggested specifications for ground waters including limits for "toxic minerals" that ranged from 0.05 mg/l for domestic water supplies to 1.00 mg/l for irrigation waters. In this report, toxic substances are not grouped by that classification; rather each potentially toxic material is treated separately. The Mersey River Board (England) proposed that trade effluents discharged to the River Alt contain no "substances toxic to fish or fish food" (2950).

# TRICHLOROACETIC ACID (TCA)

(see Chapter IX)

## TRICHLOROETHANE

 $C_2H_3Cl_3$ 

This nonflammable liquid with a pleasant odor is insoluble in water. It is used as a solvent for fats, waxes, resins, and alkaloids, and for cleaning metal and plastic molds (364). According to Garrett (2959) the TL_m toward the marine pinperch is 150-175 mg/l for 1,1,2-trichloroethane and 75-100 mg/l for 1,1,1-trichloroethane.

## TRICHLOROETHYLENE

CICH=CCl2

This nonflammable liquid with a chloroform-like odor is practically insoluble in water. It is used as a solvent and in solvent extraction by several industries, in degreasing and dry cleaning, and in the manufacture of chemicals and pharmaceuticals. The oral LD₅₀ for dogs is given as 5.86 grams/kg of body weight (364). A concentration of 55 mg/l stupified fish within 10 minutes (2977). A concentration of 660 mg/l killed Daphnia in 40 hours, but 99 mg/l had no effect (2977).

#### TRICHLOROPHENOL

(see Halogenated Phenols)

### TRICHLOROPHENOXYACETIC ACID

(see Chapter IX, 2, 4, 5-T)

TRICON OIL - SPILL ERADICTOR

# TRIDECYL METHYLHYDROXY ETHYLIMIDAZOLINIUM CHLORIDE

(see Chapter X)

## TRIETHYLAMINE

 $(C_2H_5)_3N$ 

Slightly soluble in water with an alkaline reaction, this liquid is used in the preparation of quaternary ammonium compounds. According to Gillette et al. (1442) the critical range for creek chub, a fish of moderate tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 50 to 80 mg/l, i.e. all fish survived 50 mg/l and all died at 80 mg/l. Bringmann and Kuhn (2158, 3343) reported that the threshold of toxicity toward Scenedesmus during 4 days of exposure at 24°C occurred at a triethylamine concentration of only 1.0 mg/l; but for Daphnia the threshold concentration was 200 mg/l for a 2 day exposure at 23°C and for Microregma 90 mg/l. There was no apparent effect on E. coli at concentrations up to 1000 mg/l.

#### TRIIODOPHENOL

(see Halogenated Phenols)

## TRIMETHYLAMINE

 $(CH_3)_3N$ 

Readily soluble in water, this gas has a pungent, fishy, ammoniacal odor. It is widely found in nature as a degradation product of nitrogenous matter, especially fish Industrially, it is used in the manufacture of quaternary ammonium compounds (364). Corti (146) tested rainbow trout (Salmo irideous) at a trimethylamine concentration of 268 mg/l. The resulting pH was 9.62 and the temperature was 13.0-13.5°C. The fish responded instantly in an adverse fashion, turned over in about 4 minutes, and made their last motion in 11 to 14 minutes.

## TRIMETHYL AMMONIUM CHLORIDE

# TRIMETHYL OCTADECADIENYL AMMONIUM CHLORIDE

(see Chapter X)

## TRINITROBENZENE

 $C_6H_3(NO_2)_3$ 

Symmetrical trinitrobenzene, soluble in water to the extent of about 350 mg/l, is used in explosives. According to Hiatt et al. (3350), marine fish show a slight irritant activity at a concentration of 0.1 mg/l, moderate irritant activity at 1.0 mg/l, and violent activity at 10 mg/l.

#### TRINITROPHENOL

 $(NO_2)_3C_6H_2OH$ 

- 1. General. 2,4,6-Trinitrophenol, more commonly known as picric acid, is a pale-yellow, odorless, intensely bitter, crystalline substance which explodes when heated rapidly or struck. It is used in explosives, matches, tanneries, textile mills, glass manufacture, and chemical industries.
- 2. Cross References. Nitrophenol, Dinitrophenol, Explosives, Phenol.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The ingestion of one to two grams of 2,4,6-trinitrophenol causes severe poisoning in humans (364), but the likelihood of such ingestion is slight inasmuch as small concentrations of the substance are objectionable. The minimum concentration detected by taste in drinking water has been given as 0.5 to 1.0 mgl (460). The salt, ammonium picrate, from shell-filling factories can be detected in drinking water at 0.5 mg/l, while 1.0 mg/l is objectionable (655). In addition to the bad taste, picric acid imparts a yellow color to the water, which is not removed by ordinary treatment processes (871). Furthermore, passage through the soil into ground-water reservoirs does not appear to neutralize or remove picric acid (872).

Confiscated Japanese picric acid, dumped into a harbor in Japan and picked up in water used for distillation by American ships, was believed to be the cause for hematuria in seamen (873).

b. Fish and Other Aquatic Life. Minnows can withstand approximately 30 mg/l of pieric acid in neutral solution, but at a concentration of 200 mg/l they overturned in 26 hours (617). Concentrations of 20 mg/l

have been reported (3740) as non-toxic, but high concentrations may be deleterious. Fish showed a preference for water containing trinitrophenol and prolonged their stay in higher concentrations of the chemical; but concentrations greater than 65.7 mg/l appeared to be repellant and fish in this solution showed signs of distress (3739).

For the alga Scenedesmus the threshold toxicity occurs at 240 mg/l after 4 days exposure at 24°C; for the protozoan Microregma at 900 mg/l; for the crustacean Daphnia at 88 mg/l after 2 days at 23°C; but for E. coli, 1000

mg/l was not toxic (2158, 3343).

#### TRINITROTOLUENE

 $(NO_2)_3C_6H_2CH_3$ 

(see also Explosives, Nitrotoluene)

TNT, or 2,4,6-trinitrotoluene, is a crystalline solid that is soluble in water to the extent of 200 mg/l at 15°C. It may occur in wastes from munitions and shell-loading plants. According to Schott and Ruchhoft (543), a typical waste from a TNT plant contained 1700 mg/l of total solids, 892 mg/l of ash, and only 29 mg/l of suspended solids. The acidity was 1700 mg/l, the sulfate ion content 610 mg/l, and the nitrate nitrogen was 27 mg/l. When diluted 1:1000 by a stream, this waste still had a color greater than that permitted by the U.S.P.H.S. standard and gave rise to objectionable tastes when the water was chlorinated. During World War II, according to Mohlman (542), drinking water standards were relaxed to permit the color of TNT-polluted water to be as high as 20 mg/l in the treated water. In river waters, color from TNT as high as 75 mg/l was accepted.

Degani (544) reported that about 40 mg/l of TNT in tap water killed minnows in 87 to 110 minutes, carp in 455 minutes, and bullheads in 556 minutes. In distilled water, however, the same concentration killed the various fish in about two-thirds the time required for tap water. According to Orton (874), a block of TNT in sea water exercised no recognizable effect on organisms within a few inches of it (concentrations not given).

According to Mohlman (542), TNT wastes in a river at dilutions necessary to reduce color to 20 mg/l caused no appreciable reduction in alkalinity, no odor, no killing of fish, no toxic effect in drinking water, and no objectionable tastes and odors. Dilutions of about 1:10,000 were necessary for drinking water, and 1:3000 for non-drinking water. Fish lived in combined wastes of TNT processes at a 1:800 dilution but not at a 1:400 dilution.

LeClerc (2942) observed that the minimum lethal concentration of TNT for minnows during a 6-hour exposure was 4.0-5.0 mg/l in either distilled or hard water at 23°C. The lethal concentration for fish has also been reported as lying between 1.5 and 2.0 mg/l (2977) and between 2.0 and 3.0 mg/l (3347).

In weak concentrations, TNT is subject to biochemical degradation. In concentrations of 0.5-1.0 mg/l the self-purification of water is slightly retarded; but beyond 1.0 mg/l deleterious effects occur (1721). The Soviet Union has established a maximum permissible concentration of 1.0 mg/l of TNT in surface waters (3107).

According to Mathews et al. (3347), waste waters from explosives-loading plants rapidly develop color when exposed to sunlight, owing to the formation to a TNT com-

plex brought about by photochemical reactions. The maximum concentration of this TNT complex that was not harmful to fish was found to be 3 mg/l whereas the upper limit of harmlessness for the regular TNT was 2 mg/l (3347).

## TRIPOTASSIUM PHOSPHATE

(see Potassium Phosphate, Tribasic)

## TRISODIUM PHOSPHATE

(see Sodium Phosphates)

## TRIVALENT CHROMIUM

(see Chromium)

#### TRYPTOPHANE

 $C_{11}H_{12}N_2O_2$ 

This amino acid is used medically as a nutrient, especially for the treatment of pellagra. Schaut (362) found that 17.1 mg/l of tryptophane in stabilized tap water produced no noticeable effect on minnows during a 24-hour exposure; but the dissolved-oxygen content of the water was decreased 53 percent. In Lake Huron water at 12-13°C, 5.0 mg/l of tryptophane had no effect on rainbow trout, bluegill sunfish, or sea lamprey during a 24-hour exposure (2976).

## TUNGSTEN

1. General. Also known as wolfram, tungsten occurs in nature in the minerals scheelite, wolframite, tungstite, tunstenite, and ferritungstite. Salts of tungsten are used in metallurgy, in the filaments for incandescent lights, as plating materials, for fireproofing and waterproofing fabrics in production of pigments, and phonograph needles (364, 2121). Calcium, magnesium, and iron salts of tungsten are insoluble in water; hence they are not likely to occure in natural waters or to remain in solution in waste waters from industry. Sodium and potassium tungstates are highly soluble.

- 2. Cross References. Selenium
- 3. Effects upon Beneficial Uses.
- a. Irrigation. Hewitt (1473) has shown that 62 mg/l of tungstate ion (46 mg/l of tungsten) in a nutrient solution was harmless to sugar beets in sand culture.
- b. Stock and Wildlife Watering. The addition of 2.5 to 5.0 mg/l of soluble tungsten in the drinking water reduced slightly the toxicity of selenium to rats fed a ration containing 11 mg/l of selenium (1481). The tungstate ion reduced the typical liver damage caused by seleniferous diets and decreased the mortality of rats. All other elements used in this regard tended to increase mortality. It appears, therefore, that tungsten is antagonistic toward the toxicity of selenium to animals and in low concentrations may be beneficial in certain waters (921).

According to Kinard and van de Erve (3741) complete mortality of rats was produced by 2 percent of tungsten in sodium tungstate and 5 percent of tungsten in ammonium paratungstate in the diet. On the other hand, 1000 to 5000 mg/l was not acutely toxic to rabbits but did retard growth.

c. Fish and Other Aquatic Life. Using water from the River Havel, from which the test organisms were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of tungsten added as sodium tungstate. For Daphnia the median threshold effect during 48-hour exposure at 23°C occurred at 350 mg/l of tungsten; for Scenedesmus at 24°C for 4 days the median threshold level was 110 mg/l as tungsten; for Microregma it was 502 mg/l as tungsten; and for Escherichia coli at 27°C it was at 167 mg/l of tungsten.

## TURBIDITY

1. General. The turbidity of water is attributable to suspended and colloidal matter, the effect of which is to disturb clearness and diminish the penetration of light. Turbidity may be caused by micro-organisms or organic detritus; silica or other mineral substances including zinc, iron, and manganese compounds; clay or silt; or sawdust, fibers, or other materials, either as a result of natural processes or erosion or as a result of the addition of domestic sewage or wastes from various industries, such as mining, dredging, logging, pulp and paper manufacturing, and others.

The turbidity of a water sample is a measure of the extent to which the intensity of light passing through is reduced by the suspended matter. Although in some of the literature the terms "turbidity" and "suspended solids" (or other equivalent words, such as "suspended matter" and "suspensoids") are used almost synonymously, the degree of turbidity is not equal to the concentration (or quantity) of suspended solids, but is an expression of only one effect of suspended solids upon the character of the water.

The measurement of turbidity recommended by Standard Methods for the Examination of Water and Wastewater (469) is based upon a comparison of the amount of light passing through the given water sample with that passing through a standard sample. Turbidity is measured in standard units, defined in terms of the depth of water to which a candle flame can be clearly distinguished.

In his studies of waters suitable for fish, Ellis has introduced another system of measurement based upon the determination of the depth at which the light that penetrates the water is reduced to one-millionth of its intensity at the surface. This depth is designated the "millionth intensity depth" of light penetration, abbreviated as m.i.d. (313, 790, 801). The penetration of light, is also measured by the Secchi disk and by the hydrophotometer.

- 2. Cross References. Suspended Solids, Silt, Settleable Solids.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The 1962 USPHS Drinking Water Standards (2036) specify that turbidity shall not exceed 5 units. Bean (1745) has proposed a much stricter limit, viz, 0.1 units for ideal drinking water. State and interstate agencies that have adopted systems of stream classification and standards sometimes designate limits for turbidity in streams that are used for domestic water supply, with values ranging from 5 to 250 units but most commonly the limits of turbidity

are expressed in general terms. For further details of state and interstate standards, see Chapter III.

b. Industrial Water Supplies. Turbidity is undesirable in waters for laundries, ice making, bottled beverages and brewing, textiles, pulp and paper, steam boilers and turbine operation, and other industrial processes.

A summary of the limiting values as recommended in the literature is shown in the following table:

# RECOMMENDED LIMITS OF TURBIDITY FOR VARIOUS INDUSTRIAL USES OF WATER

Y 7	Turbidity	•
Industrial Use	Units	Reference
Beverages	1–2	•
Food products	10	463, 184, 152
Breweries	1-10	173
Boiler feed water	1-20 (ac	186, 152 cording
Paper and pulp		pressure) 159
Alkaline pulps	25	245
High-grade paper	5-25	552, 879
Fine writing and book naper	10	350, 551
Unbleached kraft paner	100	351
Bleached kraft paper	40	351
Groundwood paper	50	2 <del>44</del>
Textiles	- +	232
Nitrocellulose	0.5	2405
Rayon	1	
Cotton	25	550, 405 256
Cotton (callaway mills)	0.3-0.5	
Baking	10	255 150
Cooling water	50	152
ice making	1-5	152
Tanning	20	152
	~~	152

c. Fish and Other Aquatic Life. Excessive turbidity in water affects fish in the following ways:

1. By interfering with the penetration of light, it militates against photosynthesis and thereby decreases the primary productivity upon which the fish-food organisms depend (313, 347, 664, 684, 781, 790, 800, 880, 881, 2780, 3742, 3743). As a consequence, fish production is diminished.

2. At very high concentrations, the particulate matter that produces turbidity can be directly lethal (780, 881, 2409, 3210, 3659, 3745).

3. By excluding light, turbidity makes it difficult for fishes to find food. Conversely, smaller fish may be similarly protected from predators (560, 882, 2780, 3743, 3746).

4. Turbidity modifies the temperature structure of ponds. Bottom temperatures are generally lower in turbid ponds than in clear ones (2731). In many ponds, lower temperatures mean lower productivity.

With respect to productivity, Buck (3742) investigated several farm ponds, hatchery ponds, and reservoirs over a two-year period. For farm ponds, the following results were obtained:

Average turbidity, units Fish yield, lbs per acre Ratio of volumes of pet plantton	Ponds less than 25	94	Muddy Ponds over 100 29.3
Ratio of volumes of net plankton	12.8	1.6	1

In reservoirs, the average volume of plankton in surface waters was 13.8 times greater in the clear reservoir than in the turbid one.

With respect to direct lethality van Oosten (881) concluded from a literature survey that average turbidities

as high as 200 units are harmless to fish. Ward (560, 882) has reported that turbidity as high as 245 units is not harmful to fish. Van Oosten (881) maintains that fish thrive in water with turbidities that range over 400 units and average 200 units. Kemp (780) states that turbidities of 3000 units are considered dangerous to fish when maintained over a 10-day period. In the constantly turbid waters of the Powder River, Oregon (from 1000 to 2500 units), eyed rainbow trout eggs were destroyed within a 6-day period (3659).

Wallen (3745) made a comprehensive study of the effects of turbidity produced from montmorillonite clay with respect to 16 species of fish. His results are sum-

marized as follows:

	T	Average	Fatal T	urbiaity i	$n mg/\iota$
Common Name of Fish	Range of Temper- ature °C	Time of Test, Days	Mini- mum	A verage	
Golden shiner		7.1	55,000	166,000	200,000
Mesquite fish	20-28	16.5	120,000 90,000	181,500 197,000	225,000 270,000
Goldfish	24-32	12.0 5.5	50,000	166,500	225,000
Black builhead	22-32	17.0	175,000	222,000	270,000
Red shiner	22-32	9.0 9.6	175,000 105,000	183,000 165,000	190,000 250.000
River carpsucker		7.6	52,000	101,000	150,000
Pumpkin seed	16-22	13.0	16,500		120,000 200,000
Orangespotted sunfish	22-32	10.0 9.3	100,000	157,000 85,000	200,000
Channel catfish Blackstrip top-minnow		19.3		175,000	
Black crappie	28-29	2.0		145,000 38,250	
Rock bass		3.5		30,200	

At turbidities causing death, the opercular cavities were found to be matted with soil and the gills had a layer of soil on them. Symptoms of distress generally appeared at turbidities much lower than those producing death. Harmful effects were observed as the turbidity approached 20,000 units.

Wallen (2780) also found that bullfrog tadpoles and crayfish can withstand over 150,000 units of turbidity

without death under laboratory conditions.

Ellis' study of more than 5000 samples of interior waters has indicated a general range of turbidity values from about 84 to 53,887 millimeters, as millionth intensity depth. Only in very clear mountain streams, however, was the figure 53,887 mm; in polluted streams protected from undue erosion, the m.i.d. never dropped below 6000 mm even after heavy rains. In swamp areas, with little erosion silt, the m.i.d. varied from 1000 to 20,000 mm. Ellis has recommended that the millionth intensity depth of water for good fish production should exceed 5000 mm (5 meters) (308, 313, 790, 801).

d. Shellfish Culture. It has been reported that excessive turbidity inhibits feeding and restricts the growth of some species of oysters and fresh-water mussels (331, 804). On the other hand, studies by Lunz have indicated that increased turbidity of water in the vicinity of dredging operations in no way increased the mortality of oysters (795). It is also a fact that some oysters live and propagate successfully in waters carrying large quantities of silt and clay (804). Yet, according to Korringa (1448), silt and other turbidity-producing substances such as kaolin or chalk at concentrations by weight as low as 0.1 mg/l reduced the rate of pumping by oysters.

#### TURPENTINE

(see Resins)

## URANIUM

1. General. Uranium and many of its salts are reported to be highly toxic (364, 2129, 2972), but the literature does not always confirm this observation. In addition to its significance in atomic energy, uranium has been used in photography, in glazing and painting porcelain, and in chemical processes. Many of the salts of uranium are freely soluble in water and, hence, they may constitute a health hazard if present in a water supply. Roubault et al. (3744), however, imply from a limited study of certain areas that natural uranium in the soil, which is absorbed by persons through the water and foodstuffs grown on the land, may be a limiting factor in the incidence of leukemia.

Most of the literature concerning uranium in water relates to the radiological hazards. Results are expressed in terms of radiation parameters rather than in concentrations of uranium in mg/l. Such references are covered in Chapter VIII, Radioactivity. The criteria in the following paragraphs deal with chemical effects without

reference to radiological hazards.

2. Cross References. See Radioactivity, Chapter VIII.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supply. The Division of Industrial Hygiene, Ontario Department of Health, has suggested a maximum allowable concentration for neutral uranium in drinking water of 500 to 1000 micrograms per liter (3747).

b. Stock and Wildlife Watering. In tests using two uranium-fluorine compounds, the insoluble uranium tetrafluoride, UF4, and and soluble uranyl fluoride, UO2F2, Maynard et al. (3748) found that 2 percent of UF4 and 0.05 percent of UO₂F₂ had no toxic effect in the diet of rats. Interference with growth and a depressed body weight were observable during the second year in animals on dietary concentrations of 20 percent UF4 and 0.15 percent of UO₂F₂. Some tendency toward anemia was discovered in male rats fed diets containing 0.25 and 0.5 percent UO2F2. While only mild injury was found in the kidneys of rats whose diets contained 20 percent of UF4, definite renal tubular damage was found in rats fed diets of 0.15 percent or more of UO2F2. In a one-year feeding experiment on dogs the same authors observed doses of  $0.\bar{0}1$  g/kg  $UO_2F_2$  and 1.0 g/kg  $UF_4$  were without effect on body weight, but animals fed 5 g/kg of UF4 did not gain weight as almost all other animals did. The minimum dose given for one year that provided unmistakable renal damage in dogs was 0.025 g/kg/day for UO2F2 and 0.2 g/kg/day for UF4. Moxan and Rhian (1481) reported that a concentration of 5 mg/l of uranium in the drinking water increased mortality among rats being fed a ration containing 11 mg/l of selenium.

c. Fish and Other Aquatic Life. Hoffman (769) examined the water of the River March between Czechoslovakia and Germany and found that it contained 0.001 mg/l of uranium. Much of this uranium was absorbed by algae but it was not toxic to them. The alga Ochromonas was reported to concentrate natural uranium (U-238) by a factor of 330 from water in 48 hours (3386). In a study of the Black Sea, Pshenim (2919) found yeasts to be more active than bacteria in taking up uranium.

Tarzwell and Henderson (2154) found the 96-hour  $TL_m$  of fathead minnow in soft water (pH = 7.4, alkalinity = 18 mg/l, hardness = 20 mg/l) was 2.8 mg/l for uranyl sulfate,  $UO_2SO_4.3H_2O$ , 3.1 mg/l for uranyl nitrate,  $UO_2(NO_3)_2.6H_2O$ , and 3.7 mg/l for uranyl acetate,  $UO_2(C_2H_3O_2)_2.2H_2O$ . In hard water (pH-8.2, total alkalinity = 360 mg/l, hardness = 400 mg/l), the 96-hour  $TL_m$  of uranyl sulfate was increased to 135 mg/l. Thus it appears that uranium compounds are considerably more toxic in soft water than in hard water (2407, 2410, 2973).

In Japan, it was observed that 250 mg/l of uranyl nitrate in sea water inhibited the formation of the fertilization membrane in *Urechis* eggs and led to polyspermy (3749). Bringmann and Kuhn (2158, 3343) using River Havel water, reported the threshold effect of uranyl nitrate on *Daphnia* to be 13 mg/l, on *Scenedesmus*, 22 mg/l, on *E. coli* 1.7 to 2.2 mg/l, and on a protozoan (*Microregma*) 28 mg/l, all expressed as uranium.

# UREA $H_2NCOH_2N$

This product of the decomposition of protein is used for fertilizer, organic syntheses, and the production of resins and plastics. Schaut (362) reported that 17.1 mg/l of urea in stabilized tap water had no noticeable effect on minnows during 24 hours of exposure. The dissolved-oxygen content of the water dropped only 2.0 percent. According to Gillette et al. (1442) the critical range for creek chub, a fish of average tolerance, exposed for 24 hours in well-aerated water at 15-21°C, was 16,000 to 30,000 mg/l, i.e. all fish survived at 16,000 mg/l but all died at 30,000 mg/l.

# VANADIUM

Metallic vanadium does not occur free in nature but minerals containing vanadium are widespread. The metal is used in metallurgy to increase the hardness and malleability of steel, and the salts are used in the manufacture of glass, in photography, and as a mordant in dyeing and printing fabrics (364, 2121, 3750).

In its salts, vanadium may have valences of 2, 3, 4, and 5. The tetra- and penta-salts are generally soluble, but the trifluoride, trioxide, and trisulfide are insoluble. Vanadium forms the vanadyl cation (VO) the salts of which are soluble. It also forms the anion vanadate  $(VO_4)$ . It is likely, therefore, that any vanadium salts, occurring in waste water will remain in solution.

Trace amounts of vanadium (0.02-0.15 mg/l) have been found in the waters of certain areas of New Mexico (3751). Vanadium occurs in many soils, with a concentration as high as 470 mg/kg being reported. It also occurs in vegetation grown in such soils, with some plants containing as much as 10 mg/l. In animal tissues, it is widely distributed in trace amounts. Although vanadium has not been demonstrated to be essential in human nutrition, there is evidence that it has certain beneficial biological functions (2121).

According to Mountain et al. (3752), 100 mg/kg of vanadium in the form of  $V_2O_5$  in the diet lowered the free cholesterol and phospholipid content of the liver of rabbits. Vanadium appear to inhibit the synthesis of cholesterol and accelerate its catabolism. Workmen exposed

to vanadium dust were found to have a lower serum chloresterol than a control group (3753, 3754). Stockinger (3751) reported that the incidence of coronary heart disease is-lowest in New Mexico, where natural waters contain trace amounts of vanadium. He also noted that vanadium lowered the serum cholesterol levels in men by 20 percent, at which time the urinary excretion of vanadium averaged 0.046 mg/l.

It has also been reported that vanadium in drinking water at concentrations of 0.03 to 0.22 mg/l reduced the incidence of dental caries in both primary and permanent teeth (2253).

Vanadium fed as calcium vanadate in the diet of chicks inhibited growth at levels of 20 mg/kg (as vanadium), while the  $\mathrm{LD}_{50}$  level was between 300 and 350 mg/l as vanadium (2927). In the drinking water administered to rats on a ration containing 11 mg/l of selenium, the addition of 5 mg/l of vanadium increased mortality (1481).

It is believed that small quantities of vanadium stimulates the growth of plants and may reduce the effects of iron deficiency (2121). In nutrient solution 0.1 mg/l of vanadium had no effect on the growth of soybeans and flax, but 10-20 mg/l was harmful (1595). According to Hewitt (1473) a concentration of about 50 mg/l of metavanadate ion,  $VO_3$ , equivalent to about 26 mg/l of vanadium was slightly injurious to sugar beets grown in sand culture. Up to 0.1 mg/l of vanadium increased the growth of the green alga Scenedesmus, and it is possible that vanadium is an essential micro-nutrient for all green plants (1602).

In exploratory tests, Tarzwell and Henderson (2154) investigated the toxicity of vanadium compounds to the fathead minnow. They found the 96-hour TL_m, expressed in terms of vanadium, to be 4.8 mg/l in soft water and 30 mg/l in hard water when vanadyl sulfate was used. The corresponding values when vanadium pentoxide was employed were 13 and 55 mg/l. Similar tests with the bluegill sunfish gave 96-hour TL_m values of 6 mg/l in soft water and 55 mg/l in hard water for vanadyl sulfate, expressed as vanadium.

#### VANILLIN

 $C_6H_3OHOCH_3CHO$ 

This 4-hydroxy-3 methoxybenzaldehyde solid is highly soluble in water. It is used as a flavoring agent in beverages, confectionery, foods, and perfumes. It also occurs in the raffinate wastes from pulp mills. According to Helbig (3494), the odor of vanillin becomes perceptible when its concentration in water reaches 0.15 mg/l. The State of Washington Department of Fisheries (2091) conducted tests with fingerling chinook salmon exposed to raffinate wastes containing 22.1 percent solids (vanillin content not specified). The critical tolerance level was between 500 and 100 ppm by volume. For yearling silver salmon in aerated sea water, it was between 2082 and 2549 ppm. According to Palmer and Maloney (2041) vanillin at a concentration of 2.0 mg/l is slightly inhibitory to the growth of the alga Gomphonema but not toxic to 5 other species of algae at this concentration.

## VERSENE ACID

(see Ethylenediaminetetraacetic Acid)

#### WEED KILLERS

(see Chapter IX)

# WETTING AGENTS

(see Chapter X)

#### WINTERGREEN OIL

(see Methyl Salicylate)

#### WOLFRAM

(see Tungsten)

# WOOL-SCOURING WASTES

(see also Soaps, Synthetic Detergents, Alkalinity)

Wool-scouring wastes contain the detergents and alkalies used for cleansing and the waxes, fats, dung, blood, urea, sweat, and soil from the wool. Schaut (362) tested a dilution of 1:240 in stabilized tap water and found that it distressed fish but did not kill them, despite the increased turbidity and alkalinity. At a dilution of 1:2400, fish were normal.

# **XYLENE** $C_6H_4(CH_3)_2$

Xylene is a constituent of coal tar, with the commercial form being a mixture of the three isomers, o-, m-, and p-xylene. It is a flammable liquid that is insoluble in water. Commercially it is used as a solvent and cleaning agent, and in the manufacture of dyes and organics. The oral  ${\rm LD}_{50}$  for white rats is reported (3348) as 4300 mg/kg of body weight. According to Middleton et al. (2983) a concentration of 0.3 to 1.0 mg/l of xylene causes a detectable taste or odor in water.

The concentrations of xylene reported to kill fish vary from 10 to 90 mg/l, depending on the species, temperature, and isomer. In general, m-xylene appears to be most toxic and o-xylene least toxic (363, 461, 463, 2977). In Lake Huron water at 12°C, a concentration of 5 mg/l of m-xylene had no apparent effect on rainbow trout or sea lampreys during a 24-hour exposure, but this concentration caused illness to the bluegill sunfish within 10 hours (2976).

# **XYLENOLS** $(CH_3)_2C_6H_3OH$

(see also Cresols, Cresylic Acid, and Phenols)

As a diemthyl phenol, this crystalline compound has six isomers, which are only slightly soluble in water. As constituents of cresylic acid, xylenols are used in the manufacture of resins and coal-tar disinfectants.

Ruchhoft (459) quotes references to the effect that, in chlorinated water, 1, 3, 4-xylenol could be tasted at a concentration of 0.001 mg/l and 1,2,5-xylenol at 0.002 mg/l.

The toxocity of xylenols toward fish and other aquatic life varies with the exposed species and the isomer of xylenol, as well as with temperature, time of exposure, and the synergism or antagonism of other substances. The following information on the toxic or harmful effects of specific xylenols has been reported:

	on Time of Exposure	Fish	Effect Refe	rence
A. 1. 2. 4-xyl	enol (m-xylenol)			
4.0	24 hours	salmonide	TLm at 13°C	3404
		embry os	threshold of toxicity	2904
5.0		bream, bleak	threshold of toxicity	2904
10	·	carp	lower toxic limit	3405
11		perch	TLm at 18°C	3404
17.8	24 hours	tench	lethal limit	3405
20	61 minutes	minnows	TLm at 18°C	3404
21.1	24 hours	carp	lethal limit	3405
26	10 minutes	perch	ICCIDE TONIES	
B. 1. 3. 4-x	ylenol (o-xylenol)		1 torda limit	3405
4		perch	lower toxic limit threshold of toxicity	2904
8		bream, bleak	threshold of toxicity	2904
10		carp	TLm at 18°C	3404
13	24 hours	tench	lethal limit	3405
16	10 minutes	perch	lethal limit	3405
20	15.9 minutes	minnows	TLm at 13°C	3404
27.7	24 hours	embry05	TLm at 18°C	3404
30	24 hours	carp	Him at 10 C	
C. 1. 2. 5-x	ylenol (p-xylenol)		v . 4	3405
2		perch	lower toxic limit threshold of toxicity	2904
5		bream, bleak	threshold of toxicity	2904
10		carp	lethal limit	3405
12	10 minutes	perch	lethal limit	3405
20	5.7 minutes	minnows	lethal limit	3405
20	31.9 minutes	eels	Tetuat imme	
D. 1, 2, 6-xy	lenol		t min Yamal	346
7-9		trout	toxic level	040
E. 1, 3, 5-x3	rlenol			2904
15		perch	threshold of toxicity	2904
18		bleak	threshold of toxicity	2904
20		bream	threshold of toxicity	2004
50	24 hours	salmonide		3404
• • • • • • • • • • • • • • • • • • • •		embryos	TLm at 13°C	3404
51.5	24 hours	tench	TLm at 18°C	3404
53	24 hours	carp	TLm at 18°C lethal at 9°C	910
70	4.5 hours	reach	iethal at 9 C	010
F. 1, 4, 5-x	vlenci			
2	24 hours	salmonide	1000	3404
-		embryos	TLm at 13°C	3404 3404
9	24 hours	tench	TLm at 18°C	3404
10	24 hours	carp	TLm at 18°C lethal at 11°C	910
	4.5 hours	reach		

Southgate (610) reports that sub-lethal concentrations of 1, 2, 6-xylenol increase the toxicity of p-cresol, but sub-lethal concentrations of p-cresol do not appreciably affect the toxicity of xylenol.

The sperm of carp and the eggs of that fish and of tench were found to be more resistant than the adult fish to 1, 2, 4-, 1, 3, 4-, 1, 3, 5-, and 1, 4, 5-xylenol (3404).

Xylenols begin to effect the taste of bleak at 1.0 mg/l and carp at 5.0 mg/l (2904).

Toward lower aquatic life, the xylenols do not appear to be as toxic as they are toward fish. In River Havel water with exposures of 48 to 96 hours, Bringmann and Kuhn (2158, 3343) found that the beginning of threshold effects occurred at the following concentrations:

	T	Threshold Concentration in mg/l for			
	Daphnia		Microregma	E. coli	
Isomer	at 23°C	at 24°C		at 27°C	
1. 2. 4-xylenol		40	70	>100	
1, 3, 4-xylenol		40	10	500	
1, 2, 5-xylenol	10	40	50	>100	

Bandt (2904) reports that the toxic effects of 1, 3, 4-xylenol occur at 77 mg/l for ciliates and rotatoria, 46 mg/l for crustacea, 108 mg/l for molluses, and 154 mg/l for mastigophora.

#### YTTRIUM

(see Chapter VIII)

# ZDD (ZINC DIMETHYL DITHIOCARBAMATE) (see Chapter IX)

# ZEPHIRAN CHLORIDE

#### ZEPHIRAN LEAD

(see Chapter X)

#### ZINC

 $\mathbf{Z}\mathbf{n}$ 

1. General. Occurring abundantly in rocks and ores, zinc is readily refined into a stable pure metal and it is used extensively for galvanizing, in alloys, for electrical purposes, in printing plates, for dye-manufacture and for dyeing processes, and for many other industrial purposes. Zinc salts are used in paint pigments, cosmetics, pharmaceutics, dyes, insecticides, and other products too numerous to list herein (364, 2121). Many of these salts (e.g., zinc chloride and zinc sulfate) are highly soluble in water; hence it is to be expected that zinc might occur in many industrial wastes. On the other hand, some zinc salts (e.g., zinc carbonate, zinc oxide, zinc sulfide) are insoluble in water and consequently it is to be expected that some zinc will precipitate and be removed readily in most natural waters.

In zinc-mining areas, zinc has been found in natural waters in concentrations as high as 50 mg/l (152) and in effluents from metal-plating works and small-arms ammunition plants it may occur in significant concentrations (657, 1031); but, in most surface and ground waters, it is present only in trace amounts. There is some evidence that zinc ions are adsorbed strongly and permanently on silt, with a resultant inactivation of the zinc (3755).

2. Cross References. See also Zinc Salts, Chapter VIII (Radioactivity) Chapter IX (Pesticides).

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The U.S. Public Health Service Drinking Water Standards of 1962 set a limit of 5 mg/l of zinc in acceptable water supplies when no alternate sources are available (2036). From 1942 until 1962, the limit had been 15.0 mg/l, but this standard was lowered because the taste threshold for zinc occurs at about 5 mg/l. Furthermore, the WHO International and European standards for drinking water prescribe a permissible or recommended limit of 5.0 mg/l (2328, 2329).

Zine has no known adverse physiological effects upon man except at very high concentrations. An emetic concentration requires 675-2280 mg/l. In fact, zinc is an essential and beneficial element in human nutrition (2121, 2129). The normal human intake of zinc is estimated at 10-15 mg per day (2121). A summary of literature relating to the toxicity of zine (977, 978) reveals that families and communities have used waters containing 11.2, 17, 18.5 and 26.6 mg/l with no ill effects. One water supply containing 23.8 to 40.8 mg/l of zine gave no harmful effects to 200 persons stationed at a depot. On the other hand, another supply containing 30.8 mg/l of zinc caused nausea and fainting spells. Hinman (219) reported that spring water in Missouri containing 50 mg/l of zine was used for a long time without harmful effect. From these references, it would appear that the WHO and USPHS limits are conservative insofar as physiclogical effects are concerned.

From esthetic considerations, however, high concentrations of zinc in domestic water are undesirable. At a concentration of 30 mg/l, zinc gives water a milky appearance (555) and causes a greasy film on boiling

(980). Indeed, concentrations as low as 5.0 mg/l are characterized by a greasy film on boiling (969).

All readily soluble salts of zinc have an unpleasant, astringent taste and can be detected in less-than-dangerous amounts in drinking water (979). Taste thresholds have been reported at 40 mg/l (555, 3756), 25 mg/l, and as low as 2 mg/l (3300). In tests performed by a taste panel at the R. A. Taft Sanitary Engineering Center (3301) with three zinc salts in distilled water and in mineralized natural spring water, the taste threshold was lower with zinc sulfate than with the nitrate or chloride. In the case of zinc sulfate in distilled water, the estimated taste threshold of 50 percent of the panel was 17.6 mg/l of zinc, but the most sensitive 5 percent of the panel were able to detect zinc at 4.3 mg/l. The taste was less noticeable in spring water, the median threshold being 27.2 mg/l and the 5 percentile at about 6 mg/l. These tests were partly instrumental in changing the USPHS Drinking Water Standard from 15 to 5 mg/l of zinc.

b. Industrial Water Supplies. According to Negus (633) zinc-bearing water should not be used in acid drinks like lemonade because zinc citrate and other organic zinc compounds that will result may be poisonous.

e. Irrigation Water. Kelley and Brown (277) report that small amounts of zinc are needed for nutrition by most crops, but toxicity results when concentrations exceed a very low level. A deficiency of zinc causes poor growth, a dwarfing of the leaves of fruit trees, and chlorosis in corn. Soils vary widely in their zinc content, from near zero to over 100 mg/kg. The addition of 2 mg of zinc per kg of dry soil increased the nitrogen content of peas (2926). Zinc is present in most plants in amounts varying from 1 to 10 mg/kg and in cereals up to 140 mg/kg (2121).

Wilson (1730) found that two species of pine tree (as seedlings) each required about 0.1 mg/l of zinc in nutrient solution for normal growth.

The following concentrations of zinc in nutrient solutions have been reported to be toxic to plants:

	_	pacanto,	
Concentration of Zinc, mg/l	$Compound \\ Tested$	Plant	Reference
3		Orange and mandarin	
≥5 ≥10	<del></del>	seedlings Flax	1524 $1458$
25-100	ZnSO ₄	Water hyacinths Oats	1525 1462

On the other hand, 10 mg/l of zinc caused no apparent injury to oat plants (1462). The presence of 2 mg/l as zinc in water suppressed a fungus disease that infected the roots of watercress, without harming the plants (2658).

During an observation period of 18 days, 54-436 mg/l of zinc in nutrient solution delayed germination and greatly retarded the growth of cress and mustard seeds in solution culture (1479).

d. Stock and Wildlife Watering. Rats fed on water containing 50 mg/l of zinc showed no harmful effects (977), and an average daily dose of 2 mg was not detrimental (353). A total of 390 grams of zinc per pig over a period of three months (about 3.9 grams per day) caused no ill effects, but lameness and malnutrition were caused by feeding milk containing 1000 mg/l of zinc as

lactate for two months (353). Cats were not injured by doses of 50 mg of zine as malate per day for 10 days to two months. Zine in concentrations of 2500 mg/kg fed as chloride or carbonate in the diet was completely without effect on rats (2121). In another test, 1000 mg/kg of zine carbonate in the diet of rats produced no effect; 5000 mg/kg was slightly toxic; and 10,000 mg/kg caused a cessation of growth and some deaths (2129). On the other hand, a concentration of only 5 mg/l of zine in the drinking water increased the mortality among rats on a high selenium diet (1481). When 10,000 mg/l of water soluble zine sulfate (2320 mg/l of zine) was added to the drinking water of six laying hens, egg production dropped, water consumption decreased, and there was a loss of body weight (3761).

The radioisotope Zn-65 is concentrated on pasture grass irrigated with Columbia River water and subsequently transferred to grazing animals and milk (3762, 3763). In rats fed concentrated reactor effluent water for periods up to one year, the radioisotope accumulated in highest concentration was Zn-65 (3764).

e. Fish and Other Aquatic Life. It is toward fish and aquatic organisms that zinc exhibits its greatest toxicity. In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/l have been reported to be lethal, but calcium is antagonistic toward such toxicity. Jones (573) reports that for mature fish the lethal limit for zinc in water containing one mg/l of calcium is only 0.3 mg/l but in water with 50 mg/l of calcium, as much as 2.0 mg/l of zine is not toxic (see also zine sulfate and other zinc salts). The antagonistic effect of hardness toward zinc toxicity has been confirmed by Cairns and his colleagues (2934, 2936, 3519, 3759). Zinc is thought to exert its toxic action by forming insoluble compounds with the mucous that covers the gills (2411, 2920, 2941), by damage to the gill epithelium (3757), or possibly as an internal poison (2112, 3758).

The sensitivity of fish to zinc varies with species, age and condition of the fish, as well as with the physical and chemical characteristics of the water. Some acclimatization to the presence of zinc is possible, and survivors from batches of fish subjected to dissolved zinc have been less susceptible to additional toxic concentrations than fish not previously exposed. It has also been observed that the effects of zinc poisoning may not become apparent immediately, so that fish removed from zinc-contaminated to zinc-free water (after 4-6 hours of exposure to zinc) may die 48 hours later (1444, 1731).

The presence of copper appears to have a synergistic effect on the toxicity of zinc. Doudoroff observed that test fish in soft water could tolerate a concentration of 8 mg/l of zinc alone for 8 hours; however, most of the fish died within eight hours when exposed to a solution containing only 1 mg/l of zinc plus 0.025 mg/l of copper (1459, 1528, 2409, 2410, 3104, 3561, 3760).

The Water Pollution Research Board of England tested the synergistic action of copper and zinc salts in hard water (320 mg/l as CaCO₃) with rainbow trout, at a 6 to 1 ratio of zinc sulfate to copper sulfate (74). In contrast to Doudoroff's findings for soft water, it was shown that there is no synergism between zinc and copper in hard water. Indeed, in soft water (15-20 mg/l

as CaCO₃), synergism between zinc and copper was evident at high concentrations; but the threshold concentration for the mixture (0.56 mg/l for zinc and 0.44 mg/l for copper) is about that to be expected on the assumption that there is no synergism.

The Water Pollution Research Board also found that there was little toxic action of the zinc precipitated from solution in alkaline water, almost all of the toxicity being attributable to the zinc remaining in solution (2112). They also showed that the toxicity of zinc salts to sticklebacks in soft water is reduced by the addition of calcium chloride, even more so than the addition of calcium carbonate; hence the calcium ion rather than the carbonate ion appears to be the antagonistic factor (2112, 3757).

The toxicity of zinc salts is increased at lower concentrations of dissolved oxygen in about the same proportion as for lead, copper, and phenols, e.g., the lethal concentration at 60 percent saturation of dissolved oxygen is only about 0.85 that at 100 percent saturation (1816, 2954, 3321, 3322, 3757).

An increase in temperature decreased the survival time of rainbow trout in solutions of zinc sulfate in hard water, but the threshold concentration was not appreciably affected by changes in temperature (3757) nor was the 96-hour TL_m (2936, 3519, 3759).

Sticklebacks develop an avoiding reaction to dilute solutions of zinc sulfate and will stay out of 0.0003 N zinc sulfate (about 10 mg/l of Zn) (2920).

Affleck (1444) found that 0.04 mg/l of zine in soft water prevented the hatching of rainbow-trout eggs, but Goodman (1731) reported that young rainbow trout hatched successfully in the presence of 1.0 mg/l of zine.

Doudoroff (2157, 3561) experimented with the toxicity of metal cyanide complexes toward minnows. He found that the zinc-cyanide complex, unlike nickel cyanide, dissociated in very dilute solutions, which have been found to be even more toxic than comparable solutions of cyanide without zinc, apparently because of cynergism (2109, 3409).

The following concentrations of zinc have been reported as lethal to fish in the time specified:

Concentration as Zinc, mg/l	Type Te	mpera- ture °C	Exposure Time	Fish	Reference 1444
0.01				Trout eva and young Young rainbow trout	1459 1444
0.01-0.4 0.13			12-24 hrs	Rainbow fingerlings	2921
0.13				Guppy Salmon fry	2153
0.15				Trout	1732
0.15	===			Mature fish	573
0.8	Soft			Sticklebacks	1444, 2941 1459
0.3 0.3-0.7				Fish	1459
0.3-0.1	Soft		6 days	Fish Mixed warmwater fish	
0.5		÷	3 days	Fingerling rainbow	
0.5	Soft		3 days	trout	2112
0.5	Soft		3 days 12 hrs	Rainbow trout	3057 1459
0.65	<del></del>		24 hrs	Sticklebacks	2920
1.0	Soft Soft	30	96-hr TLm		3759, 3519 1459
1.9-3.6 2.0	Soft		18 brs	Fish	3759, 3519
2.9-3.8	Soft	20	96-hr Tl-m	Bluegill sunfish Fingerling rainbow	0100,0024
8.0	Soft	·	8 hrs	trout	2112
			48 hrs	Peinhow ITY	1731
3.0		30	08 he 197 -	Rluerili senfish	2936
<b>3.</b> 5 <b>3.</b> 5	Soft Std. dil. water	20	98-hr TLm	Bluegill sunfish (medium)	2934

15.0 20.0 25-50	Type To of the control of the contro	empera- ture °C 20  18 & 30 20 & 30	48 hrs 8 hrs 96-hr TLm 96-hr TLm 96-br. TLm 8 hrs <6 hrs	Fish Young trout Fish Bluegill sunfish Trout Bluegill sunfish Bluegill sunfish Fish Fish	Reference 3057 2936 1459 1731 1528 2957 1731 3759, 3519 2936 1731 1459
200	Soft			Rainbow trout	1459
	~		3.5 hrs	Fish	1459

The following concentrations of zinc have been reported not to have caused harm to fish during the time specified:

Concentration as Zinc, mg/l 0.003 0.003 0.13 1.0 2.0 2.5-3.5 3.0 4.0 8.0-11.0	Type of Water  Hard Hard Hard Hard Hard	48 nours	Fish  Rainbow alevins Brown trout fingerlings Brown trout fingerlings Sticklebacks Mature fish Rainbow trout Fingerling rainbow trout Young trout Some individual trout	Reference 1444 1444 2920 578 3757 2112 1731
-------------------------------------------------------------------------------------------------------------	--------------------------------------------	----------	-------------------------------------------------------------------------------------------------------------------------------------------------------------------------	---------------------------------------------

Daphnia and other crustacea are susceptible to zinc but most of the literature surveyed gives the results in terms of the zinc salts; therefore, see zinc chloride, zinc sulfate, etc. Zinc, however, is somewhat less toxic than copper (575).

Zine has a toxic effect toward protozoa and bacteria, but not nearly as pronounced as copper (3323). As little as 0.1 mg/l of zine will cause an effect upon biochemical oxygen demand and 62.5 mg/l of Zn will cause a 50 percent drop in the 5-day BOD (2922). In concentrations up to 1.0 mg/l, zinc is reported to stimulate nitrification, but 10 mg/l is inhibitory (2977).

The Mersey and Severn River Boards in England have adopted working standards that limit the concentration of zine, in combination with all heavy metals, to 1.0 mg/l (1756, 2950).

For effects of zinc on kelp, see zinc sulfate.

f. Shellfish Culture. In very small amounts, zinc has been reported to be dangerous for oysters and in large amounts to impart a blue-green color (317). Toward snails, toxic action by zinc has been reported at 1.0 mg/l in natural water (3765) and as low as 0.05 to 0.10 mg/l in distilled water (2733). Toward the pond snail (Physa heterostropha), Cairns and Scheier (3759) found the 96-hour TL_m for zinc in soft water to be 0.79 to 1.27 mg/l at 20°C and 0.62 to 0.78 mg/l at 30°C. In hard water the results were 2.67 to 5.57 mg/l at 20°C and 2.36 to 6.36 mg/l at 30°C. Hardness of the dilution water had a greater effect than did the temperature.

Oysters and other shellfish concentrate zinc-65 from their environment, often by a factor of 100,000 (2438, 2442, 2443, 2446, 3766). A large part of this concentration occurs in the plankton on which oysters feed (2440, 2442, 2447, 3386). For more detail, see Chapter VIII, Radioactivity.

# ZINC ACETATE

 $Zn(CH_3COO)_2$ 

This white crystalline substance, highly soluble in water, has a faint acetous odor and an astringent taste. It is used as a mordant in dyeing and for veterinary

treatments (364). Daily doses of 10 to 15 mg of zine acetate for four months caused no injury to rats (353).

#### ZINC CHLORIDE

 $ZnCl_2$ 

Zinc chloride is highly soluble in water, one gram dissolving in 0.5 ml of water (364). It is used as a deodorant, disinfecting, and embalming material and in the manufacture of paper, dyes, glues, and many other processes.

A dose of six grams of zinc chloride has been reported as fatal to man (353). Practically all recorded cases of poisoning and deaths from zinc have involved either the chloride or the sulfate (969).

Young carp were killed within 24 hours by 1.0 mg/l of zinc chloride in tap water (1459). The highest concentration of zinc chloride tolerated by young eels for more than 50 hours was 0.14 mg/l, and 0.65 mg/l as zinc killed eels in about 12 hours (1459). For medium-sized bluegill sunfish in standard dilution water at 20°C, the 96-hour TL_m for zinc chloride was 7.20 mg/l (2933, 2934, 2935). Another observer (1731) reported that 15 mg/l of zinc chloride killed fish within 8 hours. On the other hand, exposure for one hour to 17.1 mg/l of zinc chloride in stabilized tap water had no detrimental effect on minnows (362).

According to Cairns and Scheier (2957) the 96-hour TL_m values for bluegill sunfish exposed to zinc chloride were 8.02 mg/l of zinc at normal oxygen tensions, but when the dissolved oxygen was periodically lowered to 2.0 mg/l, the TL_m was only 4.9 mg/l as zinc.

Anderson (598) quotes references to the effect that 1.36 mg/l of zine chloride in pond water killed Daphnia magna in less than five days, and in Lake Erie water at 25°C the threshold concentration for immobilization of Daphnia magna was found to be very much less than 0.15 mg/l of zine chloride. The hardness of water appears to affect markedly the toxicity of such zine salts.

#### ZINC NITRATE

 $Zn(NO_3)_2$ 

Highly soluble in water, zinc nitrate is a colorless, odorless salt used as a mordant in dyeing (364). Ellis (313) quotes references to the effect that tadpoles survived a three-month exposure to 1.89 mg/l of zinc nitrate but failed to develop limb buds, that 5.7 mg/l killed most tadpoles, and that 94.7 mg/l killed tadpoles quickly. Anderson (598) reports that zinc nitrate concentrations of 189 mg/l in well water killed Daphnia magna in 15 hours, but for stickleback fish the toxic threshold was only 0.87 mg/l.

## ZINC OXIDE

 $\mathbf{Z}$ nO

This white, or yellowish-white, amorphous, odorless powder is insoluble in water (364). It is used extensively as a pigment in white paints, in cosmetics, tires, printing inks, and other products. It is also employed as a mild astringent and antiseptic in skin diseases (364).

A concentration of 900 mg/l of zinc oxide in the nutrient solution retarded the germination of maize and barley seeds (1479). In a review of the literature, Anderson, Reinhard, and Hammel (977) report that well water containing 32.4 mg/l of zinc oxide caused vegetables to

turn green on cooking and intestinal distress on drinking. Dosages of 0.5 to 34.4 mg of zinc oxide per day for one month to a year did not harm rats and 175 to 1000 mg of zinc oxide per day for 3 to 53 weeks showed little evidence of harm to dogs and cats (353).

#### ZINC SULFATE

 $ZnSO_4 \cdot 7H_2O$ or ZnSO₄·H₂O

- 1. General. This colorless, odorless, crystalline or amorphous substances, highly soluble in water, is used as a mordant in calico printing, for preserving wood and skins, and for electroplating of zinc (364). It has been employed as an emetic, but 45 gms are reported to be fatal.
  - 2. Cross References. Zinc, other zinc salts, Sulfate.
  - 3. Effects Upon Beneficial Uses.
- a. Irrigation. Davies (990) reports that zine sulfate is toxic to plants. Dwarf French beans grown in solutions of 100 mg/l of zinc sulfate died in a few weeks. Brenchley found that 10 mg/l of zinc sulfate in nutrient solution was toxic to pea plants (1479). However, 24.7 mg/l of zinc sulfate caused no apparent injury to oats (1462).
- b. Fish and Other Aquatic Life. Using zinc sulfate, Jones (1460) found the lethal concentration limit for sticklebacks to be 0.3 mg/l as zinc. In different concentrations, the average survival times were as follows: four days at 0.7 mg/l and one week at 0.4 mg/l as zinc. Jones (467) claims that fish detect and avoid concentrations of zine sulfate as low as 24 mg/l, although the salt is not extremely toxic.

The following concentrations of zinc sulfate, as the salt or as zinc, have been reported lethal to fish in the stated time of exposure:

mg/l 0.13 (as Zn) 0.3 (as Zn) 0.4 (as Zn) 0.7 (as Zn) 0.8 1.5 3-6 (as Zn) 4.0 6.0 (as Zn) 1.1 10 10 16* 25 25-50 (as Zn) 100 400 1000	Type of Water  Soft Tap  Tap  Fresh Fresh Distilled	Time of Exposure  Long term 7 days 4 days 144 minutes 24 hours 144 minutes 14 hours 72 minutes 30 hours 48 hours 20 hours 133 mintues 2 bours 5 days 200 minutes 1-4 hours	Guppy Sticklebacks Sticklebacks Sticklebacks Sticklebacks Sticklebacks Sticklebacks Tout Minnows Trout fingerlings Minnows Fish Trout Minnows Young eels Rainbow trout Rainbow trout Goldfish Minnows Goldfish	Reference 2921 1460 1460 1460 1460 991 2977 1731 991 1731 991 459 1459 617 1731 313, 598 313 313
*Approximately				

The following concentrations have been reported as not harmful in the time specified:

$\begin{array}{ccc} Concentration & Reported \\ in mg/l & as \\ 2.6 & Zinc \\ 2.5-3.5 & Zinc \\ 4.0 & Zinc \\ 100 & Zinc sulfate \\ 200 & Zinc sulfate \\ 1000 & Zinc sulfate \\ \end{array}$	Type Time of of Expo- Water sure 24 hours Hard 14 days 24 hours Hard 4 days Sea 1 day	Fish Young trout Rainbow trout Old trout Fish Minnows Trout	Reference 1731 3757 1731 1459 1459 1459
-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	---------------------------------------------------------------------------------------	-------------------------------------------------------------	-----------------------------------------------------------

According to Rudolfs, Barnes, et al. (574), studies by different people indicate that the effects of zinc sulfate on plankton forms in soft water were as follows: concentrations up to 500 mg/l were tolerated by larvae of stonefly, caddis, and water boatman but 10 mg/l killed many small crustacea. Daphnia in an Idaho lake were killed by 0.65 mg/l in three days and 0.3 mg/l was the minimum tolerance for mayfly nymphs, 0.2 mg/l for fresh-water snails and shrimps, and 0.1 mg/l was toxic to some organisms during long exposures. Anderson (598) reported that 0.024 mg/l of zinc sulfate killed Daphnia magna in hard water but some survived 0.24 mg/l in soft water. In Lake Erie water at 25°C the threshold concentration for immobilization of Daphnia magna was found to be less than 48 mg/l (358). Naumann (654) claims that 10 mg/l of zinc sulfate had no effect on Daphnia magna during the first five hours of exposure, but thereafter signs of poisoning appeared. The animals may live for some days but their color fades and they lose their power of reproduction.

Using water of the River Havel from which the test organisms were recovered, Bringmann and Kuhn (2158, 3343) studied the threshold effects of zinc added as ZnSO_{4.7}H₂O on various species during an exposure of 2-4 days. For Daphnia the median threshold effect occurred at 1.8 mg/l of zinc, for E. coli at 1.4-2.3 mg/l, for Scenedesmus at 1.0-1.4 mg/l, and for Microregma at 0.33

Cleland (3328) found various abnormalities in the fertilization and cleavage of eggs of sea urchins when zinc sulfate was added to the sea water at concentrations as low as 0.16 mg/l of zinc.

Clendenning and North (2106, 2107) tested the effect of zinc sulfate on the giant kelp, Macrocystis pyrifera. During a 4-day exposure, 1.31 mg/l, as zinc, showed no appreciable effect on the rate of photosynthesis but 10 mg/l caused a 50 percent inactivation of bottom kelp fronds.

#### ZrZIRCONIUM

Generally regarded as a rare metal, zirconium actually constitutes a higher percentage of the earth's crust than do copper, lead, or zinc. It occurs as zirconium silicate (zircon) primarily in beach sands from volcanic areas. It is used in metallurgy to increase the wear resistance of alloys, in electronic manufacturing, in nuclear reactors as a shielding material, in tanneries, as a pigment in plastics, and in the ceramic and glass industry (364, 2121).

Although zirconium chloride, nitrate, and sulfates are soluble in water, the carbonate, hydroxide, oxide, and silicate are highly insoluble. As a consequence, any dissolved zirconium that reaches natural waters will be precipitated quickly and removed by adsorption or sedimentation.

Animal studies reported by Rothstein (2129) indicated neither acute nor chronic injury in response to zirconium compounds given orally for as long as two years. Even 20 percent zirconium oxide in the diet was not harmful (2129). Cochran et al. (3527) found the LD₅₀ values for oral administration of zirconium salts to rats, expressed as zirconium, to range from 853 mg/kg of body weight for the nitrate to 2290 mg/kg for sodium zirconyl sulfate.

Palange et al. (3767), 3768) conducted bioassays with fathead minnows to determine the toxicity of waste waters from a plant producing zirconium. They found that the 48-hour TL_m occurred at a 0.28 percent concentration of the zirconium phthalate filtrate and at 0.16 percent of the zirconium hydroxide filtrate. Concentrations of zirconium or pure compounds were not specified.

In exploratory tests with the fathead minnow, Tarzwell and Henderson (2154) found the 96-hour  $TL_m$  for zirconium sulfate to be 14 mg/l, as zirconium in soft water and 115 mg/l, as zirconium, in hard water. For

zirconium oxychloride, the corresponding concentrations were 18 and 240 mg/l. This latter compound was also tested against bluegill sunfish, with 96-hour  $TL_m$  values of 15 mg/l in soft water and 270 mg/l in hard water, all expressed as zirconium.

Collier (1720) reported that during a dense bloom of Gymnodium off the Florida west coast water samples analyzed spectrographically showed the presence of zirconium at concentrations of 0.34-3.4 mg/l. The origin and role of the zirconium, like titanium, was not determined.

#### CHAPTER VII

# BIOLOGICAL POLLUTANTS

This chapter is concerned primarily with the effects of living material, both plant and animal, upon the quality and beneficial uses of water. Such biological agents may be primary pollutants or corollary pollutants. Primary pollutants comprise biota that are added directly to water as a result of man's activities, e.g., enteric bacteria or viruses from sewage. These biological forms are not native to the water environment and they seldom multiply or prosper there; indeed they normally die off rapidly. Corollary pollutants represent indigenous living material that interferes with beneficial uses of the water, either by natural processes and growth (e.g., weeds in irrigation ditches) or by stimulation from man's activities (e.g., algal blooms stimulated by nitrates and phosphates from waste discharges). In the case of corollary pollutants, the interfering biological agent has not been added directly by man, but its prominence or its interference may be attributable to human endeavors.

Biological substances are significant in the evaluation of water quality in two other ways, viz, the impact of pollutants upon natural and beneficial aquatic and marine life, and the role of biota in the biochemical and biological stabilization of waste products. The effects of potential pollutants upon fauna and flora comprise a major part of this survey of water-quality criteria, as described by beneficial use in Chapter V and under many of the specific substances in Chapters VI-X inclusive.

The role of living material in the stabilization of waste material is a subject far too vast to be covered in this volume. Moreover, it is not directly relevant, for this study is concerned with the concentrations of pollutants, whether physical, chemical, biological, or radiological, on the beneficial uses of water, and not with the ultimate fate of these pollutants. Aspects of stabilization enter into the discussion of biological pollutants, however, when their levels of concentration are being related to beneficial uses and the reasons for these levels are being evaluated.

For further information the reader is referred to the classics of Ward and Whipple (15), and Whipple and Fair (16) mentioned in Chapter II. Of more pertinence to this work, however, are the English publications by Hynes (2602) and Yapp (2126). Also highly pertinent are the triennial symposia conducted by the U. S. Public Health Service at the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio (2127, 2128).

This chapter is organized in the same manner as Chapter VI, as explained in the introduction thereof, with appropriate cross-referencing, both internally and with other chapters. Biological substances are listed alphabetically by the most common designation; but where other terms are in common use they have been listed with cross-referencing.

# ACTINOMYCETES

(see also Fungi, Bacteria-General, and Algae)

The mold-like bacteria of the genera Actinomyces and Streptomyces (Bergey includes others) are commonly referred to as actinomycetes. They play an active part in the decomposition of organic matter and are largely responsible for the musty odor of freshly turned soil (2289).

According to Silvey (2516) the primary stages of the aquatic actinomycetes develop submerged in company with various plankton or organic matter rich in nitrogen. The growth requirements for the secondary (mycelial) stage include available oxygen, temperatures of 10° to 32°C, potassium, a source of organic carbon, and some form of nitrogen. As potassium is increased from minimal amounts of 2 to 4 mg/l, luxuriousness of growth is quite evident.

The aquatic actinomycetes are responsible for tastes and odors in water supplies (152, 662, 663, 1572, 1574, 2058, 2241, 2278, 2504). The primary stages are said to be associated with rather mild odors described as fishy, grassy, or marshy. The secondary stages appear to be more elaborate in the type of odor compounds they produce. These compounds include such metabolic products as aromatic amines, ketones, aldehydes, saturated fatty acids, and unsaturated aromatics (2058, 2516, 2517).

In culture medium, copper has a stimulating effect on all types of aquatic actinomycetes (2240). Calcium, sodium, and magnesium stimulate the growth of some species. Four types of actinomycetes from Los Angeles were found to require some available nitrogen in order to give rise to musty or earthy odors (2517).

Ives (2248) mentions a symbiotic relationship between Streptomyces and the alga Cladophora that causes tastes in water. However, many tastes and odors mistakenly attributed to algae are reported to be due to actinomycetes (2241). The spores of Streptomyces are very small and therefore may pass through rapid sand filters. Such spores can lodge in deposits in the distribution system and cause tastes and odors not found in water leaving the treatment plant (2058).

Silvey studied the relation of irrigation run-off to tastes and odors (1573). Results indicated an imperfect relation between algae and actinomycetes which, in the absence of sufficient phosphate and nitrates, causes rapid destruction of the algae and release of the by-products of metabolism of the actinomycetes.

An obligate autotrophic actinomycete is reported as being capable of destroying cyanide (2518).

# **ADENOVIRUSES**

(see also Viruses and Chapter V-Swimming and Bathing Waters)

The adenoviruses are associated with upper respiratory infections, particularly in children. These spherical viruses are somewhat larger than most enteroviruses, being 60 to 80 mm in diameter. They are excreted in large numbers in the stools of infected individuals (2159). The adenovirus is also known as the APC virus after adenoidal-pharyngeal-conjunctival.

Although adenoviruses have been isolated from sewage, no outbreaks of human infection from drinking water have been reported. Two papers have been published concerning adenovirus outbreaks that appear to be associated with swimming pools. One was manifest in an epidemic of conjunctival fever in which 74 of the 112 cases studied originated in a swimming pool (2160,

2161).

# ALGAE

1. General. In 1956, Palmer and Ingram pointed out the confusion that reigns in classifying of algal forms (2163). The same article offered a system of classification to the water-pollution specialist based upon the oxygen-consuming or oxygen-producing characteristics of the organisms. Palmer, in subsequent publications (2164, 2165, 2166), has made use of a four-part classification; (a) blue-green algae; (b) green algae; (c) diatoms; and (d) flagellates. The algae, in this second edition of WATER QUALITY CRITERIA, have been divided into three groups based largely on the convenience of Palmer's latter organization: (a) algae; (b) diatoms; and (c) marine flagellates.

The algae constitute a group of life forms that may be unicellular or multicellular, motile or immobile, of which practically all have photosynthetic pigments. None posess a multicellular sex organ with a sterile jacket such as the bryophytes (15). Since the algae occur naturally in surface waters, they fall into the category of corollary pollutants. They can be beneficial to waters because they add oxygen, remove carbon dioxide, are significant in self-purification processes, and serve as food for certain aquatic fauna (16, 366, 367, 368, 369). However, Heukelekian (2144) notes that since algae require inorganic materials such as phosphate, ammonia, nitrate, and carbon dioxide which are then photosynthetically transformed into cellular organic materials and oxygen, the algae should be considered as producers rather than destroyers of organic matter.

Growth or types are reported to be influenced by pH (2167, 2168), turbidity (370, 2169), sunlight (371, 2162), sulfates—more than 0.5 mg/l being needed (2203), temperature, water velocity, silica, nitrates, carbonates, phosphates, and manganese (373, 374, 375, 376, 377, 378, 379, 439, 2171). Others have cited proteinderived ammonia, oxygen, oxidizable organic content (2172), alkalinity, iron, and the relative concentrations of carbon, nitrogen, and phosphorus (1451, 1452, 2173, 2174, 2202). Phosphorus is repeatedly cited as a critical factor in plankton growth (2170, 2173, 2175, 2176, 2177, 2178, 2179, 2180, 2181). However, turnover of inorganic phosphate under natural conditions appears to be caused

by aquatic bacteria. Bacteria and algae may compete for inorganic phosphate (2140). Sawyer studied the relationship between the production of algal blooms and the nitrogen: phosphorus ratios in a group of Wisconsin lakes. For some algae, N:P ratios of 30:1 were found to be optimal; for other algae, ratios of 15-18:1 appeared to be most favorable. Sawyer suggested 0.01 mg/l of inorganic phosphorus as the maximum concentration that can be permitted without danger of supporting undesirable growths (1450, 2182). If the assets of inorganic nitrogen and phosphorus from wastes exceed 0.3 and 0.01-0.015 mg/l respectively at the start of the growing season, nuisance blooms of algae may occur (2183, 2519). Tucker (2184) has suggested that nutrient elements (other than phosphorus) combined with ferric complexes may be responsible for the blooms that occur following overturn in deeper lakes. In a study of a small artificial pond, chrysomonads were not found when the water contained more than 0.02 mg/l phosphate but cryptomonads increased at this concentration (2185). Inorganic nitrogen stimulated several green algal species but did not affect Eugleninae. Similarly, green algae development was related to phosphate concentration, but Eugleninae were not affected. Organisms of questionable algal status, Cyanophyceae and Cryptomonadinae, reacted similarly to Eugleninae. Algae can absorb and concentrate radioactive substances from water. For various concentration factors, see Chapter VIII, Radioactivity.

An Israeli study of fishpond phytoplankton showed that, although blooms of blue-green algae occurred in all ponds, diatoms predominated in ponds of high salinity, green algae in ponds of low salinity. Organic manure was an effective source of nutrients over a long period; chemical fertilizers had more rapid but less lasting effect (2186).

Primary effluent from a small sewage treatment plant in an Ohio stream characteristically causes an increase in some green flagellates, Euglenophyceae, and the disappearance of yellow-brown flagellates, Chrysophyceae (2520).

Temperature effects in relation to algae have been the subject of several papers. Release of cold impounded water affects stream biota. Plant populations in some tailwater areas is dominated entirely by algae (2187). Elevated temperatures of stream water of 2.8°-5.5°C caused no significant increase in plankton, but differences in fish populations were noted (2188). However, another report on a stream subject only to temperature pollution. indicated that blue-green algae became more abundant, green algae less abundant. Marked irregularities in the behavior of the periphyton population not related to temperature were believed due to chlorination of condenser water. Hale (422) reports that blue-greens favor 15°-27°C, green algae 10°-21°C, and yellow-green algae 4°-10°C (2189). Cairns cites the best growth temperature of blue-green algae as 30-40°C, and green algae 25-35°C. He also notes that in mixed populations from a normal healthy stream, a large number of species of diatoms were present at 20°C, dominating the culture. But at 30°C, only two species of diatoms were numerous and blue-green algae predominated (2190). Ingram and Towne (2197) state that high temperature may alter the entire biosphere, eliminating many organisms and allowing a few heat resistant blue-green algae to predominate, thereby giving rise to unfavorable stream conditions. Early seasonal development of Cladophora glomerata owing to warmer water temperatures occurred on the Tween and Teviot Rivers in England (2181). Some green algae have adapted to extremes of temperature. Protococcus nivalis is found in arctic regions, and Tribonema has been noted in water at 45°C. Phormidium, a bluegreen alga, is heat tolerant (2183). Anabaena and Coelosphaerium seldom give any trouble unless water temperatures exceed 21°C. Aphanizomenon apparently prefers colder water than most Cyanophyceae. It is present in some ponds even when the surface is frozen (16). In a discussion of temperature, light, and nutrient affects on the green alga Chlamydomonas reinhardi Dangeard, McCombie (2191) states that temperature acts as a typical controlling factor governing the rate of growth by determining the rate of metabolism. The concentration of nutrient salt shifts the temperature optimum for growth. According to Smith (2192), temperature rarely plays a direct role in acclimatization of algae, but has an important effect on rate of growth. However, it can be a limiting factor as is shown by cases where tropical algae have not been able to survive overwintering conditions.

Fichter (2193) reports that plankton were 13 times more abundant in clear, and 1.5 times more abundant in moderately turbid water than in muddy Oklahoma ponds. Algae were significantly fewer in samples from silted zones of the Truckee River in California (2194). Nigrosine dye was used in Arizona to limit light intensity for aquatic weed control. This change was reflected in a lower bottom temperature and a temporary increase in plankton (2195). Neel, however, reports that in observations made on the Missouri River after the reservoir system went into effect, algae began active growth soon after the water cleared. Attached filamentous forms, previously absent, became common. Algae concentrations in the nuisance range caused tastes and odors at Yankton, S.D., and extended all the way to Omaha (2169). Light exclusion is one of the most important effects of suspended matter on algae, for it interferes with their photosynthetic action, depriving them of active growth (2196).

In a study of productivity of British Columbia lakes, it was stated that the concentration of total dissolved solids was the most important factor (2198), although this factor could not be used to predict the numbers of plankton, bottom fauna, nor fish. Casey and Webb (2199) observed a fair correlation between total dissolved solids and amount of plankton, noting that greatest plankton populations were present in lakes having total dissolved solids over 100 mg/l. Smith (2192) states that algae of soft-water regions are largely desmids and certain species of Chrysophyceae, Myxophyceae, and Chlorophyceae, that pH of water is limiting, and that Birge and Juday related the greater abundance of algae in hard-water lakes as compared to soft-water lakes to the bicarbonate content.

Truly halophilic algae have been found that will develop in concentrations of sodium chloride greater than three molar (2192). Yet, the alga responsible for red patches on fresh-snow surfaces resides in near-distilled water (2200). Studies are underway on the feasibility of using algae that concentrate sodium chloride as a means of desalting sea water (2201). This study has revealed that both fresh and marine algae have surprisingly wide salinity tolerances. Fresh water species grew well in 50 percent sea water whereas marine species grew well in 25 percent sea water.

In studies of nitrogen and phosphorus removal from sewage plant effluents with Chlorella and Scenedesmus, the removal of phosphorus was never complete but continued long after the absorption of nitrogen had ceased (2204). The complex phosphate additives of synthetic detergents (2205) undergo a slow hydrolysis that tends to yield a continuously renewed supply of available phosphate for algal nutrition and prevents phosphate concentrations in streams from reaching low levels (2172).

Negative relationships of algae to some environmental factors are not lacking in the literature. A thesis noted that no correlations could be made between phytoplankton numbers and changes in the chemical environment in a study of 18 consecutive months duration (2206). No relation between phytoplankton pulses and concentrations of bound phosphorus were observed on four ponds in North Carolina (2207). Lund (2208) states that phosphate shows no variation related to algal production, but nevertheless, addition of phosphate is often followed by an increase in algae. He then describes avenues by which phosphate may be secondarily involved in such blooms. Lund also cites similar arguments with respect to nitrogen and other essential nutrients.

Gerloff and Skoog (2209) note that Microcystis can store nitrogen and phosphorus in excess of its needs. Hence, the amount of nitrogen and phosphorus in the water may be a poor measure of the alga's reproduction capacity. This factor also casts doubt upon the effectiveness of phosphorus removal processes for sewage treatment plant effluents to limit algal blooms (2209). Critical levels—the minimum cell contents required for maximum growth-of nitrogen and phosphorus are to some extent a function of the carbohydrate content of the cells (Microcystis aeruginosa) (2210). Sodium is required for the normal growth of M. aeruginosa. Another effect of sodium is to reverse the inhibitory effects of excess levels of potassium. Concentrations of manganese that are toxic in synthetic culture media were found to be non-inhibitory in lake water owing to antagonistic effects of calcium (2211). Critical levels for maximum growth for iron and manganese were 100 and 4 mg/l respectively (2212). Waters low in calcium but high in nitrogen are likely to develop large numbers of bluegreen algae (2213).

Some algae are believed capable of excreting substances toxic to bacteria (2012, 2214, 2215, 2216, 2217, 2218) or other algae (2219, 2220). Coliforms have been reported to be suppressed by algal growth (99). A bacterial contaminant has also been mentioned in connection with a slow-death factor in cultures of Microcystis aeruginosa (2219). The blue-green alga Anabaena cylindrica, as well as other species, excretes a polypeptide that can form complexes with other ions including copper, zinc, ferric iron, phosphate, and certain organic substances. This phenomenon may be important in making phosphates available to algae and in making toxic ions less toxic (2222). For an excellent summary of algal nutrition see Provasoli's review (2202).

The blue-green alga Oscillatoria rubescens is reported to be a notorious indicator of pollution in many lakes (2133, 3351). Lackey cautions investigators in the use of the terminology "characteristic of" and "indicative of" as applied to algae and organic enrichment. He concludes that the indicator value of the algae is still not clear (2230). However, Bucka reports studies that successfully correlated phytoplanktonic flora with the trophic classification system (2521). Palmer (2223) writes that a particular species or genera is not a reliable indicator of pollution, but when the whole community of algae is considered, the group may be reliableeven to the extent of indicating the degree of purification that has occurred. An interesting study of marine plankton as indicators of pollution has been published in Japan (2224). In this work B.I.P. is defined as 100

where A is the number of chlorophyll-containing

organisms in a volume of water, and B is the number of organisms containing no chlorophyll. Highly polluted sea water gives a B.I.P. of over 80; slightly polluted water of 51 to 80; normal water of 21 to 50; and clear water less than 21. For a discussion of algae in the recovery of polluted streams, see Bartsch and Ingram (2143).

The decomposition of organic matter and the drainage from rich farmlands serve to stimulate algal blooms (16, 346, 380, 381, 382, 1992). Pollution from a duck farm entering an estuary favored the growth of Nannochloris and Stichococcus over native estuarine phytoplankton. However, low salinities are also mentioned as a possible mechanism (2225).

An important chemical effect of algae is the removal of carbon dioxide from the water during daylight hours. Chlorella metabolizes as a phototrophic organism in the light, but in the dark it obtains energy from reduced carbon compounds, thereby competing with bacteria for food. The Euglenophyceae do likewise (2012). The daytime process brings about an alteration in the relative amounts of soluble (unbound) carbonic acid, intermediately soluble (half bound) bicarbonates, and the nearly insoluble (bound) monocarbonates, often causing precipitation of some of the latter. All of this produces a decrease in total hardness (2166, 2226). Vigorous growths have been known to reduce hardness by as much as one-third. These activities also result in pH variations (2126, 2181, 2226, 2227, 2228), the pH increasing in the daylight, decreasing at night. These extremes have been recorded as high as 10.5 at 4 p.m. and 7.8 at night (2229).

A most important action of algae, of course, is its effect on dissolved oxygen (2126). Indeed, Hull coneludes that during the critical warm months the amount of photosynthetic oxygenation is relatively more important than atmospheric oxygenation in Baltimore Harbor (2522). Heavy crops may produce oxygen supersaturation in the daylight and depletion at night (2012). This metabolic oxygen depletion can result in fish kills (2183). The highest figure noted in the literature was 300 percent supersaturation (418). A report from the Tweed

River Purification Board in England notes repeated daytime supersaturation with oxygen to the extent of 150-200 percent, accompanied by night values of 50 percent or even less in the vicinity of sewage outfalls (2181). A net photosynthetic gain of 1.7 mg/l of dissolved oxygen per mile of river has been observed, the figure being a daily average (not just daytime changes). Bottle tests show that oxygen production exceeds oxygen utilization in BOD reactions, resulting in a net gain (1992). Westlake also notes that pH and dissolved oxygen can be raised to levels that may be detrimental to the blooms that created the conditions. Cladophora is cited as an example of species capable of adding considerable dissolved oxygen to a stream (2126).

Phenol has been reported as coming from algal blooms (2232). Algae may interfere with disinfection (2227, 2234), coagulation (2166), and filtration (2227, 2234). They add a very large organic burden in heavy concentrations (1992), but in lower concentrations may be an asset rather than a liability (2166). When masses of algae die, dissolved oxygen is depleted faster than it can be absorbed from the air (2226). The electrokinetic (zeta) potential of algae has been studied (2234). Under all conditions studied, 14 genera of naturally occurring fresh-water algae and 8 genera of artificially cultured

algae exhibited a negative electric charge.

Algae have been implicated in the disintegration of submerged concrete blocks (2233), and in corrosion (2227) of metal sedimentation tanks (397, 399, 400, 401, 2166). The Department of Agriculture and the Bureau of Reclamation jointly studied the biological corrosion of concrete (2235). Algae, lichens, and fungi were involved in studies over a five-year period. When the sulfite content of the mortar was 0.6 percent or greater, pitting by the plants was very pronounced. Where the sulfite content was only 0.2 percent, pitting was much reduced. The report suggests that gelatin present in the plants plus their organic acids, viz., carbonic, oxalic, and salicic acids, corroded the surfaces with plants growing on them when sulfite content was high.

Lackey (2012) recognizes three benefits of algae: (1) reoxygenation; (2) mineralization; and (3) production of a food chain; and three ills: (1) algal toxicity; (2) esthetic harm, including tastes and odors; and (3) buildup of a BOD. Also, many blue-green algae produce mucilaginous envelopes that harbor bacteria and may protect coliforms and possibly pathogens such as Salmo-

nella from chlorination.

2. Cross References. Protozoa, Oxygen, Ammonia, Nitrates, Phosphates, Polioviruses, Diatoms, Marine Flagellates, Coliform Bacteria, Salmonella, Actinomycetes. Gastroenteritis Organisms, Bacteria-General, Pathogenic Bacteria, Settleable Solids, Nitrogen, Weeds, and Chapters VII, IX, and X.

3. Effects on Beneficial Uses.

a. Domestic Water Supplies. Algae have been frequently cited in the literature as responsible for tastes and odors in water supplies (16, 210, 369, 383, 384, 385, 386, 422, 428, 429, 430, 738, 1573, 1755, 2058, 2164, 2166, 2169, 2182, 2189, 2196, 2213, 2221, 2226, 2234, 2236, 2237, 2238, 2239, 2241, 2242, 2243, 2244, 2245, 2246, 2247, 2248, 2249, 2250, 2251, 2252, 2253, 2254, 2523,

2524). The reader is referred to Palmer's book "Algae in Water Supplies" (2166), which gives algae species involved, type of taste or odor produced, and color illustrations of selected species. Taste- and odor-producing algae are said to be as common to rivers as to hard-water lakes and reservoirs (2221). At one time, according to Fox (2250), odors in water from organisms were believed to be due only to microbial decay. Decomposition products from organic matter, including dead microorganisms, were listed as among the most significant causes of tastes and odors in water (2213). Now it is well known that many living organisms through their metabolic products impart an odor to water (2213, 2250). Palmer notes that sometimes certain types of algae are responsible for tastes and odors in small or moderate concentration, citing Synura and Euglena in the State of Texas. When tastes and odors result from the decomposing of large quantities of algal material, the algae are likely-in the south-central states-to be a limited genera of blue-greens during the summer months, and a mixed growth of greens and flagellates in the spring and fall (2213).

Although it is difficult to establish limiting or threshold values for algae, the Metropolitan Water Commission of Boston sets the following allowable limits at which treatment is begun (2255):

1000
. 000
. 200
. 10
200 200

Fox (2250) and Swartz (2189) report that low (500-1000 Standard Areal Units/ml) concentrations of bluegreen algae cause a grassy or moldy odor, while at higher concentrations a pigpen odor is evident. The green algae produce a grassy or nasturtium odor at high (2000 units/ml) concentration, and the yellow-green algae can cause noticeable odor even at low 100-500 units/ml) concentrations.

Palmer and Poston (2247) report that as few as five colonies of Synura per ml can cause taste and odor trouble. See Palmer's book (2166) for more complete information. Ives (2248), in a discussion on the effects of algae in water, reports that the symbiotic relationship between Streptomyces (an actinomycete) and Cladophora causes tastes and odors in water. In studies on Oscillatoria, Russian workers reported that O. splendida gave an odor when the cells were damaged mechanically, dried, or frozen, and also when there was insufficient nitrate. O. agarháii gave an odor under unfavorable environmental conditions, including an accumulation of wastes, insufficient nitrogen supply, lack of ferrous iron, etc. The acrid taste imparted by this organism reportedly disappears in the presence of added nitrate and an organic carbon source (2256). In 1953, Silvey published his work on the algae-actinomycetes relationship and the production of tastes and odors in water (1573).

Algae growths can impart color or turbidity to water (369, 2164, 2182, 2213, 2226, 2249). Reservoirs in Glendale, Pasadena, and Los Angeles, California, have had

to be roofed because of public complaint about green water (2257).

Algal contamination of drinking water has been suspected as a factor in outbreaks of gastroenteritis of unknown etiology (390, 424, 2166, 2429, 2523). Moreover, the accumulation of dead and dying plankton in filter sand offers an excellent substrate for the growth of such bacteria as Pseudomonas. Because some species of Pseudomonas are concerned with gastroenteric disturbances in man, algae may be indirectly connected with waterborne gastroenteritis (2182). Also, two cases of allergy to blue-greens of the subgroup Oscillatoriaceae (genera not mentioned) have been reported by Heise (2258). Wheeler, et al. (391) have pointed out that algal poisons usually act on the central nervous system and skin rather than on the gastrointestinal tract; on the other hand, Steyn, of South Africa, believes that algal poison is one of the most virulent poisons known to the science of toxicology and is capable of producing a "mysterious" cirrhosis of the liver and/or of reducing the resistance to disease of many human beings (381, 391, 392, 393, 406). The possible relationships of such compounds to cancer and geriatric disorders are currently under study (2523).

Algae may interfere with water treatment processes, including rapid sand filtration and disinfection (210, 369, 385, 395, 396, 397, 398, 2164, 2165, 2166, 2182, 2226, 2234, 2239, 2248, 2251, 2254, 2259, 2260). Long filamentous organisms such as Oscillatoria are more effective in clogging filters than shorter or nearly spherical organisms (2254). Plankton such as Cryptomonas and Euglena disintegrate readily on coagulation and filtration and do not clog the filters (2182). At Chicago, plankton counts of 60,500 per square foot on filter surfaces resulted in 41-hour runs and 4,572,700 in 3.5-hour runs. In another case, water became impossible to filter owing to a massive crop of Ceratium hirundinella, the numbers of which exceeded 10,000 per ml (2261). Records of plankton counts as high as 100,000 per ml have been obtained on Indiana's White River (2182). Burnson (2253), however, considered filters to be more efficient in the summer when microscopic plant and animal life are abundant than in the winter.

In studying tastes due to Oscillatoria, Uspenskaya (2239) noted that their growth varied with the organic content of the bottom muds, and that the more oxidizable the mud, the stronger was the taste imparted to the water. To avoid such tastes, reservoir mud should not contain over one percent nitrogen.

The increased organic content in water resulting from algae may serve as nutrient for organisms in the distribution system. Algae also reduce the useful capacity of reservoirs by concentrating at certain depths in the water or along the shallow margins or bottom (2226, 2238, 2249). Other problems caused by algae in domestic water supply include clogging of intake screens and reduced pipeflow (2166, 2213, 2262).

b. Industrial Water Supplies. Algae are undesirable in water for a variety of industrial uses, including butadiene manufacture (251); condensers, cooling towers, and sprayers (208, 210, 2263); paper manufacture (402, 2524); laundries, dyeing, photography, and chemical in-

dustries (369, 385); beverage bottling (403, 404); and rayon processing (405).

A heavy growth of green algae in an impounding reservoir resulted in the incrustation of pipe lines and the failure of pumps (2264). The incrustation was largely calcium carbonate caused by the algae.

c. Irrigation Waters. Interference by algal growth in irrigation distribution systems has been the only information published linking algae with this beneficial use of water (2213, 2226, 2265, 2525). Cladophora and Rhizoclonium are by far the most important algae in this

respect (2265).

d. Stock and Wildlife Watering. From many different parts of the world, including the United States, there have been reports of rapid deaths of a great variety of animals after drinking water containing high concentrations of blue-green algae, such as Anacystis, Aphanizomenon, Nostoc rivulare, Nodularia, Glocotrichia, Gomphosphaeria, and Anabaena. The first recorded occurrence of a waterbloom toxic to domestic animals is attributed to Francis in Australia (2266). The organism responsible was Nodularia spumigena. Fresh algae have been reported to be more toxic than decaying algae. Fatal poisoning has occurred among cattle, pigs, sheep, dogs, horses, turkeys, ducks, geese, and chickens, and also among experimental animals, such as rabbits, rats, guinea pigs, and mice. It is believed that such algae may be toxic to all warm-blooded animals. Algae poisoning is considered a menace to migratory waterfowl, and has been suspected as a cause of mass deaths of ducks. Fatal doses can be very small, of the order of a few milliliters of water suspension taken orally, but animals vary in their susceptibility. Waterbloom poisoning is reported to be very similar to shellfish poisoning (2429).

At least two poisons appear to be involved, and efforts are being made to isolate and identify them. One affects the nervous system and liver; another, the algal pigment phycocan, becomes concentrated in the skin, where it absorbs ultra-violet light, causing burns, sores, and possibly death (381, 391, 395, 406, 407, 408, 409, 410, 411, 1454, 1455, 1456, 2012, 2166, 2213, 2267, 2268, 2269, 2270, 2271, 2272, 2273, 2274, 2275, 2276, 2277, 2278).

An Anacystis toxin has been isolated and identified as an alkaloid (2278). A Nostoc rivulare toxin administered to mice in food and drink gave the same results as intraperitoneal injections. Heat-toxicity studies of N. rivulare suspensions showed that autoclaving destroyed toxicity, and the minimum lethal dose to mice is 0.0933 mg of algae per gram of body weight. The toxic factor is soluble in ethanol, and affects the neuromuscular and respiratory systems (2277).

Samples of blue-green algae were randomly collected at different times from two Canadian lakes. Present were Anacystis aeruginosa, Coelosphaerium, Anabaena, Aphanizomenon, Gloeotrichia, and Lyngliya. These were injected into mice for different incubation periods. All samples produced symptoms of toxicity. Fresh material had no lethal effect. Toxicity increased to a maximum after 18-26.5 hours incubation. Incubation for longer periods reduced toxicity. The toxicity of one sample was markedly reduced by storage at 3°C for 18 days, followed by incubation at 27°C for 18 hours. The authors conclude that toxicity develops only gradually

in blooms, and decreases again as the algae decompose (2276).

Aphanizomenon, Anabaena, and Anacystis blooms were found in water samples taken from a Canadian lake. Animals had reportedly died very shortly after drinking water from this lake. The relative numbers of the three algae were 99:0.9:0.1 respectively. The mixture killed laboratory mice and rats within 20 hours. The filtrate was not lethal. The residue, resuspended in distilled water, was toxic. Chromatographs of acctone and ether extracts yielded definite green, yellow, and brown bands, but the toxic material was not isolated and identified. Although it is not known which species was more important, it is believed that Aphanizomenon (flosaquae) would be the more important because of its numerical predominance (2267).

e. Fish and Other Aquatic Life. Algae can be severe pollutants to fish in two respects: (a) they can cause heavy fish mortality through direct poisoning or (b) they can be responsible for oxygen imbalance, thereby killing fish through oxygen depletion or oxygen supersaturation of the waters (373, 410, 412, 413, 414, 415, 416, 418, 427, 2012, 2269, 2279, 2280, 2281, 2282, 2283,

2524)

It has been suggested that possibly Haff's disease (acute attacks involving muscle pain, vomiting, etc.), a European disease always associated with consumption of fish or fish liver, may be the result of absorption by the fish of toxic substances from algal-infested water (406).

A fresh-water dinoflagellate, identified as either a Gymnodinium or Glenodinium, is believed to be responsible for the first recorded mass death of fish (plankton-feeding shad) in fresh water. The water reportedly had

a blood-red color (2213).

Prescott found that fish introduced into a water containing decaying blue-green algae died within two hours. An analysis showed that both hydroxylamine and hydrogen sulfide were present in sufficient concentrations to kill fish (2274).

Dead algae have caused the death of fish by clogging their gills (419, 2495), and by accumulating in a mat on the surface so dense as to prevent a barrier to the penetration of oxygen under the algae (2166).

Anacystis (formerly Microcystis) suspensions and extracts were tested on frogs and carp (2526). The toxin was found to be soluble in water, 96 percent ethanol, and methanol, but insoluble in chloroform, ether, acetone, and absolute alcohol. In neutral solution it was stable to heat at 120°C for 30 minutes, but was readily destroyed by alkali. The minimum lethal dose of dried Anacystis for carp weighing 8-10 gms was 1-2.5 mg; 60-80 gms, 5-10 mg; and 300 to 500 gms, 25-50 mg.

Fish poisoned by algae and in turn consumed by grebes have been assumed to be responsible for the death of grebes (2285). Algae growths reportedly foster increased growth of insect larvae and water fleas in ponds and reservoirs (388, 389, 2213). Bottom fauna have been seriously affected by the smothering effect of thick growths of algae. Welch reports the physical effects of dense growths of the green algae Cladophora as possibly inhibiting the supply of desirable fish-food organisms (2286).

Oscillatoria in water can give fish a muddy taste (414). Cyanogen compounds from blue-green algae have been considered as being involved in fish deaths (413).

Chlorella effected a change in the pumping rate of oysters at concentrations greater than  $2\times10^5$  cells per ml, or approximately 15 mg/l (2985). Another report cites  $2\times10^6$  cells per ml (1448), or 3000 Euglena per ml.

Poisonous plankton organisms consumed by mussels are the cause of paralytic shell-fish poisoning in humans (421). However, the mussel is apparently not readily harmed by the algae or their toxins. See Marine Flagel-

lates and Chapter V-Shellfish Culture.

f. Recreational Use. Excessive growths of algae destroy recreational and esthetic values of lakes, and also cause accidents (210, 369, 378, 395, 2012, 2262, 2524). The filamentous marine alga, Lyngbya majuscula, was believed to have been responsible for numerous cases of dermatitis in beach areas of Hawaii (2287). Although the toxin's chemical nature is not known, it was found to be fairly stable.

Algae can be an esthetic nuisance in another way. Wave action may concentrate a large mass of algae on shore where, if not removed immediately, decomposition will cause the usual annoyances of septic odors (2288).

#### APC VIRUSES

(see Adenoviruses)

# BACTERIA, GENERAL, SAPROPHYTIC

1. General. Although a few bacteria, viz, the pathogens, are inimical to man's welfare, the vast majority of bacteria are beneficial. Together with the molds and yeasts, they are responsible for the dissolution of organic matter and for the concentration of vital elements without which the green plants, and hence man himself, could not survive (2289). The dissolution of organic matter is the prime role of bacteria in the self-purification of streams. Secondarily, they also serve as food for protozoa and other aquatic animals, and therefore are the very foundation or beginning of the food chain that terminates in man.

Although bacteria are unicellular, they may occur singularly or in aggregates. Each cell in an aggregate or colony is physiologically independent. Nevertheless, it is influenced by the environmental changes effected by its neighboring cells. The study of bacterial associations and antagonisms is a fascinating and difficult area. Weindling (2152) listed some of the antagonistic factors, including competition, inhibition, antibiosis, parasitism, and predation (all of which may affect other life forms) (2219), and also some associated effects, including balanced growth, succession, stimulation, and symbiosis. The various associations and antagonisms are important factors in studies of viability of pathogens.

Bacteria have an extraordinarily broad range of biochemical activity. They perform a major role in the life processes on earth by concentrating the elements essential to life itself for use by other species and other forms. The use of radioactive isotopes in bacterial metabolic studies is yielding enlightening information regarding this complex science. The reader is referred to Chapter VIII for some information on concentration factors of certain elements by bacterial species.

Bacteria also make available again essential nutritional factors that have been stored until death in the bodies of plants and animals. Because of this role, they are the workhorses of biological sewage treatment plants and of the natural purification phenomena of lakes and streams (2144).

Insofar as water quality is concerned, bacterial pollution can be divided into two types: (1) primary pollution, which is manifest by the direct introduction of pathogens or other organisms into a body of water, and (2) corollary pollution, in which the naturally occurring aquatic bacterial saprophytes proliferate, thereby becoming pollutants because of:

- a. The introduction of toxic chemicals which may cause bacterial increases by providing additional food substrates in the form of dead plants and/or animals.
- b. The introduction of certain materials and chemicals, such as organic matter and phosphorus (432), which results directly in their extreme proliferation.
- c. The introduction of material, such as an oxygendemanding waste, that will alter the properties of the stream thereby enabling less desirable bacterial species to proliferate.

Bacteria, in addition to being categorized as pathogenic or saprophytic, are also grouped on the basis of their reaction to the presence of nascent oxygen in the immediate environment. Those that require oxygen are aerobic, those to which oxygen is toxic are anaerobic. Organisms that can adapt to either environment are facultative. This grouping is of importance to the water pollution worker. A stream or body of water into which wastes are discharged must remain aerobic for reasons other than appearance, smell, corrosivity, effect on fish and aquatic life, etc., since the aerobic stabilization of organic matter proceeds at a more rapid rate than does anaerobic stabilization.

The use of monomolecular films of hexadecanol to retard evaporation has led to the finding that saprophytic bacteria of the genera Pseudomonas, Flavobacterium, and Alcaligenes attack these films. The incorporation of a bactericide in the film in order that the film may last longer has been suggested (2290). In one lake studied, Pseudomonas and Alcaligenes species increased in numbers but the extent of the increase was not considered sufficient to affect water quality adversely (2291, 2292, 2293). The rate at which hexadecanol films are consumed by bacteria at 26°C increases geometrically with threeweek intervals of time. When the film is removed, the numbers of organisms drop off again, this period also being about three weeks. Pseudomonas and Alcaligenes consume most monomolecular films at the rate of 0.03 to 0.4 lb/acre/day based on laboratory work (2294), a more median rate appearing to be 0.2 to 0.3 lb/acre/day.

Dratchev et al. (2295) studied the distribution of saprophytes in water and foam. They found that the surface film of water has 2 to 10 times, and foams have 100 to 1000 times, the bacterial concentration as the water below.

In lake sediment studies, no significant reduction in bacterial numbers with depth was found in the top five em. Below this, however, a gradual reduction occurs (2296).

Rigler (2140) noted that turnover of phosphate under natural conditions appears to be caused by aquatic bacteria, and that bacteria may compete with algae for the available inorganic phosphate. Watt (2141) added an antibiotic and found that the increase in phosphate turnover time was accompanied by an increase in radioactive phosphorus accumulated in algal tissues. This finding suggests that the aquatic bacteria take up dissolved inorganic phosphorus and release it again in an organic form not immediately available to the alga.

Bacteria that produce vitamin B-12 have been mentioned as a possible triggering mechanism in the blooms of planktonic organisms such as the "red tide" (2297). Bacillus subtilis and Proteus vulgaris are reported to deactivate rapidly the toxin of the phytoflagellate Prym-

nesium parvum (2298).

The bifid bacteria, Lactobacillus bifidus, were investigated as an indicator of fecal pollution. Bifid bacteria are 10 to 100 times more numerous in the feces of man than the coliforms and enterococci. At 4°-6°C, fecal suspensions inoculated with the three types of organisms showed the enterococci to have the highest survival. At 10°-20°C, for the first two days, coliforms and enterococci multiplied, but the bifid organisms dropped in numbers. The third day the coliforms and bifids both dropped at the same rate, whereas the rate of decline of enterococci was lower. The investigators said that water composition and size of inoculum did not influence the survival tests (2300).

Four types of bacteria, Serratia marcesans, a variety of Streptococcus faecalis (S. zymogenes), Chromobacterium violaceum, and two strains of Bacillus globigii were tested as ground-water tracers. S. zymogenes was found most suitable, being isolated over 50 feet away from the dosing well. It was also found to survive over a year in dialyzing sacs, although the number dropped

from  $150 \times 10^6$  to  $5 \times 10^3$  per ml (2151).

Spores of the nonpathogenic (to man) Bacillus thuringiensis are utilized as a living pesticide that is known as Thuricide (2299, 2527) (see also Chapter IX, Pesticides).

Joseph (2301) made a microbiological study of acid mine drainage streams with pH of 2.0 to 2.9. There was a clear paucity of numbers of bacteria. However, the genera Escherichia, Aerobacter, Bacillus, Micrococcus, Sarcina, Thiobacillus, Crenothrix, and Microsporium were identified.

2. Cross References. Pathogenic Bacteria, Coliform Bacteria, Iron Bacteria, Sulfur Bacteria, Slime Bacteria, Fecal Streptococci, Algae, Protozoa, Insects, Crustaceae, Marine Flagellates, and Chapters V, VIII, and IX.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Bacteria antagonistic to E. coli have been isolated from surface waters. They include Micrococcus, Sarcina, Pseudomonas, Flavobacterium, and others. Their presence serves to reduce the numbers of E. coli (435). Pseudomonas, of which most species are not pathogenic, is sometimes associated with gastroenteritis. Two papers have been published urging that P. aeruginosa be included in the sanitary examination of drinking water (2302, 2303). Other saprophytic bacteria such as Pseudomonas, Flavobacterium, and Chromobacterium can discolor water supplies, but other-

wise they are generally not harmful. Bacterial growths can also impart tastes and odors to water either because of waste products of their own metabolism or by transformation of sulfate, proteins, or other chemicals (152).

Many surface and ground waters are said to contain sufficient organic matter to support abundant growths in filters. Such growths have been mentioned as a principal cause of caking and short circuiting (2304). The accumulation of dead and dying plankton in filter sand is said to offer an excellent substrate for the growth of such forms as Pseudomonas. Hence, because some members of this genus may be associated with gastroenteritis (2305), rich plankton growth may be indirectly connected with intestinal disturbance in man (2182). Proteus has been mentioned as a possible pathogen (2305).

Russian workers, in a report on microorganisms causing the appearance and disappearance of tastes and odors in water, report that the odorous gas produced by Actinomyces can be used as a carbon source by other soil and water organisms. The periodic disappearance of odor from water was attributed to these forms, all of which were Pseudomonas strains (2256) (see also Ac-

tinomycetes).

In water below a thermocline, the dissolved CO2 resulting from decomposition processes can redissolve settling, precipitated normal carbonates, thereby producing an increase in hardness (2304).

b. Industrial Water Supplies. Growth of bacteria in water may interfere with many industrial processes such as the manufacturing of leather products (254), paper (212, 436), textiles (212, 405, 450), breweries (170, 171, 175, 449, 2308) and food processing (179, 223, 224, 437).

Iron, manganese, nitrogen, and sulfur bacteria are a nuisance in waterworks, boilers, and many other industries because of their corrosive action on metals, concrete, and rubber (198, 208, 438, 440, 442, 443, 444, 448, 449, 1050) (see also Iron Bacteria and Sulfur Bacteria).

A Pseudomonas infestation of nuclear reactor cooling water has been reported (2309). Concentrations of 108 organisms per ml were thriving on the carbon and nitrogen released by the disintegrating resin of the deionizers

used in treating the water.

In an investigation of organic fouling of anion exchange resins, Frisch and Kunin (2310) inoculated such resins with various water microorganisms in trace salt solutions but found the rate of attack to be negligible.

The fall in pH of cooling water has been reported as due to the formation of nitrous and nitric acids from ammonia through the action of nitrosofying and nitrifying bacteria (2311).

- e. Irrigation Waters. Although saprophytic bacteria play an essential role in the growth of all plants, no publications pertaining to the effects upon irrigation farming of any sewage saprophytes in polluted waters have been encountered. Most such work appears to be concerned with the ultimate fate of pathogens. Biological growths in soil are a factor that influence soil permeability, hence rate of percolation (2312).
- d. Stock and Wildlife Watering. No papers dealing with the effects of saprophytic bacterial pollutants of water upon animal watering were found. However, in eggs experimentally infected with Pseudomonas, subsequent washing of the eggs in waters containing one to

five mg/l of iron may introduce iron into the egg in sufficient quantity to increase the rate of spoilage (2306).

e. Fish and Aquatic Life. Occasionally bacteria that are ordinarily considered saprophytic have infected fish and caused disease (445, 446). Oxygen utilized by bacteria during decomposition may significantly deplete dissolved oxygen and result in fish kills, especially in winter with an ice cover (447). Sewage decomposition by bacteria stimulates development of plant growth (such as algae) increasing the supply of fish-food organisms (367). Bacillus subtilis was preferred by ciliates as a food over other bacteria tested (see Protozoa) (2313).

f. Recreational Use. Alcaligenes faecalis is reported to have been found in a swimming pool where it was highly resistant to halogen disinfectants. This nonpathogen is widely distributed in decomposing organic matter and has no significance in the sanitary analysis of swim-

ming water (2315).

Levine et al. (2316) suggest that Streptococcus salivarius, Neisseria catarrhalis, and N. sicca (also Staphylococcus aureus—see Pathogenic Bacteria) are worthy of consideration as indicator organisms for swimming pools.

A report to the British Ministry of Health in 1953 recommended that 75 percent of 37°C total plate counts should not exceed 10 colonies and that the remainder should not exceed 100 colonies (2317). The same report found that Neisseria catarrhalis was seldom isolated where free chlorine residuals exceeded 0.1 mg/l. Alphahemolytic streptococci and staphylococci were too resistant to chlorine to be suitable indicators.

Russian standards for swimming pool waters include a total bacterial count requirement of less than 1000/ml (2592).

## BACTERIOPHAGES

(see also Viruses and Coliform Bacteria)

Bacteriophages are submicroscopic parasites of bacterial cells. They are highly host specific, and this property is used in the laboratory to differentiate between various strains of the same bacterial species. Specific bacteriophages active against many pathogenic bacteria have been found in sewage-polluted waters. This relationship has prompted a number of investigations to explore the use of phage as an indicator of pollution. Results show that bacteriophage counts cannot be correlated with water potability (456), nor with Escherichia coli content (coliphage not studied) (2318). An interesting observation has been reported from Europe where, in polluted stream stretches, the Vi-phage curve was similar to that of chemical and bacterial criteria of pollution (2319). One report mentions agreement between coliform counts and salmonella phage content (2320). Four reports cite the insignificant role played by bacteriophage in the reduction of bacterial numbers or in the purification process (451, 453, 455, and 740).

With respect to bacteriophages in sea water, Guelin has published two papers, both of which concluded that a direct relation exists between the amount of bacteriophage and numbers of bacteria, hence fecal pollution of the sea (452, 2321). A recent study by Carlucci and Pramer, however, in which phages active against E. coli, Aerobacter aerogenes, and Serratia marinorubra were

isolated without difficulty with suitable enrichment procedures, observed that the effectiveness of coliphages was dependent on the presence in sea water of sufficient nutrients to support growth and multiplication of host cells (2156). The same workers reported that coliphages were inactivated rapidly in natural sea water but persisted in filter and heat-sterilized sea water. Diernert (454) in 1944 stated that a bathing water was usually satisfactory if no bacteriophages were present in 20 ml of the water. Gilcreas and Kelly report that at 60°C, phage is more resistant than either animal viruses or coliforms. Differences in survival rate between coliforms and phage is dependent on temperature rather than upon response to pH levels (2322).

#### BEAVERS

A study of beaver activities on water quality concluded that such impoundments have considerable organic matter, marked color, increased coliform and total bacteria counts, increased chlorine demand, increased water temperatures in summer months, but no apparent effect on palatability (2307, 2314).

#### B. COLI

(see Coliform Bacteria)

#### BIRDS

The Ninth Pacific Northwest Symposium on Water Pollution Research pointed out that the covering of all finished waters in the Pacific Northwest is long overdue and the problem of bacterial contamination by birds of such waters often underestimated. Five cities in Washington could not meet bacteriological standards during 1960 because of contamination by birds (2528).

#### CARP

One report has named carp as a pollution problem in some rivers because they tend to dominate the waters they inhabit. Since they are bottom feeders they agitate bottom muds making it more difficult for other fish to find food, and making the water unfit to drink and unpleasant for swimming (2529).

# CHIRONOMIDS

(see also Insects, Mosquitoes, and Chapters VIII, IX, and X)

Chironomids have appeared frequently in the water pollution literature. They are sometimes mentioned as pests in potable supplies, sometimes related with varying types and densities of pollution, and sometimes mentioned as a part of the beneficial fauna of polluted waters. There is a question, apparently, as to their location in the scheme of biological classification (2420). However, it is the larvae of Chironomus and not the adult midge that has attracted so much attention in the water field. It is a red-colored larva commonly called a bloodworm since many species have hemoglobin in their blood (15). Since some entomologists assign them to the genus Tendipes in the order Diptera of Insecta, the names Chironomus and Tendipes can be used interchangeably. Unidentified or non-chironomid midges are discussed under Insects.

Chironomid infestation of potable water supplies is discussed by Ingram and Bartsch (2420) and by Palmer (2213). A Cincinnati case resulted from migration of chironomids from an uncovered clear well into the distribution system. The clear well had an accumulation of leaves and algae on the bottom, forming an ideal habitat for the bloodworms. Chironomids in a glass of drinking water are probably more revolting than nemotodes because of their red color. Bloodworms in finished water tanks have been observed in other locales also-but all were believed to originate from the direct ovipositing of eggs by the adult female midge and not by penetration of the worm or larvae through the filtering system. A very strong taste and odor from minute red worms (presumably Chironomus) has been reported (2530). Chironomus larvae are tube-building creatures, and in slow sand filters these tubes allow water to pass through upper sand layers without filtration (2420). Chironomus is quite sensitive to chlorinated hydrocarbon and organic phosphorous insecticides, Silvey quoting toxic values in the range of 0.006 to 0.04 mg/l. However, they are quite resistant to chlorine, Silvey noting that seven mg/l in 24 hours is necessary for destruction (2531). Ritter describes controlling a slight infestation with 100 mg/l of chlorine as hypochlorite in one year, and the following year a severe infestation with 0.01 mg/l DDT. Small amounts of chlorinated hydrocarbons reportedly prevent Chironomus from building tubes (0.005 mg/l BHC, 0.02 mg/l DDT) (2532). Nevertheless, Averett (2533) notes a report by Webb (2534) that chironomids were the first to reappear in a stream that had been polluted with DDT. See Chapter IX, Pesticides, for more information on specific insecticides.

Chironomids, as do all aquatic life, concentrate certain elements (2535). For various concentration factors and further information in this respect, see Chapter VIII, Radioactivity. However, *Tendipes plumosus* and *T. attenuatus* fourth instar larvae cannot be used as indicators for P-32 or F-59 because their rate of uptake is too low (2536).

Effects of Chironomus riparius on activated sludge that had been allowed to settle and consolidate for six months was to raise the pH value and the oxidation-reduction potential. The pH of the water above was increased, as well as the concentration of ammonia, and the concentration of oxidized nitrogen reduced (2537). Experiments showed that the addition of chironomids increased the decomposition of cellulose (2139). Midge breeding (Chironomus novaezealandiae) is reported to be confined to environments of low salinity (0.47 percent chloride) or fresh water, but is unrelated to pH (2538). Chironomus are among the most sensitive fishfood animals tested against synthetic detergents (2116). See Chapter X, Surface-Active Agents.

In Florida, the adult midge is called a "blind mosquito"—even though it doesn't bite. Overproduction of chironomids has been linked to excessive nutrients such as come from a sewage treatment plant effluent. The major chironomid pest, Glyptotendipes paripes, breeds on sand bottoms irrespective of depth, turbidity, pH and alkalinity, and feeds on algae non-selectively to the extent of 99 percent (2539).

The presence of certain chironomid larvae in large numbers is characteristic of grossly polluted areas (2540, 2541, 2542). Predatory chironomids such as Anatopynia dyari and Pelopia stellata have a wider range and their use as indicator organisms is limited. Four red-blooded chironomids showed a considerable difference in pollution tolerance, C. riparius confined to septic and recovery zones, and Stictochironomus varius and Microtendipes pedellus to clean water areas, but C. decorus were ubiquitous (2543). The tendipedids make their appearance in the sequence of recovery sooner than the mayflies and stoneflies (2544).

Larvae of *C. riparius* have been recorded in densities exceeding 100,000 per square meter (74). Butcher (2545) reports that organisms associated with gross pollution include "sewage fungus," tubificid worms, and *Chironomus* larvae. Sediment is least likely to bother tube-building creatures such as chironomids (2546).

The oxygen consumption rates of *C. riparius* have been studied (2547). In badly polluted waters they can lower the dissolved oxygen in a river by over 1.0 mg/l per mile at 15°C (2548) or 1.5 mg/l per mile (2126).

Bartsch and Ingram note that sludge worms such as Tubifex and Limnodrilus are found in great numbers closer to the source of pollution than any other bottom dwelling animals. In turn, they are replaced by Chironomus, and they by Asellus (2143). Since chironomids require at least a very small amount of dissolved oxygen, they will not be found in completely septic waters.

# COLIFORM BACTERIA

1. General. The direct search for the presence of a specific pathogen in water is too uneconomical, slow, and unwieldy for routine control purposes. Instead, water is examined for an indication of fecal contamination, and when such indication is found, it is assumed that the water is potentially dangerous.

Several chemical and bacteriological tests for sewage pollution have been tried and found inadequate, including the total bacterial plate count on agar at 37°C. Now, however, the demonstration of the presence of coliform organisms in a water sample is regarded as evidence of such pollution and has served for many years as a basis for water-quality criteria (2549). For judicial expression in this regard, see Chapter IV.

The coliform group of organisms includes, by definition, "all aerobic and facultative anaerobic, Gram-negative, nonspore-forming, rod-shaped bacteria that ferment lactose with gas formation within 48 hours at 35°C, and is equivalent to the B. coli and coli-aerogenes groups of early editions of Standard Methods for the Examination of Water and Wastewater (469). It embraces organisms of diverse origin among which the best known are (a) Escherichia coli strains, which are usually, but not always of fecal origin, and (b) intermediate and Aerobacter aerogenes strains, which are usually, but not always, of soil, vegetable, or other non-fecal origin. E. coli has been frequently proposed as a more specific and reliable indicator of fecal pollution than the broader coliform group (470, 471, 472). Delaney recommends thorough comparative studies between E. coli and coliform tests for any individual supply, and as an interim

standard in all water except drinking water suggests that the maximum limit for E. coli be one-half the pres-

ent coliform standard (2550).

Nevertheless, there is still enough doubt as to the significance of the various types of coliform organisms that their differentiation in routine water analysis is unwarranted. At times, however, it may be advantageous or desirable to identify the organisms further as, for example, in a study of unexpected coliform densities that might be explained by the multiplication of nonfeeal forms on materials such as jute packing in the

distribution system (473, 2551). The effect of the use of the coliform group instead of E. coli as the basis for standards is to make the water relatively safer. However, since the coliforms are only indicative of pollution rather than specific, there is some question as to whether they can stand the test of rigid court examination (481, 482). An Illinois court decision (482) held that rather than being positive proof of contamination, high counts of coliforms occurring over a long period of time without outbreaks of typhoid fever might even indicate safe water (see Chapter IV). In doubtful cases, therefore, it may be advisable to com-

plete further tests for E. coli for legal protection.

Until 1936, the results of the coliform tests were expressed officially as the coliform index, or B. coli index, the reciprocal of the highest dilution in which a positive result was obtained when a geometric series of samples was planted. Since 1936, the number of coliforms present have been expressed generally in terms of the most probable number (MPN), a value now regarded as more precise though still subject to error (334, 469). One result of the change in terminology has been some confusion in the literature, especially engineering review articles; in many papers, also, there is insufficient comprehension of the difference between B. coli group (coliform organisms) and E. coli (152, 330, 334, 469, 715). The British use the term B. coli group to refer to the coliform group, of which E. coli is a member.

The effectiveness of the coliform standards has been demonstrated by the decrease in incidence of waterborne enteric diseases, although the standards adopted have often been criticized as arbitrary. Their use has also been justified by studies of the relative death rates of coliforms and enteric pathogens under natural conditions (487, 488, 489) and when exposed to various bactericides (302). Under certain conditions, such as at different pH values and temperatures, some strains of Salmonella, Shigella and M. tuberculosis (301) may be more resistant to disinfectants than the coliforms, particularly E. coli. Such data are suggestive that occasionally, as a measure of the effectiveness of purification processes, the significance of the absence of coliforms may be open to doubt (490, 491, 492, 493, 494). The increasing importance placed upon virus-transmitted illness in water supplies serves to cast further doubt (121, 2528, 2552). A study of the bacteriophage titer and E. coli counts indicated no relation (2318). The enterococci were reported to be useful when E. coli were absent or present only in small numbers (1503, 2553). In a discussion of coli determinations, it has been suggested that other organisms (germs of the coli group) be considered (2554).

While a discussion of the efficiency of treatment methods is beyond the scope of this report, it is believed that the subject should be briefly noted inasmuch as it points to the need to continue to search for more accurate and reliable indicators and techniques for water examination. There is a need also for indicators of bacterial contamination of non-intestinal origin, particularly organisms responsible for eye, ear, and nose and throat infections (495, 496, 497), as well as for viruses, protozoa, and worms (330).

On the other hand, the status of the coliform test has been strengthened by analytical studies of the relationship between the coliform index and the probable number of S. typhosa of different supplies (489). It has appeared likely from these statistical analyses that the pathogen/coliform ratio remains reasonably stable throughout the purification process up to about 99.9 percent reductions from contaminated water, although after that it is possible that the coliforms die off more rapidly. Further studies are needed, especially to explain the occurrence of occasional outbreaks of typhoid caused by water supplies that meet the accepted standards but have already undergone over 99 percent purification and are in the doubtful ratio-value area.

Other potential indicator organisms have been suggested to supplant or supplement the coliform tests, but although better and more rapid procedures are constantly being sought, the coliform test still remains the most

practicable (see Fecal Streptococci) (2552).

In a Louisiana survey, water samples with high total counts also had high counts of coliforms, E. coli, and enterococci. In polluted surface waters, numbers of coliforms increased in heavy rainfall. But in heavily polluted drainage ditches, numbers decreased. The difference between the most and the least polluted waters in this survey was better indicated by the enterococci than the

coliforms (2555). Connecticut River samples over a two-year period gave a coefficient of correlation of E. coli and enterococci of +0.84. The density of the enterococci was 7.6 times that of E. coli (2556). The work of Kenner, et al. (2557) shows that the densities of fecal streptococci in various polluted waters are of the same approximate order of magnitude as the confirmed MPN coliform density. In classifying the extent of fecal contamination of bottom deposits, the numbers of E. coli and S. faecalis together

constitute the best criterion (2558).

Actually, an effort is made in practice not to give undue weight to the results of the bacterial tests alone, and it is required that the interpretation of quality of a water should be based on the combined findings of the bacterial examinations and a sanitary survey of the area in question, covering such items as potential sources of pollution, opportunities for self-purification, tides, and currents (334, 469, 481, 483). In studies of the ocean, for example, no coliforms have been found in open waters at places remote from possibilities of contamination from land, but they are often found in bays and estuaries, and in high densities near outfalls (484, 485, 486).

Coliform organisms may gain access to water from many sources, primary among which are excretions from human beings, animals (476), amphibians (477, 478), and birds (479, 480); surface run-off; and the multiplication of non-fecal forms on fibrous and vegetable substances in the water. More coliforms are discharged by healthy individuals than by sufferers of diarrhea (2559). Inasmuch as the bacterial flora vary from one source of supply to another, standards must not be interpreted too rigidly. A recommended practice is to rate each individual supply on the basis of frequent examinations, and to suspect at once any deviations from the usual quality (469). Nevertheless, many state and interstate water-pollution-control agencies have established standards or criteria for coliform densities in surface waters. For details regarding such standards, See Chapter III and the appendices thereto.

Not only the variety of sources, but also the complexity of microbial interrelations is deserving of mention. Vinberg and Sivko (2560) note that the viability of B. coli is greately reduced by profuse growth of green plankton. Also, Neel and Hopkins (99) point out that coliform bacteria in sewage lagoons are markedly reduced during seasons of prolific algal growth. Indeed, the antagonistic relationships of some pathogens and coliforms (1504) has raised the question as to whether it is desirable to exclude coliforms from water entirely

when promulgating standards (1383).

Studies of the survival of coliform organisms under a variety of environmental conditions continue to accumulate. Buck et al. (1506) studied survival in estuary water in the laboratory and reported results ranging from 293 to 450 days. Public Health Service laboratory studies with sea water, temperature 2.5-5°C, demonstrated significant survival after 15 days for both *E. coli* and *Salmonella* (1509). Carlucci and Pramer (2155) conclude that the reaction and salinity of natural sea water do not favor survival of *E. coli*.

Vaccaro et al. 486 report the viability of *E. coli* in sea water to be less in summer than winter. Sterilized sea water (boiled, autoclaved, pasteurized, or chlorinated) has less bactericidal activity than raw sea water. Addition of organic matter decreases bactericidal activity. See also De Balsac (1508).

Ketchum et al. (1507) state that dilution is the least important and bactericidal action the most important factor in the decrease of coliforms in sea water.

Coliform organisms were inoculated into sea water and incubated at 5°, 18°, and 30°C. The 18° and 30° samples behaved similarly, showing a rapid decrease after a stable one- to three-day period. The 5° samples showed insignificant changes for periods up to 7 days. In these studies, it was demonstrated that viability in fresh water was not appreciably greater than in sea water and at times it was even less (2561).

Viability studies in water from Great Salt Lake indicated 8-hour survival at 23°C was of the order of 1 to 2 percent, whereas at 6°C, 50 percent survived 24 hours (2562). B. coli is reported to be less viable in the pH range 6 to 7 than at 5 to 6 or 7 to 8 (2563). Carlucci and Pramer (2155) noted that pH 5.0 was more favorable than alkaline reactions for the survival of E. coli in both sea water and in 3 percent NaCl solutions. Studies of coliforms in sediment around marine sewage outfalls disclosed that generally they were found in

areas beneath the path of movement of the effluent field in the surface water (2564).

The presumptive coliform count was found to be unsatisfactory for studies of pollution in harbor areas where old sewage was returned by wind and tidal action (2567). Two Sardinian waters of alkaline bicarbonate type were inoculated with E. coli suspensions and maintained at cold and room temperatures in the dark. Results showed 20-day survival at the cold temperature, 28 days at room temperature (2565). At 8°-10°C, E. coli in water survive 3 to 5 weeks, and at 20°-30°C they multiply and will still be present to an extent greater than their original numbers after 40 weeks (2566). Czechoslovakian work on the coli-aerogenes group in different waters showed survivals of 8 to 12 months (2568). An E. coli titer of 0.004 ml (25,000/100 ml) remained constant for 160 days in a water containing humus (2569). B. coli type I was reported to survive much longer in alkaline than in acid soils (2570).

Season is reported to be a major factor in the occurrence of coliforms in wells, higher counts reported for warmer months, lower counts for colder months (2571). Some evidence was obtained showing that percolation of rain increased numbers, none that rainfall decreased numbers by dilution.

The numbers of *E. coli* in foams were reported to be 100-1000 times the number present in the body of the water (2295).

Many papers have been concerned with the percolation of polluted water through soils and the likelihood that ground waters will subsequently become infected. Rudolphs et al. stated that the distance pollution travels from bored latrines to ground waters depends mainly on the velocity of the ground-water flow. This distance varies with soil structure, gradient of the water table, and other factors (1382). Subrahmanyan and Bhaskaran (1399) believe that the safe distance between a borehole latrine and a ground-water source is the distance represented by about 8 days of ground-water travel. Stiles et al. reported that B. coli have travelled 1 to 232 feet from the source of pollution, and Caldwell found that coliforms travelled only 10 feet from a pit privy (1511). For more complete information, see the references cited in Chapter II, section on Natural Purification in Ground Water.

In studies on water-saturated sand columns, coliforms did not penetrate much beyond six feet in 417 days (water velocity 0.4 ft/day). Doubling the velocity reduced coliform arrival time at four feet from 114 to 82 days (122). Underground travel of  $E.\ coli$  of 250 feet is reported from Washington (1467a).

The question of the time factor in sewage saturated ground is pointed up in Minnesota experience (97). Fifty percent of well samples in older communities and 10 to 20 percent in young communities contained coliform organisms.

Wyss (2572) reports that there is still no evidence of coliform organisms attaining any resistance to chlorine in spite of the large scale use of chlorine for over 40 years.

For an excellent discussion of the entire coliform group of organisms, see Senn (2573).

- 2. Cross References. Pathogenic Bacteria, Protozoa, Fecal Streptococci, Mycobacterium tuberculosis, Pasteurella tularensis, Viruses, and Chapters IV, V, VIII, IX, and X.
  - 3. Effects on Beneficial Uses.

The first bacteriological a. Domestic Water Supplies. standard for water adopted by the U.S. Public Health Service, at that time in the Treasury Department, was devised for waters supplied to the public by common carriers in interstate commerce. It has been pointed out (498) that the standard was established for drinking water in specific conditions where judgment must be based on laboratory analysis alone and without the benefit of repeated tests and information about the sources of supply. As the application of this standard came to be extended to water supplies in general all over the country it was open to criticism as being too strict, arbitrary, and impractical for many municipal supplies. On the other hand, it has been held that the standard is not strict enough (499, 500, 501, 502, 503, 1744, 1745, 1746) and that the ultimate goal should be the elimination of all coliform organisms from drinking water. Orchard (504) has reviewed the early history of the Treasury Department Standard and made comparisons in effect in other proposed or tentative requirements in effect in various states. The most recent revision in the USPHS Drinking Water Standards, dated 1962, still bases bacteriological requirements solely on the coliform group (2574).

Reviews of the development, history, and significance of drinking-water standards in the United States have been presented by Buswell (1513) and by Gilcreas (1514). The limits of coliform bacteria used as guides in several American countries, as described by Caballero

(1457), are given in Chapter V.

The incidence of water-borne disease attributable to public water supplies in the U.S. has dropped markedly since the beginning of this century and most of the few outbreaks in which public supplies have been incriminated have been traced to accidents or breaks in the sanitation (417, 507, 508). One exception that has gained wide attention is an epidemic of gastroenteritis in Minneapolis, unquestionably water-borne although the water conformed to the standard (334, 671). While it is possible that the outbreak was caused by some other factor than bacteria, it has been suggested that possibly a standard based on a presumptive coliform test only might be safer.

Although pathogenic coliforms were reported as far back as 1929 (520) and 1936 (711), studies of these forms seem not to have created interest until the past decade (see Pathogenic Bacteria). It is perhaps unfortunate that the pathogenic coliforms were overlooked for so long, since a decision such as that rendered by the Supreme Court of the State of Illinois could not possibly have been made (see Chapter IV, People v. Bowen (1941) 376 Ill. 317, 33 N. E. (2d) 587).

Pathogenic serological types of *Escherichia coli* reported from Russia include 0111, 0125, 026, 055, and 408 (2575); from Yugoslavia 025 and others (2305); from France 111:B4 (2576); and from Hungary 0124:K72 (B17): H 32 (2577). All varieties were associated with gastroenteritis in young children. The Russian paper

reported the above strains to be quite resistant, surviving four minutes in water heated to 90°C, and from 10 days to 165 days under various environmental conditions. Burdin and Schmitt (2578) regard the pathogenic forms as further argument in favor of regarding water nonpotable if it contains Escherichia coli.

Nevertheless, H. A. Thomas, Jr. has estimated that as typhoid incidence and carriers decrease among the general population, the capacity of a water with a fixed coliform density for transmitting typhoid fever also decreases. It has been suggested, therefore, that the present U. S. standard could be relaxed without loss of safety to permit 35 percent of 10 ml tubes to be positive (503).

Although the foregoing discussion is of general interest to most sanitary engineers, it is relevant to this investigation of water-quality criteria only in that it provides background information for, and leads up to, a consideration of allowable coliform densities in raw water in streams, lakes, and ground-water basins. The U.S. Public Health Service has established a classification system for raw-water sources according to the kind and degree of treatment they will require in order to bring them up to the standard set for drinking water.

The first such raw-water standard was adopted prior to World War I by the International Joint Commission of Canada and the United States for sources of water located in the international boundary waters between the two countries. A yearly average B. coli index not exceeding 500 per 100 ml in the raw water was fixed as a limit on the advice of a board of expert sanitary engineers. This limit was predicated on the assumption that waters carrying such a bacterial load actually could be purified by methods in use at the time to meet the drinking-water standard, i.e., an index of two per 100 ml (334, 340, 509).

Shortly after this standard was promulgated, H. W. Streeter of the USPHS, began a comprehensive series of field and experimental investigations of the efficiency of current treatment systems under actual operating conditions in order to establish an empirical basis for rawwater criteria (156, 337, 509, 510). Using the information gathered over a period of years, the USPHS has made certain recommendations for limiting coliform densities in raw-water. By no means mandatory and without the effect of law, these recommendations are interpreted as a guide in the field of water sanitation. The 1946 recommended classification which is still in effect is quoted in Appendix Q.

It is of interest to note that in the Chanute, Kansas, drought experiment (2119), in which a treated sewage effluent was cycled through a domestic water reservoir, the number of coliform organisms in the raw water was less than that found when the river was flowing normally. The tap water during this emergency consistently met Drinking Water Standards for bacteriological quality.

b. Industrial Water Supplies. The bacterial requirements for industrial water vary widely depending on the purpose to which the water is put. In the food-handling industries, bacterial quality requirements may be more stringent than for domestic water supplies inasmuch as bacterial contamination may result in fermentation, taste changes, and/or spoilage. For further details relating to

specific industries, see Baking, Brewing, Carbonated Beverages, Confectionary, Fermentation Processes, Food Canning and Freezing, Food Equipment Washing, Food Processing—General, and Ice Manufacture, in Chapter V. In many such industries coliform organisms are used as indicators of contamination, although where fermentation and spoilage are involved, a total plate count would appear to be more indicative.

The California State Board of Public Health has prescribed standards for water used in fish canning operations. The *E. coli* standards for untreated waters is 7/ml, and for treated waters 3/ml. In the whole fish handling operation, 20 percent of the samples may equal or exceed the bacterial standard, whereas in the cut fish handling operations only 5 percent may equal or exceed the standard (2579).

c. Irrigation Water. Few studies have been made of the sanitary quality of irrigation water, and there are differences of opinion among health authorities as to the health hazards involved. There is a definite need for basic data (511).

Norman and Kabler (1515) made coliform and other bacterial counts in samples of river and ditch waters, and of soil and vegetable samples in the fields to which these waters were applied. They found that although the bacterial contents of both river and ditch waters were very high, both soil and vegetable washings had much lower counts. For example, where irrigation water had coliform counts of 230,000 per 100 ml, leafy vegetables had counts of 39,000 per 100 grams and smooth vegetables, such as tomatoes and peppers, only 1000 per 100 grams. High enterococcus counts accompanied high coliform counts in water samples; but enterococcus counts did not appear to be correlated in any way with coliform counts in soil and vegetable washings (1515). Dunlop et al. (2580) obtained ratios of 255,000 coliforms and 4,800 enterococci to one Salmonella, computed from the median values.

British workers filtered a gallon of type I coliforms in peptone water (150 x  $10^6/\text{ml}$ ) through 18 inches of uncultivated garden soil and found no reduction in numbers. Two days later, sterile distilled water was filtered through the same place and yielded a type I count of  $1 \times 10^6/\text{ml}$ . Three months later, a count of 100 per ml could still be obtained in this manner (2581).

Bringmann and Kuhn (2582) studied B. coli on plants from the sprinkler application of sewage under controlled conditions of relative humidity. They could not remove all the bacteria from leaf surfaces so they planted plant parts in a liquid medium, incubated for 24 hours, and then streaked Endo plates. Although their studies with plant extracts demonstrated that some were bactericidal or bacteriostatic, neither mechanism was observed when using the plant part. B. coli counts were stable at 100 percent humidity, lower humidities giving shorter survival. At 40 to 60 percent humidity, B. coli frequently did not survive the 6-day experimental period.

In later studies on clover, they found that Endopositive clover leaves of sewage-sprinkled plants dropped in the first 12 to 14 days to the same level as controls and remained at the same value for up to 26 days. Sunshine was observed to have a restricting influence on bacteria survival, but rainfall had little effect (2583).

The work of Bringmann and Trolldenier (2584), however, states that although the percentage of coli-positive leaves reached a constant value after 14 days, this constant value was always higher than that of controls not watered with sewage. The later paper also discusses secondary infections of clover leaves which give higher counts and which depend on rainfall and relative moisture.

In a discussion of bacterial and chemical pollution of ground water (2585), bacterial build-up in the soil is reported to occur owing to the long survival time of *E. coli* in comparison with percolation rates. Coliforms are reported to have travelled from 10 to 232 feet with

ground water.

In the absence of widely accepted bacterial standards for irrigation, health authorities in this country have recommended a high degree of treatment for sewage effluents to be used in irrigation. The California State Department of Health (512, 513) adopted in 1933 the following rules, in part, regarding the use of sewage effluents for crop irrigation purposes: Partially treated or disinfected effluents shall not be used to irrigate garden truck, berries, or low-growing fruit. Nursery stock, cotton and field crops (to be processed after harvesting) may be watered with such partially treated or disinfected effluents provided that no milk cows are pastured on land moist with sewage or have access to ditches carrying such sewage. These restrictions do not apply to well-oxidized and disinfected effluents which meet the following bacterial standards: "In any 20 consecutive samples from which five 10-cc. portions each are examined, not over 10 portions shall be positive for members of the coli-aerogenes group, and in no single sample shall over half the 0.1 cc. portions of the sample of effluent be positive for the above organisms." In addition the effluent must be inoffensive.

The Conference on Polluted Irrigation Waters at El Paso, Texas, in 1950 recommended that for use in cultivation of human foodstuff, especially that to be eaten raw, water reclaimed from sewage should be sterile (511).

Studies of the use of sewage-contaminated irrigation water indicate that bacteria, both pathogenic and coliform types, do not penetrate the whole unbroken skin of fruits and vegetables. However, superficial contamination of food may be caused by splashing or other accidental means, and slightly cracked or injured fruit may then be attacked by surface bacteria and become heavily infected internally (302, 511, 514, 515, 516). On crop surfaces and in sewage-irrigated soil, intestinal bacteria of many kinds can survive for periods varying from a few days to many months, long enough to render foods infectious to human beings. The work of Rudolfs et al. (515) has demonstrated the survival of E. coli for as long as 35 days. Outbreaks of enteric bacterial diseases among people have been linked with the consumption of raw foods which have been sewage irrigated (272, 511). On the other hand, it has been declared that over a period of one hundred years during which sewage farming has been carried on, in South Africa particularly, extremely few or no epidemies among humans or animals

have been traced directly to this practice (301, 517, 518, 1027)

It seems that still further studies, both laboratory and epidemiological, are needed in order to clarify and evaluate the relationship between the use of contaminated irrigation water and the health hazard of eating vegetables irrigated with such water.

d. Stock and Wildlife Watering. Limiting concentrations of coliform organisms in contaminated water used for stock watering have not been found in this survey. Few studies have been made on the degree of pollution safe for natural waters consumed by stock, and there is a difference of opinion as to the need for regulation. It is recommended that more work be done to determine whether cattle and other livestock can be infected by the bacteria found in sewage (301, 303), even though cows have been reported to remain free from disease when their only source of water was contaminated by sewage and pathogenic bacteria (299, 300, 301, 302). See Fecal Streptococci, Mycobacterium tuberculosis, Pasteurella

tularensis, Pathogenic Bacteria, and Viruses.

e. Fish and Aquatic Life. Guelin (2321) compared the coliform flora of fish caught in the open sea in the Mediterranean with fish caught in coastal waters. In open-sea fish, he found no Escherichia coli, no coli bacteriophage, and no other bacteria that would ferment lactose. Among the coastal fish however, he found E. coli, coli phage, and other organisms from the human intestine. Several years later (2586) he studied the possibility of using fish as a means of testing the sanitary quality of the water in which they were found. He found that fish placed in contaminated (E. coli-containing) water became contaminated themselves and within a 60-minute exposure, organisms could even be isolated from the viscera. If the fish were transferred to fresh (presumably uncontaminated) water, they freed themselves of the

organisms in a 6 to 7-day period.

f. Shellfish Culture. Outbreaks of typhoid fever and other intestinal diseases have been directly traceable to the consumption of contaminated oysters (334, 522, 523, 524). In 1925, following widespread shellfish-borne typhoid epidemics, the USPHS was requested by state and local health authorities and the shellfish producers to exercise supervision over the sanitary quality of shellfish shipped in interstate commerce. The Surgeon General appointed a committee from a panel of health officials to formulate recommendations. With regard to shellfish-growing areas, the committee's report stated that the beds should be free from any justifiable suspicion of dangerous contamination with disease-producing microorganisms, as well as other deleterious contamination. Subsequently, many studies of the quality of growing areas were made by the USPHS and state personnel, and the sanitary status of all of the important shellfish-producing areas was generally determined (523, 525, 526).

On the assumption that evidence of sewage pollution in a shellfish-growing area must be looked upon as a potential hazard, limits have been prescribed for the bacterial concentration of the water overlying beds used for the production of marketable shellfish, including oysters, clams, and mussels (527). However, it is recognized that the bacterial counts of shellfish cannot always

be correlated with those of the water, since the counts vary with the temperature, tides, and the physiological activities of the individuals (334, 528, 869). Also studies in Manila waters showed no correlation between seasonal variations in the coliform content of the waters and the coliform content of the oysters taken (1518).

E. coli appears, in some respects, to be a more suitable indicator for such waters than the coliform group (334, 472, 529, 2452); nevertheless, in the absence of practical routine methods for E. coli determinations, bacterial criteria applied to shellfish waters have been based on coliform concentrations and E. coli differentiations are optional. According to the Manual of Recommended Practice for Sanitary Control of the Shellfish Industry (481), the coliform group shall be considered as including all organisms which upon transfer from a positive presumptive test show fermentation in brilliant-green lactose bile broth, the confirming medium for coliforms, without proof of the presence of E. coli; although, if there is a possibility that the examination may become the basis for legal action, it is recommended that all tests for E. coli be completed. The results of the bacteriological examinations of water samples are not accepted alone as sufficient evidence for judging the quality of a water, but must be interpreted as an integral part of a thorough sanitary survey.

The first tentative standard suggested for controlling the bacterial contamination of shellfish waters provided that the waters should not ordinarily show the presence of coliforms in one-ml amounts when tests were made in 10-, 1.0-, and 0.1-ml volumes, a standard equivalent to a limiting coli index of 10 per 100 ml. A modification of this proposal, permitting waters to show coliforms in 50 percent or less of the one-ml volumes tested, or a maximum coli index of 50 per 100 ml, was for many years recognized as the "unwritten standard" of the U. S. Public Health Service (334, 509, 523, 530).

At the present time, on the basis of a survey plus bacterial results, waters are classified as: (a) approved; (b) conditionally approved; (c) restricted; (d) prohibited. Approved waters show a median coliform density (as MPN) not in excess of 70 per 100 ml when tests are made on a series of samples determined by the survey to be most probably exposed to fecal contamination. Restricted waters show contamination of probably human origin and the median coliform density does not exceed 700 per 100 ml. Prohibited waters are subject to continuous or intermittent pollution and have a median coliform density greater than 700 per 100 ml.

Shellfish from approved areas may be marketed directly; from restricted areas shellfish must be cleansed before marketing. Shellfish from prohibited waters must be relaid and thoroughly cleansed before marketing (2431). Water used for conditioning or cleansing shell-fish from approved or moderately polluted areas must meet drinking-water requirements pertaining to bacteria.

A recent study (2452) investigated the potential of bottom deposits as contributors to the coliform content of water and oysters. Bottom materials consistently showed higher MPN values than overlying water. Hence, during periods of turbulence, resuspension can occur thereby effecting an increase in the coliform content of

the water and possibly an increase in the ovster coliform

After studying Virginia tidal waters and shellfish beds, the Virginia State Department of Health recommended that effluents from sewage plants located near shellfish waters should carry a MPN of not over 500 coliform bacteria per 100 ml. Plants farther from the shellfish areas need not meet so stringent a requirement

Studies of oysters in Galveston Bay, Texas (2587), indicated that coliform counts of oysters and water decreased in the Spring, remained low from July to December, and increased to high values in January. This finding is verified for the Gulf Coast area in a later re-

port (2452).

This observation is in contrast to North Atlantic Coast findings where coliform counts (of oysters) decrease as water temperatures fall. The authors attribute this difference to the temperature of the water of the Gulf Coast area not dropping low enough to cause hibernation of the oyster. Nevertheless, ratios of coliform counts in water to counts in oysters did not correlate with other factors studied. The ratio of E. coli to total coliform content of the water over the oyster beds increased when stream flow into the bay was minimal, and decreased as stream flow increased.

In a study of mussels (2588), coli-aerogenes bacteria did not grow well in water from the mussel's shell cavity. Nor did the organisms survive in sea water that had been chlorinated, dechlorinated, and filtered by mussels during cleansing. E. coli survived in oysters between 7 and 17 days according to one report. In another report, there was a 458 percent increase in E. coli in shell liquor of shucked oysters in 12 days at 5°-8°C. In living shell oysters at 5°-8°C, E. coli is usually gone in 60 days. E. coli have survived 49 days of oyster storage at 5°C. (2448, 2589).

g. Recreational Use. While it is recognized that harmful contamination of outdoor bathing beaches may be caused by sewage from dwellings, hotels, sewer systems, and boats, by the dumping of refuse, and by the individual bathers themselves, the transmission of disease by bathing waters has not been established epidemiologically as a major public-health hazard. The condition of bathing waters varies from day to day and season to season, and it may be altered by permanent sources of pollution, the incidence of disease among the local population, the bathing load, wind, weather, temperature, and composition of the water. Before effectual bacterial standards can be developed for such waters, several questions remain to be answered, such as, how important is the small amount of water swallowed while bathing as an etiological factor, which diseases are transmissible by bathing waters, and to what degree are diseases contracted at beaches through exposure to infected water, infected people, and infected bathing appurtenances, respectively (531, 532, 2590).

The U. S. Public Health Service has recently supported statistical studies of illness in relation to natural bathing-water quality in an effort to secure epidemiological data adequate for the development of definitive and logical criteria. The first study on Great Lakes waters concluded that bathing in natural fresh water with a

median coliform density of 180/100 ml appears to present no general hazard to public health. The second study on inland rivers concluded that waters with a median coliform density of 2300/100 ml may possibly cause an increase in gastro-intestinal illnesses, but outdoor pool swimming in chlorinated water with 93 percent of samples having MPN less than 3/100 ml resulted in more eye, ear, nose, throat, and skin infections than river swimmers. The third report on coastal waters shows no evidence of illness related to water quality (2149). These studies are discussed in Chapter V in the section on

Swimming and Bathing Waters.

Among the diseases whose possible transmission by bathing needs further investigation are not only gastrointestinal maladies, but also eye, ear, nose, and throat ailments (see Adenoviruses), skin irritations (see Pathogenic Bacteria), tuberculosis (see Mycobacterium tuberculosis), leptospirosis (or Weil's disease—see Leptospira), and others (495, 496, 497, 519, 533). For bathing waters especially, an indicator of contamination of other than intestinal origin is needed, one that will give warning of the potential presence of nasopharyngeal or skin organisms. Levine et al. (2316) suggest that Staphylococcus pyogenes, Streptococcus salivarius, and possibly Neisseria catarrhalis, and N. sicca are worthy of consideration.

Sea water samples collected in the vicinity of a sewage outfall on the Mediterranean demonstrated the presence of fecal coliforms within a 1200-foot radius, and of nonfecal coliforms only near the outfall. Although the authors rate swimming in polluted water as less hazardous to health than eating shellfish therefrom, they recommend that sea water at approved bathing beaches contain no fecal coli (2767).

A survey during the summer of 1951 of 25 beaches on Lake Erie and its tributary rivers revealed that at 11 beaches the average number of coliforms exceeded the maximum allowable count of 1000 per 100 ml. At 7 beaches near Cleveland the average number of coliforms was approximately 30,000 per 100 ml (1521).

In a 1953 summary of the results of the latest surveys of Connecticut beaches, Scott again pointed out the lack of evidence to incriminate natural bathing waters in the spread of intestinal or other ailments, even in states where coliform values of 2400 or more per 100 ml are permitted. He commented that although bathing in grossly polluted waters could not be recommended, on the other hand, the setting of unreasonably strict or arbitrary standards should be avoided because they might force the closing of many beaches, causing considerable hardship and financial loss, in the face of no evidence that they have ever been a source of disease

In addition to the USPHS epidemiological studies of bathing and illnesses, another highly significant study of the same type was concluded in England (2468). The Committee on Bathing Beach Contamination made a 5year bacteriological and epidemiological study of more than 40 popular bathing beaches on the coasts of England and Wales, the waters of a great majority of which were subject to contamination with sewage. Surveys for the rough grading of beaches were generally planned to ensure representative sampling from the areas on the beaches where bathing actually took place, and whether the grading was effected on the basis of results of the presumptive coliform test or on fecal coliform counts, a similar order of ranking was obtained. The median presumptive coliform counts varied from 40 to 25,000 per 100 ml. Meteorological and other factors played a part in the degree of pollution of bathing waters. The isolation of pathogenic organisms from sea water was restricted to the Salmonella group although Staphylococcus aureus was occasionally isolated (see Salmonella, Pathogenic Bacteria, Polioviruses).

The general conclusions of the committee were that bathing in sewage-polluted sea water carries only a negligible risk to health, and where the risk is present it is probably associated with the chance contact with intact aggregates containing infected fecal material. Unless the water is so fouled as to render the bathing beach esthetically revolting it would seem that public health requirements are reasonably well met by the present policy of preventing the pollution of waters with undisintegrated fecal matter. Coetze (2591) refutes the applicability of these conclusions to South African beaches.

It has been agreed by the Joint Committee on Bathing Places of the American Public Health Association and the Conference of State Sanitary Engineers, that on the basis of information available it is not possible to establish a precise standard to distinguish between bathing waters that are safe and those that are unsafe (335). This committee recommended that the following classification system of Connecticut be used as a basis for further study, with a view particularly to clarifying the position of the intermediate classes of water:

Class	Description	Average Coliform MPN
A	good	0-50 per 100 ml
$\mathbf{B}$		51-500 per 100 ml
$\mathbf{G}_{\cdot}$		501-1000 per 100 ml
$\mathbf{D}$	very poor	over 1000 per 100 ml

This classification (337), based on bacteriological analysis, was found to agree well with the results of concurrent sanitary surveys of the beaches.

At the present time there is still no uniform system of classification in effect. The quality of water for bathing is regarded as a local problem to be solved by state or local health agencies, and existing codes relative to bacterial concentrations vary so widely in their requirements that the limiting values in effect in various parts of the United States range from 50 to 3,000 coliforms per 100 ml. For a more complete discusson of the standards in effect throughout the U.S., see Swimming and Bathing Waters in Chapter V.

Bathing in Berlin is permitted in waters with a coli titer of 0.1, 1.0, or 10.0. The coli titer is used in some foreign countries to express coliform counts, and is defined as the minimum quantity of water that yields a positive result. It is not related to bacteriophage terminology. Hence, in American parlance, the above coli titers would amount to coli indices of 1000, 100, or 10 per 100 ml. When coli titers in Berlin rise to 0.01 or 0.001 (10,000 or 100,000 per 100 ml), bathers are warned of the risk (2461).

Two foreign papers express coliform standards in another manner. Kedrov (2592), in discussing indoor and

outdoor pools in Russia, states that the coli titer must not be more than 100 per ml and the total bacterial count not more than 1000 per ml. It is interesting to note that the Russian standards also require that a sample volume of at least 100 ml must be used in testing for "pathogens and coli," and that the pool volume must be displaced each 45 days (2592). Dubois (2458), in a similar Belgian discussion, suggests that pools have a B. coli titer of not more than 100 per liter. From the manner in which "titer" is used in these cases, one suspects that the translators used this word in place of "count".

Levine et al. (2316) favor an "E. coli index," or ratio of E. coli to coliforms, as the most practical criterion of pollution of marine beaches. See the similar statement in the discussion on Fish and Aquatic Life immediately preceding this section whereby the same criterion is favored for oyster waters.

#### CLAMS

(see Mollusks)

#### COXSACKIE VIRUSES

(see also Viruses, Polioviruses, and Worms-Free-Living)

The Coxsackie virus is relatively small and spherical, measuring 25-30 m $\mu$  in diameter. It causes a number of diseases ranging from obscure fevers to an illness that is clinically indistinguishable from poliomyelitis. Two groups of Coxsackie virus are known. Group A with 28 serotypes causes extensive damage to the skeletal musculature of suckling mice. Group B with 6 serotypes affects the brain, pancreas, heart muscle, and subdermal embryonic fat pads of newborn mice (2159).

Although Coxsackie viruses have been isolated from treated sewage (2119, 2593), no outbreak of Coxsackie infections has been attributed to water. The virus resembles poliovirus in its size, ability to withstand a wide pH range, and method of spread (1722). All strains tested at room temperature survived pH 2.3 to 9.4 for one day, and 4.0 to 8.0 for 7 days. With respect to heat, most strains tolerated 49°C, but 30 minutes at 53°-55°C inactivated all (2594). They survive storage at 8°-10°C for up to 40 weeks, and at 20°-30°C for 30 weeks (2566).

Clarke, Stevenson, and Kabler (2595) performed an extensive series of tests on the survival of Group A Type 2 Coxsackie virus in sewage, distilled water, raw Ohio River water, and autoclaved Ohio River water, all at two temperatures, 8° and 20°C, on four different river waters at 20°C, and on samples of the same river water that were withdrawn from different points at 20°C. These results demonstrated that a water relatively free of microorganisms and dissolved organic materials (namely distilled water) permitted the longest survival (over 272 days at 8°C. Autoclaved river water also permitted lengthy survival (over 171 days at 8°C). However, at the same temperature of 8°C, all viruses were dead in 117 days in sewage and in 24 days in raw river water (1722). For further information on storage effect on several enteric viruses see Clarke and Chang's review (2596). Coxsackie A9 virus, when ingested by the nematode Diplogaster nudicapitatus, is completely protected from the action of chlorine (2597).

#### CRUSTACEA

(see also Chironomids, Rotifera, Insects, and Chapters IX and X)

The Crustacea compromise many groups of microscopic fauna, the majority of which are aquatic. Respiration is accomplished by means of gills or directly through the body surface (15). Ingram and Bartsch (2420) cite three groups of the Crustacea as organisms of interest in potable water supplies: Cladocera (Daphnia, Bosmina), Copepoda (Cyclops), and Isopoda (Asclus). In polluted waters, crustaceans along with rotifers predominate in the latter stages of the zone of recovery. The Crustacea, as with the Rotifera, are not primary pollutants. As corollary pollutants, any detrimental effects appear to be rather insignificant compared to the probable good they do as fish food.

The only detrimental effects attributable to crustaceans have been: (1) shortened filter runs resulting from Cyclops and Daphnia (2420, 2598); (2) the esthetic problem of their swimming about in a glass of water about to be consumed (2599); (3) a report that attributes a depletion of dissolved oxygen in a lake to an enormous population of copepods, namely Diaptomus ashlandi (2600); and (4) heavy populations that choked and killed fish (389).

The oxygen consumption rate of Asellus has been measured (2601). It was found to be approximately proportional to the 0.7 power of the net weight. The work involved A. aquaticus, which is found in polluted streams, and A. meridianus, which is usually not found in polluted waters. Butcher reports that in polluted streams, Asellus replaces Chironomus with increasing distance from the source of pollution, populations of over 100,000 per square meter having been reported (2126, 2545). Although the "Asellus zone" in the recovery of polluted streams is recognized by European workers, Americans do not mention it. Hynes (2602) states that this is probably because the Asellus community in America consists primarily of mollusks and leeches.

In water made turbid with suspended yeast cells, Mysidium gracile, a sea-water crustacean, showed a significant preference for swimming perpendicular to the plane of admitted polarized light. In carefully clarified sea water, this preference is not shown (2603). The survival of marine crustacea in varied salinities has been studied (2604). The maximum percent salinity changes that allowed survival as long as controls were for Brachyuran larvae ±20 percent, for Amphipoda -15 to +5 percent, and for Copepoda -7 to +5 percent. In the Delaware River Estuary, Neomysis americana was not found above the 4-percent isohaline. That larger animals were located in the upstream area was attributed to their increased age (2605). Similarly, the brackish water tolerance of fresh-water crustaceans has been studied (2608). Among Daphnia species, D. magna could withstand a salinity of 5.8 parts per thousand, but D. pulex and D. longispina had high mortalities at 2.9 parts per thousand. Asellus also gave variable results. The existence of a limiting value of chlorides for smaller crustacea has been mentioned (2542).

In a lake that was "acid-trophied" by wastes from a powder factory, only two species of Cladocera (Daphnia cristata and Bosmina coregoni) could be found (2168). Daphnia magna was unable to survive for 24 hours in sewage in which NH₃ was demonstrable (2606). Gammarus pulex tolerates heavy pollution provided that the dissolved oxygen content of the water is not too low (2607).

The Crustacea are important also because of their value as tools of toxicity. Owing to its transparency and role as a fish food, *Daphnia* has been repeatedly utilized in toxicity studies. Crustacea can concentrate radioisotopes from water (see Chapter VIII, Radioactivity). *Daphnia* can be used as a specific indicator of radioactivity in reservoirs, according to Lebedeva (2609).

Crustacea are sensitive to many insecticides (2610), although Tarzwell cites an increased population of copepods in small ponds seasonally treated with DDT (2611). Turner used the insecticide pyrethrum to eliminate an infestation of Asellus aquaticus from a distribution system (2612). Only 0.005 mg/l of pyrethrum was necessary to kill the organism efficiently. DDT and DDD are also effective (74). Rotenone markedly reduced populations of Daphnia and Diaptomus (2613) (see also Chapter IX).

Various suspended materials were tested on Daphnia magna (2614). Charcoal and montmorillonite were toxic at 100 mg/l; ground glass at 98 mg/l; chlorite at 120 mg/l; illite at 264 mg/l. Pond sediments were not toxic at any level tested—presumably as high as 1,458 mg/l based upon the abstract available. Lackey et al. (2615) report that silt can be quite detrimental to Daphnia or ostracods.

Haynes (2602) states that the major controlling factor in the distribution of aquatic invertebrates is the nature of the river bed, with hardness (approximately 20 mg/l) a relatively unimportant second factor.

Experiments with phenol on *Planaria* (worm), *Daphnia*, *Gammarus*, and *Tubifex* (worm) showed *Gammarus* to be least resistant, *Tubifex* most resistant (2616).

Infestation of oysters in Puget Sound by Mytilicola orientalis, a copepod parasite, ranged from 0 to 62 percent. Heavy infestations can result in oyster death by secondary bacterial invaders (2415).

#### DIATOMS

(see also Algae, Protozoa, and Chapter IX)

Diatoms are unicellular algae characterized by a siliceous cell wall of varying thickness. Because of obvious morphological distinction provided by the siliceous cell wall, these algae are readily distinguished from other forms of algae. Indeed, the cell walls also provide means of differentiating individual species of diatoms.

Since all diatoms secrete a gelatinous material that covers the cell wall, they may grow singly, in colonies, or in strands. The jelly also provides a mechanism for attachment to substrate in fast-moving streams (15).

Patrick has suggested that diatoms can be useful as indicator organisms of pollution (2617) since (a) they need no special treatment for preservation; (b) they constitute a great variety of species which lends itself to statistical treatment; (c) a great deal is known of their

sensitivity to various ecological conditions; and (d) some species are sensitive to environmental changes whereas other species are not (2618). However, she emphasizes that great care should be exercised in interpretation of results (2617). In a study of the biological succession in a polluted river from which the pollution was markedly reduced, certain algal species and diatoms reappeared first (2544). Alfimov and Mironov (2619) found that the numbers of diatoms varied inversely with ammoniacal nitrogen content. A British report found it possible to estimate the maximum areal productivity of a lake by means of photosynthetic rate measurements, the rate of increase of Asterionella populations, and the rate of depletion of silica in the water (2623).

Diatoms appear to require silica (2202) in concentrations above 0.5 mg/l (1453), small quantities of iron (2620), and grow best at temperatures of 15°-30°C (2190, 2621). The brackish water diatom Nitzschia filiformis grows best at 26° and shows no growth at 34°C. The tolerant fresh-water diatom Gomphonema parvulum grows best at 22°C and still shows considerable growth at 34°C. The least tolerance to high temperatures is shown by the sensitive fresh-water diatom Nitzschia linearis which grows best at 22°C and shows little or no growth at 30°C. Although growth of N. linearis was inhibited at 4°C, the cells remained in good condition. For mixed populations from a normal healthy stream, a large number of diatom species were present at 20°C and dominated the culture. At 30°C, only two species of diatoms were numerous and blue-green algae predominated (2190). Investigations on a pollution-free river into which heated condenser water was discharged showed that diatoms of the family Fragillariaceae became more abundant. However, irregularities in the population not related to temperature were noted and were believed attributable to chlorination of condenser water (2622). Silicic acid has led to the development of diatoms (2171). During periods of maximum growth there was a marked decrease of silica in the water (2186). Asterionella blooms have been known to use up all the available silica in their environment, thereby creating conditions detrimental to their own survival (2126).

Diatoms discolor water (414, 2164, 2245), cause taste and odor problems (386, 409, 414, 422, 2166, 2213, 2221, 2236, 2242, 2244, 2246, 2247, 2252, 2624), and shorten filter runs (428, 738, 2166, 2221, 2625, 2626), Synedra being particularly important in both respects in the Chesapeake Bay area (2165). A heavy growth of diatoms was implicated in reducing normal filter runs from 50-110 hours to 5 hours (2627). Another report associates counts of 4800 cells of S. delicatissima per ml with reducing filter runs from a normal 50 hours to less than 1 hour. An upstream water treatment plant, with a maximum count of 20 Synedra per ml, had no difficulty (2628). However, Baltimore reports no filter-clogging difficulty despite (what was termed) high counts of diatoms (2629). Also, in the Loch Raven Reservoir, pH changed from an average of 7.0 to 9.0 in an area where diatoms were abundant. pH was normal where diatoms were scarce.

Gamet and Rademacher (2630) studied the relationship between lengths of filter runs on Lake Michigan water and diatom counts. In general, there was a relation between high counts and short runs, but exceptions occurred. Tabellaria appeared to have the greatest influence on shorter filter runs of all organisms studied (3256). They conclude that possible nannoplankton, excreta from micro-organisms, or siliceous gel also contribute to short filter runs. The diatoms Asterionella and Fragilaria are identified as taste- and odor-producing forms (2196, 2246, 2624), Tabellaria, Synedra, and Melosira as filter-clogging forms (2166).

Diatoms have developed in "very low" concentrations of phosphate, but higher concentrations stimulated growth. Numbers of diatoms were inversely related to the concentration of nitrate nitrogen and unrelated to ammonia nitrogen (2186). Bamforth (2185) reported that diatoms grew at 0.02 mg/l of phosphate (see also 2202). Diatoms are reported to occur in larger numbers in alkaline ponds than in acid ponds (2202). Diatoms have been reported to grow when doses of 3 mg/l copper sulfate removed Oscillaria (389). Seasonally, they appear in the Spring, are replaced by green or blue-green algae in the Summer, and reappear in the Autumn (371). An Israeli study of fishpond phytoplankton showed that although blooms of blue-green algae occurred in all ponds, diatoms predominated in ponds of high salinity, green algae in ponds of low salinity (2186). Diatoms have also been identified as cooling water contaminants (208). They have also been reported to flourish during blooms of the Florida "Red Tide" (420). Whereas certain flagellates may be important food sources for shellfish (Mya arenaria), diatoms are probably of little importance (2631). Nevertheless, concentrations of 75,000 Nitzschia per ml markedly reduce the pumping rate of oysters (1448).

In a study on the antibiotic effects of Nitzschia palea, it was found that the effect was greatest in cultures 4-8 days old, and was pronounced against B. coli, Proteus vulgaris, and Pseudomonas fluorescens, but not against other organisms tested (2632).

When the biological balance of a Delaware reservoir was upset by DDT spray from an airplane, the diatom Synedra multiplied until the high count of 10,000 per ml was reached. At this level the color was 15 mg/l and turbidity 20 mg/l (2245).

Palmer (2213) states that sometimes certain diatoms in small or moderate numbers are responsible for tastes and odors, citing *Melosira* and *Synedra* in Alabama. The Metropolitan Water Commission of Boston sets allowable limits in Standard Units per ml for *Asterionella*-3000, *Tabellaria*-2500, and *Synedra*-3000, at which treatment is begun (2255). Fox (2250) reports diatoms to be most prominent in the Spring and Fall, and that concentrations of 2000 units/ml of *Asterionella* and *Tabellaria* are troublesome (see also 384, 385, 386).

#### ECHO VIRUSES

(see Enteroviruses)

#### EELS

The presence of eels in cistern water supplies on the island of Pantellaria, Italy, are reported to have no effect on the hygienic quality of the water (2633).

#### ENTEROCOCCI

(see Fecal Streptococci)

#### **ENTEROVIRUSES**

(see also Viruses, Coxsackie Viruses, Polioviruses, and Infectious Hepatitus Viruses)

Enteric viruses are found in the gastrointestinal tract and feces of man and many lower animals. Some of the enteroviruses invade beyond the confines of the alimentary canal, and most have a higher incidence in children than in adults. The incidence is seasonal, being highest in the summer months, the period when enteroviruses are most readily isolated from raw sewage and polluted waters. This group of agents is transmitted generally by the oral-fecal route; hence, presumably all viruses of this group have the potential for transmission in polluted waters (2159).

In the past 15 years over 70 newly discovered viruses have been added to the original list of enteric viruses known to be present in human wastes (125).

Enteric viruses, other than those mentioned separately (see Coxsackie Viruses, Infectious Hepatitis Viruses, and Polioviruses) include the ECHO viruses and reoviruses. These latter two have not been incriminated in waterborne illness.

The ECHO (enteric-cytopathogenic-human-orphan) viruses constitute 28 serotypes of 30 mµ-diameter spheres that have been isolated from human feces. The first ECHO viruses were discovered in the feces of healthy persons during studies of poliovirus. At the time no illness was associated with these ECHO types. However, later studies found a number of clinical syndromes associated with these types. An array of similar such agents is found in other animal species such as swine, cattle, chickens, monkeys, dogs, etc. But the relationship of these latter viruses to human disease is poorly understood, although some are pathogenic to man. The ECHO viruses are readily isolated from sewage (2119, 2159, 2634).

The recoviruses constitute a small group (four serotypes) of viruses possessing certain characteristics common to both ECHO and Coxsackie viruses. The recovirus is a large spherical particle, about 72 mµ in diameter and has a very broad host range. It is responsible for enteric and respiratory infections in children and has been encountered in chimpanzees, monkeys, and calves. The role of water in the transmission of recoviruses is not known (2159).

## ESCHERICHIA COLI

(see Coliform Bacteria)

# FECAL STREPTOCOCCI

(see also Protozoa, Coliform Bacteria, and Pathogenic Bacteria)

The fecal streptococci include, in addition to the enterococci, the *Streptococcus mitis—S. salivarius* group, *S. bovis, S. equinus*, and an atypical group resembling the enterococci. Interest in the use of the fecal streptococci as an indicator of potential pathogen contamination by intestinal wastes (2635) stems from the appearance that this group is characteristic of fecal pollution, that they

do not multiply in surface waters, and that they rarely occur in surface soil or on vegetation not contaminated

by sewage (1501, 2636).

The enterococcus group, suggested by Sherman in 1937 as indicator organisms of fecal pollution, includes Streptococcus faecalis, S. faecalis var. liquefaciens, S. faecalis var. zymogenes, and S. durans (2637). The enterococci have also been suggested as indicator organisms for soil and vegetables contaminated by sewage, whereas E. coli was unreliable (1502). Recently, Kabler (2636) stated that undue emphasis has been placed on the enterococci (as an indicator group) with little or no consideration for other streptococcal strains present in the intestinal tract of warm-blooded animals. He quotes studies in the Cincinnati area that revealed the enterococcus group represented only 77 percent of the total streptococci present in humans, 25 percent in sheep, 12 percent in cows, and 10 percent in swine. Bartley and Slanetz (2635) conclude that the "membrane filter tests for fecal streptococci are more practical, efficient, and accurate than the coliform tests for evaluating the sanitary quality of almost all types of water.'

Ritter (2638), in comparing enterococci with coliforms in well-water samples, stated that the test for the entire enterococcus group-including atypical strains-was to be preferred to tests for Streptococcus faecalis only. Morris and Weaver (2639) claim a good correlation between coliforms and streptococci on both freshly collected and 24-hour stored samples (room temperature). Leininger and McCleskey (1501, 2555) reported that pollution of water from drainage ditches was more readily detected by enterococcus counts than by coliform counts. A South African paper by Keller (2553) reports that enterococci survived longer than Escherichia coli and therefore can be regarded as "delayed indicators" of pollution when E. coli is absent or present in small numbers. In a two-year series of samples on the Connecticut River, the density of enterococci to E. coli was approximately 7.6:1. But water samples from the harbor of New Haven, Connecticut, indicated a ratio of 63:1 of E. coli to enterococci (2556). The Water Pollution Research Board in England reported laboratory studies on settled sewage from three different sewage-treatment plants. The samples were maintained at different temperatures between 5° and 25°C and counts of B. coli and S. faecalis determined at intervals. At temperatures above 10°C, B. coli multiplied whereas S. faecalis did not (2640). In a study to determine the extent of fecal pollution of mud from lakes and estuaries, British investigators (2558) state that counts of B. coli and S. faecalis together probably constitute the best index (1505), although few such organisms are present at depths of more than two inches.

British workers also report that S. faecalis is less viable in the pH range 6 to 7 than in other ranges studied (pH 5.0 to 8.0) (2563), and also that S. faecalis persisted for a much longer period in alkaline soils than in acid soils (as did B. coli type I). This explanation was suggested for the greater fecal pollution found in surface water supplies in limestone areas than occurs in waters from acid areas (2570). B. coli and S. faecalis survived longer in Thames River water having a salinity of 20.8 per thousand than at 30.8 per thousand. Also,

S. faecalis survived appreciably longer than did B. coli. Kenner et al. (2641), in quantitating fecal streptococci from man and various animals, recorded the following totals per animal per day:

 HUMAN
 450,000,000

 CHICKEN
 619,000,000

 COW
 30,680,000,000

 SHEEP
 42,900,000,000

 PIG
 226,800,000,000

Hence, surface drainage from agricultural land, feeding pens, and grazing areas can be expected to contribute substantially to the bacterial contamination of streams. Kenner et al. (2557) also shows that densities of fecal streptococci in various waters is of the same order of magnitude as the confirmed MPN coliform density.

Mallman (1503) suggested the enterococci as a supplementary indicator group to *E. coli* in rural areas, since the absence of *E. coli* indicates a satisfactory water but presence does not necessarily indicate an unsafe supply.

High enterococcus counts in irrigation water samples accompanied high coliform counts in water samples; but enterococcus counts did not appear to be correlated in any way with coliform counts in soil and vegetable washings (1515).

#### **FUNGI**

(see also Sulfur Bacteria, Iron Bacteria, Algae, Yeasts, Slime Bacteria, and Chapter V)

The true fungi are the chlorophyll-free organisms of the phylum *Thallophyta*. The algae comprise the other division of this phylum and are the chlorophyll-containing forms. Although the fungi lack chlorophyll, they closely resemble green algae in their structure and mode of reproduction. Many species of the fungi are aquatic, many are terrestrial. The fungi include the yeasts which are discussed in this book separately. The term "molds" is applied to those fungi which are multicellular and filamentous (2289).

In the sanitary engineering field, the term "sewage fungus" is frequently used. This is a general term applied to a number of organisms which may include bacteria and even protozoa as well as fungi. Sphaerotilus, for example, is often termed a "slime fungus" because of its appearance (2642). Waldichuk describes a greygreen fungal slime, possibly Sphaerotilus, that is characteristic of sulfite-liquor pollution (1949). Among the more important organisms in this heterogeneous group are Sphaerotilus, Carchesium, Leptomitus, and Fusarium, only the latter two of which are fungi.

Naturally occurring water fungi are generally not primary pollutants although some such as *Penicillium* may be present in waste discharges from the manufacture of penicillin (661). However, the most important water-pollution problem presented by fungi is that of corollary pollution, namely the heavy growth of "sewage fungus" as referred to above, which is the result of wastes rich in organic matter (see Slime Bacteria) (457, 1191, 1192, 1193, 2542).

Hohnl's work (2643) on waste-water fungi notes that the bacteria *Sphaerotilus* was the primary organism at pH values of 5.8 to 9, but when the pH reached 5.2 to 5.6, the fungi *Fusarium* and *Mucor* predominated. *Fu*- sarium aqueductum and Sporotrichum, cultured in a medium containing glucose, hydrolyzed casein, and mineral salts, grew over a pH range of 3 to 10, optimum growth being over the wide range of 4 to 9. Oospora fragrans grew best at pH 3 to 9, but did not grow at pH 2. Sepedonium (not identified in Ward and Whipple) (15) had a narrow optimal range of pH 7 to 8 (1540). The growth of the fungus Sepedonium in the presence of small amounts of metals indicated that zinc, calcium, and manganese are essential elements, but that molybdenum is not. Results for iron and copper were inconclusive. For best growth, zinc of 0.5-1.0 mg/l and calcium of 5 to 12.5 mg/l were required (2640).

Sepedonium and Ascoidea rubescens require organic nitrogen, Oospora fragrans and Sporotrichum can utilize ammonium salts or organic nitrogen, and Fusarium aqueductum is capable of using nitrate as well as other

forms of nitrogen (1540, 2644).

Cooke (2645) identified Trichoderma viride, Myrothecium verrucaria, Aspergillus fumigatus, and Penicillium ochro-chloron as very active among the organisms helpful in the decomposition of cellulose. Gliomastix convoluta, Cladosporium cladosporiordes, and Geotrichum candidum showed no significant activity in this respect. Pullularia pullulans was unable to use cellulose. A report of the mass development of Achlya prolifero downstream from a wood fiber plant has been reported in Sweden (2646). Some fungi can use rubber as a source of carbon (666).

Nutritional studies on the Peronosporales and Blastocladiales indicate a need for thiamine. All Saprolegniales investigated were capable of producing all the vitamins they need. The Chytridiales include both self-sufficient and thiamine-deficient species (2623).

DDT has been observed to accumulate on aquatic mosses as a result of aerial spraying and results in the

death of aquatic organisms (2647).

Fungi are among the organisms that metabolize hexadecanol evaporation—retardant films (2293, 2648). Increased stream temperatures are mentioned as encouraging to the growth of "sewage fungus" (2649). Optimum temperature for "sewage fungus" is 20° to 30°C (2602, 2650). Lichens, a symbiotic relationship of fungi and algae, have been associated with concrete corrosion (see Algae) (2235). Species of Fusarium have caused extensive corrosion of turbine blades. Decomposition of the organisms liberated sulfur which combined with iron surfaces to form iron sulfide (400).

The indicator value of fungi towards pollution has been the subject of several papers. Heukelekian (2278) mentions a study that reports the absence of some fungi from heavily polluted waters, the presence of others in moderately polluted areas. Aphanomyces had an affinity to polluted matter. Cooke (2651) reports the isolation of 105 species of molds from a stream subject to primary effluent pollution. Of these, 6 were present in all samples collected in the 12-month survey, and 48 were present in 4 or more of the 8 stations. Little correlation was noted between the number of species and number of colonies produced (2651, 2652). Although fungi are commonly associated with decaying organic matter, Cooke concludes that they cannot be used as indicators of pollution largely because of their ubiquitous nature (2653, 2654).

Leptomitus lacteus is described as a fungus found in polluted water. Among problems associated with it are the blocking of weirs, pipes, and fishing nets, and objectionable odors upon decomposition (949). Fungus growths have been linked with problems of eaking and

short circuiting through filter sands (2304).

In a study of Lytle Creek in Ohio, fungi showed definite response to stream pollution. At the outfall of a primary treatment plant, fungal populations were suppressed. In the downstream clean water zone, they surpass the populations of the clean water zone above the plant. It is assumed that the fungi contribute to the purification of the stream (2655).

Fungi have been discussed as a pollutant of cooling waters (2263) and as a factor in the deterioration of

wood in cooling towers (2656).

The increased use of sewage effluents for irrigation may lead to outbreaks of plant diseases from pathogenic fungi (2657). Crook root disease of watercress is caused by a water-borne fungus. Contamination by zinc from galvanized piping of a tap water resulted in 2.0 mg/l zinc in the water and completely suppressed the infection (2658). At least 18 species of fungal plant pathogens have been identified in sewages and sewage-polluted waters. See Cooke and Kabler (2659) and Cooke (2644) for the species and their diseases.

Labrynthula appears to cause disease in eelgrass which is resulting in the disappearance of eelgrass from both American and European shores and subsequent depletion of foodstuffs of both fish and wild fowl (667). Other fungi, Saprolegnia and Ichthyosporidium hoferi for example, cause diseases in fish (308, 384, 2260). The collective term "sewage fungus" has been applied to mats covering the bottom of streams where they destroy spawning beds, benthic organisms, and impede fish migration (see Slime Bacteria) (1575, 2661). A decline in the oyster industry of the Gulf Coast has been reported to be due to Dermocystidium marinum, a parasitic organism related to the fungi (2415).

# GASTROENTERITIS ORGANISMS

(see also Copper, Pathogenic Bacteria, Salmonella, Shigella, and Algae)

Water-borne outbreaks of gastroenteritis of unknown etiology sometimes occur in communities whose drinking water appears to meet the bacteriological standards of the U. S. Public Health Service. Several possible causative agents have been suggested, including heavy growths of blue-green algae, anaerobic decomposition products of decaying algae, chemical toxins, or irritants of other biological origin, decomposing organic matter, toxic pollens or dusts, miscellaneous bacteria of non-sewage origin, viruses, various streptococci, staphylococci or other bacteria not detected by conventional techniques, or bacteria of the colon-typhoid-dysentery group present because of a temporary excessive raw-water contamination and inadequate purification (152, 393, 424, 492, 669, 670, 671, 672, 1272, 2124, 2429).

Petersen and Hines (2662) related the morbidity rates of summertime gastro-intestinal illnesses in Rocky Mountain communities to the sanitary quality of the drinking water. Contaminated water supplies were associated with an attack rate of 14 percent, whereas non-contaminated supplies were associated with a 9 percent attack rate. Among the users of contaminated supplies, those who had been exposed for over two years had only one-half the attack rate of those exposed for less than two years.

An outbreak of 8,000 to 10,000 cases of human gastroenteritis involving suspected water gave strong circumstantial evidence that algae blooms which existed at the time were responsible (2274).

#### INFECTIOUS HEPATITIS VIRUSES

The etiological agent of infectious hepatitis has been suspected as being of viral nature for several decades. Proof, however, has been only recently established. The incidence of this illness has increased dramatically in recent years. The mortality from infectious hepatitis, although low, is highest in older children and older adults. The incidence can be high in troops and also is not uncommon in overcrowded, understaffed, public institutions housing the sick. Hence, its incidence is generally related to unhygienic conditions. The major route of transmission is probably by direct contact (2159, 2663).

The virus of infectious hepatitis has resisted efforts at laboratory cultivation thus far. Hence, definitive studies are scarce. Nevertheless, some illuminating work has been done, particularly that by Neefe and Stokes (2664). Their work demonstrated that the virus of infectious hepatitis would survive storage in relatively clean (well) water for at least 4 weeks and possibly up to 10 weeks, and be virulent at the end of that time. A report from Europe indicates that the virus remains virulent in ground water for at least a month (2665). The virus is quite resistant to heat, especially when suspended in protein. Exposure to 56°C for 30 minutes failed to render the virus noninfective, since 3 of 4 men who ingested it contracted the illness (2666). Exceedingly minute amounts of infective excreta can cause the disease when taken orally. Human volunteers have developed it from as little as a 10⁻²⁰ dilution of infected feces (2667). According to Clarke and Chang's literature review (2596), a 30-minute chlorine contact period protected all of 12 volunteers. The conditions of these findings were: fecalborne infectious hepatitis virus suspended in distilled water, room temperature, pH range 6.7-6.8, initial and final free chlorine residuals of 3.25 and 0.4 mg/l. There is need for more information (2528).

- 1. Cross References. Viruses, Enteroviruses.
- 2. Effects on Beneficial Uses
- a. Domestic Water Supplies. Many outbreaks of infectious hepatitis have been reported to have originated from contaminated water supplies (883, 885, 2573, 2667, 2668, 2669, 2670, 2671, 2672, 2673, 2674, 2675, 2676, 2677). The massive outbreak in Delhi, India, was reported to be the first of its kind in the world (2678). More probably, it was the first to be recognized and reported. The plant that treated the water at Delhi apparently turned out a safe supply when the water was prechlorinated to a free residual of 0.7 mg/l. When sewage backed up to the waterworks intake, however, sufficient ammonia was present to destroy the free chlorine and to produce a low, combined chlorine residual

(2676). The latter treatment, nevertheless, rendered the water safe according to incomplete coliform testing results, but it apparently did not destroy viruses of hepatitis. Records of a water plant in New York State, which supplies water for two communities in both of which a simultaneous epidemic of jaundice (infectious hepatitis) occurred, showed flash orthotolidine residuals of not less than 0.35 mg/l during a one-month period (2671). For more information on treatment, see Senn et al. (2573).

b. Fish and Other Aquatic Life. The virus of infectious hepatitis can also be transmitted by shellfish. Coetze (2591) quotes Roos' finding in Sweden (2453). See also Jensen (2454), and Chapter V—Shellfish.

c. Recreational Use. Coetze (2591) also quotes Buttiaux as concluding that of the virus diseases, especially poliomyelitis and infectious hepatitis, there is little convincing evidence for the part played by bathing places in the spread of the disease, and none at all relating to sea water.

#### INSECTS

(see also Chironomids, Mosquitoes, Chapter VI—Hardness, Chlorides, and Chapters VIII and IX)

Although most insects are terrestrial, a great number are aquatic, occurring almost entirely in fresh water (15):

Generally speaking, each group of aquatic insects is most abundant in certain fresh-water habitats. For example, damselflies and dragonflies are predominantly pond species, stoneflies and mayflies are running water forms, and caddis flies are abundant in well-aerated streams and lakes (15). Hynes generalizes aquatic fauna with respect to hardness (2602). In very soft water (presumably less than 20 mg/l of calcium) stoneflies and mayflies are dominant creatures; in slightly harder waters mayflies and chironomids become more abundant; and in hard waters, shrimps, snails, worms, and caddis flies dominate.

Aquatic insects are natural fauna and not primary pollutants. As consumers of minute plants and animals and as food organisms for fish, insects and their larvae and nymphs are an integral part of stream life, and their destruction can have far reaching consequences upon the biological nature of streams. However, the presence of insects in excessive numbers can be highly obnoxious and render water undesirable for various uses. The multiplication of many types of insects such as flies, midges, mosquitoes, etc., is encouraged by heavy algal growths and decaying vegetation (388). Certain insect larvae, such as rat-tail maggots and bloodworms, thrive best in sewage-polluted waters and have been useful as indicator organisms in studies of natural purification of streams.

Because of the large number of references to chironomids and to mosquitoes, these groups of aquatic insects are discussed separately.

Among the insects of interest in potable water supplies, Ingram and Bartsch (2420) list *Chironomus* (see Chironomids), the predacious diving beetle, *Dyticus*, the whirling beetle, *Gyrinus*, and the water strider, *Gerris*. Other than the clogging of traps in water lines by large numbers of *Dyticus*, they are apparently fairly innocu-

ous creatures. Some insect larvae that flourish in treated water reservoirs may reach the consumer in a state of partial decay (388). An increase in the number of midges has been reported to result in an increase in the number of bacteria (682).

Although mosquitoes predominate as an insect problem associated with irrigation waters, biting black flies are also mentioned (2679, 2680). A German organization called the Association of Beekeepers has protested against the spray irrigation of crops by sewage in areas where bees are numerous. Their argument is that if bees become contaminated with pathogenic bacteria, the organisms might be transferred to humans by their stings (2681). In a study of aquatic fauna associated with several species of submerged aquatic plants, midge larvae and freshwater annelids together made up 59 to 93 percent of the population (2682). Aquatic insects concentrate radioactive elements. Concentrations of P-32 in Hydropsyche of 370,000 times that in the surrounding water have been reported. See Chapter VIII, Radioactivity.

The application of monomolecular films for retarding evaporation from reservoirs results in a lowering of the surface tension of the water. This action may have an effect on emergent insect populations such as mayflies of up to 70 percent (2683, 2684). The storage of waters behind dams with subsequent change of temperature of the released water is reflected in changes in the insect population. The most abundant in one study were Tendipedidae, Simulidae, and Hydropsychidae. However, another study of mayfly nymphs reports that temperature and dissolved oxygen have little, if any, effect on their distribution in a lake (2685). Sediment may cause a marked change in the insect fauna (2615, 2686, 2687). The bottom tube-building forms may increase (2686).

The midge Cricotopus bicinctus was found to be particularly resistant to electroplating wastes containing hexavalent chromium (25mg/1), cyanide (3.2mg/1), and copper (2.2 mg/l), all accompanied by a low dissolved oxygen level. Another midge, probably Pentapedilum, was also present (2688). In general, a population containing numerous gill-breathing forms such as mayflies, stoneffies, and caddis flies indicates clean water and their absence denotes organic pollution and/or low dissolved oxygen (2542, 2689). Insect larvae are among fourteen indicator forms of the saprobic classification system used by Stammer in tests of hydrogen sulfide (2690). The once abundant mayfly nymphs of Lake Erie (which averaged about 400 per square meter of lake bottom) have declined today to about 40 per square meter (2136). In Europe, Hynes remarks that organic matter causes a decline in Ephemeroptera but only slight sewage pollution may increase the caddis worms (2607). Caddis fly larvae can apparently adapt to wide levels of dissolved oxygen (2691). Mayfly nymphs showed a tolerance to chlorides less than that of fish (see Chapter VI, Chlorides) (2692). British streams polluted with 3 to 6 mg/l of lead have an animal fauna restricted to the midge Tanypus nebulosus and the mayfly Closon simile (2693).

The rat-tailed maggot, *Eristalis tenax*, is not dependent on oxygen in the water and is one of the few survivors in heavily polluted waters from which most other animals have disappeared (2143). In the recovery of

streams, the tendipedids, dragon flies, and damsel flies together with the beetles make their appearance sooner than the mayflies and stoneflies. The caddis flies seem to be a more variable group (2544). Because individual species of water beetles are extremely variable in their tolerance of pollution, these predaceous organisms have been suggested as an indicator group (2697).

Pesticide effects have been extensively studied. For more information see Chapter IX, Pesticides. Forest spraying of insecticides can have disastrous results on aquatic insects. Since they are a major fish food, spraying is reflected in a declining fish population (2694). The immediate effect is a drastic reduction in the emergence of all insect forms for several weeks. Chironomids show the first recovery but represent only minor fish-food volume. One to two years later, total numbers of emerging insects exceed prespray figures, but they are much smaller in size and represent only ½ to ½ of prespray volume. After the chironomids come the mayflies and stoneflies. Caddis flies are virtually eliminated and do not recover until 2 to 4 years later. Other insects severely reduced include blackflies and Dobson flies (2533, 2534, 2695).

The use of DDT to control Simulium damnosum in Africa resulted in most species of Ephemeroptera and Trichoptera being eliminated (2696). The fish that fed on these insects and were able to change their diet to other forms of plant and animal matter survived, and those that couldn't moved away or died.

In Saskatchewan, Simulium arcticum feed on suspended solids and the single application of DDT at rates as low at 0.09 mg/l destroyed the larvae for distances of 40-98 miles downstream. This mortality was much higher than that suffered by other aquatic insects (2698).

The seasonal effects of routine DDT applications to small ponds resulted in decreases of the insects, viz., chironomids, Hemiptera, Coleoptera, and Ephemeroptera, but increases in nematodes, viz., Oligochaetes, copepods, and gastropods (2611).

Gaufin (2699) found that there is a considerable difference in resistance of aquatic flies to insecticides, the larger being more resistant than the smaller to the insecticides studied.

# IRON BACTERIA

(see also Iron, Manganese, Sulfur Bacteria, Bacteria-General, and Slime Bacteria)

Detrimental or inimical growths of iron bacteria in natural waters that result from man's activities can classify such organisms as "corollary" pollutants. Such growths may occur in surface streams that receive acid mine drainage, spent pickling liquor, or sugar wastes. They may also be found in ground waters that leach soluble ferrous compounds from the soil (346).

The principal iron bacteria are Leptothrix ochracea, Gallionella ferruginea, and Crenothrix polyspora. These are also the most common microorganisms causing trouble in water supplies (2189). Leptothrix and Gallionella appear to require ferrous iron for proper nutrition and utilize it for sheath and cell structures (2700). Crenothrix derives energy from the oxidation of iron, but does not embody iron in its sheath (1036). These

organisms can thrive in water containing less than 0.1 mg/l of iron (1219, 1220). Wolfe has isolated a large, sheathed bacterium, tentatively described as Clonothrix putealis, that concentrates iron and manganese in its sheath and which flourishes in a water supply containing by chemical analysis no detectable manganese and less than 0.02 mg/l iron (2701). Leathen, et al. (2702) reports that ferrous sulfate in water is rapidly oxidized by Ferrobacillus to ferric sulfate, which then hydrolyzes (2703) to insoluble ferric hydroxide. The iron compounds deposit as a sludge, leaving the stream acid.

Detriment to natural waters is caused when these organisms form slime growths on rocks, bottoms, pipes, and other surfaces. Frequently the growths are red, and at times they die or slough off to form red or brown sludges or deposits. These bacteria, therefore, are indicators of iron in the water and foretell its unsuitability for use in boilers, laundries, tanneries, paper mills, beverage plants, and other processes where iron and/or the

iron bacteria may be inimical (239, 665).

Well screens and gravel packing around wells in iron-bearing ground waters become clogged with growths of iron bacteria even when the water contains as little as 0.2 mg/l of iron (1050). Hem (2704) has rendered an excellent discussion of this subject. Most sedimentary rock contains iron in the form of pyrite. The rapid increase in solubility of pyrite with an increase in redox potential suggests that pyrite is likely to be relatively unstable in most ground-water environments. Colonies of iron bacteria may become established in or near wells and they accelerate oxidation and precipitation of the iron from the water. Occasionally, the precipitated iron will break lose and be pumped from the well. Also see Oborn and Hem (2705) for more on microbiota and vegetation and their relationship to iron in waters.

The metabolism of iron bacteria has been associated with the corrosion of iron and steel (1037, 1222, 1223). These organisms remove soluble ferrous compounds or free ions from the water and deposit it in their sheaths or separately as ferric-oxide tubercles (2700). In so doing they may augment and accelerate the electrolytic phases of corrosion of iron and steel.

Another mechanism associated with iron bacteria and corrosion is reported by Wolfson (2700). These bacteria can build up many layers thick, clogging pipes and screens, and providing anerobic conditions underneath for corrosive bacteria to multiply (see Sulfur Bacteria).

A Russian report (2706) indicates that an oxygen deficiency prevents the growth of Gallionella. Earlier, Suzuki (2707) reported that Gallionella ferruginea required more oxygen than Leptothrix ochracea. Both agreed that iron had to be present in order for growth to occur.

Carter (2238) mentions that the combination of chlorine with iron bacteria has resulted in chlorophenol tastes. *Crenothrix* and *Sphaerotilus natans* have been cited as causing tastes and odors (2226, 2242).

## LEPTOSPIRA

(see also Pathogenic Bacteria)

Various Leptospira species distributed throughout the world have caused outbreaks of leptospirosis (also known as Weil's disease or hemorrhagic jaundice) in man (520). When transmitted through water, the organism originates in the urine of infected animals, most frequently including dogs, rodents, foxes, skunks, raceoons, and opossums. Hence, it is most generally transmitted to swimmers exposed to contaminated waters, and is an occupational hazard to rice-field workers, sewer workers, miners, etc. In the United States, L. icterohemorrhagiae, L. canicola, L. autumnalis, and L. pomona have been recovered from human cases. At least 21 serogroups containing 59 serotypes are recognized (2663).

Leiguarda (2708) examined 348 samples of untreated surface and ground water and 25 samples of sewage in Argentina. He recovered *Leptospira* from 44 percent of the surface-water samples, 14 percent of the groundwater samples, and all of the sewage samples. Treated potable water did not contain *Leptospira*. Coagulation and sedimentation were ineffective, but chlorination de-

stroyed them all.

A Yugoslavia epidemic is reported which originated with a poorly constructed well. Rats and even a cat had access to a chamber at the top of the well (2709). Leptospirosis among rice-field workers is described from Italy (2710). A report attributes one epidemic to harvest mice

(2711).

L. icterohemorrhagiae survived in river water at 5°-6°C for 8-9 days, 25°-27°C for 5-6 days, and 31°-32°C for 3-4 days. In bacteria-free tap water at pH 7, they survived more than four weeks—with small amounts of nutrients present. High and low pH values were both detrimental. Survival in sewage was limited to 12-14 hours, but when diluted with 99 parts of tap water rose to 7-8 days. The organism survived 18-20 hours in sea water (710).

Russian workers have found that Leptospira persisted a maximum of 36 days after infection of river water. Freezing temperatures apparently are quite destructive to the organism in the water environment (2485). Other Russian work identified a water fever in an endemic area as leptospirosis. The main source is the field mouse, and water has played a leading role in the spread of the disease. Areas with acid soils are not associated with this so-called water fever (2712).

An Australian investigation demonstrated the presence of *L. australis* in drainage water from infected soil for up to 24 days. The pH of this soil ranged from 6.1 to 6.2, and of the infected water from 6.6 to 7.6 (2713).

Smith and Turner (2714) studied the relationship of pH to leptospiral survival. Survival in the laboratory under pH 7.0 ranged from 10 to 117 days, and over pH 7.0 from 21 to 152 days. In soil extracts, however, they found no such correlation. They observed that Bentonite clay absorbed about half the leptospires from a suspension and recommend further studies of this observation.

A probable connection between human cases and piggeries is reported from Israel. Bathing and drinking of lake water into which the pigsties drained is thought to be the route of transmission (2486, see also 2715).

In the United States, three additional papers have been published relating leptospirosis with swimming. These originated in the States of Alabama (2490), South Dakota (2489), and Idaho and Wyoming (2487). A fourth investigation found leptospires in raccoons near a military establishment in North Carolina, noting that human infections had occurred among the soldiers who had been quartered near a potentially infected stream (2716). According to Galton (2488) recognized cases of leptospirosis in the United States have appreciably increased, and the disease in cattle has spread rapidly. Leptospirosis associated with swimming has been reported by others (1627, 1628). Rat access to a closed swimming pool was found to be a source of Leptospira to swimmers in Czechoslovakia (2491).

Foxes at a fox farm have contacted leptospirosis from drinking water drawn from a rat-infested pond (1629). In Denmark (2305), 91 percent of cases of leptospirosis are thought to be due to direct contact with water (18 percent accidental contact, 60 percent bathing, and 13 percent working in water).

#### MARINE FLAGELLATES

(see also Algae, Diatoms, Bacteria-General, Worms—Free-Living, and Chapter V—Shellfish Culture)

Marine flagellates are responsible for two highly toxic situations, viz., they are the source of shellfish toxins that can cause illness and even death in man, and they are the agent of the so-called "poisonous tides," one of which is better known in the United States as the "Red Tide" off Florida's Gulf Coast (420, 539, 545, 749, 750, 2427, 2429, 2717, 2718).

Gonyaulax catenella has been reported present in Alaskan shellfish and is said to be preventing the further development of the shellfish industry in Alaska. The toxin can be present in certain clams during every month of the year (2429). Shellfish feed upon these organisms (751) and concentrate the alkaloid toxin which is not harmful to them (2428). Gonyaulax catenella toxin from shellfish was ingested by a man and his wife in Marin County, California. Each had consumed more than 15,000 mouse units of toxin (both recovered) (2719). See Chapter V, Shellfish Culture.

In a discussion of toxic shellfish in British Columbia, a suggestion has been made to investigate the use of clam types as plankton indicators (2433). Waldichuk's review of the British Columbian outbreak states that Pacific oysters, Crassostrea gigas, as well as various species of clams and mussels were involved. Toxicities of 200 mouse units or less are considered harmless. When toxicity exceeds 400 mouse units, a ban is usually imposed on collecting shellfish (2430). The toxin is described as ten times as potent for mice as strychnine (2427). Flagellates, nevertheless, constitute an important source of nutrition for some shellfish (Mya arenaria) (2631). For a thorough discussion of shellfish poison, see the work of McFarren et al. (2429).

Salinity has been studied as an ecological factor in marine flagellates and phytoplankton. Syracosphaera carterel had an optimum salinity of 30 parts per thousand; Amphidinium grows best at "low" salinities, while the optima for Exuviella trochoideum, Prorocentrum micans, and Cryptomonas are 15-20 per thousand (2720). Gymnodinium brevis, the "Red Tide" dinoflagellate, grew well throughout the salinity range of 27 to 37 per thousand. The organism could not survive in a

salinity of 13.7 per thousand, indicating that salinity may be a factor in limiting natural distribution (2721). A high light intensity, vitamin B-12, and sulfides are all essential for mass development of the red-tide organism (2722).

The toxin from Gymnodinium veneficum consists of a large molecule that cannot penetrate a dialysis bag, is soluble in water and lower alcohols, insoluble in ether and chloroform, unstable in acids, decomposed by hot alkali and thermostable in neutral solution (2723). It is toxic to a wide range of animals to a greater or lesser extent, but not to polychaetes. Death in fish is due to respiratory failure, and the action is on the nervous system (2724). Bacteria-free cultures of G. brevis were as toxic to fish as cultures containing bacteria. Concentrations of G. brevis used in these studies were 0.6 to 4.8x10 6/liter (2725).

A reduction in estuarine pollution, with a consequent reduction of nutrients in coastal water, "might help" control blooms of G. brevis. Plankton blooms are believed to be initiated by natural characteristics of near-shore waters, but once started the nutrients contributed by sewage may increase the bloom (2726). Another paper suggests that a high phosphorus content in Florida rivers draining into the Gulf may be related to Gymnodinium blooms (2718). Total phosphorus in the colored water of Gymnodinium blooms is 10 to 20 times as great as in adjacent waters (2727). Significant quantities of titanium and zirconium are also present in bloom waters (2722). Phosphorus rate of uptake was found to be 25 times greater in Cladophora than in Fucus. Both rate and productivity were porportional to algal surface per (water) volume ratio. Under conditions of high surface to volume ratio and favorable light conditions, uptake is related to potential productivity and not to existng metabolic level (2179). Copper sulfate at 20 lbs/acre reduced the count of G. brevis from several million per liter to none, but in two of five test areas, the organisms rose to lethal concentrations to fish 10 to 14 days later. The technique is recommended only for temporary use in relieving an area of the respiratory irritation caused by the airborne toxin (2728, 420).

Prymnesium is another fish killer (648, 2012). The toxin from Prymnesium is rapidly inactivated by the bacteria Bacillus subtilis and Proteus vulgaris. The toxin appears to be a substance of high molecular weight with some of the properties of protein that have a pronounced liability to oxidizing agents.

Collier (2297) writes that the sudden increase in multiplication rates of the organisms is caused by a complex of biological factors with physical factors playing a major role in effecting mechanical concentration. Naturally occurring organic factors are important, as may be succeeding concentrations of bacteria that produce vitamin B-12. Interaction between environmental copper and hydrogen sulfide may be a factor. Once started, the bloom may replenish the required nutrients through the decomposition of the fish that are killed. Particulate iron could not be related as a limiting growth factor for phytoplankton in inshore waters (2729).

The brown color of the Thames Estuary and other waters along the English coast during summer months

is caused by great numbers of brown flagellates and dinoflagellates (752).

Davis observed no toxic effects upon oyster larvae when to larval cultures of *C. virginica* were added flagellates at concentrations up to 15,000 cells per ml per day. For some flagellates, concentrations of 25,000 cells per ml of water were harmless. Davis reported that although Korringa obtained good growth of oyster larvae in water containing 10,000-20,000 flagellates per ml, he later recommended "that water containing initially more than 5,000 flagellates or a commensurate great number of other phytoplankton, should be mistrusted" as it may contain toxic concentrations of phytoplankton excretory products (1647).

Hexamita, a marine flagellate, causes a winter disease in oysters of the Gulf Coast, and has been implicated in oyster mortalities in the Gulf of St. Lawrence (2415).

# MOLDS

(see Fungi, Yeasts, and Actinomycetes)

#### MOLLUSKS

(see also Insects, Weeds, Worms—Parasitic, and Chapter IX)

Mollusk pollutants include both snails and clams, either of which can be important natural or corollary pollutants. Snails are primarily troublesome because they are the intermediate hosts of trematodes that are parasitic to man and animals. Snails and clams both are troublesome in potable water supplies because of their sheer physical presence in large numbers. Records of mollusk infestation of water supply systems in the U. S. concern mainly the faucet snail, Bythinia tentaculata. This organism accumulates in pumping station wells (also of irrigation systems), chokes service lines, and plugs up faucets. Other genera reported include the snails Pleurocera, Helisoma, Physa, and Goniobasis, and the Asiatic clam Corbicula (2418, 2420, 2421).

Mollusks have been included as pollution indicators. They are reported to be intolerant of heavy metals (2607), and in the succession of recovery of organically polluted streams appear after Asellus has replaced Chironomus (2545), i.e., they appear in a lesser polluted area than that occupied by the worm fauna (2540). The fingernail clam, Pisidium, was more prevalent in polluted areas than Sphaerium or Musculum, but none can survive the severe conditions of pollution tolerated by tubificids (2729, 2730). Ide (2541) explains how animals exhibit various degrees of tolerance to oxygen deficiency based on their respiratory mechanism. All clams and snails, except for pulmonate snails which are lung breathers, respire by means of blood gills or by the general body surface.

Temperature rise to 40°C has wrought disastrous effects on clams (2731). In French domestic and industrial water systems the warm water mussel *Dreissenia polymorpha* is a nuisance and can be controlled by flushing water at temperatures over 40°C through the systems for 15 minutes (2426).

Ecological studies of water infested by planorbid snails in Brazil show a wide variation in pH, 4.9 to 8.8, and also of sulfates and ammonia, but low total hardness,

iron, nitrites, nitrates, phosphates, and chlorides (2732). In studies of the distribution of Australorbis glabratus, it is suggested that large amounts of carbonates and bicarbonates relative to the amounts of chlorides and sulfates may account for its absence from some habitats, such as limestone streams, and that copper and zinc may be limiting quantities in those waters that are low in dissolved solids (2733). Other studies on A. glabratus in Puerto Rico showed water temperature to range from 21° to 35°C, and pH 6.0 to 9.1. The snail can be maintained about two weeks in redistilled water (2734). Hynes (2602) notes that shell-forming creatures require at least a minimum amount of calcium, about 20 mg/l. This hardness is the limiting value between hard and soft waters from the biological point of view. Extremely heavy pollution is unsuited to the snail, but light pollution provides an abundant food supply (2735). Organic pollution and lowered oxygen tension killed off two species of snails in Africa, one of which is an intermediate host of the liver fluke (2736). Streams treated with the molluscacide, sodium pentachlorophenate, (see Chapter IX, Pesticides) become repopulated with A. glabratus within four months (2737). For field tests of 33 compounds against the snail, see this latter reference. In stagnant water, 10 mg/l—sometimes as little as 1 mg/l -effecting 99-100 percent kills included pentabromophenol, pentachlorophenol, sodium and copper pentachlorophenates, bis (3, 5, 6-trichloro-2-hydroxyphenyl) methane and its sodium salt, and phenyl mercuric acetate.

The snail, A. glabratus, infected with cercariae of Schistosoma mansoni, has a lesser resistance to an anaerobic environment than normal snails. The shedding of cercariae is greatly reduced under anaerobic conditions. But infected snails, after six hours or longer in an anaerobic environment, shed normal cercariae when returned to an aerobic environment (2738). Most infected snails died if kept under anaerobic conditions for 16 hours.

The snail intermediate hosts of Fasciola hepatica, the common liver fluke, inhabits wet-weather springs, slowly moving fresh water, stagnant water, swampy and marshy lands, banks of ponds, streams, and ditches, and in mud (2739). Snail intermediate hosts of the schistosomes not specific for man can nevertheless release cercariae which penetrate man's skin causing swimmer's itch or cercarial dermatitis (2495, 2740).

Snails have been found in increasing numbers in Canadian streams that have been treated every year with aircraft-sprayed DDT (2534). Snails are reported to be quite adversely affected by silt (2615).

# MOSQUITOES

(see also Insects and Chapter IX)

The problems caused by mosquitoes as a corollary pollutant appear to be on the increase. The larvae of Culex pipiens, also known as "sewage mosquitoes", feed on the organic compounds of sewage. When such mosquitoes emerge from their aquatic habitat, they will have contributed to BOD removal and therefore have been referred to as "flying BOD" since their emergence represents BOD taken out of the water (2143).

Heavy breeding of mosquitoes in areas of water impoundments and under irrigation has always been a difficult problem. A report from Russia mentions an increase in malaria among inhabitants along the shores of the Ribinsky impounding reservoir (2741). Encephalitis (2680) is the major U.S. illness associated with irrigation (2679). In both illnesses mosquitoes are the vector.

Although Culex pipiens is associated with polluted waters, most other mosquitoes prefer cleaner waters. Hence the environmental requirements of some mosquito larvae have been studied and some mosquito species have been considered as possible indicators of pollution (2543). The larvae of Anopheles punctipennis, Culex tarsalis, and Aedes vexans were found not to be affected by high concentrations of salts. Therefore it was concluded that oil-well brine pits would constitute suitable larval habitats (2742). Although mosquitoes vary considerably in their reaction to salinity, it is thought that the combination of salinity and organic matter better indicates optimum conditions than salinity alone. Also, the type of salinity may be an important factor (2736).

Surface tension studies revealed that Culex pipiens (as well as C. fatigans and C. molestus) developed normally in water of lowered surface tension. Aedes aegypti, the yellow fever vector that lives in close association with man (breeding in such artificial water retaining places as tin cans, tires, flower vases, etc.) prefers higher surface tensions. The malaria vector, Anopheles quadrimaculatus, demonstrated the most limited tolerance to surface tension change (53-73.5 dynes/cm) at which normal development occurs (2743). Therefore, changes in the surface tension of water because of pollutants may be responsible for changes in the type of mosquito life in the environment.

Mosquito larvae appear to be quite sensitive to temperature. Water temperatures of 40°-45°C fcr a five-minute exposure will kill many species of larvae. Shallow tanks in the tropics can reach 40°C and streams can reach 34°C. The rate of temperature change is also of importance.

In mosquito ecology, dissolved oxygen is not indicated as a factor of great importance and therefore has not been the subject of much study. Nevertheless, organic content is a factor of great importance to anopheline mosquitoes. Most anophelines prefer clean water. It is interesting to note that the larvae themselves are unaffected by degrees of pollution up to 20 or 30 times that in which the female refuses to oviposit. Further, although Anopheles gambiae will tolerate a considerable degree of fecal pollution, it is very sensitive to the organic pollution of decaying vegetation. An anopheline of India shows a preference for waters in freshly dug tanks or borrow pits, and as these waters eutrophy, larval density declines.

Odom and Sumerford (2744) demonstrated that mosquito (Culex) pupae are more resistant to DDT than are its larvae. Less than 0.001 mg/l effected 100% kill of the larvae, whereas 0.025 mg/l were required for an equivalent kill of pupae. See Chapter IX, Pesticides.

#### MYCOBACTERIUM TUBERCULOSIS

(see also Pathogenic Bacteria)

Although the transmission of bovine tuberculosis by drinking unpasteurized milk from infected cows has long been acknowledged, transmission through polluted waters is not mentioned in the American Public Health Association's official report of 1960 (2663). Nevertheless, the organism appears hardy enough and the potential real enough for researchers to continue to probe the dangers.

Klein (1756) cites a paper by Christiansen and Jepsen in which they report that cows drinking brook water polluted by waste waters from a slaughterhouse remained free from tuberculosis in spite of 8 of 15 water samples containing Mycobacterium tuberculosis (see also 519,

2492, 2745).

In 1954, Miller and Anderson (2493) reported two cases of primary tuberculosis in children following immersion in sewage-contaminated water. Hence, Greenberg and Kupka (2482), in reviewing the literature on tuberculosis transmission by waste waters, state that the danger is most marked with swimming or near-drowning.

In a series of laboratory investigations in which sewage was added to various pathogenic cultures, it was found that sewage had an inhibitory effect on tubercle bacilli (2746). However, Dedie (2403) reports that the tubercle bacillus can remain infective for three months in waste waters, and up to six months in soil. The Yearbook of Agriculture on "Animal Diseases" states that tubercle bacilli dropped in stagnant pools with manure may remain alive for a year or longer (2402). Haigo (2747) verifies the presence in feces of other organisms antagonistic to the tubercle bacillus, but estimate survival in natural waters and sewage as about one month. In a study of sewage sludge, Jensen (2748) reported that it took 11 to 15 months before the organism could no longer be demonstrated in sludge-drying beds.

Experiments with guinea pigs injected with milk from tubercular cattle show an inoculating dose to be 30 bacilli. The same paper gives an interesting account of the dangers associated with feeding cattle on land sprayirrigated with waste water from a German dairy, using actual figures obtained in a study. These figures show that cattle would be exposed to 111 virulent organisms

in each square meter of soil (2404).

In terms of distance, tuberculosis bacteria have been found over one mile downstream from a sanitorium sewage outfall (1382, 2305).

#### PASTEURELLA TULARENSIS

(see also Pathogenic Bacteria)

Pasteurella tularensis is the etiologic agent of tularemia. This disease can be transmitted in a number of ways of which the drinking of water contaminated by infected animals is probably a lesser avenue. Nevertheless, a Russian paper notes a tularemia epidemic among muskrats that infected hunters and fishermen (2749); another associates the illness with washing and bathing in infected waters (2305, 2494); and a third discusses the nature of outbreaks associated with wells as compared to outbreaks associated with surface streams (2750). Outbreaks associated with wells generally involved a large

number of people drinking the water in a short time. The source of difficulty, usually small rodents falling into wells through unsound casings, is easily corrected and eliminated. Outbreaks associated with streams, however, result in only a few patients at a time over a much longer period of time and greater geographical area. Also, elimination of the source is much more difficult, the only rational method being to provide the population with clean drinking water (see also 2492).

Banfield (2751) reports the first demonstration of *Pasteurella tularensis* in the natural waters of Canada. It was associated with an epizootic among beavers and muskrats that died in the water. However, no known

human cases resulted.

Ten years earlier, Parker et al. (2752) had observed a tularemia epizootic among muskrats and beavers in the northwestern part of the U. S. This occurrence resulted in a number of human cases, but transmission through water was not involved. Nevertheless, Parker stated that water transmission was potentially possible and that under favorable conditions such contamination could persist for periods of at least seven months and at any season of the year. In 1942, Jellison (2753) published the results of an investigation of tularemia among beavers in Montana. At this time he indicated that tularemia could possibly be transmitted among animals via contaminated water and also suggested that *P. tularensis*-contaminated stream water may be the occasional source of human infection in the U. S.

In 1950, Jellison et al. (2754) described tularemia among humans that was traced to an infected domestic rural water supply. Although farm animals had been fenced out of the area of the spring, ferral rodents had

access to it.

Pasteurella tularensis was isolated from 14 of 37 samples by workers who were studying tularemia infection in a population of voles (2755). Quan et al. (2756) calculated the  $\mathrm{LD}_{50}$  of P. tularensis suspensions in drinking water of mice as  $10^7$  organisms. In a series of experiments by intubation into the stomach with a blunt-nosed hypodermic needle, the  $\mathrm{LD}_{50}$  was calculated at  $10^6$  organisms.

#### PATHOGENIC BACTERIA

(see also Coliform Bacteria, Salmonella, Shigella, Mycobacterium tuberculosis, Leptospira, Pasteurella tularensis, Protozoa, and Insects)

Bacterial diseases that have been transmitted to human beings or livestock by contaminated water supplies include not only intestinal illnesses, such as dysentery, typhoid fever, paratyphoid fevers, cholera, and gastroenteritis (497, 520, 533, 702, 703, 704) but also, though less frequently, tuberculosis (302, 573, 1382, 1383, 1626), anthrax (346, 497, 520), brucellosis (497, 705), tularemia (671, 706, 707, 708), leptospirosis (330, 423, 520, 709, 710, 1382, 1627, 1628, 1629), and other infections. Occasionally strains of coliforms may be pathogenic, although they are ordinarily harmless (711, 2575, 2576, 2577, 2578). Some diseases, such as brucellosis, tuberculosis, tularemia, and salmonella infections are common to man and certain animal species. Conceivably, therefore, they may be transmitted in water polluted by animal discharges (301, 334).

Except for the intestinal pathogens, most disease organisms do not gain access to water in any great numbers and can survive in it for only a limited time, so that their spread by this route has been rare. In recent years, however, more attention is being directed towards an understanding of the factors involved in the spread of disease by water, because greater demands are being made upon limited water supplies in populated areas and it has become necessary to draw sometimes upon questionable sources for various uses.

The survival of disease organisms is dependent on many factors, both physiological and environmental. Among the more important physiologically are (a) their ability to form resistant spores, (b) reaction to heat, cold, and chemicals, and (c) competition with other organisms. Factors that are environmentally significant include oxygen supply, pH, temperature, sunlight, nutrient supply, sedimentation, dilution (619, 712, 713, 714), and the antibiotic and competitive activity of other organisms (301, 302, 435, 487, 715, 716, 718).

On the other hand, whether pathogenic organisms can cause infection depends on other factors, such as their virulence, chance of ingestion by proper hosts, and the

resistance of the hosts (301).

Because of the operation of so many independent variables, public-health practice is based not on the probability but on the possibility of infection. It is not concerned with defining limiting or threshold concentrations of pathogenic organisms, because the limit is zero. It is concerned with providing "safe" water, which may be consumed internally or otherwise used without menace to the health of the consumer. It is hardly possible for water to be so safe that absolutely no risk is taken in using it; on the other hand, it is possible to provide water safe to such a degree that the danger involved is small enough properly to be disregarded (152, 334). Nevertheless, both France and Belgium have standards for drinking water that specify "no" pathogenic organisms (717).

According to Maxey (719), to be considered waterborne a disease must meet four criteria: (a) it must be associated with insanitary conditions; (b) its incidence must be reduced when water-supply improvements are made; (c) it must increase with epidemic rapidity when water supplies are subject to temporary pollution; and (d) it must be of greater incidence among those using a suspected supply than among others using different supplies, alike in all other aspects. The isolation of pathogenic organisms from water does not constitute procof that the diseases they cause are water-borne unless this evidence can be supported by epidemiological data. The intestinal diseases are commonly accepted as water-borne because they have met the conditions listed. At the present time, the water route of transmission of other diseases is still considered epidemiologically unimportant, even though they may occasionally be spread by water supplies.

Kruse (2122) discusses a "so-called water fever" that appears immediately after infection of a water supply and precedes a true typhoid epidemic. There has been some concern expressed for a reappraisal of water-borne ailments, for many aspects are not clearly understood (2123).

Vibrio comma was isolated from 12 of 89 samples of water taken from the River Hooghly and associated canals in Calcutta, India (2757). Vibrio survived 81 days in sterilized harbor water, 64 days in sterilized open-ocean water, and less than 32 days in polluted fresh water. Other reports state that the organism survived over 36 days in heat-sterilized sea water, 10 days in harbor water, 47 days in sea water (2589), 7 days in Yugoslav river water, and 1 day in badly polluted water (2305). Cholera bacteria in drinking water can be destroyed by adding HC1 to give a concentration of 0.06 N (pH about 4.0) for 10 minutes (2758).

Infection by tetanus after a bathing accident led to the examination of water samples from the Elbe River.

Of 30 samples, eight were positive (2759).

Brucellosis infection may occur by water (2305). So may listerosis (sheep), coccidiosis (sheep, goats, and poultry), and pullorum disease (2402). Brucella can survive up to 90 days in distilled water, and up to 72 days according to another author. Others have claimed up to 120 days in tap water. Frogs have been experimentally infected with Brucella melitensis, as were a tortoise and carp. Brucella were isolated from internal organs of the latter two in 15 to 40 days after placing in a contaminated aquarium. The strain lost virulence as measured in guinea pigs (2760). See Koser (2745) for Brucella in sewage-irrigation water.

In a review of anthrax infection, Gillissen (2761) concludes that infection by the water-borne route is rare, but that the potential is still sufficiently strong so that drainage from leather factories should not be permitted

to enter meadows and fields (520).

An epidemic of granulomatous skin lesions caused by an acid-fast Mycobacterium which secondarily invaded abrasions in the skin of swimmers in Sweden was first reported in 1951 (2479). In 1954, the new bacterium was described as Mycobacterium balnei (2762), and the disease called "swimming pool disease" or mycobacteriosis balnearea (2480). Cases from Canada and Sweden were reported in 1957 (2481). In 1959, an epidemic of considerable proportions occurred in Colorado, involving 262 cases. M. balnei was found in both water and tissues (2476, 2477, 2478).

Staphylococcus aureus was found to be harmful to some ciliates (2313). This organism was occasionally isolated from sewage-contaminated sea bathing waters in a 5-year study of illness associated with bathing in such waters (2468). S. aureus reportedly succumbs rapidly in polluted sea water (2589). Less than 15 lbs. of a dried, purified Staphylococcus enterotoxin in one million gallons of drinking water would poison the greater part of the exposed population.

The toxin of *C. botulinum* is even more potent. Less than 10 lbs of partially purified toxin in one million gallons of drinking water would infect more than 90 percent of the exposed population (2763). *Clostridium botulinum* partially purified type A toxin, in the pH range 7.0-10.0, is inactivated to the extent of 99.90-99.99 percent in 15-30 seconds at 25°C by free available chlorine (see also 2764, 2765). Chloramines are relatively ineffective (2766). There have been undocumented statements that decaying algae can support the growth of *Clostridium botulinum*, which in turn can result in the

death of water fowl (2012, 2285). Chickens have contracted botulism from drinking pond water. The toxin was found in the water even though decomposing animal matter was not present (1629). Sea water samples collected in the vicinity of a sewage outfall in the Mediterranean showed Clostridium welchii (perfringens) to occur up to 1200 feet from the outfall (2767). Fish caught in coastal waters were reported to contain C. perfringens, those caught at sea did not (2321).

Erysipelas is a skin inflammation caused by hemolytic streptococci. This infection may arise from skin punctures obtained while handling fish (1630, 2768). Listeria monocytogenes and Erysipelothrix rhusiopathiae (insidiosa) were isolated from surface waters, sometimes along with Pasteurella tularensis, as well as from ferral rodents. This occurrence resulted in a recommendation that when combatting epidemics of illnesses caused by these organisms among either humans or animals, the waterborne route must be considered (2769). E. rhusiopathiae was found in 10 of 30 samples of sewage in Konigsberg, and in 5 of 52 samples in Munich. Slaughterhouses were believed to be the sources (2770).

Furunculosis of fish is caused by Bacterium salmonicida (Aeromonas salmonicida), an obligate parasite that survives longer in polluted than unpolluted waters—up

to 67 days (2771).

An Association of Beekeepers (Germany) has protested against the application of sewage to ground as a spray in areas where bees are numerous. Bees flying through the spray may become contaminated with pathogens and these may in turn be transmitted to humans by stinging (2681).

Water free from disease-producing organisms may still be capable of harming milk. Such water should be treated to give a "low" colony count at 22°C and should contain no milk-souring organisms in 10 ml samples

(2772).

### **POLIOVIRUSES**

1. General. The polioviruses comprise a group of three primary types, Type I being the most prevalent. It is a relatively small sphere 25-30 mµ in diameter, indigenous to man but capable experimentally of infecting other primates and some rodents. The majority of infections caused by poliovirus are inapparent or abortive, the most common clinical manifestations being febrile illness and enteric disturbance. On occasions, however, the virus will affect nerve tissue, causing aseptic meningitis and paralysis of varying kind and severity (2159).

The British Medical Journal reports that a patient with poliomyelitis may excrete in one gram of feces enough virus to infect one million monkeys. Half the patients are still excreting virus after 3 weeks and some continue to excrete it up to 12 weeks (2773). It is, therefore, not surprising that the virus has been found in sewage, in the early stages of disposal processes at treatment plants, or even in treated effluent (533, 719, 721, 722, 723, 724, 727, 884, 2119, 2593, 2774). Earlier work (724, 725) indicated that the virus can be transported in sewage for at least \( \frac{1}{8} \) mile, and can persist in water or refrigerated feces for several weeks. Russian workers in 1956 (2775) reported that the poliovirus remains viable

in human feces for over 6 months, in milk at room temperature for 31 days and at 10°C for over 150 days, and in experimentally polluted water for at least 118 days. A 1950 Canadian paper reported that a strain of poliovirus in stools survived at least 188 days after addition to river water, temperature 4°C. Dilution was 1:200. and the virus retained its ability to induce paralysis in monkeys (2776). German experiments with the Columbia-SK-virus reaffirmed Maxcy's statement that the virus is unable to grow and multiply while suspended in sewage (723). The same work showed that virulence of the virus in moderately or highly polluted river water continued for up to 6 days, and in sterile physiological salt solution for over 11 days (2496). The virus has been inactivated when inoculated into cultures of sewage protozoa (726).

Poliovirus reportedly resembles Coxsackie virus in its ability to withstand a wide range of pH. All strains tested survived pH 2.3-9.4 for one day and 4.0 to 8.0 for 7 days at room temporature (2594). With respect to heat, it is reported that the virus is destroyed by the higher pasteurization temperature when the virus is present in such concentrations as are "to be expected in milk" (2496). Lawson (2777) states that a rodent poliovirus is 95% reduced in infectivity when exposed to 45°C for 30 minutes, but requires 60°C for 30 minutes to be 99.9% or greater inactivated. Robinson (2594), using a Y-SK strain, reports no infectivity after 30 minutes at 53°-55°C. Also, an MM strain demonstrated more heat tolerance but still lost most infectivity at 62°-64°C for 30 minutes.

- 2. Cross References. Viruses, Coxsackie Viruses, and Infectious Hepatitis Viruses.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. There is still no positive evidence to prove that polio is spread by drinking water. Epidemiologically, polio does not behave like a water-borne disease (719, 722, 723, 724, 883, 2124). Nevertheless, two polio epidemics have been reported in which water-borne poliovirus is highly suspect. A Canadian outbreak is reported to have had all the characteristics of a water-borne epidemic postulated by Maxcy and Howe, namely incidence correlated with poor supplies, and explosive outbreaks occur in widely scattered areas of the municipal supply (2778). Also, the epidemiological investigation of a Nebraska epidemic strongly indicated that back siphonage from sewage was responsible. In this study, an absence of chlorine and presence of coliforms in the water at a date later than the epidemic were observed (2779). South African studies, as interpreted by Russian workers in the light of their own experience, were also highly incriminating of a waterborne source of virus in a polio epidemic (2774). Earlier papers that reported a possible association between lower fluorides and a higher polio incidence, and also between low nitrates and lower polio incidence remain unconfirmed (729, 730, 1033).
- b. Irrigation Waters. The mode of transmission of polio and the role of contaminated food have not been established (302). Bingel and Engelhardt (2496) state that since the poliovirus is sensitive to temperatures of 85°-100°C, fruit and vegetables can be disinfected by

immersion in boiling water. Also, soil studies show that the virus can reach ground water, but it is so dilute that chlorination would be quite effective.

c. Fish and Other Aquatic Life. Crovari (2455) studied Type 2 poliovirus and mussels. His conclusions: (1) If mussels are left for some hours (he used 3 hours) in sea water containing poliovirus, they become contaminated. (2) Passage of the virus through the mollusk does not—affect its pathogenicity. (3) Virus can be recovered from infected mussels even after 24 hours cleansing in running sea water, but not after 48 hours.

One investigator has pointed out similarities between the effects of poliomyelitis and mussel poisoning, relating both to poisoning by cyanogen compounds, possibly produced in water by cyanophore glucosides of plant origin. Sulfocyanates and cyanides are said to be capable of producing gastrointestinal and neurological symptoms identical with those of polio. It is suggested that the virus might be a cyanolytic enzyme in the human body, or an endogenous protein produced in the body by cyanophore compounds (421, 731, 732).

On the other hand, a detailed comparison of the symptoms of polio with those of cyanide poisoning has shown such clear-cut differences between the two symptom-complexes that it is hardly likely that the two could be related or should be confused (733).

d. Recreational Use. Certain studies of localized polio epidemics have indicated that swimming at polluted beaches has been second to direct contact (722, 734, 735). Moore (2468) states that a statistically controlled epidemiological study of the bathing histories of 150 poliomyelitis cases in children living permanently by the seaside gave no evidence that sea bathing played any part in causing the disease (also see 2469, 2470). Van Den Bossche concludes that swimming pools were not a factor in a Belgian epidemic (2498). An investigation of an epidemic in Germany concluded that swimming in untreated or in purified water had no effect on incidence (2497).

### **PROTOZOA**

1. General. The occurrence of protozoa in a water can be either beneficial or a nuisance. Protozoa have been found to be factors in the elimination of viruses and pathogenic bacteria from water, and are an important part of the food chain for higher forms of animal life. They also assist bacteria in the processes of decomposition of organic matter (726, 736, 737, 740). Apparently not all bacteria affect protozoa in a similar manner, however (2313). Escherichia coli and Salmonella typhimurium were found to be harmful to Paramecium caudatum, Chilodonella uncinata, and Colpidium colpoda, as was Staphylococcus aureus although after a longer period. Salmonella enteritidis and Bacillus subtillis were not harmful. B. subtilus was soon preferred by the above three experimental ciliates. Protozoa may occur as part of a biological slime or sewage fungus (see Slime bacteria, Fungi). Heukelekian (2144) ascribes to the role of the protozoa the second order of importance in the biology of the self-purification of waters, because of their ingestion of small organic particulates, utilization of soluble organic material, ingestion of bacteria, and role

as food for higher organisms. Common protozoans include Epistilis, Vorticella, Colpidium, and Stentor (2143).

A number of protozoa are intestinal parasites of man (2492), a few of which are pathogenic. They may be regarded as primary polluting substances, whereas the protozoa that proliferate because of high bacteria and algae counts in waste waters would be corollary pollutants.

Stammer (2690) tested fourteen indicator organisms of the saprobic classification system against hydrogen sulfide and ammonia. The protozoa of these tests all had a low resistance to these chemicals in the absence of oxygen, regardless of the position of the protozoa in the saprobic system. Nevertheless, some species of protozoa, such as Stentor coeruleus, become abundant in anaerobic situations (2780). The formation of slimes containing the methane-oxidizing bacteria Methanomonas methania and protozoa has caused the blocking of filters (2781). Prechlorination can sometimes lengthen filter runs by killing small, motile, gelatinous organisms such as Monas which otherwise would not settle out (2260).

Mohr (2782) has discussed the protozoa as indicators of pollution. Intestinal protozoa are fragile and distinct from the forms commonly found in water, except when encysted. Identification of protozoa is difficult (2503). Protozoa may be more sensitive to temperature changes than many other life forms. Trembley mentions that green algae and many protozoa became less abundant in heated waste waters (2622). Protozoan populations of swamp-drainage and sewage areas of a Pennsylvania lake were-similar except that more species were associated with the area of sewage pollution (2783). Seasonally, protozoa have been reported in the fall (738), and reflect the size of the bacterial population. Acid waters show a great decrease in protozoa. Some of the Ctenostomata and Metopus have been found a few times at pH 6.5, but a bottom dwelling Pelomyxa is the sole acid water organism (2503). In a stream from which pollution was greatly reduced, protozoa and algae became diversified more quickly than the insect fauna (2544).

In a study of ciliate ecology, it is reported that growth is best in cultural conditions closest to that of the natural environment. In enriched cultures, most species die out. Most ciliates are sensitive to high bacterial concentrations. However, ciliates have a wide range of sensitivity to carbon dioxide and oxygen tensions. Species sensitive to acid conditions were likewise sensitive to high carbon dioxide tensions, whereas less sensitive forms tolerated higher carbon dioxide tensions (2784). Lackey (2230) reports that oxygen depletion of a stream tends to eliminate all but a few species of anaerobic ciliates and colorless flagellates. After many years of study the status of indicator species seems little near clarification (see also 739).

A Baltimore reservoir with an average pH of 7.0 rose to 9.0 in a portion where diatoms were abundant. Where the pH was normal, protozoa were abundant and diatoms scarce (2629). Another paper states that pH will increase if blue-green algae are present but if protozoa become abundant, the pH would go down (2628).

Studies on cellulose decomposition showed that a potassium deficiency hinders protozoan development (2139). The succession of organisms in the decomposition

of cellulose approximates that of digestion: small bacteria and small flagellates, followed by small ciliates, and finally larger ciliates, amoeba, and rotatoria. In a study of a small artificial pond, chrysomonads were not found when the water contained more than 0.02 mg/1 phosphate but cryptomonads and diatoms increased at this concentration (2628). See Provasoli's work (2202) for further information on protozoan nutrition, and also see Johanna Resigs' work (2790) on marine protozoans of the order Foraminifera and their relation to pollution.

Cationic and nonionic surfactants in low concentration were toxic to *Pelomyxa carolinensis*, but low concentrations of nonionics were growth-stimulating. Protozoa have been associated with the metabolism of hexadecanol evaporation-retarding films (2293). In the harbor of Hamburg, Germany, ciliates predominate among the plankton during the winter (2785). In a German river, all aquatic life was snuffed out by a discharge of phenols. First protozoa appeared when the DO reached 5.3 mg/l and phenols dropped to 4.3 mg/l. In increasing from zero to 2.0 mg/l, phenols generally decreased the variety and quantity of protozoa with no relation to its saprobic classification (2786). Laboratory tests showed the protozoa could not utilize phenols directly.

Bartsch and Ingram show that counts of ciliates reach their greatest numbers in the zone of decomposition in polluted streams (2143).

Cysts of Endamoeba histolytica are well recognized for their durability (744, 745). Chang's work (2787) showed that they survive in feces and in distilled water at 0°C for 62 days. Below 0°C, the lower the temperature, the more rapidly the cysts are killed. The cysts die out quickly upon drying out, but survive months in water and sewage (720, 745). They pass quite readily through biological sewage treatment processes (743, 746, 2788). Emile and Tomasic (2305) relate survival not only to temperature but to the number of bacteria in the water. If "a lot of microbes" are present and the temperature is 27-30°C, cysts may disappear within nine days. At 22°C and with fewer bacteria, cysts may subsist for 29 days. In pure water without organic matter (no temperature mentioned) cysts may survive several months. In Denver, 46 percent of the Endamoeba coli cysts survived primary treatment and chlorination which removed 99 percent of coliforms and enterococci (2789).

Protozoa concentrate radioactive materials (2109). See Chapter VIII, Radioactivity.

- 2. Cross References. Bacteria—General, Slime Bacteria, Fungi, Algae, Polioviruses, and Chapter X.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Ingram and Bartsch (2420) have compiled a booklet of animals associated with potable water supplies. Among the protozoa most frequently mentioned are Paramecium, Didinium, Arcella, and Difflugia. Pathogenic protozoa include Endamoeba histolytica, Giardia lamblia, and Balantidium coli which may be transmitted by infected drinking water or sewage-irrigated foods that are eaten raw (497, 745).

As recently as 1949, the water transmission of amoebic dysentery was not universally acknowledged (742). However, a factor in this slow recognition may be explained by findings of the germ-free animal studies. They

show that amoebic dysentery in animals does not occur unless other intestinal microflora are present (2791). Persons afflicted with acute diarrhea discharge trophozoite forms in their stools and few cysts. The trophozoites are fragile forms, not capable of lengthy survival under adverse environmental conditions (2305). Chronic amoebiasis sufferers discharge few trophozoites, but many of the hardy cyst forms (720).

The water treatment processes of coagulation, sedimentation, and filtration are partially effective as removal processes, but chlorination cannot be relied upon for destruction of the cysts as it can with pathogenic vegetative bacterial forms (741, 2305). The drought experience at Chanute, Kansas, in which treated sewage effluent was recycled through a water supply reservoir (2119) did not disclose any *E. histolytica* cysts in the treated water. However, cysts of free living amoebas comparable in size to *E. histolytica* were found regularly in the treated water.

Vorticella has been associated with bitter taste as well as odor in Valparaiso, Indiana (2247). Bursaria is another odor-producing form (2242).

A violent outbreak of amebiasis occurred among industrial workers in Indiana in 1953 (2792, 2793). Chlorination had successfully abolished bacteriological evidence of contamination, but did not influence the cysts. Rendtorff and Holt (2794) performed some interesting human studies on the transmission of Endamoeba coli and Giardia lamblia in drinking water. Cysts of both species were introduced into a bottled water dispenser from which 20 men drank. Four became infected with Endamoeba, none with Giardia. In another experiment, cysts were added to aerated tap water maintained at 8°C and fed to volunteers from 0 to 16 days after storage. Endamoeba infected 70.6 percent, Giardia 64.7 percent.

Ratios of amoebic cysts to coliform bacteria of 1:100,000, and of carriers to the general population of 1 or 2 to 20, have been reported (747). Cysts have been reported to be non-infective until they have matured for 24 to 48 hours (748).

- b. Industrial Water Supplies. Protozoa are undesirable pollutants for various uses, such as the bottling of carbonated drinks, papermaking, dyeing, and photography (346, 403).
- c. Irrigation Waters. The use of *Endamoeba*-polluted irrigation water may cause dysentery among consumers of uncooked produce. Waterborne epidemics occur in temperate climates only as a result of massive quantities of fresh pollution, and are rare in the United States. Rudolfs et al. (748) contend that in the temperate zone field-grown crops subject to contamination by cysts are safe, and can be eaten raw, one week after contamination has stopped. In wetter, tropical regions, however, they are safe only after two weeks (2795). This contention is likely to be disputed by many public-health authorities.

A study of the degree of intestinal parasitism of urban sewage workers with *Endamoeba histolytica* revealed a 14 percent rate; that for workers in irrigation fields, a 9 percent rate (2912).

d. Fish and Aquatic Life. Parasitic protozoa are known to cause disease in fish (308). Protozoa serve as food organisms for shellfish.

#### RICKETTSIA

The only rickettsial agent reported in connection with polluted water found in this survey is Rickettsia burneti. This rickettsia, also known as Coxiella burneti, is the causative agent of Q fever, a relatively mild illness of benign nature with a negligible fatality except for the aged. Its mode of transmission is commonly airborne in or near contaminated premises or infected animals (2663). Out of 19 water samples collected on 6 ranches in California (an endemic state), 6 samples contained Rickettsia burneti in detectable amounts (2796). However, Q fever is not a waterborne disease.

### ROTIFERA (ROTATORIA)

(see also Crustacea)

The Rotifera are a group of small, usually microscopic animals, that have attracted much attention from microscopists because of their wide-spread distribution in waters of all kinds, and the great abundance in which they frequently occur (16). Among the small aquatic animals, the Rotifera and Crustacea comprise groups with which the water pollution specialist generally has a limited amount of familiarity. However, there exist many other groups of small aquatic fauna.

These aquatic fauna are not primary pollutants. They may become corollary pollutants owing to the development of ideal conditions for their growth in abundance by means of certain waste discharges. For example, Bick (2139) cites the succession of organisms in the decomposition of cellulose as corresponding approximately to that of digestion: small bacteria and small flagellates followed by small ciliates, and finally by larger ciliates, amoeba, and Rotifera. Also, Bartsch and Ingram (2143) cite the predominance of rotifers and crustacea in stream purification in the latter stages of the recovery zone. However, there was not uncovered in this survey a single reference as to any detrimental effects that large numbers or any particular species of Rotifera may have on any of the beneficial water uses. Rather, since they are a part of the aquatic food chain, one would suspect that large numbers of rotifers may eventually lead to an increasing fish productivity.

In a study of acid mine pollution, it was noted that the predominant aquatic population remaining after an excessive amount of acid had drastically reduced the plankton population consisted entirely of rotifers (2797). However Järnefelt (2168) reports only one species of Rotifera as being present in a lake that was "acid-trophied" by wastes from a powder factory.

Ingram and Bartsch (2420) cite two Rotifera as of interest in potable water supplies, viz, *Philodina* and *Brachionus*. Rotifers are commonly found in uncovered finished water reservoirs and have been reported to penetrate filters in England.

#### SALMONELLA

1. General. The genus Salmonella is responsible for some of the most severe diseases in man. Salmonella typhosa causes typhoid fever, and S. paratyphi, S. schottmuelleri, and S. hirschfeldii cause paratyphoid fever

(2289). The genus Salmonella includes a large number of species. Bergey's Manual (2637) lists 343 serotypes that were recognized by the year 1955. The species S. typhosa, known also by the names of Bacterium typhosum, Bacillus typhosus, Bacillus typhi, Bacillus typhi abdominalis, Bacterium typhi, Eberthella typhi, Salmonella typhi, etc. (2637), has been studied most extensively. Although it differs in some respects from the others, being somewhat longer lived and more resistant to bactericides, it is fairly representative of the other intestinal pathogens as a group (302).

Considerable research has been directed toward determining the survival times of various salmonella species in a variety of media. Some of the data pertinent to water pollution are tabulated in Table 7-1. The bulk of the organisms, when thrust into unfavorable media, undergo an initial rapid die-off such that for most, survival is for only a few days (488, 716, 2492). A few, however, can survive for considerable periods of time, and on occasion have been known to multiply outside the human body (716, 720, 2467, 2798). One investigation (2799) reports survival in terms of distance; salmonella was recovered from a stream 15 to 21 miles below a sewage outfall. Unidentified factors in waters antagonistic toward salmonella have been reported. These waters include ground water (deep well) (2800) and a saline lake water (2801).

Salmonella were isolated from 83 percent of the water samples taken from a canal in Argentina. Recovered salmonella included 11 species, the more common of which were, respectively, S. newport, S. typhimurium, S. muenster, S. bredeney, S. montevideo, and S. anatum. These six species were also isolated from children suffering from enteric disorders with the same respective frequency (2802). S. panama was recovered from a harbor water in the neighborhood of a patient infected with the same organism (2803). S. typhosa has been isolated from gull feces (479). Sea birds excrete typhoid and paratyphoid bacteria for long periods after removal from access to polluted waters (2804).

- 2. Cross References. Pathogenic Bacteria, Algae, Protozoa, Worms—Free-Living, and Chapter V—Swimming and Bathing Waters.
  - 3. Effects on Beneficial Uses
- a. Domestic Water Supplies. Salmonella in humans was attributed to gulls that were contaminated while scavenging in the area of sewage outfalls and later polluted the community surface-water supply. Cultures from the gulls and two hospitalized patients were identical (2813). Kruse (2122) states that infection (with typhoid) is not conveyed by drinking polluted water but by contact of the water with some easily polluted food stuff under suitable conditions of temperature and growth of the bacteria. Nevertheless, improvements in the quality of a potable supply have been followed by a reduction in the typhoid fever rate among the population and thus the incidence of typhoid fever in a community has served as a measure of the sanitary quality of the water supply. The number of S. typhosa organisms in a supply is dependent, of course, on the past history of typhoid in the community; thus a reduction in incidence with a consequent reduction in the

TABLE 7-1
SURVIVAL DATA FOR SALMONELLA

Type Organism Reported	Media and Conditions	Survival Time	Refer- ence	Type Organism Reported	Media and Conditions	Survival Time	Refer- ence
S. typhi S. enteritides	Spring water	10% survived 44 hours	2805	E. typhosa	Sea water, heat sterilized	25 days	2589
S. paratyphi S. typh <b>i</b>	) Synthetic well water, pH 5.9, 5°-25° C	7 days	2806	$E.\ typhosa$ $E.\ typhosa$	Sea water, raw San Francisco Bay, 10° C	9 days 12-28 days	2589 2589
S. typhi	Synthetic well water, pH 7 & 9, 5° & 21° C	77+ days	2806	E. typhosa	San Francisco Bay, filtered, 10° C	14-34 days	2589
S. typhi	Synthetic well water, pH 8, 5° & 21° C	196+ days	2806	S. typhimurium	Sea water	Few died in 24 hours	2589
Typhoid bacilli	Tap, well, and distilled	2 weeks to 80 days	2589	E. typhosa E. typhosa	Tidal water Sea water	>2-3 weeks 14 days	2589 2589
S. typhi	Tap and distilled water, innoculum 1 × 10°/ml	211 days	2807	Typhoid organisms Paratyphoid bacteria	Sea water Sea water	12-16 hours 21 days	2589 2589
	Distilled water, innoculum $5 \times 10^3/\text{ml}$	59 days	2807	S. paratyphi B.	Sea water, innoculum 10 × 10 ⁶ /ml	2 months	2466
	Distilled water, innoculum $1  imes 10^8 /  ext{ml}$	494 days	2807	S. typhosa S. typhosa	Sea water Sea water	>30 days >32 days	487 488
S. paratyphi B. Typhoid bacteria	Surface water Water 0° C Water 5° C Water 10° C	3 months 9 weeks 7 weeks 5 weeks	2808 2809	Salmonella group S. schottmuelleri	Muddy waste water Sludge banks and ditch water	180 days 1.5 years	2403 2810
g	Water 18° C	4 weeks	2520	Typhoid bacilli S. typhi	Septic sewage Water with humus	5 weeks 85-104 days	2589 2569
S. typhi S. paratyphi A.	Water without humus Tap water, aged	58-69 days 29 days	$2569 \\ 2798$	S. typhosa	added Polluted water	>4 days	488
S. paratyphi B.	24 hrs. Tap water, aged 24 hrs.	25% remaining in 29 days	2798	E. typhosa Typhoid bacilli	Imboff tank sludge Oysters	11 days 9-42 days	2589 2589
S. typhiabdominalis	Tap water, aged 24 hrs. + 0.2 gm/l steri- lized feces, 16°-18° C	Multiplication	2798	S. typhosa S. schottmuelleri Typhoid bacteria Typhoid bacteria	Shell oysters Oysters, 5° C In gut of fish Carp	14-60 days 49 days 7-9 weeks 4-6 weeks	2589 2589 1630 2768
S. typhosa	Water or sewage, warm weather	Several days	533	Salmonella	Soil and potato (surface)	40+ days	2811
S. typhosa	Water or sewage, cold weather	months	533		Carrot (surface) Cabbage and goose-	10 + days 5 + days	2811 2811
S. typhosa	Fresh water	4 days	488		berries (surface)	-	
S. typhi S. enteritides	Sea water	50-60% survived	2805	Typhoid bacteria	Excreta Septic tanks	10-84 days >27 days	488 488
S. paratyphi S. typhi	) Autoclaved sea water	44 hours Several days	2588	S. typhosa	Within gut of Nema- todes of Rhabditidae	3-4 days	2812
S. paratyphi B.	Autoclaved sea water	Several days	2588		family		

number of carriers results in a corresponding reduction in the contamination of the water. Typhoid may be contracted from infected shellfish, milk, and other foods; nevertheless, over the years, the incidence of typhoid has dropped enormously in this country, so that under the present favorable conditions there is less likelihood that water pollution will result directly in serious epidemics of typhoid fever, although pollution can still cause widespread outbreaks of other enteric diseases.

Less than one pound of a preparation of Salmonella anatum added to one million gallons of drinking water is required to produce salmonellosis in 50 percent of the exposed population. HCl added to water to give a 0.06 N solution (pH about 4.0) for 10 minutes will destroy

salmonella (2758).

b. Irrigation Waters. In studies lasting several years, salmonella including S. typhosa, were isolated from over 50 percent of sewage contaminated irrigation waters. However, only one isolation was made from vegetables to which the water had been applied (1516, 2788). Previous workers had essentially the same results, viz., they re-

covered salmonella from the water samples but none from vegetable washings (1515). Ratios of enteric organisms computed from irrigation water samples were 255,000 coliforms: 4,800 enterococci: 1 salmonella (2580, 2814). The median value of salmonellae in eleven irrigation waters was 0.9 per 100 ml (1383). The work of Rudolfs et al. (515) showed that salmonellae could not survive on the surfaces of vegetables more than one week under the prevaling atmospheric conditions (see also 2795, 2816). Salmonella organisms have survived for 15-46 days on the surface of sewage-irrigated soils, and for as long as 10 weeks in the lower layers (2817) (see also 2745).

c. Stock and Wildlife Watering. Fowl typhoid caused by S. gallinarium was successfully treated by the addition of 0.0375 percent sulfaquinoxaline in the drinking water (2815). Calf typhoid was traced to hay which had been grown on ground flooded in the spring by a stream polluted with sewage. The bacteria deposited in the grass were experimentally demonstrated to survive natural drying and remain virulent in the winter (2814).

d. Fish and Aquatic Life. S. typhimurium was found to be harmful to ciliates; S. enteritides not harmful (2313). Fish may act as carriers of typhoid and paratyphoid (1630).

Survival of S. schottmuelleri in shell oysters was similar to that of S. typhosa, which is about 15 to 60 days in shell stock. S. schottmuelleri persists at least as long as E. coli, but the rate of reduction during storage is not as great as that for E. coli. S. schottmuelleri seldom multiply in animals in marketable condition. However, increases do occur on prolonged storage (2448).

e. Recreational Use. Five different strains of S. typhosa were found in water at an Australian beach where 10 people contracted typhoid fever. A nearby sewage treatment plant effluent was implicated as the source (2475). Two cases of typhoid fever were attributed to swimming in a river (2474). Two other cases of typhoid fever in Spain were attributed to bathing in the sea (2473). None of the above cases were adequately documented (see Chapter V—Swimming and Bathing Waters).

In a 5-year study of sea-bathing waters and illness of bathers, the British Committee on Bathing Beach Contamination encountered small numbers of salmonella in a high proportion of samples; as many as 40 percent of those samples containing over 10,000 coliforms per 100 ml had salmonella. Although the most frequently isolated salmonella was S. paratyphi B. (see also 2818), a total of 33 different species was encountered (2468). Possibly a million or more salmonellae would have to be ingested before clinical infection results (2470). See Chapter V, Swimming and Bathing Waters, Coliform Bacteria—Recreational Use. A Polish study reported the same findings as the British study (2464).

According to Moore (2466), S. typhi could be recovered from sewage sediment in samples maintained at room temperature although the organism was not present in the supernatant. Later, Steiniger found salmonellae in North Sea water (again mostly S. paratyphi B.) and calculated that the numbers could not be explained in terms of numbers in sewage reaching the harbor area. Hence, he assumed the organisms were multiplying—a conclusion supported by Guelin (2467).

# SEWAGE FUNGUS

(see Fungi)

#### SHIGELLA

(see also Pathogenic Bacteria, Salmonella, and Worms —Free-Living)

The genus Shigella is the chief cause of dysentery (bacillary) in man. Important species include S. dysenteriae, S. flexneri, and S. sonnei (2289). The Shigella group does not come within the definition of the coliform group in one respect—it does not produce gas in lactose. Shigella has been implicated in water-borne epidemics on several occasions (2492). The seventh edition of Bergey's Manual lists five species in addition to the above three (2637).

The Shigella species are not as hardy as are the salmonellae. Concentrations of  $1 \times 10^9/\text{ml}$  in tap water, distilled water, and normal saline of S. sonnei, S. flex-

neri, and S. shigae did not remain viable as long as Salmonella typhi (211 days) at room temperature, diffuse daylight, and aerobic conditions. Inoculations of  $5 \times 10^3$ /ml of the following species in distilled water gave viable results as indicated: S. sonnei 107 days; S. flexneri 238 days; and S. shigae 7 days (2807). Inoculation densities of  $1 \times 10^9$ /ml gave the following results: S. sonnei 197 days, S. flexneri 391 days, and S. shigae 7 days (2807).

In a synthetic well water, pH 5.9 and temperature 5°-25° C, S. boydi survived at least 469 days. At pH 7 or 9, and temperatures of 5° and 21°C, S. sonnei, S. shigae, and S. flexneri survived at least 77 days, and at pH 8, both temperatures, at least 196 days (2806). The viability of S. flexneri in water was increased from 98-111 days to 160 days by the addition of humus (2569).

In other viability reports, dysentery bacteria (presumably Shigella) were largely destroyed within 12 hours when placed in sea water, but a few persisted for up to 12 days (2819). In an unidentified water at room temperature, S. flexneri and S. boydi survived 52 days, and S. sonnei 105 days (2820). Studies of S. flexneri in Black Sea water, Lake Tekirghiol water (saline), well water, and a piped supply indicated survival was dependent upon size of inoculum, exposure to sunlight, and salt content. Survival in non-sterilized water usually did not exceed one or two days (2801).

The work of Rudolfs et al. (515) showed that Shigella could not survive on the surfaces of vegetables for more than one week under the atmospheric conditions that prevailed (see also 2795, 2816). Shigella survived 3-4 days within the gut of worms of the Rhabditidae family (2812).

### SLIME BACTERIA

(see also Iron Bacteria, Sulfur Bacteria, and Fungi)

The collective term "slime bacteria" as used in this report includes a host of slime-forming organisms. As differentiated from chemical slime, biological slime refers to films of microorganisms that form slippery layers on wetted surfaces. This term is applied to the larger, often filamentous aggregates of sphaerotilus, zoogleae, and fungi that occur in polluted streams (2821). Most commonly reported in the literature of water pollution among the slime bacteria are the iron or higher bacteria and certain fungi.

Terminology among these corollary pollutants is quite confusing. In order to minimize this confusion, the nomenclature as set forth in the 1957 edition of Bergey's Manual (2637) will be followed. Where an investigator utilizes a name that differs from the above guide, the Bergey's terminology is presented immediately following within parentheses.

The literature on slime bacteria most frequently concerns Sphaerotilus, occasionally Leptothrix. These bacteria have one point in common, viz, they belong to the family Chlamydobacteriaciae. Bergey's Manual recognizes three genera in this family, Sphaerotilus, Leptothrix, and Toxothrix. The latter genus is a group of iron bacteria and has not been referred to specifically in the literature as being among the slime pollutants.

One of the main reasons for the confusion in the nomenclature is that the same organism can assume two or possibly three different physiological forms. Wurtz (2822) states that Sphaerotilus natans appears in the more polluted streams while the other physiological form known as Cladothrix dichotoma (Sphaerotilus dichotomus) is produced in less polluted streams. Bahr (2823, 2824) also concludes that Cladothrix dichotoma (Sphaerotilus dichotomus) is the form that Sphaerotilus natans takes during unfavorable environmental conditions. The National Council for Stream Improvement has sponsored a considerable amount of research on slime bacteria, and one of their bulletins (2825) states that Sphaerotilus natans, Cladothrix dichotoma (Sphaerotilus dichotomus), and Leptothrix ochracea are one and the same organism (2821). Also, that Sphaerotilus discophorus (not in Bergey's) and Leptothrix discophorus (L. discophora) are the same organism.

Eldridge (2826), in summarizing a conference held on the sphaerotilus problem, notes that the term "sphaerotilus" includes a large association of organisms and that these apparently take three forms; the slime form, a "pond" form that does not produce slime, and a third form that is associated with iron. Hohnl (2643) makes the same statements but also cites varying environmental conditions. Slime growths require, in addition to the usual organic and inorganic nutrients and suitable environmental conditions, 18 amino acids, and a sugar content of 20 to 50 µg/1. S. natans predominated at pH values of 5.8 to 9, S. dichotoma (S. dichotomus) at pH 6.4, and when the pH dropped to the range of 5.6 to 5.2, the fungi Fusarium and Mucor predominated. However, the fungi most frequently mentioned among the slimes is Leptomitus (2823), more specifically, Leptomitus lacteus (2825, 2827).

Sphaerotilus problems are frequently associated with sulfite waste liquors. Concentrations of 25 to 100 mg/1 have been responsible for abnormal growths (2642). Jenkins (2828) notes that in streams receiving paper-mill effluents, conditions responsible for S. natans growth were a biological imbalance resulting from the addition of organic matter giving a high dilution, near neutral pH, and insufficient dissolved oxygen. It is an aerobic organism and its growth is inhibited by salt water and also by ammonia (2826). Nevertheless, a pH limit of 4.6 to 8.0 and E_h (redox potential) limit of 200 to 500 v for the growth of Sphaerotilus in estuary studies has been cited (2829).

The major nutrient requirements include mono- and disaccharides, organic acids (acetic and lactic), amino acids, nitrate nitrogen, organic nitrogen, and phosphates.

Hexose sugars appear to be more available to the organism than pentose sugars. There is some question as to its need for iron. Phosphate is a major factor controlling growth, extremely small amounts (0.01 mg/l) being required to implement growth. There is little growth below 3°C. The temperature range for growth is 5° to 24° C, with growth being more rapid at the higher temperatures. pH values below 5.0 and above 11.0 will prevent growth, optimum being between pH 6.0 and 9.0. Stream velocities influence growth (2826). Individual cells of S. natans are motile when set free (2830).

Among the statements cited by Eldridge in his summary of the sphaerotilus conference was that this organism is not associated with gross pollution. There appears to be an overwhelming amount of disagreement in the literature with this statement. Two examples among several include statements by Dondero (2821) and Butcher (2545). Dondero states that Sphaerotilus is a dominant organism in zones of heavy pollution resulting from sewage and wastes containing mono- and disaccharides, lower organic acids, alcohols, and amino acids. Butcher maintains that with gross organic pollution the flora of a river consists of sewage fungus, chiefly Sphaerotilus natures.

Hohnl (2831) found that dilutions of as little as 1:694,000 of spent sulfite liquor, 1:470,000 of spent yeast waste, or 1:350,000 of spent liquor from alcohol fermentation would support growth of S. natans.

The major problem involved with Sphaerotilus growths is interference with commercial and sports fishing by the large floating masses. The slime reduces benthic organisms, hence has an influence on the biology of the stream. If the growth occurs on salmon-spawning beds, it can smother the eggs (2826). Ingram and Towne (2183, 2197) eite additional problems, viz, a cause of tastes and odors upon decay, nuisance to swimming, water skiing, and boating, and clogging of rapid-sand filters. An unusual problem related to slime growths but not specifically to Sphaerotilus occurred in refinery wastes (2502). When the slimes deteriorated in the receiving waters, large amounts of entrained oil were liberated creating an objectionable appearance. The same paper states that spent and regenerated caustic wastes containing phenols effectively controlled slime growths in the refinery's cooling waters.

Secondary effects from Sphaerotilus may be even more serious than the primary effect of being esthetically offensive or a nuisance to fishermen. The detached growths can settle in sludge banks many miles from their origin, giving rise to anaerobic decomposition and the subsequent offensive effects (2500). The oxygen demand of dead Sphaerotilus sludge is reported to be 11 times that of living Sphaerotilus (2821).

One control method under study is the method of intermittent discharge (1920, 2832). It has been applied to sulfite waste liquors, which are stored for 5 days and then released to the river in a 24-hour period. It is estimated that such intermittent discharge has reduced slime growth by 80 to 90 percent (2833, 2834). Cawley (2835) succeeded in reducing growth by intermittent discharge but could not control the growth by this technique.

Another possible control method is reported by Waitz and Lackey (2836). In studying Sphaerotilus natans, they noted that the addition of 1 mg of copper sulfate per liter of medium completely inhibited growth. However, this was not studied in vivo. The same paper suggests that, on the basis of the characteristics exhibited in these experiments, Sphaerotilus could be more accurately classified as a sulfur than as an iron bacterium.

Wolfson (2700) reports that in waterflood systems, the primary slime formers are *Pseudomonas*, *Flavobacterium*, *Escherichia*, *Aerobacter*, and *Bacillus*, many of which are capable of growing in a 10 percent NaCl en-

vironment. Such slimes allow anaerobic organisms to thrive underneath the layers where sulfate-reducing bacteria can thrive.

#### SNAILS

(see Mollusks)

#### SPHAEROTILUS

(see Slime Bacteria)

#### STREPTOCOCCUS FAECALIS

(see Fecal Streptococci)

### SULFUR BACTERIA

(see also Slime Bacteria, Fungi, Iron Bacteria, and Chapter VI—Sulfur)

The sulfur bacteria constitute a heterogeneous group of autotrophic bacteria of varying forms. They are found in soil containing large amounts of sulfur and in the mud of lakes, rivers, estuaries, and harbors. Some species live only in aquatic habitats (2289).

When excessive growths of sulfur bacteria occur in surface or ground waters as a result of man's activities, such growths are considered to be corollary pollutants. Sulfur bacteria may occur as thick slimy growths in streams that are subject to direct pollution of sulfides from tanneries or paper mills, or to the indirect formation of sulfides resulting from anaerobic decomposition of organic matter.

Sulfur bacteria include sulfate-reducing forms (Desulfovibrio) and sulfide-oxidizing forms (Thiobacillus, Beggiatoa), and others. The sulfate reducers are strict anaerobes and are found in large numbers only in places where sulfate is present in abundance. The oxidative forms, also called colorless or white, filamentous, sulfur bacteria, are restricted to places where H2S is present but can flourish only where oxygen is available. Hence, they are generally found in areas where one body of water with an adequate oxygen content borders on another which supplies the H₂S (15). An example is furnished by the Aitolikon Lagoon in Greece. Here a saline bottom water devoid of oxygen content underlies a fresh water of high oxygen content. Periodically, H2S rises in large masses to the surface waters, resulting in patchy blooms of sulfur bacteria (2837).

Another group among the sulfur bacteria are the photosynthetic forms. They include the sulfur purple and green bacteria and they differ from the colorless forms in that they require light and an absence of oxygen. They utilize sulfide in much the same way, but being anaerobes do not occur frequently in natural waters (1036).

Filamentous white sulfur bacteria, such as Beggiatoa alba, obtain the energy necessary for their growth by oxidizing sulfide ion to colloidal sulfur, which is then stored in the cells. This stored sulfur, however, eventually disappears, being itself oxidized to sulfate to yield more energy (1036).

Lackey (2838) published studies on certain sulfur bacterial, viz., Beggiatoa gigantea, B. arachnoidea, and Thiodendron sp. He reports that they tolerate a wide range of most environmental conditions but that all re-

quire  $H_2S$ —as little as 0.2 mg/l or less, and also at least a trace of oxygen—0.1 mg/l or less. The above three require a "high-salt" water of approximately one-half strength sea water or more, and all prefer alkaline waters of pH 7.0-8.4—the latter not necessarily limiting. Beggiatoa, generally presumed to indicate presence of pollution and anaerobiases, actually simply demonstrates the presence of  $H_2S$  (2503).

Mutze and Engel (2839) added thiosulfate to samples of water from the Elbe River. The rate at which thiosulfate was oxidized was found to be a function of the number of sulfur-oxidizing organisms present. Thiobacillus thiooxidans and T. dentrificans were isolated from these samples. Another report (2703) mentions the accelerating effect that T. thiooxidans and T. thioparus have on the hydrolysis of sulfur compounds, partly si-

multaneously and partly alternately.

The corrosion or deterioration of concrete exposed to waters or atmospheres rich in hydrogen sulfide appears to be attributable in part to sulfide- and sulfur-oxidizing bacteria such as *Thiobacillus thiooxidans* (1039, 2358) or *Thiobacillus concretivorous* (198, 1040). Where such organisms are introduced or fostered in natural waters, concrete corrosion may be accelerated. CO₂ and H₂S react on the surface of fresh concrete lowering the pH from 11 to 7.5 and producing sulfate. Then *T. thiooxidans*, *T. thioparus*, and similar sulfur-oxidizing organisms can develop. These organisms oxidize the sulfur compounds to H₂SO₄ (2358, 2840).

Iron and steel are corroded by sulfate-reducing bacteria. This type of corrosion is rapid and is not self-stifling, as is rusting, where the adherent oxide film partially protects underlying metal (2358). Harbors and estuaries are considered as offering ideal conditions for this type of corrosion because the bottom mud is rich in organic matter and anaerobic conditions develop quite readily (2841, 2842). A study of harbor mud from 46 different areas of the world indicated that the amount of sulfur increases with the amount of organic matter—as determined by loss on ignition.

The addition of ferrous iron causes an increase in the rate of corrosion of east iron based on studies with Desulfovibrio desulfuricans (2843). Mortensen (2844) states that corrosion of steel in soil where no oxygen is available is due mainly to sulfate-reducing bacteria, but in harbors, it is mainly an electrolytic form of corrosion.

The sulfate-reducing Desulfovibrio bacteria are most common and important in water flood systems (2700). They are obligate anaerobic (facultative) autotrophic organisms with an optimum growth pH of 7, but a growth range of 5.5 to 8.5. Optimum temperature range is 24°-43°C, but they are found to exist at 0°-100°C. They can grow in fresh water or brines of up to 30 percent NaCl. Such organisms in pipe lines cause corrosion in several ways: (1) The H₂S released is corrosive and this action is accelerated in the presence of O₂. (2) Electrochemical reactions are propogated by the organisms. (3) Chemical corrosion itself enhances the growth of these organisms, and leads to more corrosion.

Sulfides in the Thames Estuary are believed to be formed mainly by sulfate-reducing bacteria rather than by the breakdown of sulfur-containing organic compounds by sulfhydryl-splitting bacteria. The loss of reduced sulfate is a small factor in the over-all oxygen

balance of the estuary (2845).

Sulfate-reducing bacteria liberate H₂S in anaerobic environments. This gas not only corrodes various surfaces, but is also ordorous and highly toxic. Such organisms are of the Desulfovibrio desulfuricans type (1037, 1038). Springer reports that heavy growths of water weeds may lead to anaerobic conditions, which in turn permit the growth of sulfate-reducing organisms, the  $H_2S$  from which can kill oysters (2424).

In H₂S-bearing ground water, sulfur bacteria may occur on well screens or gravel packings, or in pipes and reservoirs receiving such water. Sulfate-reducing bacteria are reported to be the most common organism found in the slimes that plug up tubes of cooling systems, or line the tube walls thereby acting as insulators

and decreasing efficiency (2846)

Drummond and Postgate (2847), in an attempt to control hydrogen sulfide odors emanating from a waterlogged sanitary landfill, found that concentrations of chromate acted bacteriostatically on sulfate-reducing bacteria thereby controlling odors. Furness (2848) introduced cultures of sulfide oxidizers (Chlorobium and Chromatium) in an unsuccessful effort to reduce odors.

A colored sulfur bacterium, Rhodocapsa, caused taste and odors and a purplish-pink color in a service reservoir. Gulls feeding at a sewage works, and resting on the reservoir at night were believed to be responsible (2849). Beggiatoa has also been responsible for tastes and odors (2226, 2242).

#### TREES

(see also Phenols)

Alder trees are reported to be undesirable growths when adjacent to water reservoirs. The leaves discolor the water and impart an unpleasant taste. Leaf worms attack the tree in great number, covering the ground with offal. Hence, it was recommended that they be cleared from areas 100 to 150 feet around impoundments and conifers planted in their place (2314, 2850).

A blue-violet color of a pond in Poland was found to be a complex of tannins and iron, the tannins originating from fallen alder leaves (2851).

Maple leaves were reported to have an oxygen demand equivalent to 75 percent of their weight, whereas oak leaves and pine needles exerted only a 50 percent demand (2852, 2853).

Some trees, such as cottonwood and willow, transpire enormous quantities of water and when located along irrigation canals the water loss is substantial. Such plants, whose root systems extend into the ground water, are known as "phreatophytes." The reader is referred to a USGS publication of that name (2854).

Investigations were made on the influence of vegetation on the quality of drinking water from dunes in the Netherlands to ascertain whether afforestation would have a beneficial or a harmful effect. Water from pine and oak forests showed higher values of color, oxygen consumed, bicarbonate ion, hardness, and chloride content than water from soil with a natural low vegetation. Pine gave lower values for color and oxygen consumed than oak or birch, but higher values for chloride and hardness. An oak forest with elder undergrowth showed high nitrate values for the retained water (2855)

The latest study of the effects on water quality of trees and other vegetation left intact on the ground that was to form the bed of a reservoir again substantiates earlier work that no adverse effects are observed (2856).

Afforestation with spruce and red cedar are said to affect trout streams adversely (2857). Lackey (2503) reports that cypress leaves so soften and color waters as to reduce their recreational, fishing, and domestic-use attractiveness. Tupelo gum leaves blacken swamp waters and inhibit the development of certain plants and animals. He also mentions Hoaks' work that demonstrated the production of phenolic compounds by decaying oak leaves.

# TUBERCULOSIS BACTERIA

(see Mycobacterium tuberculosis)

#### TULAREMIA BACTERIA

(see Pasteurella tularensis)

#### VIRUSES

(see Enteroviruses, Adenoviruses, Coxsackie Viruses, Infectious Hepatitis Viruses, and Polioviruses)

Collectively, the viruses are infectious agents of both plant and animal cells. They are ultramiscroscopic, obligate intro-cellular parasites that manifest their presence by destruction or impairment of the host cells. Most viruses fall in the size range of 10 to 500 mm. Morphologically they vary, some being rod-shaped, some spherical, and some appear as crystals. Whether viruses are organisms in the strict sense is still a point of controversy. However, it appears that they are devoid of any intrinsic metabolism, depending entirely upon the host cell for development and replication. All viruses contain a core of ribonucleic (RNA) and/or deoxyribonucleic acid (DNA) surrounded by a coat of protein. Some viruses contain additional substances. The vital portion of the virus particle is the nucleic acid core which in some cases can alone establish infection. Among the characteristics of virsuses is their high degree of host specificity, their affinity to certain tissues, and their ability to elicit the formation of antibodies in suitable hosts.

The viruses tend to fall in groups or "families," each member of the family sharing certain basic properties with the others but having certain individual properties. Hence, there usually exists a number of types within each family. The type is identified by its antigenic specificity and is referred to properly as a "serotype." In addition to serological tests, identification requires several other tests-host range, nature of infection in an experimental animal, type of cytopathic effect, ability to elump red blood cells, etc. (2159).

The problems associated with viruses in waters are of increasing concern. Seventy-six viruses are now known to be pathogenic to man (2062). Viruses found in polluted water include the adenoviruses, Coxsackie viruses, ECHO viruses, viruses of infectious hepatitis, polioviruses, and reoviruses. Of the illnesses caused by these organisms, only infectious hepatitis is known sometimes to be water-borne. However, the implication that poliovirus and adenovirus infections can at times be transmitted by polluted water is quite strong. These findings are of considerable importance to the water industry and have been responsible for a great deal of speculation as to the adequacy of water treatment processes and of the coliform tests as a measure of the water's sanitary quality.

The control of pathogenic viruses appears to require greater chlorine residuals than do vegatative bacteria. Also, viruses require that the chlorine be of the free form (2858), the combined form being substantially less effective. Hence, the treatment generally afforded water in the control of enteric bacterial infection is, at times, apparently not sufficient for the control of viruses (1772, 2859). For more information on the effects of chlorine and other disinfectants, see the reviews by Kabler, Clarke, Berg, and Chang (2860), and by Clarke and Chang (2596). No further information has developed with respect to the association of viruses with goiter (887, 1368).

Viruses causing pretibial fever and inclusion conjunctivitis have been associated with swimming (883).

#### WEEDS

1. General. Weeds can be defined as any plants growing in an unwanted place. However, water weeds are those aquatic growths that have a root system and are attached, thus, in main, differentiating them from freefloating growths such as algae. There are a few freefloating species, however. They include duckweed (Lemna), bladderwort (Utricularia vulgaris), Canadian pondweed (Elodea canadensis), and sometimes normally rooted plants that are found as free-floating plants, such as Myriophyllum species (2861). Plants and animals in an aquatic environment exist in complex communities in a state of dynamic balance. It is not a state of stable equilibrium, for change is inherent and is due to the many varying factors that affect the abundance of any one member of the community which in turn reflects upon all others (2693).

Water weeds can be grouped into two types, emergent and submerged (2861). Up to a certain point, either or both types can serve a worthwhile purpose. Beyond this point they have a nuisance value. In a polluted river, lush growths of *Elodea* and *Potamogeton* are likely to occur in the recovery zone (2143, 2541). The heavy growths of aquatic plants in the Potomac River below Washington, D.C., are due partly to the sewage of that city (2012).

Heavy growths of plants are indirectly related to such human diseases as malaria and schistosomiasis since these allow protected breeding sites for the Anopheles mosquitoes and feeding areas for snail intermediate hosts of the trematode. Water weeds may be directly associated with human illness, such as a dermatitis from the smartweed (Polygonum hydropiperoides) or pollinosis from aquatic grasses (2495).

Plants such as the water hyacinth (Eichormia crassipes), parrot-feather (Myriophyllum brasilliense) sometimes grow so thick that the backwater buildup floods marginal land. In one situation, sewage backed up into a populated area (2495).

Such dense growths have an effect on the water also. E. crassipes can cut off light, exhaust nitrates and phosphates, and exclude oxygen (2012). Water lettuce (Pistia) can accumulate sulfates thereby limiting plankton production (2503). Dense mats of Trapa natans can cause the water underneath to become stagnant (2165, 2505).

A study of macrophytes in polluted and unpolluted reaches of a river suggested that the pollution that prevailed was not responsible for the changes in the community, enrichment by sewage discharge having no obvious effect. In this study, growth is believed to be primarily determined by the amount of available solar radiation. Net primary productivities of 0.31, 0.47, and 0.85 grams of organic carbon per square meter per day and efficiencies of utilization of solar energy of 0.19, 0.24 and 0.25 percent were recorded. The average increase in dissolved oxygen due to the plant growth (March to June) in the area of maximum growth was about 1.2 mg/l/mile (2862). Another report by the same authors quotes 1.65 mg/l/mile (2863).

Aquatic vegetation contains large amounts of iron and is quite important in adding or removing iron in water (2705).

The use of aniline dyes to inhibit aquatic weeds by excluding light led to the finding that the following year normally semi-emergent weeds failed to reach the surface (2195).

An edible seaweed has been used as one of several criteria in limiting discharge of radioactive effluents (2864). See Chapter VIII, Radioactivity, for further information on this item and on concentration factors for isotopes of several weeds. Kelp is a commercially important seaweed off the California coast. Apparent indications that kelp beds were being damaged by sewage pollution led to a series of investgiations on kelp ecology and effects of various pollutants. The effects are given in Chapters VI, IX, and X under the name of the polluting substance. Of pertinence to this chapter however, is the discovery that effects on photosynthesis of kelp is one of the most sensitive parameters used in biological assays that has yet been found. Thus far in these studies, however, sewage pollution of sea waters does not appear to be an important contributing factor to the decline of kelp in those areas of the Pacific coast that were studied (2106, 2107, 2108, 2503, 2865, 2866, 2867, 2868, 2869, 2870). The presence of water lilies and bladderwort serves as an excellent indication of the presence of desmids (freshwater algae) according to Palmer (2213). Such waters tend to be brownish in color, low in nutrients, and neutral to acid in reaction.

Pest plants reported in the south-central states include Myriophyllum, American Iotus, cattails, sawgrass, water hyacinth, pond lily, duckweed, floating evening primrose, watermilfoils, sedges, and water fern (2213).

An added risk to the over-abundance of plant growth is the danger of secondary pollution from dead plants (2610). Lush vegetation on exposed flats during a dry year presents a considerable organic loading for the following year when the flats are submerged (2514). This condition has been suggested as an explanation of high manganese content in the waters.

The effects of water weeds are usually much greater in rivers than in lakes (2872). In addition to the chemical effects exerted in both bodies of water, the physical effects of weeds in restricting water movement which are reflected in water level, velocity, silting, and flooding, all have an additional indirect influence on pollution.

Turbidity of water exerts a considerable influence on aquatic vegetation (1355, 2873). Potamogeton pectinatus is said to be somewhat unaffected by excessive sedimentation because of its thin leaves (2286, 2546). Nevertheless, fine solids render water opaque and plant growth nil (2546, 2615, 2874). On the other hand, large-sized grit settles and leads to a decline in number of weed beds (2875).

The application of hydrated lime to increase alkalinity of an unproductive lake led to a marked increase in Myriophyllum tenellem over a previous barren bottom. An incidental observation was the increased bottom life underneath Myriophyllum (2174). Alkaline waters destroy the effectiveness of copper sulfate for the removal of water weeds (2876) (see Chapter IX, Pesticides).

- 2. Cross References. Insects and Chapter IX.
- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Weeds, living or decomposing, may impart bad tastes and odors to water supplies (152, 858, 889, 2213, 2424, 2877, 2878). Significant reduction of water quantity may be caused by transpiration (2525). Other problems include the clogging of water intake pipes, and imparting of color to water (2424, 2878).
- b. Industrial Water Supplies. There is no information available relative to any specific industrial use. However, the change in water quality, such as decrease of carbon dioxide, increase of dissolved oxygen, increase of pH and chlorine demand, and associated effects of heavy weed growths can cause problems to various industrial users (858).
- c. Irrigation Waters. Heavy weed growths can choke irrigation channels (858, 889, 891, 1355, 2226, 2262, 2265, 2525, 2879), impede metering devices and piping (2265, 2525, 2880), and cause water loss though transpiration (890, 2525, 2880). Losses from aquatic and ditch bank weeds in 17 western states have been estimated at 1,272, 480 acre-feet annually (2881). The reduced flow causes increased sedimentation (2525). Water losses from aquatic weeds were more than three times those caused by ditchbank weeds (2525). Flow reduction from floating weeds such as water hyacinth can be as much as 40 percent; that from submerged weed such as naiad and pondweeds as much as 97 percent (2880). Grass-type weeds are among the more troublesome problems in the more humid states (2882).
- d. Stock and Wildlife Watering. Decomposing aquatic plants washed up in windrows on shores serve as breeding areas for the stable fly, Stomoxys calcitrans, which attacks man and domestic animals quite viciously. Cattle and sheep are sometimes poisoned by eating leaves of arrowgrass, Triglochin maritima. Weeds also offer protected breeding areas for mosquitoes including types that transmit encephalitis (2495). Eurasian watermilfoil (Myriophyllum spicatum, M. exalbescens) is reported to be increasing in one area such that it could have a serious

effect on the distribution of the total canvasback population (2883).

e. Fish and Aquatic Life. As shelter for fish-food organisms and small fish, weeds are beneficial to fish production. In addition, they help to maintain favorable stream conditions for aquatic life by consuming carbon dioxide and producing oxygen during photosynthesis (667, 589, 858, 889, 892, 2174, 2682). However, there is some question as to just how thick vegetation should be to make conditions ideal for fish life (2884).

Decaying weeds reduce dissolved oxygen, resulting at times in fish kills (2495), or otherwise ruin waters for fish (2012, 2495). They make it difficult to harvest fish (891, 2424, 2495, 2878, 2884). In a study of the animal population on seven species of submerged plants, it was found that Myriophyllum spicatum and Potamogeton crispus were more densely populated than the rest. Midge larvae and freshwater annelids together made up 59 to 93 percent of the population on most plants. Myriophyllum averaged a greater population than Potamogeton (2682). The growth of the alga Anabaena has been reported to be suppressed by the growth of water weeds (2885). This condition can be expected when the waters are shaded by the plants, and has led Krecker (2682) to remark that a beneficial effect of watermilfoil is that it may occupy areas that might otherwise be occupied by objectionable algae.

Heavy stands of Eurasian watermilfoil seriously affect oyster growth by smothering oyster grounds or reducing water movement, which affects food supply, eirculation, and temperature, and may lead to anaerobic conditions, the growth of sulfur bacteria, and release of toxic hydrogen sulfide (2424, 2883). The presence of aquatic plants has been reported to reduce the effect of copper salts used to control the snail Australorbis glabratus, intermediate host of Schistosoma mansoni (2886).

- f. Recreational Use. Both living and dead weeds may be objectionable because of appearance or odors. Massive growths can impede fishing, boating, swimming, and other recreational uses (858, 889, 2012, 2262, 2495, 2878, 2883). Bathing sites may be made unpleasant by the spiny caltrops of the water chestnut, *Trapa natans*, or by the cercariae of swimmers itch which comes from snails dependent upon aquatic vegetation (2495). Swimmers have become entangled in weeds and drowned (2262). Surber has published an excellent booklet pertaining to improved fishing by means of weed control (2887).
- g. Navigation and Drainage. Heavy growths of water weeds impede the movements of boats and the flow of drainage waters through ditches (589, 858, 889, 891, 893, 2495).

#### WORMS, FREE-LIVING

(see also Phenol, Insects, Chironomids, Crustacea, and Chapter X)

The recognition of free-living nematodes associated with public water supplies is of long standing. Whereas the pathogenic worms are all primary pollutants, the free-living forms are all either corollary pollutants in that they develop in waters as a result of some direct or indirect facet of man's activities, or are just naturally occurring. Even in this latter case, however, it is difficult

for an individual, who is about to consume a glass of water and notes the presence of small worms, to believe that this is not pollution of the most vile form.

Interest in the free-living worm has been increasing in the past decade, probably for two reasons. First is the interest that is being expressed in their pollution-indicating value, and second, the papers that have been published about their occurrence in finished-water supplies.

Tubificid populations have been linked with heavy organic pollution in a number of articles (2126, 2143, 2540, 2542, 2545, 2688, 2888). Tubificids can reach enormous populations, 1.7 million per square meter being reported found in the River Elbe. The respiration of such masses is comparable with that of the microflora of the water (2126). Surber (2888) reports that an abundance of tubificids in excess of 100 per square foot apparently represents polluted habits, but cautions against non-judicious use of this figure especially since severe pollution can destroy even these resistant life forms. Phenol kills Tubifex worms at a minimum concentration of 200 mg/l although 150 mg/l was not lethal in five days (2889). Tests with Planaria, Daphnia, Gammarus and Tubifex showed Tubifex to be the most resistant to phenol (2616). Tubifex were reported to be common among benthic invertebrates in river water containing concentrations of chromium as great as 25 mg/l, copper 2.2 mg/l, and cyanides 3.2 mg/l, accompanied by a low dissolved-oxygen content (2688).

Goodnight discussed the entire group of oligochaetes as indicators of pollution (2890). Results of this study are not yet conclusive. Sludge formed on river bottom from wood fiber is said to influence the benthic fauna, favoring the oligochaetes (2891, 2892). When a stream becomes organically polluted, clean water Insecta such as mayflies, caddisflies, and stoneflies become replaced by oligochaetes and others (2533) providing that the former clean, firm stream bottom also changes. Sediment deprives cryptic animals of hiding places, and covers surfaces of rocks and stones rendering ineffectual various hold-fast mechanisms. Organisms that survive such conditions include the tube-building oligochaetes and chironomids (Insecta). Sodium arsenite, however, is reported to be directly toxic to oligochaetes (2893). On the other hand, results of aerial forest spraying with DDT in Canada indicate that oligochaetes (and snails) are found in considerably larger numbers in a stream sprayed every year than in any other stream including the control (2534). Results from England state that 2 lb/acre of DDT and DDD are not toxic to tubificid worms (74).

Tubifex, also referred to as "sludge worms," although dependent upon dissolved oxygen in the water, adjust well to levels as low as one-half mg/l. The Tubificidae protrude their tails above the mud into the water and wave them rhythmically. The lower the dissolved oxygen content, the further the tails protrude. Their blood contains hemoglobin which is an efficient collector of oxygen and the oxygen collected in this manner is pumped down to their front ends buried in the mud (2602). They feed directly on the sludge, removing some organic matter from it and reducing the BOD. Sludge worms one and one-half inches long and the diameter of a needle have been observed to pass fecal pellets totaling five feet nine

inches in a 24-hour period. These pellets have been found to have one-half the BOD of the surrounding sludge (2143). Hence, the sludge worms aid the self-purification process of polluted streams (2894).

A report on the degradation of Lake Erie water states that pollution-tolerant worms have increased from 12 to 551 per square meter from 1929 to 1961 (2136). The effects of siltation from logging operations on bottom fauna have been reported showing fewer organisms in the silted areas (2895). Annelids and turbellaria are among the indicator organisms of the saprobic classification system (2690). Turbellaria are intolerant of heavy metal pollution (2607). A bad taste from mineral oils can be transmitted from oil-containing muds to fish meat when the fish ingest mud-dwelling tubificids (2904).

Marine forms of free-living worms are also being studied. In the Los Angeles-Long Beach Harbor, Capitella capitata is being investigated (2896, 2897, 2898) as an indicator of pollution as well as other forms (2506). Reish (2898) reports that in this area a healthy bottom is characterized by a large number of polychaetes with Tharyx parvus, Cossura, and Nereis procera predominating; a semi-healthy area by Polydora (Carazzia) paucibranchiata and Dorvillea articulata; a second semi-healthy area by Cirriformia luxuriosa, and a polluted area by C. capitata. A very polluted bottom area has no animal life.

Mass development of marine forms also occurs where sedimentation of nutrient matter occurs and current is sufficient (2785). Newell reports that the lugworm in estuaries lives as well in water one-fifth saturated with dissolved oxygen as in water fully saturated, and that another polychaete *Scoloplos armiger* grows faster and lives longer at one-fifth saturation (2899).

Marine Bankia species bore holes in wood. Logs sprayed with sodium arsenite have been tested as a temporary means of protection from teredo (2900). However, another means of controlling borers has been suggested (2506). Since borers are more prevalent in clearer waters and since large early populations of fouling organisms (amphipods and polychaetes) appear to restrict borers, it may be possible to admit small continuous supplies of organic waste particles that would favor growth of the fouling organisms.

Felice has studied the bottom fauna of San Francisco Bay quite extensively. In 1954, he stated neither pH nor dissolved oxygen correlated with the presence of waste waters (2901). In 1958 (2902), he adds that neither pH nor dissolved oxygen correlated with any species distribution of bottom fauna, and also that salinity strongly influences species distribution. However, even in the latter case, there were some unusual responses, such as Capitella capitata being found in two widely separated areas at opposite ends of the salinity gradient. Felice's 1959 paper (2903) remarks that there is little doubt but that C. capitata displays an unusual tolerance for pollution. Since Felice's work involves much more than worms, the reader is referred to his papers. Also, see Olga Hartman's work in the Southern California area (3383).

Among the more prominent worms associated with potable water supplies according to Ingram and Bartsch (2420) are the roundworm, *Diplogaster nudicapitatus*, and the segmented worm, *Nais*. For descriptions of these

animals, see Ingram and Bartsch's work. Diplogaster, as well as Monhystera and Seinura, have been found in filter influent, effluent, and tap water. Tribolus gracilis has been reported from English slow-sand-filter effluent. Other worms reported from England include Dorylaimus and Rhabdolaimus. Nais has been found in unfiltered, chlorinated supplies in California, but, although they are reported to pass through slow-sand filters, they have not been reported to pass through rapid-sand filters.

Chang, in reporting on a nematode in a water supply, identified it as Diplogaster nudicapitatus. Pathogens, such as Salmonella, Shigella, and Coxsackie A9 virus, ingested by the worm are protected from the effects of chlorine (2597). Later work reported the presence of nematodes in 16 of 22 water supplies investigated in both raw and finished water. Further, three species, D. nudicapitatus, Rhabditis limicola, and Cheilobus quadrilabiatus (latter species uncertain), liberated an odorous, oily substance that produced a distinct earthy or musty odor when only one drop was diluted with one liter of water (2905).

D. nudicapitatus and C. quadrilabiatus are extremely resistant to the action of chlorine, such that 50-60 percent survived a 5-minute contact with 95-100 mg/l chlorine. Pathogens ingested by the worms were completely protected even when as many as 90 percent of the worms were immobilized by chlorine. About 5 to 6 percent of ingested Salmonella typhosa or Shigella sonnei and 12 to 16 percent of ingested Salmonella paratyphi or Coxsackie A9 virus survived for 24 hours (2812).

In a study of the animal populations associated with various water plants, midge larvae and annelids together made up 59 to 93 percent of the population on most of the plants (2682). Polychaetes were among the only aquatic fauna tested that were not affected to some extent by toxins from the marine dinoflagellate Gymnodinium veneficum (2724).

### WORMS, PARASITIC

(see also Worms-Free-Living, and Chapter IX-Acrolein)

The more important worm parasites of man include the ascarids, hookworms, flukes (schistosomes), and tapeworms. The worm parasites have many individual remarkable properties including host specificity (Enterobius), multiple-host requirements (schistosomes), durable ova (Ascaris), enormous size (tapeworms, up to 10 meters long), and many others.

The parasitic worms are primary pollutants, even though some species have free-swimming secondary stages in which form they were not introduced, such as the cercarial stage of the schistosomes. Although water may be essential to the completion of the life cycle of many worms, infection by drinking is generally one of the less hazardous methods of acquiring infection. The ova of parasitic worms are quite resistant to sewage-treatment processes (743, 745, 902, 2589) as well as to chlorination (741) and have been studied quite extensively in the application of sewage to various crops (2745, 2906, 2907).

The life cycle of the schistosomes, briefly, commences with the infected individual or animal passing ova in

urine or feces, and subsequent hatching of the free-swimming miricidia. The miricidia must locate and penetrate a suitable snail host (such as Australorbis glabratus for Schistosoma mansoni), in which further change occurs and from which the cercariae evolve. Free-swimming cercariae must then locate a suitable animal host and penetrate its skin in order to complete its life cycle. Oxygen studies of cercariae of S. mansoni and Australorbis snails show that the cercariae cannot survive outside the snail in an anaerobic environment. Those within the snail were unaffected although the snail itself cannot tolerate more than 16 hours exposure to a lack of oxygen. As little as five percent of oxygen in the environment permitted normal shed and survival of cercariae (2738). The schistosome egg is not likely to be harmed by usual chlorination processes, although the miracidia and cercariae are quite susceptible (585, 908). Since the ova may not hatch until it has passed through the sewage treatment plant, control of the snail intermediate host has been studied and utilized as a method of controlling schistosomiasis (907). Humans contact the illness by bathing, wading, or working in infested streams. Drinking water is of secondary importance (497) since the cercariae cannot survive stomach acid. They must penetrate the mucous membranes of the mouth before being swallowed in order to complete their life cycle (2305). Filtration is an effective screening device for ova (840) but miracidia and cercariae can penetrate filters.

Schistosomes of other animals, especially of aquatic birds (2908), are the source of considerable annoyance to humans since the organism manifests itself as an itch or a cercarial dermatitis, commonly known as "swimmers' itch." The syndrome is spreading (906) southward from the major foci of the U.S.-Canadian Great Lakes area into the Tennessee Valley area (2484), and has since been reported in Washington, Oregon, and southern California. In spite of a decreasing waterfowl population, cases of swimmers' itch are increasing. Marine forms of cercarial dermatitis also occur on California's coast (2483).

The common liver fluke Fasciola hepatica is the most widespread of cattle liver parasites in the U.S. (2739). Sheep are extremely susceptible to infection (2910). The snail intermediate host lives in wet-weather springs, slow-moving, stagnant, swampy waters, on the banks of ponds, streams, and ditches. After development in the snail, these flukes form tiny cysts on grass or in the water. Mammals are then infected by eating this grass or drinking the water. The cysts can remain infective for several months in or out of water. Destruction of snail hosts is a primary method of control.

The heavy-walled Ascaris ova is deposited with feces from an infected individual. Under suitable environmental conditions, namely of temperature, moisture, and oxygen, the enclosed larva will mature, and after its first molt becomes infective. If it is consumed at this time with drinking water, on vegetables, or in any other manner, it will hatch in the duodenum and complete its life cycle. The ova of Ascaris are extremely resistant and long-lived (741, 1728, 2278, 2305, 2589, 2911) and are often used as criteria (1728, 1729) of effectiveness of various treatment processes or in investigations (1729, 2789, 2912) of the disease transmission potential of sew-

age-irrigated crops (2278, 2788, 2795). A study of ascarid eggs and their fate in streams has been reported (1727). Fresh cultures of ova were incubated under conditions similar to those occurring in streams. The development of the ova varied with the region of the stream, and under the same temperature conditions, varied with the dissolved-oxygen content. At 7.0-9.0 mg/l, larva developed in two months. At 5.0-5.6 mg/l, ova did not develop larva in two months. In the absence of dissolved oxygen, no development at all occurred. Percentage of eggs in water and bottom deposits remaining viable after 15 months were 11.8 and 17.1 respectively. Ascarid ova have been reported to survive for two years in irrigated soil and have been found on irrigated vegetables even when chlorinated effluent was used for irrigation (1728, 1729). According to one report, the effect of chlorine in doses up to 223 mg/l only accelerates the development of the ova (2909).

Studies of the survival of suspensions of ova on vegetable surfaces have been made (1729). Under hot, dry climatic conditions, the number of eggs decreased to 10 percent of the initial value in 27 days. Plants cannot free themselves of contamination in a month's time or even longer under more humid conditions. In a rural area of Germany, the population had a 39 percent rate of infection by Ascaris. Within a district where sewage was applied for irrigation, the rate was 90 percent (904). A later German study investigated the degree of parasitism by Ascaris lumbricoides of urban sewerage workers and workers of sewage-irrigated fields. The respective percentages for the two groups were 2 and 16 (2912). The ova of Toxocara canis, ascarid of the dog and fox, was capable of surviving the winter months of 1927-1928 in Minneapolis, Minnesota (2913). Exposure to -30°C or to desiccation in sunlight was reported to be lethal to this species.

The tapeworms include Taenia saginata (beef tapeworm), Taenia solium (pork tapeworm), Echinococcus granulosus (dog tapeworm), and Diphyllobothrium (fish tapeworm). Taenia, Echinococcus and Diphyllobothrium differ somewhat in their life cycles and therefore in their water transmission roles. Taenia species ova are passed in the feces of an infested individual. Domestic sewage applied to grazing lands is one mechanism whereby cattle or hogs are exposed and ingest the ovum (511, 746, 903, 905, 784, 2912). Within the animal host the organism penetrates the intestine and migrates to any of various tissues, forming a cyst. In order for the life cycle to be completed, man must then ingest the cyst, which may happen when meat is not properly cooked. Ordinary sewage treatment is not effective in removing tapeworm eggs (2589, 2914), the ova being quite resistant (746). Dog tapeworm ova are passed in the feces of an infected dog, and if man subsequently ingests the ova, hydated cysts will form. They may form in any area of the human body and can be quite serious, depending upon the numbers and location. Yugoslav investigations have disclosed a higher rate of Echinococcus infections where water sources and courses are not so abundant and where people depend a great deal upon cisterns as a main source of water supply. The highest rate of infection exists where people obtain their water directly from open pools (2305).

The fish tapeworm commences its life cycle with the discharge of an ovum in the feces of an infected individual into water. The coracidium, or free-swimming form, hatches and must be found by a suitable copepod host (Cyclops or Diaptomus) which ingests it. Within the copepod the organism undergoes further change and then a suitable species of fresh-water fish must ingest the copepod. Within the fish, the procercoid larva migrates to various tissues and develops into an encysted plerocercoid larva. In order for the life cycle to be completed. this larva must then be consumed (improperly cooked fish flesh) by a susceptible host (308, 720). Diphyllobothriasis in a population in Russia is attributed to discharge of untreated sewage to an impounding reservoir (2741), and the main sources of infection are the pike. eel, and river bass (2749).

Hookworm has been reported to enter the body through drinking water (909), but this is a very rare occurrence (2305). The ova are quite resistant but not nearly so resistant as the ascarid egg (746, 2305). Hynes remarks that helminth ova can be dispersed from sewage treatment plants in wind-carried detergent foams, and quotes an ova density in sewage of one to six eggs per gallon (2602).

### YEASTS

(see also Bacteria—General, Fungi, and Chapters V and VIII)

The yeasts comprise a large group of fungi that are characteristically unicellular. Ordinarily they do not form a mycelium, although a few under certain conditions produce a rudimentary mycelium. Along with the bacteria and other fungi, the yeasts perform an indispensible function in the decomposition of organic materials in water (2289) although Cooke (2644) notes that this role of yeasts has not been sufficiently studied.

The pathogenic yeast, Histoplasma capsulatum, is of the type that has both mycelial and yeast phases. It is responsible for histoplasmosis in human beings, an illness involving the reticuloendothelial system, the primary lesion generally (if not always) being in the lung. It is transmitted through inhalation of air-borne spores of saprophytic origin, rarely by ingestion of contaminated food (2663). Since surveys of skin test sensitivities to histoplasmin indicate that water may be a factor, studies on the survival of H. capsulatum have been conducted (2915, 2916). Both mycelial and yeast phases persisted in sterilized Ohio River water at 50°C and 20°C for at least 180 days, at 37°C, generally, for 140 days. The yeast phase converted to the mycelial at both 5°C and 20°C, and the mycelial phase, at least in part, converted to the yeast at 37°C (2916).

In a sterilized tap water, yeast-phase survival was demonstrated for 621 days at 4°C, 306 days at 25°C, and 62 days at 37°C. No viable cells were recovered after 3 days at 45°C. The mycelial-phase survival was 421 days at 4°C, 245 days at 25°C and 34°C, and 269 days at 37°C. Again, there was no survival after 3 days at 45°C. H. capsulatum survived alternate freezing and thawing for 198 days and survived in triple-distilled water for 28 days (2915).

Cooke (2917) identified 30 species of yeast from 136 isolates obtained from various sewages and polluted waters. No pathogenic yeasts were found. He suggests that the habitats sampled were adequate for growth and reproduction of the yeasts, the organisms thereby contributing to sewage purification.

The interrelation between Candida albicans and normal intestinal bacteria has been studied. This yeast is the etiologic agent of candidiasis (moniliasis, thrush), which is generally characterized by localized skin lesions. When systemic infection is present, the illness is ex-

tremely grave. Long or repeated exposure of the skin to water may lower resistance to this organism, although host susceptibility is considered a more important factor in clinical disease than communicability (2663). Intestinal bacteria may be inhibitory, stimulatory, or indifferent to the yeast's growth. The atmospheric environment is important in determining the degree of its activity (2918).

Yeasts have been found more active than bacteria in taking up uranium (2919) (see Chapter VIII, Radio-

activity).

#### **CHAPTER VIII**

### RADIOACTIVITY

Criteria of water quality are governed not only by potential chemical and biological pollutants but also by the physical properties of extraneous substances in water. Foremost among these physical properties is radioactivity, which is sufficiently unique to warrant special consideration in this separate chapter. Abnormal levels of radioactivity may be deleterious to several beneficial uses of water. Radioactivity in water is especially significant in relation to human health, first through the direct consumption of water and second through the ingestion of agricultural products, stock, and aquatic or marine life that have accumulated radioactivity.

Surface and ground waters may acquire radioactivity in several ways. First to be considered are natural sources such as mineral deposits. Indeed, many springs and deep well waters have high levels of radioactivity, as

described later in this chapter.

Radioactivity of natural waters may be increased by atmospheric nuclear detonations and the resulting fallout products, especially Sr-90, Cs-137, and I-131. There is no evidence to date, however, that underground nuclear explosions have raised significantly the level of radioactivity in ground water (1977). A third major source of radioactivity in water is the direct action of the atomic-energy industry in mining and separating uranium, in the manufacture of atomic weapons, and in the production of radioisotopes in piles and reactors. Finally, the radioactivity of water may be raised by the utilization of radioisotopes in medical therapy, scientific research, and industrial processes. Radioisotopes are used, for example, to detect flaws in metal bodies or welds, to note changes of grade of petroleum oil in pipelines, to locate leaks in pipes, to determine the levels of liquids in tanks, and to find the density of soil (1484, 1611, 1661, 1662, 1663, 3646, 3647, 3771, 3772).

In general, the wastes from nuclear reactor operations have a high level of radioactivity and are carefully controlled and monitored by the Atomic Energy Commission before discharge to streams. Low-level radioactive wastes, however, originate in laundries, hospitals, research laboratories, plant wash waters, and myriads of small operations. Many of these wastes are discharged to municipal sewerage systems and subsequently reach natural waters (3773).

Radioactivity is an indestructible property; that is, it cannot be neutralized or cancelled by known chemical or physical methods. Radioactive substances must be disposed of by dilution with water or stable isotopes, or by concentration and storage, according to the hazards involved. Natural decay will then reduce the radioactivity.

All radioactive substances are in a state of decay or disintegration; hence, they give off energy in the form of particles or rays. The rate of decay is expressed as "half-life," i.e., the time required for a radioactive substance to lose one half of its original radio energy. One

half of the remainder will be lost in another half-life and the process continues until the end product is substantially inert. Thus, the radioactivity remaining after n half-lives equal  $(\frac{1}{2})^n$  times the original value. Decay curves have been determined for most radioisotopes (760, 3774). Some substances give up their energy in the form of radiation and become inert quickly; others, such as radium, plutonium, and uranium, are radioactive for thousands of years. Half-lives of some important radioisotopes are shown in Table 8-1.

#### TYPES OF RADIATION

Radiation has been divided into four general categories, all of which may be encountered in polluted water.

- 1. Alpha particles are large, highly damaging, and positively charged; in fact, each alpha particle is a helium nucleus with a high velocity, often as high as 10 ° cm/sec. Although alpha particles cannot penetrate skin, they are particularly dangerous when ingested and deposited within the body.
- 2. Beta particles are high-velocity negative electrons. They are moderately damaging and moderately penetrating. Some beta particles have velocities close to that of light.
- 3. Gamma rays are a form of electro-magnetic radiation, rather than particulate matter. They are deeply penetrating but relatively less damaging than alpha or beta particles. The wavelength of gamma rays is in the range of  $10^{-7}$  to  $10^{-10}$  millimeters. X-rays are similar to gamma rays but with a shorter wavelength ( $10^{-5}$  to  $10^{-8}$  millimeters).
- 4. Neutrons are uncharged, high-speed particles, deeply penetrating and highly damaging. They make dissolved salts radioactive and consequently they can make cooling water from reactors very dangerous.

Alpha, and to a less extent beta, particles are particularly hazardous in water and food because they can be ingested and can become concentrated in specific tissues, bones, or organs where they can act for a long time. Beta particles, neutrons, x-rays, and gamma rays from radioisotopes in water outside the body can also be hazardous because of their power to penetrate skin and flesh. Table 8-1 shows which type of radiation is given up by the common radioisotopes.

### UNITS AND DEFINITIONS

Before discussing the biological effects of radiation it is well to review the terms and units used in this chapter. The two basic units of measurement of radioactivity are the curie and the roentgen.

The curie (c) was originally intended to represent the rate of disintegration of one gram of radium. It is now defined as  $3.70 \times 10^{10}$  disintegrations per second, whereas

	TABI	E 8-	1	•
<b>SIGNIFICANT</b>	<b>PROPERTIES</b>	OF	SOME	<b>RADIONUCLIDES</b>

Radionaciide	Type of decay	Specific activity (curles/gram)	Critical body part	Radioactive half-life	Biological half-tife (days)	Effective half-life (days)	Maximum permissible concentration in water for general population (pc/l)
Hydrogen-3	β	9.78 × 10 ²	whole body and body tissue	12.46 years	19	18.9	3 × 10*
Carbon-14	β	4.61	fat	5570 years	35	35	8 × 10 ⁵
Sodium-24	Ď, 7	8.74 × 10°	whole body and GI tract	15.06 hours	19	0.61	2 × 10 ⁵
Phosphorus-32	β	2.86 × 10 ⁵	bone	14.3 days	1,200	14.3	$2 \times 10^{4}$
Phosphorus-32Potsssium-42	β, γ	5.96 × 10°	GI tract	12.44 hours	37	0.51	$3 \times 10^{5}$
Calcium-45	à	1.77 × 104	bone .	164 days	18,000	164	$9 \times 10^{s}$
Iron-59	β, γ	4.92 × 104	GI tract and spleen	45.1 days	65	26.7	6 × 104
Cobalt-60	βir	1.14 × 10 ³	GI tract and total body.	5.27 years	9	9	5 × 10 ⁴
Zinc-65	β, Y	8.21 × 10 ²	total body, liver and prostate	250 days	23	21	1 × 105
Strontium-90			1 -				
and Yttrium-90	β β. γ	$1.44 \times 10^{2}$	bone	28 years	3,900	2,820	$1 \times 10^{2}$
Ruthenium-106	β, γ	3.39 × 10 ³	GI tract	365 days	20	19 7.7	$1 \times 10^4$
Iodine-131	β. Υ	1.24 × 10 ⁵	thyroid	8.08 days	180 17	7.7	2 × 10 ³
Cesium-137	β, Υ	98.5	total body, liver, spieen, and muscle			17	2 × 10 ⁴
Barium-137	β, γ	98.5	GI tract	30 years	200	196	2 × 10 ⁵
Cerium-144	<b>4 ይ</b> ሃ	3.18 × 10 ³	GI tract and bone	282 days	500	180	1 × 104
Cerium-144 Radium-226 and daughters	α, β, γ	0.98	bone	1622 years	20,000	19,400	10
Thorium-232	α, β, γ	1.11 × 10⁻⁻	bone	$1.39 \times 10^{10}$ years	40,000	40,000	$2 \times 10^{2}$
Uranium-238	σ, β, γ	$3.34 \times 10^{-7}$	GI tract and kidneys	4.51 × 109 years	30	30	4 × 10 ⁴

one gram of radium has  $3.61\times10^{10}$  disintegrations per second. The term specific activity is used to express curies per gram of a solid or curies per ml of a liquid or solution. In water quality control, levels of radiation are such that they can be expressed better as one-thousandth of a curie, or millicuries (mc); as one millionth of a curie, or microcuries ( $\mu$ c); and as  $10^{-12}$  curies, or micromicrocuries, or picocuries ( $\mu$ c). In this report, the term picocurie is used insofar as possible.

The roentgen (r) is defined as that amount of gamma or x-radiation that produces in 1 ce of air (at standard temperature and pressure) ions carrying one electrostatic unit of charge of either sign. One roentgen is equivalent to 83.6 ergs per gram of air. The original definition has been extended by common usage to include the effects of alpha, beta, and neutron particles as well as

gamma and x-rays as described below.

Strictly speaking, the term "roentgen equivalent physical" (rep) is used to describe the quantity of alpha, beta, and neutron radiation producing the same amount of ionization or energy change in tissue as does one r of x-rays. To be even more specific, the term "radiation absorbed dose" (rad) was created to quantitate the absorption of radiation by tissues. It is defined as the energy imparted to matter by ionizing particles per unit mass of irradiated material at the place of interest. Thus, the rad is the unit of dose and is equal to the absorption of 100 ergs per gram of tissue. For most considerations of radioactivity and its effect on life processes, the number of roentgens is substantially equal to the number of reps and rads. Indeed, the three terms are used interchangeably and roentgen is used for all three (3688, 3772).

Although the roentgen has been broadened in definition to cover particles as well as rays, it must be recognized that the same absorbed dose of different kinds of radiation does not, in general, produce the same biological effect. The quantitative effect of a given physical dose of radiation depends on the tissue or animal ir-

radiated, the characteristics of the radiation, and the particular effect being studied. Alpha radiation, for example, is much more damaging than most other types. The relationship among radiation classifications is expressed as the "relative biological effectiveness" (RBE). The present accepted values for RBE of different kinds of radiation are given as follows (3688):

Radiation	RBE
Gamma and x-rays	_ 1
Beta particles	_ 1
Alpha particles	_ 10
Neutrons and protons (up to 10 Mev)	_ 10
Heavy recoil nuclei	_ 20

The term "roentgen equivalent man" (rem) is the quantity of radiation producing, when absorbed by man, a biological effect equivalent to that resulting from the absorption of one r of x-radiation. Thus the unit of RBE dose is the rem, considered to be that dose which is biologically equivalent to one roentgen of gamma or x-radiation. For example, one rad of neutrons is considered to be equivalent to 10 roentgens of gamma radiation, or its RBE dose is 10 rem.

Experimental results, however, have shown that the same RBE dose of different radiation in bone does not always produce the same effect. Hence, a numerical relative damage factor has been introduced to provide for this difference, the biological effect being represented by the product of the RBE and the relative damage factor

(3688).

When the high-energy particles strike the individual atoms and molecules that make up tissue, electrons are knocked out of their orbits and these stray electrons may themselves cause further damage. The process of ejecting electrons from their atomic orbits is known as ionization. The number of ionizations caused by a radiation per unit of path length is known as "specific ionization". Specific ionization is the major factor in judging the relative biologic effect of various types of nuclear radiation (3775, 3776).

#### BIOLOGICAL EFFECTS OF RADIATION

Estimates of probable radiation injury to human beings are based largely on experimentation with lower animals; clinical studies of human beings exposed to radiation by medical treatment, accident, or war (e.g. Hiroshima); and observations made on populations living in areas of high background radiation. The 1956 report of the National Academy of Sciences-National Research Council (3777) notes that radiation injury is a complex matter and that it is not possible to extrapolate with confidence from one condition of radiation exposure to another, nor from animal data to man.

Exposure to radiation from cosmic rays and concentrations of radioactive minerals in the earth's surface has always been a part of life. Man has reached his present state of development amid radiation of the order of 80-170 millirems per year (3688). It is not known whether exposure to this level of radiation is essential to the development of biological systems or whether it is simply another deleterious force that such systems have learned to tolerate (3826).

The intensity of radiation in both air and water varies from place to place. The radioactivity of natural waters generally lies in the range of 1 to 1000 pc/l. In some radioactive springs it may reach 100,000 pc/l (3778, 3779). The radium (long-lived) content of some New York community water supplies is 0.5 pc/l (425) and the radon (short-lived) content of mineral springs has been found to be as high at 750,000 pc/1 (761). The radon content of springs and wells in certain regions of France exceeded 4000 pc/l in more than two-thirds of the samples (3780). Smith et al. (3642) found the radon activity of well waters in Maine and New Hampshire to be as high as 1,130,000 pc/l. During and immediately following the 1953 spring weapons tests, the radioactivity of rainfall in Cincinnati varied from 280 to 319,-000 pc/l as compared with a pre-bomb test background of 50 pc/l (3781). In general, it has been estimated that the radioactivity of surface waters amounts to 1 to 10 percent of that of the rainwater (3782), or for the Cincinnati area about 0.5 to 5.0 pc/l before bomb testing. Such naturally occurring radioactivity results in an average background radiation of 0.0005 to 0.002 reps per day, or about 0.2 to 0.73 reps per year (762).

The therapeutic value of naturally radioactive waters is open to question. On the other hand, many authorities maintain that the continuous consumption of such waters is dangerous, although no cases are known of radioactive poisoning from natural waters (624, 761). The problem of interest in water pollution control is how to avoid additional exposure to artificial radiation that may cause damage.

The biological effects of radiation are classified as somatic (directly affecting the individual cell and organism) and genetic (which do not apparently influence the irradiated individual but do affect his descendants, perhaps after several generations). Somatic effects may be acute or chronic. A dose of radiation will be acute if it damages a critical number of cells such that the organism cannot recover by normal cell mitosis. The same total dose delivered over a longer period may have much less adverse effect because the repair mechanisms of the

organism enable it to recover. Yet, there may be chronic long-term damage. Acute exposure can result in both immediate and delayed biological effects; but chronic exposure is usually considered to produce only delayed effects (3688).

The following table summarizes the effects resulting from acute whole-body external exposure of radiation to man (3688, 3775):

 $E_{i}$ 

cute Whole-Body	
xternal Exposure	
in Rads	Biological Effects in Man
0-25	No detectable clinical effects, but delayed effects
0-20	may occur.
25-100	Slight transient reductions in leucocytes and
20 100	neutrophils: disabling sickness not common; de-
	layed effects possible but serious effects very
	improbable.
100-200	Nausea and fatigue with possible vomiting; re-
100-200	duction in leucocytes and neutrophils, delayed
	effects may shorten life expectancy.
200-300	Nausea and vomiting followed by two-week
200-000	latent period, then loss of appetite, general
	malaise, sore throat, pallor, diarrhea, and
•	moderate emaciation; recovery likely in about
	three months unless complications develop.
300-600	Nausea and vomiting in first few hours followed
	by a latent period of 3 to 7 days, then epilation.
	loss of appetite, general malaise, and fever dur-
	ing second week; hemorrhage, purpura, pe-
	techeae, inflammation of mouth and throat,
	diarrhea, and emaciation in third week; some
	deaths in 2 to 6 weeks; possible eventual death
	to half of individuals exposed to 450 r.
over 600	Nausea and vomiting in first few hours, short
A company of the comp	latent period, then toward end of first week
	diarrhea, hemorrhage, purpura, inflammation of
	mouth and throat, fever; rapid emaciation and
	death as early as second week, and eventual
	early death of up to 100 percent of exposed
	individuals.

The effects of acute radiation, as described above, are quite well understood. They are not of primary concern, however, in water pollution control. Chronic effects that arise from frequent small doses, year after year, are much more important, but difficult to evaluate. They may include the production of eye cataracts, the induction of leukemia from irradiation of the bone marrow, the development of bone cancer from ingestion of radium, the production of skin cancer, and the reduction of life span owing to the imperceptible impairment of many bodily functions. It is difficult, if not impossible, to determine the threshold levels of radioactivity that give rise to these manifestations.

The relationship between chronic dose and effect has not been established for somatic action. Three possibilities have been considered in the literature: (a) a linear, no-threshold concept; (b) a non-linear, no-threshold concept, and (c) a non-linear, threshold concept. Authorities are not in agreement as to whether or not a threshold can be established for somatic effects. The evidence is insufficient to prove either the hypothesis of a damage threshold or the hypothesis of no threshold in man at low doses. It is prudent, therefore, to keep radiation exposure to the lowest practical level (3688).

For genetic effects, however, there appears to be no possible threshold dose below which some effect may not occur. Any amount of radiation, no matter how small, is bound to produce some mutations. Once completed, mutations are irreversible and almost all mutations are deleterious. Irradiation of a population from any source is bound to have some genetic consequences (3688, 3772, 3783, 3784).

There is an increasing reluctance on the part of knowledgeable scientists to establish radiation protection standards on the basis of the existence of a threshold for radiation damage. On the premise that there is no threshold, every type and amount of radiation involves some biological risk either to the individual or to his descendants. In contrast, however, radiation can bring numerous benefits to man in medicine, industry, and research. It is necessary, therefore, to weigh the risks against the benefits. Maximum benefits cannot be obtained without some biological risk, and the risk cannot be eliminated without loss of benefits (3688). As a consequence, radiological standards have been recommended by several scientific agencies.

Among the oldest of these organizations are the International Commission on Radiological Protection (ICRP) and the National (USA) Committee on Radiation Protection and Measurement (NCRP). Formed in 1928 by the International Congress of Radiology, ICRP is now a commission of the International Society of Radiology. The NCRP started as the Advisory Committee on X-ray and Radium Protection and adopted its present name after a reorganization in 1946. Its recommendations are generally published in handbooks of the National Bureau of Standards, one of the agencies represented on NCRP. Reports have also been published in 1956 and 1960 by the National Academy of Sciences-National Research Council for its Committees on the Biological Effects of Atomic Radiation. In general, the recommendations of all three bodies (ICRP, NCRP, and NAS-NRC) are in close agreement. The United Nations also has a Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) which published a report in 1958.

As a result of congressional hearings, Public Law 86-373 was enacted in 1959 to form the Federal Radiation Council. It is the purpose of the Council to provide a federal policy on human radiation exposure, to advise the President with respect to radiation matters, and to guide all federal agencies in the formulation of radiation standards. The 1962 Drinking Water Standards of the U. S. Public Health Service (2036), for example, are tied into the Federal Radiation Council. As of September 1961, the Council had issued two reports of background material for the development of radiation protection standards (3688, 3785). Much of the information in this chapter was drawn from these reports.

Insofar as ICRP is concerned, the major recommendations are contained in ICRP Publication 2, "Report of Committee II on Permissible Dose for Internal Radiation" (3786). This report has been abridged by NCRP and published as Handbook 69 of the National Bureau of Standards (3784). Table 1 of Handbook 69 presents the maximum permissible concentrations of radionuclides in air and in water for occupational exposure, both for a 40-hour week and a 168-hour week. Outside of a controlled area of occupational exposure the concentrations should not exceed one-tenth of that for radiation workers. The values presented in Table 8-1 of this chapter

were taken from Handbook 69 but they have been corrected by this factor of one-tenth and hence may be considered to apply to the general population. ICRP and NCRP also specify that radiation "outside a controlled area, but attributable to normal operations within a controlled area, shall be such that it is improbable that any individual will receive a dose of more than 0.5 rem in any one year from external radiation" (3784).

It is also a basic recommendation of the Federal Radiation Council that "the yearly radiation exposure to the whole body of individuals in the general population (exclusive of natural background and the deliberate exposure of patients by practitioners of the healing arts) should not exceed 0.5 rem" (3688). However, on the arbitrary assumption that the majority of individuals do not vary from the average by a factor greater than three, and since no one should be exposed to more than 0.5 rem per year, the Council recommends the use of 0.17 rem for yearly whole-body exposure of average population groups. Insofar as genetic dose is concerned, the Federal Radiation Council recommends that the exposure to the gonads be limited to 5 rems over a period of 30 years for the average population (3688). For most individual organs of the body, the permissible body burden is taken as 15 rems and for the thyroid or skin it is

Once the permissible body burden has been established, the daily intake which would not result in an accumulation over a 50-year period of more than the permissible body or organ burden is calculated. To determine the permissible intake by ingestion it is also necessary to consider the fraction of ingested material that is absorbed into the blood from the gastro-intestinal tract, the fraction of material in the blood that will be deposited in the critical organ, the rate of uptake, and the time of retention of the material in the critical organ. This last factor is expressed as the "biological half-life", or the time required for half of the material to be removed by normal metabolic processes. The "effective half-life" is a combination of radiological and biological half-lives such that

$$\frac{1}{T_e} = \frac{1}{T_r} + \frac{1}{T_b}$$

Values of these half-lives are shown in Table 8-1.

Once the permissible daily intake by ingestion has been determined, the maximum permissible concentration (MPC) in water can be derived by assuming that the total daily intake of water is 2.2 liters. The MPC values for several important radioisotopes, adjusted downward by a factor of 10 to allow for the general population, are shown in Table 8-1.

A study of Table 8-1 shows that strontium, radium, and thorium are most dangerous because they are bone seekers and have very long effective half-lives. Strontium is a serious problem also because it is produced in high yield by fission reactions (3787). Radium is especially harmful because it occurs in natural waters and it is also an alpha emitter. Calcium and phosphorus are bone-seekers with long biological half-lives, but they are not serious health problems because their radiological half-lives are short.

The Federal Radiation Council has also established the terms Radiation Protection Guide (RPG) and Radioactivity Concentration Guide (RCG). The RPG is "the radiation dose which should not be exceeded without careful consideration of the reasons for doing so; every effort should be made to encourage the maintenance of radiation doses as far below this guide as possible". The RCG is "the concentration of radioactivity in the environment which is determined to result in whole body or organ doses equal to the Radiation Protection Guide".

The Radiation Protection Guides shown below are considered by the Federal Radiation Council to represent an appropriate balance between the requirements of health protection and of the beneficial uses of radiation and atomic energy. It is recommended (3687) that the following RPG values be adopted for normal peacetime operation:

	RPG	RPG for Average of
_	fo <b>r</b>	Suitable Sample of Ex-
Organ	Individuals	posed Population Group
Thyroid	1.5 rem per year	0.5 rem per year
Bone marrow	0.5 rem per year	0.17 rem per year
Bone	1.5 rem per year	0.5 rem per year
Bone (alternate	0.003 micrograms	0.001 micrograms of
guide)	of Ra-226 in the adult	Ra-226 in the adult
	skeleton or the bio-	skeleton or the biological
	logical equivalent of	equivalent of this amount
	this amount of Ra-226	of Ra-226

By September 1961 the Federal Radiation Council had established RPG values for iodine, radium, and strontium in three ranges. Range I covers intakes that would not under normal conditions be expected to result in any appreciable number of individuals in the population reaching a large fraction of the RPG. Range II involves intakes expected to result in average exposures to populations not exceeding the RPG, but involving surveillance and routine control. Range III deals with intakes that would be presumed to result in exposures exceeding the RPG if continued for a sufficient period of time. The following values have been given for the three ranges (3687, 3785):

	Ranges of Transient Rates of Intake (in picocuries per day)			
Radionuclides	Range $\vec{I}$	Range II	Range III	
Radium-226	0-2	2-20	20-200	
Iodine-131	0-10	10-100	100-1,000	
Strontium-90	0-20	20-200	200-2,000	
Strontium-89	0-200	200-2,000	2,000-20,000	

Inasmuch as different environmental media contribute to the total daily intake, the MPC values for water will be only a fraction of the values given above. For example, the MPC of Ra-226 for drinking water (see Domestic Water Supplies hereinafter) is 3 pc/1. Assuming 2.2 liters per day per person, the intake from this source is limited to 6.6 pc/day, or about one-third of the total daily intake to remain within Range II.

The Atomic Energy Commission (3788) has established standards for protection against radiation hazards arising out of activities of licensees, including the disposal by release into sanitary sewerage systems. These standards limit the average daily concentration of radionuclides, the total daily discharge, and the average monthly concentration. Furthermore the gross quantity of licensed and other radioactive material released to the

sewer cannot exceed one curie per year. For the same radionuclides shown in Table 8-1, the AEC limits for discharges to sewers are given in Table 8-2. The quantity of any radioactive material released into the sewer system by a licensee in any one day shall not exceed the larger of columns 1 or 2 and the monthly average shall not exceed column 2. For comparison, the MPC for water is given again in column 3.

TABLE 8-2
AEC STANDARDS FOR DISCHARGE TO SEWERS

Radionuclide	Maximum Daily Discharge in Microcuries (1)	Maximum Concentration, pc/1 (2)	MPC for Water, pc/1 (3)
Hydrogen - 3	2500	$1 \times 10^{8}$	$3 \times 10^{6}$
Carbon - 14	500	$2 \times 10^{7}$	8 x 10 ⁵
Sodium - 24	100	$6 \times 10^{8}$	$2 \times 10^{5}$
Phosphorus - 32	100	5 x 10 ⁵	$2 \times 10^4$
Potassium - 42	100	$9 \times 10^{6}$	3 x 10 ⁵
Calcium - 45	100	$3 \times 10^{5}$	$9 \times 10^{3}$
Iron - 59	10	$2 \times 10^{6}$	6 x 104
Cobalt - 60	10	$1 \times 10^{6}$	5 x 10*
Zinc - 65	100	$3 \times 10^{6}$	$1 \times 10^{5}$
Strontium - 90			
+ Yttrium - 90	1	$4 \times 10^{3}$	$1 \times 10^{2}$
Ruthenium - 106	10	4 x 10 ⁵	1 x 104
Iodine - 131	100	6 x 10*	$2 \times 10^{s}$
Cesium - 137			
+ Barium - 137	10	$7 \times 10^{7}$	2 x 10*
Cerium - 144	10	3 x 10 ⁵	1 x 104
Radium - 226	1	$4 \times 10^{2}$	10
Thorium - 232	500	5 x 10 ⁴	$2 \times 10^{3}$
Uranium - 238	500	$1 \times 10^6$	4 x 104

### DOMESTIC WATER SUPPLY

The 1962 Drinking Water Standards of the U.S. Public Health Service (2036) contain limits for Ra-226, Sr-90, and gross beta activity, based on the recommendations of the Federal Radiation Council. A full statement of these limits is reproduced below.

"(1) The effects of human radiation exposure are viewed as harmful and any unnecessary exposure to ionizing radiation should be avoided. Approval of water supplies containing radioactive materials shall be based upon the judgment that the radioactivity intake from such water supplies when added to that from all other sources is not likely to result in an intake greater than the radiation protection guidance recommended by the Federal Radiation Council and approved by the President". (i.e. 20 pc/day of Ra-226 and 200 pc/day of Sr-90). "Water supplies shall be approved without further consideration of other sources of radioactivity intake of Radium-226 and Strontium-90 when the water contains these substances in amounts not exceeding 3 and 10µµc/ liter respectively. When these concentrations are exceeded, a water supply shall be approved by the certifying authority if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action.

"(2) In the known absence of Strontium-90 and alpha emitters, the water supply is acceptable when the gross beta concentrations do not exceed 1,000µµc/l. Gross beta concentrations in excess of 1,000µµc/l shall be grounds for rejection of supply except when more complete analyses indicate that concentrations of nuclides are not

likely to cause exposures greater than the Radiation Protection Guides as approved by the President on recommendation of the Federal Radiation Council."

The radiological requirements contained in the WHO Drinking Water Standards, both International (2328) and European (2329), are based on the recommendations of the International Commission on Radiological Protection (3786), but they contain an additional safety factor of 10 proposed by the Commission for water which is to be supplied to large communities. Thus, these standards are only one-tenth of the MPC values for Ra-226 and Sr-90 as given in Table 8-1. If the levels of radioactivity are lower than the following values, the water is considered to be safe for use without further investigation:

alpha emitters ______ 1 pc/l beta emitters _____ 10 pc/l

"Higher figures than those given above are safe for many radionuclides and a water with a total radioactivity exceeding the above figures may be safe for use if the absence of the more dangerous radionuclides can be confirmed by radiochemistry" (2328).

firmed by radiochemistry" (2328).

The standard for alpha emitters (1 pc/l) was set this low to allow for the possibility that all alpha activity might be due to radium and its daughter elements—otherwise, it too might be 10 pc/l. Until it is found to be practicable to analyze all water supplies specifically for Ra-226, it appears prudent to retain the lower level for all alpha emitters (2328).

Many natural waters used for water supply throughout the world fail to meet the WHO standard for radium, or even the USPHS standard. A tabulation of activities of natural waters, presented by Smith et al. (3642), shows a variation in radium activity from as low as 0.01 pc/l in the River Thames to 709,800 pc/l for spring waters in Japan. The average for all river waters was given as 0.07 pc/l and for river waters in North America as 0.03 pc/l (3642).

Ground waters, however, tend to be higher in radium content. Lucas (3643) reported that the Ra-226 activity of certain midwest water supplies ranged from less than 0.03 to 37 pc/l. Surface supplies and wells in glacial deposits or limestone formations were with rare exceptions found to contain less than 1.0 pc/l, whereas wells penetrating deep sandstones had Ra-226 contents of 1.0 to 37 pc/l. A population of 1,000,000 was identified as consuming water in excess of 1.0 pc/l and 480,000 consume water having Ra-226 activity in excess of 4 pc/l. Smith et al. (3642) measured the natural radioactivity of ground-water supplies in coastal areas of Maine and New Hampshire, finding the average Ra-226 activity of drilled and dug wells in Maine to be 66 and 73 pc/l respectively and in New Hampshire 6.9 and 4.1 pc/l respectively. It is apparent, therefore, that many existing water supplies fail to meet the WHO or USPHS standards for Ra-226 and alpha emitters.

Insofar as Strontium-90 and total beta emitters are concerned, the situation is not so serious. As a result of nuclear testing, rain water has been reported to contain from 2 to 8 pc/l of Sr-90, or close to the USPHS limit. Surface waters in the U.S., however, generally contain less than 1.0 pc/l although activities in excess of 2 pc/l have been reported (3778). Ground waters generally

contain less than 0.01 pc/l of Sr-90 (3680). Water, however, is not considered to be the major avenue by which humans ingest radiostrontium, for food is the principal source. It is estimated that less than 10 percent of the Sr-90 ingestion comes from consumption of water (3682).

Gross beta activity in all surface waters of the U.S. in 1958 averaged less than 100 pc/l (3789) and only a few rivers exceeded 500 pc/l in 1961 (3778). It is unlikely, therefore, that the USPHS limit of 1000 pc/l for gross beta activity will be exceeded by natural waters.

The first edition of WATER QUALITY CRITERIA and the 1954 Addendum contained extensive discussions of radioactivity in relation to domestic water supply. Much of that material, however, is not repeated here because it has been rendered obsolete by the recent publications of ICRP, NCRP, and the Federal Radiation Council.

#### INDUSTRIAL WATER SUPPLIES

Excessive radioactivity in water supplies may be harmful to certain industrial processes or to manufactured products such as film (762, 3790). Further details of such effects were not uncovered in this literature survey. Where water is used for cooling reactors and thus may be exposed to irradiation by neutrons, it should have a minimum of dissolved and suspended matter, especially iron, calcium, lithium, sodium, boron, and sulfur (3395, 3791).

#### **IRRIGATION**

Vegetation, in general, is more resistant to radiation than is animal life (767); however, plants can concentrate radionuclides and thereby raise the potential hazard to human beings and animals consuming such vegetation. Two questions, then, are of interest in relation to water-quality criteria, viz, what levels of radiation in irrigation water will damage crops, and to what extent will crops concentrate various radionuclides?

Without a doubt, extremely high levels of radiation will cause somatic damage to vegetation; but no attempt was made in this survey to study the literature on plant physiology to ascertain these levels. It is also probable that lower concentrations of radiation will have a genetic effect on plants, but this factor was not uncovered in this survey. Foster et al. (3762) maintain that somatic effects of radiation are not likely to be a problem insofar as irrigation water is concerned. According to Krumholz (3797) the only plant that has concentrated enough radioactive material to damage itself has been the American elm. No significant effects were observed in plants grown in soil that contained concentrations of radionuclides equivalent to 25 years of accumulation from the Hanford effluent (3762). Barley seed plots irrigated with five percent reactor effluent from Hanford showed no adverse effects, but the seeds contained less nitrogen when plots were irrigated with undiluted effluent (3792). In normal irrigation practice, genetic effects should not be evident because modern farmers almost always use seed from special seed crops rather than from the products of the irrigated soil. Kaufman (3794) noted that the maximum permissible levels of radiation for irrigation waters may well become more stringent than those for domestic water supplies; but undoubtedly he was

referring to the concentration factor rather than to direct somatic or genetic damage.

The only important radionuclides that are absorbed and possibly concentrated by plants appear to be strontium, cesium, barium, iodine, calcium, potassium, ruthenium, zirconium, zinc, and chromium (2382, 3795, 3796, 3797, 3798, 3799, 3800). The uptake by plants of various elements from the soil solution is affected by several factors, including plant species, stage of growth of the plant, the part of the plant studied, the acidity and chemical composition of the nutrient medium, temperature, light, and soil structure (3793).

At Hanford, barley irrigated with five percent reactor effluent demonstrated no increased beta activity over the controls. Plants irrigated solely with effluent demonstrated higher activity, but only by a factor of two. It appears, therefore, that little long-lived beta-emitting material is taken up by barley. Of 16 radionuclides identified in the effluent, only Zn-65 and Cr-51 were found in the barley plants (3800).

The accumulation of Zn-65 on pasture grass irrigated with Columbia River water below Hanford and its subsequent transfer to grazing animals and milk is an important biological pathway for this radionuclide to man (3762). Cesium-137 is readily adsorbed by soil, but plants can take up Cs-137 directly from the water before ions are fixed to the soil; as a consequence, animals grazing on wet lands can ingest 400 times as much Cs-137 as those on dry lands, and crops grown in standing water may accumulate high Cs-137 levels (3798).

Samples of crops irrigated with Columbia River water 30 miles below Hanford were assayed for Zn-65 to determine concentration factors. The activity of the irrigation water averaged 188 pc/l of Zn-65. The following concentration factors were observed (3763): pasture grass, 440; black-eyed peas, 2.9; tomatoes, 2.4; okra, 2.1; string beans, 1.5; corn, 0.83, and grapes, 0.47. Kaufman (3794) observed that radishes concentrate strontium 84 times.

Tsivoglou et al. (3644) studied the effects of wastes from uranium ore processing on the Animas River and its beneficial uses, especially with respect to radium. They found that the average radium content of truck vegetables and field crops (excluding alfalfa) was 2.0 pc/kg of live material for farms upstream of the mill and 3.6 pc/kg for downstream farms irrigated with Animas River water. Yet the average dissolved radium content of downstream river water varied from 12.6 pc/l immediately below the mill to 2.9 pc/l 59 miles downstream, in contrast with 0.6 pc/l upstream. Thus, while the dissolved radium content of the river increased by a factor of 4.8 to 21, the radium content of crops increased by a factor of only 1.8, thus indicating that the concentration factor was less than 1.0.

The uptake of Sr-89 by attached aquatic plants, and in particular by watercress (Nasturtium officinale) was studied by Owens et al. (3689). For five aquatic macrophytes they found concentration factors varying from 30.4 to 74.1 when the dosed hard river water had a Sr-89 activity of about 10 ⁷ pc/l. In dosed soft water, however, concentration factors were about 200. The concentration factor was not influenced significantly by the level of

Sr-89 activity in the water between the limits of  $10^5$  pc/l and  $2x10^7$  pc/l (3689).

From pond water to which  $6 \times 10^6$  pc/l of Cs-137 had been added, Pendleton (3387) found the concentration factors for aquatic macrophytes to be as follows:

water weed	1000
coontail	400
sago pondweed	700
water fern	
duck weed	500
American bullrush (culms)	50
hardstem bullrush (culms)	90
cattail (leaves)	200
spotted persicaria (leaves)	

Several authorities have reported on the uptake by plants of specific radionuclides in relation to other substances in the soil moisture (3684, 3795, 3801, 3802), especially the effect of calcium on the concentration of strontium and the inhibiting action of potassium with respect to cesium uptake. A thorough review of these relationships is beyond the scope of this report.

### STOCK AND WILDLIFE WATERING

Extensive experiments have been conducted with laboratory animals to determine the biological half-lives of various radionuclides and to find the levels of somatic and genetic effects. It is not possible, however, to transfer these results from one animal to another species, nor from any animal to man (3777). Although this survey of literature on the subject of the effects on animals of radionuclides in water was far from exhaustive, the following observations may be of interest.

Insofar as somatic effects are concerned, Dowdy and Charles (763) report that the acute LD₅₀ among most warm-blooded animals is 200 to 790 r. The chronic LD₅₀ for dogs, at a dosage rate of 10 r per day for 6 days per week was 1440 r, but three dogs survived 5000 r. At 6 r per day, the LD₅₀ was 2940 r but five dogs survived 3000 r. At 3 r per day, seven out of nine dogs survived 1500 r. For rats, 10 r per day for six days per week resulted in an LD₅₀ of 3500 r. At 8.8 r per day to mice the LD₅₀ was at 4400 r. At 8.8 r per day to guinea pigs, the LD₅₀ was at 2300 r (763). Lower forms of life are resistant to much higher levels of radiation, e.g., 200,000 r for viruses and bacterial cultures, 300,000 r for Paramecium, and 150,000 r for some insect pupae (767).

In relation to dose, the tentative LD₅₀ dose of uranium for mice was given at 27,000 to 31,000 pc per gram of weight (1681). When plutonium-239 was administered to rats by stomach tube, a dose of 88 mc/kg of body weight caused deaths but 56 mc/kg caused no deaths among six rats. The lethal dose of 88 mc/kg is equivalent to 650,000 rem over the surface of the small intestine. Rats were fed 40 mc of the alpha-emitting radionuclide Pu-239 (equivalent to 80,000 rads to the surface of the large intestine) without discernible effect (3804). On the other hand, when 3 mc of beta-emitting Y-91 were fed to rats (about 4000 rads to the large intestine), one-half of the animals were killed (3804). It is apparent, therefore, that the alpha particles from plutonium-239 do not reach the sensitive tissues in the gastro-intestinal tract. The LD₅₀ in rats for Y-91 after oral administration was 17 mc/kg of body weight. The average survival time was 9 days (3805). Sheep fed 5 microcuries/day of I-131 for five years developed thyroid tumors. The total thyroidal dose was approximately 30,000 rads (3804). A muskrat that fed on vegetation in and around a stream receiving radioactive discharges developed cancer as a result of Sr-90 accumulation (2126).

On the other side of the ledger, a daily intake of 0.15 microcurie of I-131 appears to be a safe level for sheep. This corresponds to a thyroidal dose rate of roughly 3 rads/week (3804). The thyroid glands of sows fed 45 microcuries of I-131 per day were smaller than the thyroids of normal animals but even at this level two out of eight experimental animals showed no definite histological damage (3806). The thyroids of two sheep fed 1.5 microcuries per day of I-131 for four years did not show definite evidence of damage. The total radiation dose probably exceeded 5000 rads (3803). Rats fed concentrated reactor effluent for up to one year concentrated Zn-65 more than any other radioisotope (3764), but their growth rate was not affected and no histological changes were observed (1682, 3804).

Ballou (3807) studied the metabolism of Zn-65 in the rat. Using bone as the critical organ and an estimated effective half-life of 21 days, the MPC for Zn-65 in water was calculated at  $6 \times 10^7$  pc/l. Ballou's studies, however, indicate that the effective half-life is about 100 days and hence the MPC should be decreased to  $1 \times 10^7$  pc/l.

Relatively little information was uncovered to show the direct concentration factors between animal flesh and drinking water. Most concentration factors in animals arise from ingestion of vegetation that had previously concentrated the radionuclide from irrigation water. For example, while the concentration factor of 440 existed for Zn-65 with respect to pasture grass, the factors for beef bone, flesh, and fat were only 13.4, 10.7, and 2.2 respectively in relation to the irrigation water. For cow's milk, however, the overall concentration factor for Zn-65 was 26 as compared with 440 for the pasture grass on which she fed (3763). Waterfowl have been shown to concentrate P-32 in muscle by a factor of 75,000 over the water from which they fed (3702).

#### FISH AND OTHER AQUATIC LIFE

The effects of radioactivity on fish and other aquatic life should be considered with respect to direct somatic damage or death, possible long-term genetic effects, and the accumulation of radionuclides in aquatic or marine life used as food by humans. On the basis of limited data, it appears that concentration is by far the most serious effect, i.e., levels of accumulated radionuclides that make fish and other aquatic or marine life hazardous for human consumption do not appear to be likely to release sufficient ionizing radiations to damage the organisms themselves (2109).

Radionuclides in the aquatic or marine environment may affect organisms by (a) direct radiation from the water or accumulated bottom sediments, (b) adsorption of radioactive material on the body surfaces, (c) absorption through cell membranes of soluble substances, and (d) ingestion of radionuclides along with food and water (3273, 3808). For algae, for other lower forms of life, and for higher aquatic vegetation, adsorption and absorption appear to be the principal mechanisms of accumulation. For herbivores and carnivores (e.g., crustacea, insects, worms, fish), ingestion of radionuclides concentrated by lower forms of life appears to be the major route of accumulation.

Although direct somatic damage is not likely to be a serious factor for aquatic life, it is well to establish general levels of lethal action and damage. In general, organisms of the lower phyla are more resistant to ionizing radiations than are the higher vertebrates (2439). The following comparison of susceptibility to radiation was presented by Donaldson and Foster (2439):

	Acute Dose in Roentgens Causing			
Organism	50% Mortality	100% Mortality		
Algae	8.000-100.000	25.000- 600.000		
Protozoa	10,000-300,000	18,000-1,250,000		
Mollusks	5,000- 20,000	10,000- 50,000		
Crustacea	500- 90,000	5,000- ~ 80,000		
Fish	600- 3,000	370- 20,000		

By way of comparison, an acute dose of 450 roentgen would probably cause 50 percent mortality to a group of humans. Lowe et al. (3809) reported that ionizing radiations from a cobalt-60 source required a dosage of 2,000,000 rad to give complete destruction of microorganisms in sewage, although 90 percent kills of most organisms were achieved at a dose of 70,000 rads. Ridenaur and Armbruster (3810) found that a dosage of 100,000 reps was sufficient to kill 99 percent of the bacteria in contaminated water and sewage.

When nearly mature rainbow trout were exposed to x-rays at the rate of 8.25 r per minute for as long as 64 weeks, growth was retarded by total dosages as low as 50 r; radiation injuries were caused by 500 r; more than 1000 r caused significantly high mortalities as compared with the controls; and 2500 r killed all fish in 8 to 13 weeks (771).

In White Oak Lake, which receives the radioactive waste effluent from the Oak Ridge National Laboratory, white crappies (Pomoxis sparoides) and redhorse (Moxastoma erythrurum) gradually disappeared from the fish population. The total radiation dose received by the fish in White Oak Lake was estimated to be at least 57 repper year from external radiation and was probably several times that from internal radiation. As a result of this irradiation, it is believed that the fish population of this lake may have suffered deleterious effects, as manifested by shortened life spans, slower rates of growth, and possibly decreased fertility of the breeding stock of the redhorse (3692, 3797).

Silver salmon fry held in cooled effluent from the pile area at Hanford suffered 100 percent mortality in eight weeks. Even at dilutions of 1:50 increased mortalities were evident. For eggs or fingerlings, dilutions of 1:25 or greater gave no increase in mortality (3811, 3812). On the other hand, no somatic damage was observed in fish that had accumulated P-32 to the extent of 9 x 10⁷ pc/kg of fish flesh after 9 months of exposure and only slight damage was evident in trout having 42 x 10⁷ pc/kg after 6 months of exposure. None of the fish sampled from the Columbia River itself had as much as 1/100 of the P-32 dosage that caused no damage. It can

be concluded, therefore, that present radioactivity in the Columbia River poses no direct somatic hazard toward fish (3811).

Blinks (1683) found that marine algae surviving at the most radioactive spot accessible on the Bikini Island reefs one year after the atomic explosions appeared to be normal in a number of physiological functions, except for one: catalase activity was considerably increased. No injurious genetic effects were observed, but this does not rule out the possibility that some occurred but were overlooked in the course of rapid sampling.

Genetic damage to fish appears to occur at lower levels of radioactivity than somatic effects. If genetic effects are considered in the strict sense of damage to chromosomes or genes, to the extent that modified characteristics are passed from one generation to the next, there is little to be found in published literature describing work on marine or fresh-water forms (2439).

Studies of the eggs and young produced by trout that were irradiated at the rate of 8.25 r per minute indicated that the number of abnormalities and the mortality rate among the spawn of parents receiving a total of 50 r was higher than among control eggs and young. A total exposure of 500 r to parents caused significantly higher frequency of death, slower rates of growth, and abnormality (772). Gonadal hemorrhage was observed in fish exposed to 500 r of total body irradiation (2439). Both sexes of fishes of all ages kept for periods of up to 150 days in water containing initially 200 microcuries per liter of P-32 were rendered sterile.

With respect to lower forms of life, higher levels of radiation are required to produce genetic effects. A sewage worm, Aeolosoma hemprichi, showed reproductive effects at 20,000 r and an occasional mutation (2442). Colonies of a colorless flagellate, Entosiphon sulcatum, were exposed to 500,000 r of gamma radiation from Co-60. In 72 lines with isolations every second day and each line carried for 50 generations, no effects on morphology or reproduction could be found (2442).

The concentration of radionuclides in aquatic and marine organisms is a complex phenomenon. The rate of uptake of any element or compound, and the extent of its retention in the organism, are dependent on many factors. It must be remembered that an organism does not distinguish among the isotopes of any element; hence the uptake depends on the ratio of a radionuclide to the non-radioactive form of the same element. The extent of concentration of any radionuclide is governed by the following factors (1936, 2436, 2437, 3273, 3813):

- 1. The particular element involved and its physiological importance to the organism. In the Columbia River below Hanford, for example, P-32 is the radionuclide most strongly concentrated in aquatic life, not because of any radioactive property but merely because phosphorus is a limiting element in the nutrition of aquatic organisms. Consequently any extra phosphorus in water is quickly assimilated into plant and animal life (1936, 2535, 3814, 3815).
- 2. The physical and chemical state of the element and its acceptability to the specific organism. Sulfide, for example, may be utilized and oxidized by one form of bacteria to which sulfate would be unacceptable. Also.

- particulate cerium-144 became associated with the cells of *Nitzschia* at a faster rate than ionic cerium-144 (3273).
- 3. The concentration of the element in the environment and the presence of other elements that may inhibit or enhance its uptake. The accumulation of one radioelement by an organism may be altered by the relative abundance of another in the environment by one of three ways: (a) elements of similar properties may substitute for one another, (b) some elements may have an inhibitory effect on others, and (c) one element may have a synergistic effect on others (3273). The uptake of strontium, for example, has been shown to be inversely proportional to the concentration of calcium in the water (3816).
- 4. The morphology of the organism, its life history, its condition and age, and its particular role in the food web. Closely related species may behave differently and organisms of the same species will concentrate radio-nuclids at widely varying rates depending upon other environmental conditions. Young and active organisms tend to accumulate most rapidly.
- 5. The physical and chemical characteristics of the environment. Temperature is especially important, for in cold-blooded animals it controls the rate of uptake, the animal's metabolism, and the rate of excretion of radionuclides. The pH of the water is also an important factor.

As a result of the interaction of these many factors, it is difficult to forecast the extent to which any radionuclide will be concentrated in a given organism. Some of the concentration factors that have been observed for aquatic and marine organisms are presented in Table 8-3, with each radionuclide being shown separately. A hasty perusal of this table will show that sodium, phosphorus, sulfur, and calcium are not likely to be accumulated significantly. After all, the non-radioactive forms are normally abundant in the water environment. The addition of phosphorus, iron, cesium, and zinc radionuclides, on the other hand, generally increases significantly the concentrations of these elements in the environment and this change is reflected in the organism, especially if the element is essential for nutrition and generally a limiting factor, such as phosphorus. In Table 8-3 attention is invited especially to the wide variation in reported concentration between species and even the wide range of values for the same species. This spread reflects the factors listed above.

Despite the variability of data and the fact that most information is of recent origin, Krumholz and Foster (2436) present the following generalizations:

- 1. Radioactive materials are taken into the body of an organism either through physiological processes and incorporated directly into the tissues, or they are adsorbed onto the surfaces of the organism. In general, adsorption and absorption are governing mechanisms for the lower forms of life while ingestion is the principal route for predators.
- 2. The concentration of certain radioelements reaches a higher level in the lower plant and animal forms, such as bacteria, protozoa, and phytoplankton than in higher forms such as vertebrates. In such instances there is an inverse correlation between the complexity of body struc-

ture and the concentration of the radioelement in question. This point was brought out clearly by the Columbia River studies made by the U.S. Public Health Service (3814, 3815).

3. Certain plants and animals have a predilection for concentrating specific radionuclides in certain tissues or organs. Iodine, for example, is concentrated in the thyroid, silicon in the tests of diatoms, calcium in the shells of mussels, calcium and phosphorus in the bony skeletons of vertebrates, and cesium in soft tissues.

4. Although certain radioelements may occur in amounts acceptable for drinking water, many freshwater organisms have the ability to concentrate them to levels that might be harmful.

How can the true hazard of concentration of radionuclides in fish be assessed? One way is to consider that the average person eats about 0.5 kilograms of fish per week and drinks about 15 liters of water. On that basis, the fish muscle could have a level of radioactivity per kilogram 30 times greater than the MPC per liter for drinking water before the hazards are comparable (2109). In the Columbia River surveys, the maximum radioactivity observed in plankton was  $7.9 \times 10^6$  pc/kg of weight (1684). The maximum total activity of an adult game fish was  $2.2 \times 10^6$  pc/kg of body weight (3817). Caddis flies emerging from the river area averaged  $3 \times 10^5$  pc/kg of wet weight (1936). A large percentage of this activity was probably due to P-32.

TABLE 8-3.

CONCENTRATION FACTORS FOR AQUATIC AND MARINE ORGANISMS

Radionuclide	Organism	Concentration Factor	Reference
Sodium-24	Marine invertebrates	0.5	
	Fresh-water fish	100	3375 2436
Phosphorus-32	Spirogyra	850.000	3273
-	Caddis-fly larvae	370.000	2535
	Insect larvae	200,000	3804
	Shiners	165,000	2535
	Fish	30,000-100,000	2436
`	Marine vertebrates	40.000	3375
	Algae (Ochromonas)	4,900-10,500	3386
	Algae (Platymonas)	6,300-13,600	3386
Sulfur-35	Marine invertebrates	5	3375
Potassium-42	Marine algae	25	2440
	Marine invertebrates	10	2440, 3375
	Marine vertebrates	5	2440
	Crabs (Carcinus)	·	3820
Calcium-45	Marine invertebrate, skeletons	1,000	2440
	Marine invertebrate, soft parts	10	2440, 3375
	Marine vertebrate, skeletons	200	2440
	Marine vertebrate, soft parts	1	2440
	Marine algae	10	2440
Iron-59	Algae (6 species)	720-7,500	3386
	Fresh-water fish	10,000	2436
	Marine algae	20,000	2440
	Marine invertebrates, skeletons	100,000	2440
	Marine invertebrates, soft parts	10,000	2440,3375
	Marine vertebrates, skeletons	5,000	2440
	Marine vertebrates, soft parts	1,000	2440
Chromium-51	Brown Algae	100-500	2442
Cobalt 60	Algae (Ochromonas)	1,070-1,500	3386
	Diatom (Navicula)	271	3386
	Copepods	50	2444
	Marine plankton (maximum)	10,000	3375
Copper-64	Algae. (Ochromonas)	1,840-3,040	3386
	Sphaerotilus	3,890	3386
	Marine bacteria	990	3386
	Marine invertebrates, soft parts Fresh-water fish	5,000	3375
		50	2436
Zine-65	Algae (6 species)	312-67,800	3386
· · · · · · · · · · · · · · · · · · ·	Brown algae	400-1,400	2442
	Marine bacteria	290	3386
	Marine invertebrates, soft parts	5,000	3375
•	Oysters	200,000	2446
	Oyster meat	1,400	<b>2442</b>

### **TABLE 8-3.—Continued**

# CONCENTRATION FACTORS FOR AQUATIC AND MARINE ORGANISMS

	CONCERNATION TACIONS TON AQUANC AND	MARINE ORGANISMS	
Radionuclide	Organism	Concentration Factor	Reference
Strontium-89 & 90	Algae (6 species)		
	Brown algae	100-3,060	3386
.*	Algae	8-90	2442
	Diatom (Nitzschia)	1,840-2,110	3385
	Algae	17	3690
N _p ·	Crustacea	1-40	3819
	Mussels (Mytilus)	3–8	3819
	Brine shrimp	6	3819
	Bacteria	40	3821
	Marine bacteria	10–100	3822
	Marine algae	100	3386
•	Marine invertebrates, skeleton	20	2440
	Marine invertebrates, sacreton	1000	2440
	Marine vertebrates, skeleton	10	2440, 3375
	Marine vertebrates, soft parts	200	2440
	Rudd, flesh	1	2440
	Rudd, bone	2.6	3691
	Rudd, scales	71	3691
	Fresh-water fish	209	3691
	Goldfish	20,000-30,000	2436
	Goldfish	10-150	3823
	Mosquito-fish, live	35–53	3824
	Mosquito-fish, dead	1.6-3.1	3385
Ruthenium-103 & 106	- · · · · · · · · · · · · · · · · · · ·	2.7-48.8	3385
Ratheniam-109 & 100	Algae	104,000	3385
	Algae (Ochromonas)	4,000-6,500	3386
	Diatom (Navicula)	7,900	3386
Iodine-131	Copepods	200	
•	Marine algae	10,000	2444 2440
	Marine invertebrates, skeleton	50	
	Marine invertebrates, soft parts	100	2440
	Marine vertebrates, soft parts	10	2440, 3375
Cesium-134 & 137		· ·	2440
Cestam-194 & 194	Algae (6 species)	<del>29-2,180</del>	3386
	Green algae	400-4,000	3387
	Fresh-water algae	52-1,530	3388
	Algae	342,000	3385
	Green, red & brown algae	4-30	3819
	Crustacea	10	3819
	Marine algae	1	<b>2440</b>
	Marine invertebrates, soft parts	10	2440
	Marine vertebrates, soft parts	10	2440
•	Oysters, soft tissue	50	3375
	Crabs (Carcinus)	. 8	3820
	Mussel (Mytilus), soft body	10	3819
	Flavobacterium aquatile	26	3386
	Sphaerotilus	116	3386
	Marine bacteria	15	3386
	Zooglea ramigera	558	3386
	Snail	600	3387
	Amphipods	11,000	3387
	Tadpoles	2,600-6,000	3387
	Damsel-fly & dragon-fly nymphs	800	3387
	Bullfrog, muscle	9,000	3387
	Carp, muscle	3,000	3387
	Sunfish, muscle	9,500	3387
	Atlantic prawn	25	2 <del>444</del>
Cerium-141 & 144	Algae (4 species)	5,100-28,500	3386
	Algae (several species)	2,000-4,500	3272
•	Algae	2,040,000	3385
	Algae	<b>314-4,498</b>	2442
	Red, green & brown algae	300900	3819
•	Mussel (Mytilus), soft body	360	3819
	Crustacea	230	3819
	Marine bacteria	280-1740	3386
Gross beta emitters	Algae	43,300	3385
STORE CHIEFEIS	Plankton	4,210	3825
	Bottom animals	526	3387
	Shiners, juvenile	474	3825
	Suckers, bone	263	3825
	Suckers, muscle	58	3825
	Bass, bone	184	3825
	Bass, muscle	24	3825
Mixed fission products	Algae (6 species)	1,700-16,800	3386
uppion products	Tribut (4 photops)	2,100 20,000	<b>4000</b>

Another approach is to consider the radionuclides for which limits have been set in the 1962 Drinking Water Standards of the USPHS (2036), namely radium-226, strontium-90, and total beta emitters. No information was uncovered in this survey on the concentration of radium by fish, but since radium is relatively scarce in surface waters its measurable uptake by fish seems improbable. Strontium-90, however, is present in typical surface waters of the U.S. at concentrations that frequently exceed 1.0 pc/l and sometimes 2.0 pc/l. The limit set by the new standards for drinking water is 10 pc/l. If fresh-water fish should concentrate Sr-90 by a factor of 30 in their flesh (which according to Table 8-3 is possible but not likely) and if the surface water contained 2.0 pc/l of Sr-90, the fish flesh would contain 60 pc/kilogram. A man would have to eat 2.5 kg of such fish per week to get a Sr-90 dosage equal to the permissible dosage from drinking water. Moreover, the 150 pc/week so consumed would be only  $150/7 \times 200$  or 10.7 percent of the limit set by the Radiation Protection Guide for total intake of Sr-90. It seems unlikely, therefore, that accumulation of radiostrontium in fish is likely to become a serious problem, but it warrants surveillance.

#### **SHELLFISH**

Many of the factors and principles relating to the effect of radioactivity on shellfish are discussed in the foregoing section on aquatic and marine life. The following information is specific for shellfish.

Snails vary considerably in their resistance to gamma irradiation; one species was killed by 213 r from Co-60, another by 1200 r, two species by 1750 r, but a fifth species survived 7461 r (3818).

Concentration factors for shellfish (oysters, mussels, crabs) are shown in Table 8-3. Clams can rapidly con-

centrate Zn-65, Fe-59, and Co-60 in their shells and soft tissues (2438). Oysters and clams are especially adept at accumulating Zn-65. A survey of food in Cincinnati showed that marketed oysters contained 40 to 178 pc/kg of Zn-65 in their meat compared with 3 to 17 pc/kg for other common foods (2445). Cesium is concentrated slightly by mollusks (3273, 3827). Accumulation factors for the mussel (Mytilus) are given in Table 8-3 for strontium-90, cesium-137, and cerium-144 (3819). Lobsters show a fairly rapid uptake of Sr-90; indeed they were the critical animal in limiting the discharge from the reactor at Winfrith in England (2444).

#### RECREATIONAL WATER USE

Radiation in water may be harmful to swimmers and bathers, especially when the period of contact is long. Most types of radiation, i.e., alpha and beta, can be absorbed through the skin and all types through wounds. Ideally, the radioactivity of recreational waters should be as low as possible; yet one must rationalize that the hazard from occasional bathing or swimming is not nearly as severe as that from daily ingestion. No clearly defined criteria of radioactivity for recreational waters, based on the latest standards of ICRP and NCRP were uncovered in this survey. It is assumed, therefore, that the ICRP, NCRP, and Federal Radiation Council standards for water apply to recreational waters as well as drinking water.

#### WASTE DISPOSAL

The Atomic Energy Commission, upon advice from the Federal Radiation Council, has established regulations for the discharge of radionuclides to sewers. For a summary of these regulations, see Table 8-2 and the discussion associated with it.

#### **CHAPTER IX**

### **PESTICIDES**

by Ralph Pressman, Ph.D.*

If the number of fish killed per year in the streams of the United States were the criterion of water quality problems, first place among the list of pollutants would be occupied by pesticides (2879, 3012, 3013). There is no question but that mankind has reaped bountiful awards in the form of greater productivity, improved comfort, and better health from the widespread use of pesticides (3014, 3015). It has been estimated that in the first 10 years of broad-scale use, pesticides saved 5 million lives and prevented 100 million illnesses. Yields of many crops increased 10 and 20 percent or more and were of higher quality. Nevertheless, it is apparent that pesticides will have to be used with increasing care in order to avoid tragic, secondary effects (3016, 3017).

### CLASSIFICATION OF PESTICIDES

Webster's New Collegiate Dictionary, 2nd Edition, defines pesticide as "any substance used to kill rats, insects, bacteria, fungi, protozoans, minute forms of plant life, etc." Such a broad definition includes many thousands of organic and inorganic compounds that have pesticidal properties but are not ordinarily recognized as pesticides. A simple example would be the use of common table salt to control weed growth in a homeowner's crushed-rock patio. The Federal Housing Administration report on ground-water contamination (2015) cites the following definition in Van Nostrand's Scientific Encyclopedia, 1958 edition:

"A legal definition for a pesticide is that it is any substance or mixture of substances used in the production, storage, or transportation of food which is intended for preventing, destroying, repelling, or mitigating any insects, rodents, fungi, or weeds, and other forms of plant or animal life or viruses, except viruses on or in living man or other animals."

The FHA report enlarges the definition "to include many substances used to control objectionable insects, weeds, and probably other undesirable life or organisms. (Example: Some types of fish in ponds or water reservoirs.)"

The latter definition is that which has been most nearly followed in the preparation of WATER QUALITY CRITERIA. However, only those compounds that are generally recognized as pesticides are included within this chapter. For those compounds that are primarily used or classified in other ways, see Chapters VI and X.

The common pesticidal chemicals can be categorized chemically into three general groups, (a) Inorganic, (b) Synthetic Organic, and (c) Natural Organic. Examples of each include: Inorganic—arsenicals, mercurials, bor-

ates, and fluorides; Synthetic Organic—chlorinated hydrocarbons, organic phosphates, and thiocarbamates; and Natural Organic—rotenone, pyrethrum, and nicotine (3015). They may also be classified by their biological usefulness, viz, algicides, acaricides, fungicides, herbicides, etc. Other practical means of classification are also available such as the form of use, attractant, fumigant, and repellant, etc.

In general, the inorganic pesticides are toxic to plants and humans as well as to insects. Some formulations (3018) are more toxic to mammals than to insects. Inorganic pesticides have been supplanted largely by organics which can be adapted to more specific use. The natural organics are somewhat limited in supply and popularity. Present-day trends are towards the use of powerful synthetic organic pesticides, principally the chlorinated hydrocarbons and organic phosphorus compounds (3015). Similarly, the trend in aquatic weed control is towards chemical methods (3880).

#### MAGNITUDE OF THE PROBLEM

Pesticides may gain access to ground and surface waters through direct application, through percolation and run-off from treated areas, and/or through drift during application. Gross over-application of pesticides is a common practice that augments the pollutional effects of pesticides to a considerable extent. Although knowledge is lacking regarding the long-range effects of pesticides on our water resources, it is clear that these substances with their accompanying diluents and solvents are entering our natural waters in ever-increasing amounts (3015). Fish kills occurred in at least 15 streams in the Tennessee River Valley following application of a synthetic insecticide to over 400,000 acres of cotton in 8 Alabama counties (3019, 3030). Concentrations of DDT as high as 5 to 20 µ/l have been reported in the Detroit, Missouri, Mississippi, and Columbia Rivers (2699). The biological significance of trace quantities of many of the complex organic substances is only partially understood; their persistence in natural waters largely unknown (3015, 3021, 3022).

Because of these uncertainties, official limits for organic pesticides in water in the U. S. have not been established (3015). Serious consideration was given by the U. S. Public Health Service to recommending limits for the organic phosphate and chlorinated hydrocarbon pesticides in the 1962 Drinking Water Standards. It was difficult, however, to establish acceptable concentrations. Moreover, there are no simple analytical techniques for identifying and quantitating these chemicals (2062). Bean (1745), in a discussion of limits for an ideal water, concurs with these conclusions. Nevertheless, the English

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Mersey River Board in 1953 proposed that industrial waste effluents entering the River Alt and other fishing streams contain no insecticides (2950).

In contrast with water, pesticide limits are in existence for foods. In preparing limits for pesticides on foods, several assumptions are made:

(1) Man is 10 times more prone to injury than other species of warm-blooded animals.

(2) The most sensitive individual is 10 times more susceptible to injury than is the average individual.

(3) Some individuals subsist for lengthy time intervals on diets consisting almost entirely of fresh fruits and vegetables.

(4) When two or more toxic substances are present, the allowable quantity of each is calculated as the percent of its applicable tolerance, the sum of such percentages being not more than 100.

The last assumption is said to be good for the chlorinated hydrocarbons, organic phosphates, and dinitro compounds (3023). However, the reader is referred to EPN or malathion in this chapter as examples of synergistic compounds that do not behave in this simple way.

Until a pesticide is exempt (copper compounds, pryethrum, rotenone) or given an official tolerance, no trace of the pesticide is allowed on any product (3015). A zero tolerance for any particular pesticide generally requires that the product not be used on the crop during the period when it might result in the contamination of the harvested portion of the crop (3024). With few exceptions, pesticides are not taken up from the soil by roots or absorbed through the foliage of fruit and vegetable plants and translocated (3023). However, the reader is referred to a study that reports such uptake (3025).

It must be remembered when dealing with pesticides as water pollutants that any specific pesticide will rarely. if ever, be encountered as the sole, solitary pollutant. Many solvents, diluents, or other carriers used with the pesticide also have toxic properties, e.g., the light petroleum oils used in household insect sprays. Solvents, such as xylene, alkylated naphthenes, fuel oil, or kerosene, have some toxicity. This effect is believed to be particularly evident in aquatic environments when solvents have an opportunity to be emulsified by riffles in streams (3026). Rudd and Genelly cite three important aspects of solvents or dilutents from the wildlife standpoint: (a) they may be toxic themselves; (b) they may enhance the toxicity of the pesticide directly (synergism); and/or (c) they may increase the toxicity of the pesticide by making the toxic agent more readily available. None of these effects are common, and only certain types of formulation will show any one of these effects. In general, solvents and additives reduce the available amount of toxic agent (3005).

When considering pesticidal pollution of water, toxicity is not the only aspect of concern. There are also difficult problems posed by tastes and odors. Some synthetic organics cause highly objectionable tastes and odors, as do many of their solvents also (3024).

The addition of synergists and/or various adjuvants to make a particular pesticide more effective has been practiced by the pesticide manufacturing industry for many years. A marked synergistic effect, or potentiation, of up to 50-fold in acute toxicity exists for EPN and malathion when administered simultaneously to dogs (3027). For more on potentiation and toxicities of mixtures the reader is referred to three significant references (3028, 3029, 3030). Adjuvants include wetting or spreading agents, stickers, penetrants, and emulsifiers (2998).

When, to the complexity of various formulations, one adds the differing environmental conditions and inherent biological variations, it is not surprising to find that there is a wide variation in the literature in toxicity results of these compounds to various aquatic animals. Although recognizing that it is important to duplicate test conditions such as dissolved oxygen, pII, temperature, time, hardness of water, etc., several authors (2953, 2985, 3031, 3032, 3033, 3034, 3035) have indicated that (a) not enough variables are included, (b) ecological factors are not considered sufficiently, and (e) chronic effects of sub-lethal dosages are not considered. They conclude, therefore, that a great deal of additional study is necessary. Among the more obscure areas of knowledge is that delineated by Hueper (3330) who states that, based upon animal studies, a number of pesticides and preservatives, such as DDT, aramite, carbon tetrachloride, acetamide, thioacetamide, thiourea, thiouracil, aminotriazole, and isopropyl-chlorophenyl-carbamate are capable of eliciting benign and/or malignant tumors in various organs.

There is no doubt but that more study is needed, particularly in view of the burgeoning aspects of pesticides. The 9072 commercial pesticide products of 1961 represented a 15-percent increase over the number listed in 1960, and over twice the number, 4360, listed in 1952 (2998). Although over 200 different kinds of synthetic organic pesticides are now used, fewer than 30 account for approximately 80-90 percent of the estimated 900 million pounds of finished pesticidal preparations sold annually (3015). Over 300 million acres of cultivated crop land in the U.S. are sprayed each year with over 500 million pounds of organic insecticides (2699). Woodward (3024) has made the interesting observation that division of the 1958 production of pesticides (460x106 lbs) by the annual U.S. runoff (1160 bgd) results in a concentration of 0.13 mg/l.

In the face of this enormous and expanding use of pesticides, suggestions have been offered to limit undesirable side effects. In addition to the usual plea for proper dosage and careful application, it has been suggested that consideration be given to select that insecticide most effective against the pest desired and least hazardous to other organisms (3014), and also that the least persistent types of pesticides are to be preferred (3024).

#### ACP-M-569

(see ATA) °

### ACROLEIN

CH₂=CHCHO

1. General. Acrolein has been introduced as an aquatic weed killer under the commercial name Aqualin. Also known as acrylic aldehyde, 2-propenol, or F-98, it is

a clear colorless liquid at ordinary temperature, having a pungent irritating odor. It is severely irritating to the skin and mucous membranes, and is soluble in water and various organic solvents (364, 2599, 2991).

2. Cross References. Pentachlorophenol and Pentachlorophenates.

3. Effects Upon Beneficial Uses.

a. Stock and Wildlife Watering. The principal constituent of Aqualin, 2-propenol, has an acute oral LD₅₀ for rats of 46 mg/kg of body weight and for rabbits of 7.1 mg/kg (2991). Another report cites 600 mg/kg in food being administered to laboratory animals without effect (3036).

b. Fish and Aquatic Life. Acrolein at 3 mg/l applied to a pond killed tadpoles, 500 small bluegills, and a few big walleyes, but no large bluegills or bass (2878). Other field work indicated that fish showed severe agitation when exposed to concentrations of 10 to 15 mg/l. Carp and thread-fin shad appeared quite sensitive, whereas largemouth black bass seemed more resistant (2988). Springer (3010) reports that acrolein repels fish, is toxic to rough fish at 3 mg/l, and to game fish at 5 mg/l.

For F-98, a trade formulation containing acrolein, the 24-hour TL_m value for chinook salmon at 20°C in aerated solutions was 0.08 mg/l (2988). This formulation is reported to kill carp and thread-fin shad at 1-2 mg/l (3036). All test fish exposed to acrolein at 2 and 4 mg/l were dead within one hour after their removal from the solution (2988). Chironomids, tubificids, and Tanypus were not affected at doses up to 12 mg/l (3036).

In Lake Huron water at 12° C, rainbow trout, bluegill sunfish, and sea lamprey survived a 5 mg/l concentra-

tion for 24 hours (2976).

Van Overbeek et al. (3037) reports that aerolein is twice as effective against snails as sodium pentachlorophenate, and promises to become a useful tool against the blood flukes (see Worms, Parasitic, in Chapter VII). The molluscacidal properties of aerolein were first observed during field trials in California coincident to the destruction of submerged weeds in irrigation canals. Concentrations of 10 mg/l for 3 hours killed 100 percent of snail eggs and for 24 hours killed 98 percent of adult snails. Numerous field trials in Puerto Rico against water weeds and snails are cited (3038).

With respect to plant life, concentrations of 5 mg/l for 5 hours, or 0.5 mg/l for 24 hours, are toxic to Elodia densa leaf cells (3309). A dosage range of 1.5 to 7.5 mg/l, depending upon water temperature (15°-27°C), killed Hydrodictyon, Cladophora, Spirogyra, Potamogeton, Zannichellia, Elodea, Callitriche, and Ceratophyllum (3040). Another reference cites doses of 3-6 mg/l of F-98 for the control of weeds in lakes and static reservoirs (3036).

#### ACTIDIONE

(See Antibiotics)

### **AEROSPORIN**

(see Antibiotics)

### AGROXONE

(see MCPA)

#### ALDRIN

C₁₂H₆Cl₆

- 1. General. Aldrin is the common name of an insecticide containing not less than 95 percent of 1, 2, 3, 4, 10, 10-hexachloro-1, 4, 4a, 5, 8, 8a-hexahydro-1, 4, 5, 8-dimethanonaphthalene. It is crystalline, insoluble in water, slightly soluble in oils, and soluble in most other organic solvents. It is similar to dieldrin which has an oxygen substituted for two hydrocarbons. Aldrin is used agriculturally at rates varying from 2 ounces to 6 pounds per acre, and is usually used as a dust or emulsifiable concentrate (3005).
- 2. Cross References. Chlorinated Hydrocarbons—General, Dieldrin, Isodrin.

3. Effects Upon Beneficial Uses.

- a. Domestic Water Supplies. Aldrin has moderately high acute and chronic effects by all routes of administration. A number of cases of human illness have been recorded, most of which resulted from its manufacture (3005). The estimated fatal dose for a 70-kg man is 5 grams (2995).
- b. Irrigation Waters. Aldrin from contaminated soils was absorbed by carrots, potatoes, peas, cabbage, cucumbers, beans, radishes, beets, and rutabaga. These crops contained both aldrin and dieldrin in their tissues (3025).
- c. Stock and Wildlife Watering. For aldrin, the acute oral  $\mathrm{LD}_{50}$  to rats has been cited at values ranging from 39 to 66.8 mg/kg of body weight (2992, 2999, 3002, 3042, 3043). Chronic oral doses of 100 mg/kg in the diet produced a gradual increase in esterase levels (3041). A level of 25 mg/kg for two years caused no harm (3043). However, lower dietary levels (10-12.5 mg/kg) had effects on reproduction. Other animals are more susceptible than rats, dogs being five times more susceptible in chronic feeding tests. Sheep and cattle fed alfalfa treated at 0.5 lb/acre showed no noticeable reactions (3005).

Poultry and birds appear to be quite susceptible to aldrin. Levels of 3 mg/kg in the diet retarded growth in turkeys and chickens. The LD50 value for seven-dayold chicks is 25.5 mg/kg. Ducks and other water fowl suffered significant losses from single applications of aldrin as low as 0.125 lb/acre, which also effected a heavy mortality of insects (3006). Feeding of 1 mg/kg in the diet of quail caused a decrease of 40-percent reproduction (2996), and when fed to growing quail caused high mortality rates. Young pheasants failed to survive on a diet of 5 mg/kg. Nearly all quail died when fed winter diets containing 0.5 mg/kg. Hatchability of eggs and viability of chicks are adversely affected by aldrin (3044, 3045). The oral LD50 values for bobwhite quail and ringneck pheasant, considering all stages of the life cycle, are 4 and 14 mg/kg of body weight respectively (2994, 2996). The acute oral  $\mathrm{LD}_{50}$  value for mourning doves lies between 15 and 17 mg/kg (3005).

d. Fish and Other Aquatic Life. Aldrin is highly toxic to fish. In aquarium tests there was no significant difference in toxicity between dust suspensions and emulsions of equal aldrin equivalence (3005). Aldrin dust, 2.5 percent, applied weekly for 20 weeks at 1 lb/acre (0.025 lb aldrin per acre) caused insignificant fish mor-

tality. Five lb/acre of dust killed 3.3 percent of the

fish, 10 lb/acre killed 60 percent (3046).

Doudoroff, Katz, and Tarzwell (1449) tested the toxicity of aldrin toward ten goldfish or minnows in a 15liter aquarium at 20°C with water of 75 mg/l total alkalinity. Tests were made with a dust containing 2.3 percent aldrin, 1.79 percent related compounds, and the remainder inert; and also with an emulsion comprising 22.8 percent aldrin, 17.5 percent related compounds, 50 percent petroleum products, and the remainder inert. In terms of aldrin, the effects of dust suspensions and emulsions were about the same. The concentration of aldrin fatal to 50 percent of the goldfish in 10 days (i.e., the 10-day  $TL_m$ ) was 0.02 mg/l. At 0.01 mg/l 90 percent survived, while at 0.032 mg/l only 20 percent lived 10 days. A concentration of 0.05 mg/l caused some goldfish to turn over within 24 hours, but others withstood 0.1 mg/l. For minnows, the 10-day TL_m was about 0.018 mg/l but some fish were killed by as little as 0.01

Although young fathead minnows do not differ in susceptibility from large goldfish, it appears that trout are more sensitive (3005). Exposure of 4-7 inch brown trout to an emulsified concentrate at 0.025 mg/l killed 33 percent in 48 hours, and 0.033 mg/l killed 100 percent in the same time interval (3005, 3007, 3049). The toxicity threshold of aldrin to trout is reported as 0.025 mg/l (3007, 3048). Later studies that report the fish toxicity of aldrin are tabulated below:

Concentration of Aldrin mg/l	Temperature °C	Type of Water	Type of Fish	Result	Reference
0.013	25	(3)	Bluegill	96-hour TLm	3000
0.028	25	(2 <b>)</b>	Fathead	96-hour TLm	3000
0.028	25	(3)	Goldfish	96-bour TLm	3000
0.033	25	(3)	Fathead	96-hour TLm	3000
0.033	25	(3)	Guppies	96-hour TLm	3000
0.05	20-22		Gupples	Abnormal behavior in 3 hours, death in 48 hours	2992
5.0	13	(1)	Rainbow trout	No effect in 24 hours	s 2976
5.0	13	(1)	Bluegill	No effect in 24 hours	s 2976

Lake Huron water, pH 7.5-8.2, D0 8.6-13.7 mg/l, free C0₂ 5.0-9.0 mg/l, 10-liter aquaria, 6 liters solution, one or two test specimens only.
 Hard water, pH 8.2, D0 8.0 mg/l, alkalmity 360 mg/l, hardness 400 mg/l.
 Soft water, pH 7.4, D0 8.0 mg/l, alkalmity 18 mg/l, hardness 20 mg/l.

Silvey (2531) cites the concentration of aldrin required to kill 50 percent Chironomus larvae in eight hours as 0.012 mg/l. Batte, et al. (2993) found that 4.8 mg/l of aldrin killed Lymnaeid snails in 24 hours. The estimated concentration of aldrin required to immobilize Daphnia magna in 50 hours at 20°C is 29.2 µg/l (3255).

### ALLETHRIN

(see Pyrethrum)

### AMERICAN CYANAMID (4124 and 12009)

(see Organic Phosphates—General)

#### AMMATE

(see Ammonium Sulfamate)

### AMMONIUM SULFAMATE

NH₄SO₃NH₂

This compound also known as Ammate, AMS, and ammonium amidosulfate, is used to control aquatic vegetation. It occurs as crystals and is extremely soluble in water. It has low mammalian toxicity, the acute oral  $LD_{50}$  to rats being 3.9 g/kg (364, 1724, 2997, 3009). Ammate is reported to be the best herbicide for use around water supply reservoirs. The lethal dose for an average 90 kg man is 180 grams (1723).

A formulation of 0.8 pound of the chemical in 1 gallon of water, with or without a wetting agent, was reported not to kill fish although frogs were blinded by the spray. A concentration of 10 mg/l was non-toxic to fish (1725, 3009). Rainbow trout, bluegill sunfish, and the sea lamprey survived a concentration of 5 mg/l for 24 hours in Lake Huron water (2976).

The 24-, 48-, and 96-hour LD₅₀ values for Ammate to fingerling channel catfish at 19°C were reported as 259,

206, and 203 mg/l respectively (2981).

# AMINOTRIAZOLE

(see ATA)

### AMITROL

(see ATA)

### ANTIBIOTICS

Antibiotics will not likely be found as stream pollutants. An increasing amount of research, however, is being conducted to determine their effectiveness against algae. Since they appear to show high specificity to certain types of algae, their use as algicides may very well increase in the coming years.

Actidione, which has an acute oral LD₅₀ against laboratory rats of 1.0 mg/kg (3009), was found to be effective against certain green algae and diatoms (2041, 3050). Concentrations of 2.0 mg/l inhibited the growth of 50 percent of the test algae during a 21-day incubation period at 22°C. Streptomycin inhibited all cultures of blue-green algae and 18 percent of green algae at 1 mg/l equivalent of pure base. A concentration of 0.015 mg/l retarded the growth of 25 percent of the blue-green algae tested (2041, 3050). Streptomycin sulfate at a concentration of 2.0 mg/l inhibited the growth of 66 percent of the tested algae during a 21-day incubation period at 22°C (2041).

Neomycin and terramycin were found to affect bluegreen algae (2041, 3050). Terramycin at a concentration of 2.0 mg/l inhibited the growth of 17 percent of the tested algae during 21 days of incubation at 22°C (2041).

Concentration of Aerosporin-Polymyxin B (sulfate) and penicillin G, potassium (erystalline), at 2.0 mg/l inhibited the growth of 83 and 17 percent of the tested algae respectively after 21 days incubation at 22°C (2041).

Chlortetracycline at 20 mg/l was used in oyster rinse water at near 0°C but it failed to depress bacterial growth significantly and did not prevent the development of sour odors associated with spoiled oysters. The oysters retained 3 mg/l, a concentration that decreased by 50-60 percent during 12 days of storage (3051).

### AQUALIN

(see Acrolein)

#### AQUATHOL

(see Endothal)

### AQUATIC

(see Aromatic Solvents)

#### ARAMITE

 $C_{15}H_{23}ClO_4S$ 

Aramite is the common name for a compound whose chemical name is 2 (p-tert-butylphenoxy) isopropyl 2-chloroethylsulfite. It is a chlorinated acaricide commonly used to control mites on fruits, vegetables, and ornamentals. Application rates normally range between 0.25 and 0.5 lb/acre. Residues persist for at least one week.

The acute oral  $\rm LD_{50}$  to laboratory rats has been reported as 6300 mg/kg of body weight (3002) and 3900 mg/kg (3005). The  $\rm LD_{50}$  for mice is 2300 mg/kg. Chronic toxicity studies showed that 500 mg/kg in the diet of rats and dogs for a period of 1-2 years had no effect. The lowest dietary level that produced gross effects was 1000 mg/kg (3005).

Testing fingerling channel catfish against a 15-percent Aramite solution at  $20^{\circ}$ C, Clemens and Sneed (2981) found the 24-hour  $TL_m$  to be over 15 mg/l as Aramite. In tests utilizing Lymnaeid snails, a 100-percent mortality was caused in 24 hours by 1.5 mg/l of Aramite (2993).

#### AROMATIC #80

(see Aromatic Solvents)

#### AROMATIC SOLVENTS

1. General. Aromatic solvents are used for the control of submerged aquatic weeds in irrigation channels in the United States. These petroleum or coal-tar derivatives are also used in industry as paint thinners. Bruns, et al. have published studies of the aromatic solvents as aquatic weed killers in a U.S. Department of Agriculture Circular (2873). In this report, the type of solvent is identified by a table of A.S.T.M. physical characteristics

Because the aromatic solvents are not soluble in water, emulsifiers (surface-active agents) are added. Earlier work by the Department of Agriculture utilized the petroleum sulfonates at 5-10 percent by volume of the solvents. Experience showed that the performance of these emulsifiers was adversely affected by lower temperatures or higher salt content. Nonionic type emulsifiers are now used at about two-percent concentrations and give satisfactory results (2873). The aromatic solvents are usually injected under the water surface to give a concentration of 300-600 mg/l for 30-60 minutes (2861).

- 2. Cross References. Chapter X.—Surface Active Agents, Chlorinated Benzenes.
  - 3. Effects Upon Beneficial Uses.
- a. Irrigation Waters. A 30-minute introduction of aromatic solvent at up to 1200 mg/l caused no visible or measureable damage to spring wheat. However, 2200 mg/l caused a 22-percent reduction. Irrigation for 60 minutes with concentrations as high as 900 mg/l caused no injury to potatoes, and 1250 mg/l caused no damage to sweet corn. Later studies indicated no effect by 30-minute concentrations of 1200 mg/l applied to sweet corn, potatoes, sugar beets, and beans. Although concen-

trations of 2400 mg/l for 10 minutes caused no damage to sweet corn, a 12-percent reduction was obtained from 1600 mg/l for 30 minutes. Applications of 2400 mg/l for 30 minutes did not affect oats, beans, and probably not carrots, the decreased yield of carrots at concentrations over 800 mg/l being insignificant.

Although concentrations of 400 mg/l for 40 minutes appeared to damage seedling alfalfa, new shoots developed and the plants grew normally. Mature stands suffered only the burning of lower submerged leaves. Grain sorghum was unaffected except for those plants completely submersed, which died. Cotton exhibited the same response. Other studies of 40-minute applications of up to 1600 mg/l to alfalfa, grain sorghum, and cotton exhibited temporary inhibition in growth but no decreased yields. Applications of 2400 mg/l for 30 minutes did not affect ammonifying or nitrifying bacteria (2873).

Further experiments are discussed by Bruns, et al., but the general conclusion is that the usual concentrations of aromatic solvents, when present in flood irrigation waters, will not harm crops provided that they are not in the seedling stage; i.e., provided that they are not submerged (890, 2873).

b. Stock and Wildlife Watering. Farm animals were observed to taste aromatic-solvent-treated water and then refuse to drink it. No subsequent ill effects were noted, nor are species or concentrations given. However, guinea pigs were confined with water treated with 800 mg/l and refused to drink it until the third day. Although they drank a substantial quantity (amount not specified) on this third day, no subsequent ill effects were noted (2873).

c. Fish and Aquatic Life. The aromatic solvents are toxic to aquatic life (2861). Fish, crayfish, snails, mosquito larvae, and other insects are killed when they come in contact with treated water of 150-740 mg/1 (3009).

In aquaria, 4.2 mg/l of Aromatic #80 and Socal #3 killed 40-60 percent of the white crappies tested. Dead-X, when applied in a drainage ditch at 185-200 mg/l, killed most caged fish within 1 mile of the point of introduction, but unconfined fish were observed to flee before the chemical and certain insects were little affected. An Esso weedkiller, WS-1492, with an aromatic content of 99.5 percent applied at 250-350 mg/l killed gar, mudfish, and a few minnows. Within several hours of application, the emulsion broke, rose, and evaporated, leaving the water relatively unpolluted. Fish later returned (3009, 3011).

Ortho Aquatic Weed Killer, which contains 95 percent aromatic petroleum distillate, at 50 mg/l effected a 50-percent kill of 3-inch silver salmon in 72 hours. Aerated, fresh water was used, and all survivors were obviously distressed. The level recommended for use in weed control is 370 mg/l (2091). The 96-hour TL_m values of Aquatic to shiners in soft and hard waters at 20-22°C was 75 and 78 mg/l respectively. Field studies reported that water striders (Gerridae) were the only water fauna that survived (3011).

#### ARSENIC

(see Chapter VI)

#### ARSENICALS

(see Arsenic and the specific arsenic compounds in Chapter VI: Arsenic Trioxide, Calcium Arsenate, Lead Arsenate, Sodium Arsenate, and Sodium Arsenite)

The arsenicals have been in use for a long time as herbicides, rodenticides, algicides, and insecticides. A number of compounds are still available for use, but at least as insecticides, they have been largely supplanted by synthetic chemicals. For this reason and for convenience of presentation all arsenic-containing compounds except paris green are included in Chapter VI. Arsenicals comprise chemicals with widely different compositions and uses.

The best known arsenical insecticides are calcium and lead arsenate. Until recent years they were more widely applied than any other insecticides. They are still used commonly, particularly in Europe and in the southern United States. Sodium arsenite has been used in grasshopper and ant baits. It is better known in recent years as a herbicide to control submerged vegetation and as a debarking agent in the wood pulp industry. Dust and aqueous solutions of arsenic trioxide continue in limited use in rodent baits. Paris green (copper acetoarsenite), one of the first insecticides to be widely employed, is discussed in this chapter.

### ARSENIC TRIOXIDE

(see Chapter VI)

### ASUNTOL

(see Co-Ral)

### ATA

 $C_2H_4N_4 \cdot HC1$ 

ATA, also known as amitrol or aminotriazole, is a water-soluble crystalline compound for which the chemical name is 3-amino-1-H-1,2,4-triazole. The chemical formula above is that of the hydrochloride. ATA is a weed killer that is not considered to be very toxic to animal life. The LD₅₀ to rats is reported to be 14.7 g/kg of body weight (364) and also 25 g/kg (3009). ATA is used for the control of all species of cattails (3010), and is less hazardous than 2, 4-D to sensitive crops when sprays drift (2880).

Tests with bluegills indicated that all fish would be expected to survive a concentration of 1470 mg/l. A concentration of 10,000 mg/l was necessary to kill 50 percent of the bluegills during a 48-hour exposure (3009).

Toxicity studies were made with red-sided shiners. The 96-hour  $TL_m$  values at 20°-22°C for soft and hard water respectively were 983.3 and 1370 mg/l (3011).

According to Bond (2988) the 24- and 48-hour TL_m values at 20°C for coho salmon were both 325 mg/l. Bond notes that aminotriazole failed to kill largemouth bass in 96-hour standing-water bioassays at concentrations up to 1,000 mg/l but in a constant-flow apparatus this concentration killed all test fish in six days. Largemouth bass survived 62.5 mg/l for a 14-day period in the constant-flow test. Bond also quotes other studies on the toxicity of aminotriazole to bluegills, indicating that the 24-hour TL_m is 14,300 mg/l and the 48-hour TL_m is 10,000 mg/l. Bond mentitons another report that indicates

that the concentration safe to fish is only 1470 mg/l. He also studied a formulation called ACP-M-569 using chinook salmon and found the 24-hour  $TL_m$  value to be 185 mg/l and the 48-hour  $TL_m$  value 155 mg/l. However, this formulation contained other undisclosed ingredients as well as aminotriazole (2988).

#### BARON

C11H9Cl5O3

(see also Dalapon, 2, 4, 5-T)

Baron is a trade name given to the herbicide erbon, whose chemical name is 2- (2, 4, 5-trichlorophenoxy) ethyl 2, 2-dichloropropionate. This molecule was designed to combine the selectivities of the phenoxy compounds with those of dalapon. Baron is applied to the soil as a residual nonselective systemic herbicide. It requires rainfall or irrigation to leach the compound into the soil of the root zone. It persists in the soil for a considerable period. Baron contains 41.3 percent technical grade erbon.

According to Bond (2988), the 24-hour TL_m value against bass at 20°C was 4.6 mg/l and the 24- and 48-hour values against chinook salmon were 2.62 and 2.3 mg/l respectively. Utilizing coho salmon, no mortalities occurred in 24 hours following 15- and 30-minute exposures to 5 mg/l. Bond quotes Lawrence as citing the safe concentration to fishes at 5 mg/l. Clemens and Sneed (2981) tested Baron against fingerling channel catfish at 19°C. The 24-, 48-, and 96-hour TL_m values were 7.2, 6.9, and 4.5 mg/l respectively (2981).

## **BAYER 13/59**

(see Dipterex)

### **BAYER 17147**

(see Guthion)

### **BAYER 21/199**

(see Co-Ral)

#### **BAYER 29493**

(see Organic Phosphates-General)

### BENOCLOR

(see Chlorinated Benzene)

# BENZENE HEXACHLORIDE

 $C_6H_6Cl_6$ 

1. General. Benzene hexachloride is a widely used compound whose correct chemical name is 1,2,3,4,5,6-hexachlorocyclohexane. Of its nine possible stereoisomers five are known, the gamma isomer being the powerful insecticidal principle. It is also known under the names lindane, BHC, and Gammexane (677). The name lindane is applied to commercial preparations containing 99 percent or more of the gamma isomer. Originally the wettable powder formulation of benzene hexachloride contained 6-12 percent of the gamma isomer. Newer formulations contain as much as 36 percent. BHC has a residual life in the soil approaching that of DDT (3005).

An example of stream pollution by an industrial waste containing BHC has appeared in the German lit-

erature. In this report, concentrations of BHC were not given, but varying dilutions of the waste waters were made and tested against different organisms. The report notes that the treatment plant efficiency was diminished, stream organisms disappeared, and the odor was noticeable 15 kilometers downstream as a result of the pollution (3052).

- 2. Cross References. DDT, Chlorinated Hydrocarbons—General.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The A.M.A. Committee On Pesticides reports that an estimated 600 mg/kg of body weight, or about an ounce, of technical grade BHC containing 15 percent gamma isomer would be fatal for man (3053). Other reports (2995) estimate the fatal dose of lindane for a 70 kg man as 15 grams and of BHC as 28 grams. BHC imparts a disagreeable taste to drinking water at a level of 20 µg/l (3054). Still another report (2058) notes that as a source of taste and odor in water a mild effect is still noticeable up to two years after spraying.
- b. Irrigation Waters. A most important hazard involved in irrigation water containing BHC is the tainting of the flavor of crops with a characteristic musty odor and taste. BHC has no effect on the pH of the soil or on its bacterial content (677). Crops grown in soils containing lindane absorb the insecticide into its tissues. Crops tested were carrots, potatoes, peas, cabbage, cucumbers, beans, radishes, beets, and rutabaga. Carrots accumulated lindane in higher concentrations than it was present in the soil (3025).
- c. Stock and Wildlife Watering. The acute oral  $\rm LD_{50}$  of technical grade BHC for the rat is reported as 600 mg/kg (2992, 3002, 3003), and 200 mg/kg (3055, 3056). Another report cites the acute oral toxicity of lindane against male rats as 88 mg/kg and against female rats as 91 mg/kg (2999). The beta isomer is reported to be toxic at 6000 mg/kg (3005). The chronic oral toxicity of lindane to rats fed daily for two years was found to be 5.0 mg/kg (3003).

The amount of BHC that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 250 and 450 mg/kg respectively. The amount of lindane required for the same results with the same two birds is 200 and 400 mg/kg respectively (2994, 2996). Rudd and Genelly cite LD₅₀ values of lindane for bobwhite quail as 120-130 mg/kg for males, 190-210 mg/kg for females. Yet, their own work indicated an LD₅₀ for female ringneck pheasants as being between 60 and 100 mg/kg. Mourning doves proved to be more resistant to lindane with an approximate LD₅₀ of 350-400 mg/kg (3005, 3058).

d. Fish and Other Aquatic Life. Gjulian, et al. (919), report that concentrations of 1.0 to 10.0 mg/l of gamma BHC were toxic to fish. The pure gamma isomer of BHC dissolved in acetone was highly toxic to one-inch-long rainbow and brown trout at 0.02 mg/l. Rainbow trout were killed by 0.025 mg/l but brown trout

were not affected (3007). A summary of the toxicities of alpha, beta, gamma, and delta isomers follows:

BHC Isomer and Concentration mg/l	Temperature °C	Type of Fish	Results	Reference
Alpha 5.0	21	Guppies	Abnormal behavior in 18 hours, death in 36- 48 hours	2992
Beta 0.5	· <del></del>	Trout	Toxicity threshold to fingerlings	3007
2.0		Fish	Toxic	677, 679
Gamma 0.01	= :	Trout	Toxicity threshold to fingerlings	3007
0.03		Bluegills	Toxicity threshold to fingerlings	3007
0.05		Fish	Toxic	677, 679
0.5	21	Guppies	Abnormal behavior in 5 minutes, death in 20 hours	2992
Delta 0.05	<del></del>	Trout	Toxicity threshold to fingerlings	3007
0.2		Fish	Toxic	677, 679
2.0	21	Gupples	Abnormal behavior in 45 minutes, death in 48 hours	2992

Linduska and Surber (679) state that bluegills were not killed by 0.45 mg/l of BHC. The concentration of Gammexane that will kill half a batch of trout in a day is about 5 mg/l and in 30 days it is about 1.8 mg/l (3057). However, the threshold of toxicity for rainbow trout has been reported as being in the neighborhood of 0.0125 mg/l (3058). BHC in aquarium tests at concentrations of 0.1 mg/l killed 50 percent of bluegill and bass fingerlings (681).

Mixtures of BHC and DDT show LD₅₀ concentrations in 10 days of 3.0 mg/l for goldfish (680). Cope et al. (755) claim that BHC was more toxic than DDT, chlordane, or toxaphene to fish. Trout fingerlings were disabled by 1.0 mg/l of BHC in emulsion and by 10.0 mg/l in acetone solution (755). On the other hand, Warrick (920) quotes literature to the effect that BHC is less toxic than DDT to fish.

Doudoroff, Katz, and Tarzwell (1449) studied the toxicities of BHC-DDT mixtures to ten goldfish at 20°C. A dust containing 3 percent gamma BHC, 5 percent other BHC isomers, 5 percent DDT, 40 percent sulfur, and 47 percent inert compounds showed that 0.3 mg/l as dust was the 10-day median tolerance limit. This dose is equivalent to 0.24 mg/l of total BHC or 0.09 mg/l of gamma BHC, and 0.15 mg/l of DDT. Approximately 25 mg/l as dust caused the fish to turn over within 24 hours. For further information on the toxicities to fish of mixtures of various isomers with DDT, the reader is referred to Fielding (3059). Rudd and Genelly (3005) cite the statement that fish are less sensitive to BHC than to DDT, but add that toxaphene, dieldrin, and the other newer chlorinated hydrocarbons are many times more toxic to fish.

Later studies reporting the toxicity of benzene hexachloride and the gamma isomer to fish are summarized in the following table:

Concentration mg/l	Temperature °C	Type of Water	Type of Fish	Results	Reference
Lindane (gamma isome					
0.05	6–10	(2)	Trout	Less than 50% dled in 81 days	2640
0.056	25	(3)	Fatheads	96-hour TLm	8000
0.062	25	(4)	Fatheads	96-hour TLm	3000
9.077	25	(4)	Bluegills	96-hour TLm	3000
0.138	25	(4)	Guppies	96-hour TLm	3000
0.152	25	(4)	Goldfish	96-hour TLm	3000

Concentration mg/I	Temperature. °C	Type of Water	Type of Fish	Results	Reference
25% Gamma Isomer					
0.032-0.056	14	(1)	Salmon	96-hour TI-m	2091
0.056-0.10	14	(1)	Trout	96-hour TLm	2091
BHC					
0.790	25	(4)	Bluegills	96-hour TLra	3000
2.000	25	(3)	Fatheads	96-hour TLm	3000
2.170	25	(4)	Guppies	96-hour TLm	3000
2.30	25	(4)	<b>Fatheads</b>	96-hour TLm	3000
2.30	25	(4)	Goldfish	96-hour TLm	3000

(1) Fresh water, pH 7.3, DO 9.0 mg/l, total alkalinity 73.0 mg/l, 300-liter aquaria, 16 fish per aquarium, chimook salmon 77 mm long, rainbow trout 92 mm long. (2) Fixed volume aerated aquaria, fresh solutions added daily, rainbow, yearlings. (3) Hard water, pH 8.2, DO 8.0 mg/l, akalinity 360 mg/l, hardness 400 mg/l. (4) Soft water, pH 7.4, DO 8.0 mg/l, akalinity 18 mg/l, hardness 20 mg/l.

Five treatments per year with technical BHC applied each summer for three consecutive years at a rate of one pound per acre each time (i.e., about 0.1 mg/l) resulted in no fish injury (1475).

Dusts of 3 percent gamma BHC applied at 1 lb/acre/ week for 20 consecutive weeks caused insignificant fish mortality (3046, 3060). Technical grade BHC (12 percent gamma isomer) can be applied safely as emulsions at a rate of one lb/acre at five-week intervals without damage to fish (3057). One lb/acre of wettable powder BHC was reported to have killed many fish in a small pond (3061). An aerial application of 0.2 lb BHC/acre caused heavy losses of fiddler and marsh crabs (3061). An application of an emulsified mixture of BHC at 12.3 lbs/34,848 square feet was lethal to coho salmon fry if they were within one foot of the surface, but not if they were below the one-foot depth (3062). In the study utilizing crude BHC and crabs, 65 mg/l caused death in four hours, 6.5 mg/l caused death in 24 hours, 0.65 mg/l caused no death in 72 hours, and 0.065 mg/l had no effect (3063). The 24-hour TL_m to shrimp (P. setiferus) was 35  $\mu$ g/l; for P. aztecus it was 400  $\mu$ g/l (3064).

Silvey (2531) cites the concentration of lindane necessary to kill 50 percent of Chironomus larvae in eight hours as 0.006 mg/l. Saturated aqueous solutions (10-4 g/100 ml H₂O or 1 mg/l) were tested against various aquatic organisms. Bacteria decreased in numbers during the first 24 hours then increased to former levels. Protozoa and algae were killed almost immediately, fish were injured in one to four minutes (3065).

Losses of rainbow trout due to parasitism by the copepods Lernaea cyprinacea Linn or L.carassii Tidd were controlled by a concentration of 5 mg/l of benzene hexachloride in rearing ponds. As little as 0.1 mg/l applied for 72-96 hours caused a 55-percent kill of the female copepods (3066).

Batte et al. (2993), tested the toxicity of benzene hexachloride isomers to Lymnaeid snails. Concentrations of the technical grade isomers of 10 mg/l, including alpha-beta, delta, beta, alpha, alpha-delta, beta-delta, and alpha-beta-delta failed to give any mortalities in 24-hour exposures. A similar concentration of 99.8 percent gamma isomer affected 100-percent kill, but only a 1.7 mg/l concentration of crude benzene hexachloride (five percent gamma isomer) was required for the same mortality.

Toward plankton, BHC may not be so toxic. Use of a concentration of 3.0 mg/l of the gamma isomer in rivers of the Belgian Congo (1476) to control blackfly larvae resulted in no significant change in the behavior or composition of river plankton. There is a report, however, that 5 mg/l inhibited growth of plankton presumably in

sea water (2423), which plankton serve as fish food for oysters and clams. White shrimp, two inches long, suffered 100 percent mortality within 24 hours to a concentration of 25 µg/l. In laboratory tests it was demonstrated (1476) that concentrations could be raised to 30 mg/l before a marked affect on plankton occurred. Ciliates and flagellates showed the most resistance, becoming sluggish at concentrations of 40 mg/l. Tests of various isomers of benzene hexachloride against algae at concentrations of 2.0 mg/l for 21 days of incubation at 22°C showed that the alpha, beta, and gamma isomers did not inhibit any of the test algae, the delta isomer inhibited 17 percent, and the technical gamma isomer 33 percent (2041).

### BHC

(see Benzene Hexachloride)

### **BSM-11**

#### BUFFEN 30

### BUTROL

These three compounds are grouped because they come together alphabetically and because the only water quality information found on them was published by Horn and Balch in the same paper (2986). These compounds are used in slime control in pulp and paper mills. The many variables, reported in the paper by the investigators, are not included here. In summary, the inhibiting concentration for each compound against the organism indicated was as follows:

	$Inhibiting\ Concentration,\ mg/l$				
Organism	BSM-11	Buffen 30	Butrol		
Aerobacter aerogenes		6.0	20.0		
Bacillus mycoides		0.8	2.0		
Aspergillis niger	25.0	20.0	45.0		
Penicillium expansum	25.0	30.0	30.0		
Notropis atherinoides (Emerald shiners)	0.8(MLD	0.02(MLD)	0.5(MLD)		

#### CALCIUM ARSENATE

See Chapter VI.

### CAPTAN

C9H8Cl3NO2S

Captan is an approved name for the fungicide N-trichloromethylmercapto-4-cyclo-hexene-1, 2-dicarboximide (N-trichloromethylithiotetrahydrophthalimide). It is the active ingredient in the proprietary product Captan 50-W and was formerly known as SR-406, Vancide 89, and Orthocide. Captan is an insoluble crystal product that is partially soluble in some organic solvents. Captan 50-W is a wettable powder comprising 50 percent captan, and is used as a suspension for spraying or dipping (364, 2091).

Captan is described as practically non-toxic (3067). having an actute oral LD₅₀ to laboratory rats of 15,000 mg/kg of body weight (3009) and 9,000 mg/kg (3005). The acute oral LD₅₀ for rabbits is reported as 3,160 mg/ kg. Rats fed 1,000 mg/kg in the diet for one year showed no differences from controls. Captan is readily hydrolyzed, the effective residual life being two weeks (3005).

In experiments with rainbow trout in lake water at 10°-13°C, a 50-percent kill occurred among the larger fish in 72 hours at 0.32 mg Captan 50-W per liter. The smaller fish suffered a 61-percent kill in 9 hours at 0.56 mg/l, and there were no deaths in the 0.32 mg/l concentration in 72 hours. Neither size was affected by 0.18 mg/l in 72 hours (2091).

#### CD - 68

(see Chlordane)

## CHLORDANE

 $C_{10}H_6Cl_8$ 

1. General. Chlordane or chlordan is a common name for an insecticide containing 60-75 percent of octochlorohexahydromethanoindene. It is an amber-colored viscous liquid that is insoluble in water, but miscible with aliphatic and aromatic hydrocarbon solvents. It is also marketed under the trade names of Velsicol 1068, CD-68, Toxichlor, and Octa-Klor (364).

Technical grade chlordane is a mixture of toxic compounds that have not been separated in manufacture. The material is available as a wettable powder, an emulsifiable concentrate, a dust, or a solution. High chronic toxicity prevents its use on edible crops. Customary applicable application rates are below one lb/acre (3005).

- 2. Cross References. Chlorinated Hydrocarbons-General, Heptachlor.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The estimated fatal dose of chlordane for a 70 kg man is estimated as varying from 6 to 60 grams (2995). However a 100 mg/kg dose has been reported as fatal (364).
- b. Irrigation Waters. Like BHC and other chlorinated hydrocarbons, chlordane can accumulate in the soil and conceivably be contained in return water from the drainage of treated areas. Chlordane is stable in the soil (677) and it is fungicidal.
- e. Stock and Wildlife Watering.—The acute oral  ${
  m LD_{50}}$ of chlordane to rats has been reported as 335-590 mg/kg of body weight (2999, 3002, 3003). Although daily doses of 50 mg/kg for 15 days resulted in toxic symptoms and death (1485), the chronic oral toxicity has been reported as 0.125 mg/kg fed on a daily basis for two years (3003). One sheep fed 1000 mg/kg died in 48 hours. A concentration of 250 mg/kg in the diet for 12 weeks produced toxic effects in rats. Concentrations of 660 mg/kg killed dogs in four weeks. Cattle studies indicated 91 mg/kg to be toxic, 129 mg/kg fatal (3070). Chlordane causes poorer reproduction among birds (3069). Ducks and waterfowl had suffered significant losses from single sprayings of chlordane at concentrations of one pound/ acre (3006). A concentration of 25 mg/kg in the diet will cause a 40 percent or more decrease in the reproduction of quail (2996). The amount of chlordane that will produce a 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 250 and 500 mg/kg of body weight respectively (2994, 2996).
- d. Fish and Other Aquatic Life. Chlordane dust was toxic to fingerlings of bass and bluegills at concentrations of 0.2 mg/l (681). The minimum disabling doses against

trout larvae were reported to vary from 5.0 mg/l in an emulsion to 30 mg/l in acetone solution (755). Chlordane at 0.125 mg/l killed 100 percent and 0.05 mg/l killed 50 percent of test goldfish in four days. Corresponding figures for DDT in these tests were 0.25 and 0.125 mg/l respectively (3005). The approximate toxicity threshold of bluegills and trout to chlordane has been reported as 0.03 mg/l for both fishes (3007, 3048).

Tests made on 32 species of fish in ponds gave complete mortality of black bass, adults and fingerlings, bluegill adults but not fingerlings, and of bream at concentrations of 0.2 mg/l (3005). Chlordane at 0.2 mg/l killed all bluegill and bass fingerlings in aquarium tests. In earthen ponds, 0.2 mg/l killed bass fingerlings (681). According to Surber, Stock reported that 0.041 mg/l killed 33 percent of 4-7 inch trout within 48 hours, and 0.025 mg/l killed 20 percent within 48 hours (3049). The toxicity threshold for bluegill sunfish 1.7 inches long with pure chlordane was found to be about 0.03 mg/l (3007).

In Alaskan streams chlordane emulsions proved more toxic than DDT to trout in 15-minute applications. As a suspension chlordane was not toxic at any level tested below 15 mg/l and in a few oil concentrations up to 6 mg/l no damage was observed. Chlordane appears to be damaging to some fish at one lb/acre (3005). Application at one lb/acre (10% in fuel oil) to outdoor ponds killed 87 percent of bluegill sunfish (3058). Most of the bluegills as well as other species survived an application of 0.5 lb/acre. Tarzwell reports that the fish population of ponds will be significantly reduced at a routine dosage of 0.1 lb/acre. Chlordane apparently has no significant effect on fish at a dosage of 0.025 lb/aere (3005). Most fish survived aerial applications of 0.5 lb chlordane/acre but succumbed at 1.0 lb/acre (679).

More recent studies are summarized in the following tabulation:

Concentra- tion Chlor- dane mg/l	25	(1)	Fish Bluegills	96-hour TLm	rence 3000 3000
0.052	25	(1) (2)	Fatheads Fatheads	96-hour TLm 96-hour TLm	3000
$0.069 \\ 0.082$	25 25	(1)	Goldfish	96-hour TLm	3000 2976
0.1	13	(3)	Bluegills Guppies	no effect in 24 hours 96-hour TLm	3000
0.19 0.5	25 25	$\binom{1}{4}$	Catfish	96-hour TLm	2981 2976
1.0	13	(3)	Trout Bluegills	Death in 3 hours Death in 5 hours	2976
1.0 1.0	13 13	(3) (3)	Sea	Death in 14 hours	2976
5.0 5.0	13 13	(3) (3)	lamprey Trout Bluegills	Death in 1 hour Death in 2 hours	2976 2976
9.0				mg/l. hardness 20 mg/L	

(1) Soft water, pH 7.4, DO 8.0 mg/l, alkalinity 18 mg/l, hardness 20 mg/l.
(2) Hard water, pH 8.2, DO 8.0 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.
(3) Lake Huron water, pH 7.5-8.2, DO 8.6-13.7 mg/l, free Co2 5.0-9.0 mg/l, only one or two test animals exposed for 24-hour period, technical grade chlordane.
(4) University of Oklahoma tap water, 4-gallon aquaria, 10 fingerlings per aquarium. 100 or 200 fish per experiment.

For another summary of the effects of chlordane on fish, see Fielding and Baldwin (3059). Silvey (2531) gives the concentration of chlordane necessary to kill 50 percent Chironomus larvae in eight hours as 0.015 mg/l.

## CHLORINATED BENZENES

1. General. Chlorinated benzenes are used for the control of weeds in lakes and ditches. They are characterized by high specific gravities and settle to the bottom in quiet water unless emulsified. Benoclor, a trade product consisting of a mixture of the non-emulsifiable forms of mono-, di-, and trichlorobenzene, is used in high-pressure subsurface sprays to control aquatic vegetation (897). Metadichlorobenzene is a colorless liquid, insoluble in water, and seldom used commercially. Orthodichlorobenzene, also a liquid and insoluble in water, is used as a solvent for waxes, for preserving plants, and for destroying insects such as termites. Paradichlorobenzene, a white crystalline solid with a characteristic odor, is used largely for killing moths and other insects. It is soluble in water to the extent of 79 mg/l at 25°C (364).

- 2. Cross References. Chlorinated Hydrocarbons—General, Aromatic Solvents.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. According to Rohlich and Sarles (759), the halogenation of an aromatic series markedly influences tastes and often a change from sweet to bitter is effected. Goudey (897) indicates that Benoclor has a pungent odor but no physiological effects on humans at odoriferous concentrations.
- b. Irrigation Waters. The U. S. Bureau of Reclamation (890) reports that more than 500 mg/l of Benoclor in water is required to injure crops.
- c. Stock and Wildlife Watering. Livestock were not harmed when they drank water treated with Benoclor. Mild symptoms of poisoning of sheep and cattle occurred at a concentration in excess of 2700 mg/l while a level of about 17,000 mg/l was considered to be fatal. Ordinarily these animals do not drink contaminated water because of the objectionable taste (890, 3009).
- d. Fish and Other Aquatic Life. Paradichlorobenzene was reported to be lethal at 50 mg/l to fish (313, 431). Springer notes that the chlorinated benzenes are poisonous to fish and fish-food organisms in the concentrations necessary to kill submerged plants (150-600 mg/l), and their toxicities are of long duration (3009). Orthodichlorobenzene has properties similar to trichlorobenzene but is reported to be less dangerous to fish since it diffuses less readily. A concentration of 3.2 mg/l killed 40-60 percent of fish in aquaria studies (3009). Trichlorobenzene gives fish a very disagreeable taste (3068).

No mortalities occurred in coho salmon for 24 hours following 15- and 30-minute exposures to a mixture of trichlorobenzene (50 mg/l) with five percent Colloidal X-77 emulsifier. After a 30-minute exposure to 100 mg/l, 20 percent of the salmon died within 12 hours. However a 15-minute exposure to 100 mg/l caused no death in 24 hours (2988).

Three chlorinated benzenes differentiated only by number (Nos. 1, 2, and 3) were tested in the laboratory at 2 mg/l for 21 days at 22°C against various algae. Inhibition of growth of 50 to 100 percent of the cultures was observed (2041). Trichlorobenzene at a concentration of 5 mg/l reportedly killed both fish and weeds (3068).

## CHLORINATED CAMPHENE

(see Toxaphene)

## CHLORINATED HYDROCARBONS-GENERAL

(see also DDT, Dieldrin, Chlordane, Toxaphene, Aldrin, Heptachlor, Benzene Hexachloride, Chlorinated Benzenes)

The chlorinated hydrocarbons include a large number of chemicals with high insecticidal activities. They are especially resistant to degradation to non-toxic end products, and many persist for months or years following application (2528). Chisholm and Koblitsky (3071) applied aldrin, heptachlor, and toxaphene to soil plots. The following day, about one-half of the amounts applied to the soil could be found. After 42 days, no heptachlor could be found and after 84 days only eight percent of the aldrin and 4 percent of the toxaphene could be found. Although most chlorinated hydrocarbons are sparingly soluble in water, their solubility is still greater than the 96-hour TL_m values (3015).

The toxicity of a mixture of DDT and BHC to goldfish has been studied. The dust mixture contained 5 percent DDT, 3 percent gamma BHC, 5 percent other BHC isomers, 40 percent sulfur, and 47 percent inert compounds. The 10-day median tolerance limit was about 3.0 mg/l as dust, or 0.15 mg/l DDT and 0.24 mg/l BHC. A dust suspension caused fish to turn over within 24 hours (1449).

Shell Oil Company has investigated the feasibility of deep sea disposal of mixed chlorinated hydrocarbon wastes. The effects of wastes on organisms indigenous to the disposal area were studied. Those organisms that came into immediate contact with the waste were killed or seriously impaired, but within 3-8 hours the area had again assumed natural features. For further information, which includes specific effects, diffusion studies, etc., the reader is referred to the original paper (3072). Hexachloran is a Russian insecticide that is reported to be used in reservoirs. It can be detected by smell in cold water at 0.04 mg/l, and in warm water (60°C) at 0.01 mg/l. It does not affect BOD at concentrations up to 2.5 mg/l, nor the dissolved oxygen up to 50 mg/l, nor nitrifieation up to 12.5 mg/l. The maximum permissible concentration in reservoir waters should be limited to 0.01 mg/l, the concentration at which it can be detected by smell (3257).

## CHLORO IPC

(see IPC)

## CHLORTETRACYCLINE

(see Antibiotics)

## CHLORTHION

- 1. General. Chlorthion, also known as chlorothion, is a trade name for 0, 0-dimethyl 0 (3-chloro-4-nitrophenyl) phosphorothioate, a phosphoric acid ester related to parathion and containing chlorine (364). Chlorthion is a yellow oil miscible with benzene, alcohol, and ether, and is insoluble in water. It is used especially for combating boll weevils.
  - 2. Cross References. Parathion, Organic Phosphates.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The estimated fatal dose for a 70 kg man is 60 grams (2995).
- b. Stock and Wildlife Watering. The acute oral  $\mathrm{LD}_{50}$  to rats has been reported at 550 to 1510 mg/kg of body weight (2997, 2999, 3002, 3073, 3074). Against

eattle 50 mg/kg has been reported as non-toxic, and against calves 25 mg/kg is non-toxic and 50 mg/kg lethal (3075). The amount of Chlorthion that will produce at least 50 percent mortality in bobwhite quail considering all stages of its life cycle is 700 mg/kg of body weight (2994, 2996). Fed to dogs, 15 mg/kg in the diet produced a questionable red-cell inhibition, 2 mg/kg had no effect (3076). Although no mortality occurred in rats with daily dosages of 50 mg/kg of body weight, mortality was 40 percent at 100 mg/kg (3005).

c. Fish and Other Aquatic Life. Chlorthion at 5 mg/l caused injury to both guppies and goldfish in two hours and resulted in death in 18 hours (3073). Levels of Chlorthion of 5.0 mg/l caused abnormal behavior in 2 hours and death in 18 hours to guppies and goldfish in tests conducted at 19-22°C (3073). The 96-hour TL_m value of Chlorthion to fathead minnows at 25°C in both hard and soft water was 3.2 mg/l of active ingredient

(3000).

Laboratory tests at rates of 0.0125-0.25 mg/l killed 100 percent of Psorophora larvae when exposed 24 hours. In the field, applications up to 0.074 mg/l failed to give satisfactory control. Applied in a granular formulation to test plots as a pre-flood application, applications as high as 0.5 lb/acre failed to give satisfactory control. The same formulation at 0.2 lb/acre as a post-flood treatment, however, gave 100 percent control (3082).

#### CINERINS

(see Pyrethrum)

C9H11CIN2O CMU

1. General. CMU 3-(p-chlorophenyl)-1,1-dimethylurea, is also known by the tradenames Karmex and Monuron. It is stable toward oxygen and moisture under ordinary conditions at neutral pH, very slightly soluble in water and in number 3 diesel oil, moderately soluble in methanol, ethanol, and acetone, but practically insoluble in hydrocarbon solvents (364).

CMU is a soil sterilent when used at 10 to 80 lbs/acre, and a pre-emergence herbicide in crops when used at

1 to 3 lbs/acre (3005).

- 2. Cross References. 2.4-D. Diuron.
- 3. Effects on Beneficial Uses.
- (2861)a. Domestic Water Supplies. Chancellor states that CMU at concentrations up to 180 mg/l is nonpoisonous to man. Another report cites the lethal dose of CMU for the average 90 kg man at 326 grams (1723). CMU is reported to be one of the best herbicides to use in water supply reservoir areas (1723). It is 5 times less toxic to humans than 2, 4-D (3083).

b. Irrigation Waters. CMU at concentrations of 7.4 and 18.7 mg/l in irrigation water killed tomatoes after 10 days and injured cotton plants after 41 days (3084).

c. Stock and Wildlife watering. The acute oral LD50 of CMU for rats is 3,500 mg/kg of body weight (3005, 3009). Chancellor (2861) states that CMU at concentrations up to 180 mg/l is non-poisonous to livestock. Rudd and Genelly (3005) state that apparently CMU will kill water weeds at concentrations safe for aquatic life; however, there is no predictable hazard to terrestrial animals from other use.

d. Fish and Other Aquatic Life. The initial toxicity of CMU to small golden shiners in aquaria occurred at 20 mg/l (3009). Two goldfish tolerated 14.9 mg/l of CMU for 35 days, but both fish died within a week after the concentration was increased to 59.5 mg/l (3005). The tolerance limit of 3-month-old rainbow trout is 100 mg/l over a 48-hour period (2861).

Preliminary studies with the bluegill indicate that this fish has a tolerance for CMU similar to that of coho salman. Treatment of two ponds with up to 10 mg/l caused no mortality of frogs, tadpoles, or fishes. Another report indicates that several warm water fish species can withstand 40 mg/l for 10 days. Bond notes that aeration partially detoxifies solutions of Monuron, and that Lawrence cited a safe concentration for CMU of less than 1.2 mg/l. Applications of 25-100 lbs/acre to vegetated ponds did not cause excessive mortality of largemouth bass, bluegills, and brown bullheads, but bluegills did fail to spawn. However, these effects are thought to have been due to low oxygen content resulting from plant decomposition (3009). Later work that reports various variables used in the testing procedures is presented in the following tabulation:

Concentration of CMU mg/l	Temperature °C	Type of Water	Type of Fish	Results	Reference
40	23-24	(5)	Bluegfils Green sunfish Crappie Bluntnose minnow	No effects in 23 days	2211
40.1	21	(4)	Shiners	96-hour TLm	3011
41.5	21	(3)	Red-sided shiners	96-hour TLm	8011
63.1	20	(2)	Fingerling catfish	96-hour LDso	2981
110	20	ίīί	Coho salmon	48-hour TLm	2988
230	20	(1)	Largemouth bass	10% dead in 48 hour	s 2988

- (1) Aerated, pH 7.4-7.7, methyl orange alkalimity 41-71 mg/l, 15 liter aquaria, 10
- (1) Aerated, ph 7.4-7.7, methyl orange alkalimity 41-71 mg/l, 15 liter aquaria, 10 fingerlings per aquarium.

  (2) Tap water University of Oklahoma, 4-gallon aquaria, 10 fish per aquarium 100 or 200 fish per experiment.

  (3) Soft water, pH 7.6, D0 9.0 mg/l, alkalimity 36 mg/l, hardness 18 mg/l, 10 liters solution, 5 fingerlings per jar.

  (4) Hard water, pH 8.2, D0 9.0 mg/l, alkalimity 116 mg/l, hardness 156 mg/l, 10 liters solution, 5 fingerlings (6-7 cm) per jar.

  (5) Aerated 10 to 20 liter aquaria.

No mortality to fish-food organisms (amphipods and isopods) was noted at concentrations of CMU up to 100 mg/l (3005). CMU at a few mg/l is a good general algicide (3050). A concentration of 2 mg/l of CMU prevented the growth of all blue-green algae and diatoms and of 65 percent of the green algae species tested. At this concentration, CMU is not toxic to fish (2041, 3083). Another article notes that concentrations of CMU of 0.5 to 1.0 mg/l prevented algal growth in aquaria (2211).

## COPPER ACETOARSENITE

(see Paris Green)

#### COPPER SULFATE

(see Chapter VI)

## CO - RAL

Co-Ral is a trade name for O, O-diethyl 0-(3-cloro-4methyl-coumarinyl-7) phosphorothioate (3085). Also known as Muscatox, Asuntol, and Bayer 21/199, its solubility in water is less than 18 mg/l, but it is soluble in aromatic solvents. The acute oral LD50 to rats is 56-230 mg/kg of body weight depending on the method of application (2997). The amount of Co-Ral that will produce at least 50 percent mortality in bobwhite quail con-

C₁₂H₁₃ClPSO₅

sidering all stages of the life cycle is 400 mg/kg (2994, 2996)

The 96-hour  $TL_m$  values of technical grade Co-Ral, 100 percent active in acetone, to fathead minnows in both hard (400 mg/l) and soft (20 mg/l) waters at 25°C was greater than 18 mg/l. In contrast, the 96-hour  $TL_m$  value for bluegills in soft water was reported as 0.18 mg/l (3000).

## CUBE ROOT

(see Rotenone)

2,4-D

 $C_8H_6Cl_2O_3$ 

- 1. General. 2,4-D (dichlorophenoxyacetic acid) is the best known of present herbicides. Actually, it is a plant hormone that stimulates growth, often to the extent of causing a plant to destroy itself. There are many products of 2,4-D available commercially. Various salts, amines, and esters of 2,4-D are formulated. Usually the acid equivalent is given on the label to standardize comparisons (3005). The amine salts are soluble in water and the sodium salt is soluble to the extent of 3.5 percent (364). 2,4-D is also used in combination with TCA (trichloroacetic acid). Dichlorophenol and ortho-monochlorophenol sometimes occur as impurities in the manufacture of 2,4-D (901).
- 2. Cross References. TCA, 2,4,5-T, MCPA, Silvex, Chapter VI—Phenols.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Traces of weed-killing chemicals may reach domestic water supplies as a result of eradication work along streams or railroad embankments, or from aerial spraying of fields. A most serious case of pollution of domestic water occurred, however, through an industrial waste reaching an underground stream in the so-called Montebello incident (894, 895, 896, 897). A chemical corporation in Alhambra, California, was manufacturing 2,4-D weed killer from 2,4-dichlorophenol, monochloroacetic acid, caustic soda, hydrochloric acid, diethanolamine, and acetone. It appears that a batch of the raw materials did not react properly and the chemicals were dumped into the sewer, from which they passed through the Tri-Cities sewage treatment plant (activated sludge), and were discharged to the San Gabriel River. They traveled above ground some three to five miles then seeped into the underground stream from which Montebello drew its water supply. There was relatively little combined 2,4-D in the wastes and hence no damage to plants that were watered, despite rumors to the contrary; but the unreacted dichlorophenol caused tastes and odors.

It was estimated that the original chemicals were diluted 1:10,000,000 and still produced unpleasant tastes. The taste threshold for 2,4-D is 0.01 mg/l, whereas the same concentration of dichlorophenol causes noticeable tastes (897). The period of contamination lasted 4-5 years (3086). It is reported that 2,4-D waste waters containing dichlorophenol are considerably more difficult to treat than phenolic wastes (3087).

According to Chancellor (2861), 2,4-D is non-poisonous but may give water an unpleasant taste. The lethal dose for an average 90 kg man is 62 grams (1723).

b. Irrigation Waters. Tomato plants irrigated for 22 to 44 days with tap water containing up to approximately 20 mg/l of 2,4-D were, in most instances, more vigorous than the control which, in each case, received the same amount of untreated tap water. Cotton plants irrigated for 24 days with water containing concentrations up to 11 mg/l of 2,4-D were more vigorous than the untreated controls. Such stimulation is not surprising considering the fact that 2,4-D is a plant hormone.

Flame Tokay and Concord Grape plants irrigated with tap water containing up to approximately 11 mg/l of 2, 4-D showed variable leaf abnormalities at all concentrations, probably from vaporization of 2,4-D from water containing the isopropyl ester. The check also was affected, indicating the effects noted were not due to 2, 4-D entering the roots from irrigation water. The sodium salt of 2,4-D in the concentration 16.7 mg/l did not injure tomatoes but caused some injury to cotton after 41 irrigation days (3084).

A combination of industrial wastes discharged to a lagoon in Colorado generated 2,4-D. It was first noticed in 1951 when crop damage resulted from use of well water for irrigation, and some 60 square miles of ground water were said to be contaminated (3086, 3088).

Concentrations of 2,4-D of 100 mg/l in sterile solution inhibited callus and root formation of snapbeans (3089). Muzik et al. (3090) failed to observe movement of sodium 2,4-D applied to calcareous soil with high organic content beyond one inch. Great care should be taken to prevent treated water reaching cultivated land (2861).

c. Stock and Wildlife Watering. The acute oral toxicity of 2,4-D to laboratory rats is 500 mg/kg of body weight (3009). Another report cites the acute oral LD₅₀ of 2,4-D and 2, 4, 5-T and their derivatives as ranging from 300 to 1000 mg/kg for rats, mice, guinea pigs, and rabbits (3091). Rudd and Genelly (3005) note the more specific LD₅₀ values of 375 mg/kg for mice, 666 mg/kg for rats, 800 mg/kg for rabbits, and 100 mg/kg for dogs. An oral dose of 380 mg/kg is lethal to chicks. Chronic studies showed that 20 mg/kg of food fed daily to dogs was toxic. On a weight basis, the toxicity to cattle seems to be similar to laboratory animals. The hazard to livestock and wildlife appears negligible (3091).

d. Fish and Aquatic Life. Harrison and Rees (901) found that the safe concentration to minnows was 1500 mg/l and for sunfish and catfish 500 mg/l. Some mortality of bream and bass occurs at 100 mg/l and of carp at 65 mg/l (3005). Marini (1726) reports that a concentration of the sodium salt of 2,4-D of 260 mg/l was not toxic to carp. Surber (898) described an incident at Leetown, W. Va., where water from a pond treated with 2, 4-D seeped into an adjacent pond and made the fish therein unpalatable. The chemical imparts a disagreeable phenolic flavor to fish flesh making it unpleasant to eat (898, 2861).

The 24-hour  $TL_m$  value to bluegills and largemouth bass was 350 mg/l (3092). A mixture of neutral aromatic oils (57 percent), 2,4-D (12.5 percent), emulsifiers (8 percent), and water (to 100 percent) was toxic to three-month-old rainbow trout at a concentration of 3.0 mg/l over a 24-hour period, and at 2.2 mg/l over a 48-hour period (2861).

In laboratory tests, the lowest concentration of 2,4-D to cause mortality of fish was 100 mg/l, and von Bandt notes a threshold value of toxicity to perch and bleak of 75 mg/l (2977). However, certain esters and amines of 2,4-D have been found to be more toxic and, particularly in still, shallow water, may harm fish at dosages used for weed control. Fingerling bluegills suffered losses of up to 40 and 100 percent from concentrations of 1 and 5 mg/l, respectively, of the butyl ester. The isopropyl ester was somewhat less toxic but caused complete mortality of bluegills at 10 mg/l, as did the alkanolamine at 40 mg/l. A few fish also died during a 4-day exposure to 4 mg/l of the latter material. The sodium salt was not observed to kill small rainbow trout below a concentration of 112 mg/l (3009).

The Fish and Wildlife Service (2976) tested a large number of phenoxyacetic acids and related compounds in rough screening studies in Lake Huron water at 12°C. Trout and bluegill were killed but sea lamprey were unaffected by 2,4-dichlorophenoxyacetic acid, butyl ester

during a 24-hour exposure to five mg/l.

Fish-food organisms vary in sensitivity to the derivatives of 2,4-D. Tests with the isopropyl ester showed that losses of over 25 percent were sustained by crustaceans at 0.1-0.4 mg/l, insects at 0.4-2.0 mg/l, and snails at 2.4-3.3 mg/l. These animals were more resistant to poisoning by the mixed propylene glycol and butyl esters of 2,4-D, and certain species of insects and snails were not killed

at 6.6 mg/l (3009).

Worth and McCabe (434) report that 2 mg/l of 2,4-D inhibited the growth of aerobic bacteria but not facultative or anaerobic bacteria. Organisms that require free oxygen for respiration appear to be smothered by 2,4-D. The synergistic and antagonistic effects of various substances dissolved in water are not yet understood well enough to permit the establishment of safe procedures for all kinds of waters and weeds. The concentration of a chemical that will kill weeds in one lake without harming fish life may be very toxic to fish in another lake, accord-

ing to Brown (589).

The use of 2,4-D has proved to be especially successful in the destruction of water hyacinth and other emergent water weeds. Concentrations of 2,4-D of 1000 mg/l have been sprayed on exposed leaves with successful killing. and hence the concentrations in the adjacent water will be very much less than 1000 mg/l. Application of 8 lb/acre (free-acid equivalent) to weed infested areas of the Mississippi Delta destroyed water hyacinths. Stronger growths of alligator weed were only slightly affected, but weaker growths were controlled by two applications (3093). Application of 1 ounce of Dicotex (2,4-D) per 100 square feet will kill submerged plants such as Hydrilla and Naias and rooted plants such as Vallisneria in about 20 days but will not harm fish (3096). A 6 mg/l concentration of 2,4-D controlled heavy growth of watermilfoil (3097). Application of 4-6 lbs/ acre in an oil-water emulsion spray has been effective against cattails (2880).

## $\mathbf{DALAPON} \qquad \qquad \mathbf{C_3H_3Cl_2NaO_2}$

Dalapon, also known as Dowpon, is a herbicidal chemical containing 2,2-dichloropropionic acid. It is crystalline and has a characteristic salty taste (364). Control of

cattails and a variety of grasses is possible with dalapon. It is applied in spray to noncrop lands at 20 to 40 lbs/acre (2861). It is also used in combination with amitrol (3010), and is less hazardous than 2,4-D to sensitive

crops when sprays drift (2880).

The acute oral toxicity of dalapon to laboratory rats is 6590-8120 mg/kg of body weight (3009). Rats receiving 1.08 percent dalapon in the diet showed slight histopathological changes and some changes in organ weights, but there were no effects at lower concentrations. Cattle given 1 g/kg daily for 10 days showed no serious irreversible effects. Feeding of dalapon to cows at 300 mg/kg of dry feed intake had no detrimental effects to milk production, butterfat percentage, body weight, feed intake, or animal behavior (3098).

The Lake Emerald shiner was not adversely affected when kept for 3 days in water containing 3,000 mg/l. However, all fish died when the concentration was increased to 5,000 mg/l (3005). Tests with Dowpon on red-sided shiners in both hard and soft aerated waters demonstrated very little difference in toxicity, the 96-hour TL_m values at 21°C for the two waters being 390 and 395 mg/l respectively (3011).

Dowpon was tested against largemouth bass and coho salmon at  $20\,^{\circ}\mathrm{C}$  in aerated solutions. The 48-hour  $\mathrm{TL_m}$  values were greater than 1,000 mg/l for bass and 340 mg/l for coho salmon. In constant-flow experiments, however, no bass survived 48-hour exposure to 1000 mg/l. Survival in 250 mg/l was complete over a period of seven days. Lawrence reports 3000 mg/l as being safe for fish (2988).

#### DBD

(see Guthion)

 $\mathbf{DDD} \qquad \qquad \mathbf{C_{14}H_{10}Cl_{4}}$ 

- 1. General. DDD (dichlorodiphenyldichloroethane) is the same as TDE (tetrachlorodiphenylethane), and is also known as Rhothane. It is insoluble in water, has low solubility in oils, and is freely soluble in most other organic solvents (2997). DDD has much the same general properties and is used similarly to DDT. Chemically, it has one less chlorine atom than DDT. Its insecticidal activity approximates that of DDT but its mammalian toxicity is only about one-fifth that of DDT. It is formulated as dusts, wettable powders, and emulsifiable concentrates that are applied at slightly higher rates than DDT (3005).
- 2. Cross References. DDT, Chlorinated Hydrocarbons—General.
  - 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. The acute oral  $\rm LD_{50}$  to rats is 3400 mg/kg of body weight (364, 3002, 3003). Chronic oral toxicity to rats fed daily for 2 years was 5 mg/kg (3003). Chickens fed 0.1 percent (1000 mg/kg) DDD in mash showed some mortality within a month. Domestic animals may be treated with DDD with comparative safety although calves are particularly sensitive (3005).

Repeated treatment of Clear Lake, California, with DDD for the control of gnats may be the indirect cause of death of hundreds of grebes (3014). The grebes dis-

appeared in 1950 shortly after the lake was treated with 0.01-0.02 lb DDD/acre. Treatment was repeated in 1953, 1956, and 1957. In November 1957, hundreds of grebes died, poisoned by fish they ate. DDE in fish visceral fat assayed 40 to over 2000 mg/kg (3099, 3100).

b. Fish and Other Aquatic Life. All bluegill sunfish died in aquaria receiving 0.2 mg/l of pure DDD. The approximate toxicity threshold to fingerling bluegills of DDD is 0.03 mg/l (3007). Using fingerling channel catfish, Clemens and Sneed (2981) found that the 96-hour  $TL_m$  was less than 2.6 mg/l at 20°C. Rainbow trout were not killed by immersion for 7 days in water that had been left in contact with sludge to which 2 lbs/acre DDD had been applied. Gudgeon fed on dying larvae (from a dose of 1 lb DDD/acre) at a rate of 20 larvae per day for four days were not killed (74).

Lindquist et al. (1585) reported that a concentration of 0.014 mg/l of an emulsion of DDD controlled gnats in Clear Lake, California, with no harmful effects on fish and other aquatic organisms (but see 3a above). A concentration of 0.013 mg/l controlled Chaoborus larvae in 35 days and temporarily eliminated chironomid larvae without affecting fish. These larvae, however, make up 10-20 percent of the fish diet and consequently the long-term effect may be harmful. DDD at 2 lbs/acre was not toxic to tubificids nor to Aelosoma (74).

In the Clear Lake gnat control program, concentrations of 0.013 to 0.022 mg/l affected an appreciable fish loss among black crappie. There was drastic temporary reduction of some fish-food organisms but recovery was rapid and no permanent reduction occurred (3005). However, subsequent analyses showed that all fish, bird, and frog samples contained DDD, the amount found in all flesh samples exceeded the application rate on an mg/kg basis, and flesh samples of largemouth bass and Sacramento blackfish hatched 7-9 months after the last DDD application contained 22-25 mg/kg and 7-9 mg/kg of DDD respectively. All areas of the lake contained DDD-contaminated fish (3101).

Rudd and Genelly (3005) cite work reporting the TL_m of DDD to goldfish as being 1.0 mg/l, and the following work by Tarzwell based on lb/acre applications:

Application Rate in lbs/acre	Form	Effect on Fish
0.025	Spray	Insignificant loss
0.05	Spray	Some mortality
0.1	Dust	Insignificant loss
0.1	Spray	Destroyed all fish

 $\mathbf{DDT} \qquad \qquad \mathbf{C_{14}H_{9}Cl_{5}}$ 

1. General. Dichlorodiphenyltrichloroethane, commonly known as DDT, is a white amorphous powder that is used as an insecticide. Practically insoluble in water, dilute acids, and alkalies, it is readily soluble in many organic solvents. It has a low volatility and is not normally decomposed by sunlight; hence, it has high residual powers. It is used in a 5-percent solution with kerosene and xylene as the solvent, as a 25-percent emulsion in several types of vehicles, or as a dust diluted with talc or other inert substances. It is also used in paints and wall washes. The diluent or vehicle is very important in determining the toxicity of DDT (919).

DDT has been used so widely that it is stored to some extent in the body of almost everyone in the U.S. (3001). Its safety has been proven by a large body of experimental work and by extensive experience and it is the best insecticide we have (3258). DDT has been recovered from five major river-water sources in concentrations of 5 to 20 µg/l (3004, 3102).

- 2. Cross References. Chlorinated Hydrocarbons—General, Benzene Hexachloride.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Men who have been exposed to DDT for as long as 6.5 years, and consequently absorbed an average of 200 times as much DDT as the general population does in its food, have evidenced no chronic poisoning (3103). The oral ingestion of 0.7 gm DDT will produce a sensation of burning or itching of the tongue, lips, and part of the face. At 1.0 gm, tremors and convulsions may commence. However, men have recovered from swallowing as much as 20 grams. DDT in the diet at a level of 35 mg/day in human volunteers for 18 months caused no toxic symptoms (3104). The estimated fatal dose for a 70 kg man is about 30 grams (677, 2995). Water that has been treated with technical grade DDT can be used for domestic supply if the concentration does not exceed 2 mg/l. If an organic solution is used, the concentration should not exceed 0.25 mg/l (678, 1131, 3055, 3105). However, DDT has been cited as a source of taste and odor in water (2058, 3106). The Soviet Union established maximum permissible concentrations (MPC) for polluants based upon a most sensitive parameter. For DDT, the parameter was odor and the  $\widehat{MPC}$  set was 0.2 mg/l (3107).
- b. Irrigation Waters. In general, plants are not harmed by DDT applied to kill insects (1132). The breeding of anopheline mosquitoes in water used for irrigating rice fields was controlled by the addition of 1.0 mg/l of DDT as an emulsion, without damage to rice plants (1154). DDT has no effect on soil pH or bacterial content, and it is not toxic to soil fungi or nitrifying organisms (677, 678).

Crops grown in soils treated with DDT absorb the chemical into their tissues. Crops tested were carrots, potatoes, peas, cabbage, cucumbers, beans, radishes, beets, and rutabaga (3025).

DDT is very stable in soil, decomposing at a rate of about 5 percent per year (dependent upon soil type). The growth of squashes, cucumbers, tomatoes, strawberries, and some peas and beans may be retarded by DDT at levels of 25 lbs/acre (3006).

c. Stock and Wildlife Watering. The acute oral LD₅₀ of DDT to rats has been reported as 250 mg/kg of body weight (2992, 3002, 3003) and against males and females as 113 and 118 mg/kg respectively (2999). Other papers cite values from as low as 150 mg/kg for mice to over 1300 mg/kg for chickens (1132, 2994, 2996, 3108). Drinking water containing 10 mg/l of DDT, 30 mg/l of xylene, and a triton emulsifier had no effect on 10 mice for 75 days. Another 10 mice received 50 mg/l of DDT, 150 mg/l of xylene, and triton emulsifier for 58 days without deleterious effect (1131). Nevertheless, DDT is stored in the body and daily ingestion of sub-lethal doses may be accumulative and fatal. When fed a dietary level of 5

mg/kg, rats developed a detectable amount of liver damage (677, 1132, 3109).

A considerable literature on the toxic effects of DDT applied on an areal basis (lbs/acre) exists. A dosage of 1 lb/acre to water 5.0 ft deep, equally distributed, gives a concentration of 0.0735 mg/l. Hence, an assumption of 1 lb/acre approximating 0.1 mg/l is sometimes made. It cannot be positively said, however, that effects to land animals are due only to the contamination of the animal's drinking water sources.

An areal application of DDT at 5 lbs/acre is required in order to produce direct mortality in mammals. Indirect effects, however, are noted at applications as low as 0.5 lb/acre. Such an application, for example, kills most crayfish and forces raccoons subsisting on them to change their diet (to acorns and mussels). Four annual aerial applications of 2 lbs/acre and one of 1.1 lbs/acre caused reductions of 28-44 percent in treetop bird species. Five lbs/acre caused a reduction of 80 percent. Although the daily consumption by adult birds of as little as 8.5 mg for two months may have no overt effect, it produces significant reductions in reproduction and in fertility of eggs and survival of young (3110). The effect of 5 lbs/acre on birds, however, is not gradual since this level reduced the Maryland yellow-throat by 63 percent in 24 hours and the prairie warbler by 93 percent in 48 hours (3111).

It has been reported that a concentration of DDT of 100 mg/kg in the diet of quail will cause a 40 percent or more decrease in reproduction (2996, 3044, 3045). The amount of DDT that will produce at least 50-percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 500 and 300 mg/kg of body weight respectively (2994, 2996).

Terrestrial reptiles are reported to suffer losses at 2-3 lbs/acre (3110). Levels of 0.5 lb/acre were observed to have no ill effects on mammals, birds, reptiles, and amphibians when applied as a mosquito larvacide (3112). Adult birds have been reported to eat insects poisoned by DDT without harm (3069). See Von Oettingen for a detailed discourse of the toxicity of DDT (3292).

d. Fish and Other Aquatic Life. Most aquatic organisms are more susceptible to DDT than are terrestrial forms (3006). It is reported that fresh water animals on the Island of Cyprus have been devastated by DDT spraying for mosquito eradication (3113). The effects of DDT are persistent and widespread when employed in flowing streams. As a control operation against Simulium arcticum, a single application of 0.09 mg/l for 16 minutes was effective for 40-98 miles downstream (2698). Cope (3114) reports finding DDT in fish 85 miles downstream from sprayed areas, as well as in all control fish, in fish from an untreated stream, from a hatchery, and from a fish market. In standing waters, its effects persist for months. Earthen ponds treated with 0.4 mg/l wettable powders remained toxic to bluegills for several months. Emulsifiable applications at 0.1 mg/l remained toxic to fingerlings for a month, longer at higher concentrations (681). However, it is to be noted that rainbow trout were not killed by immersion for 7 days in water

that had been left in contact with sludge to which 2 lbs DDT per acre had been applied (74). The accumulation of DDT on plants or in benthal deposits downstream may continue to cause insect and fish mortality. One month after spraying, moss contained as much as 128 mg/l six miles downstream from the area sprayed (2647).

The toxicity of DDT to fishes has been subjected to considerable study. Among the variables that have been cited are the type of water course and bottom, depth, vegetation, silt, turbidity, hardness, temperature, dissolved oxygen, organic content, species and age of fish (1133, 3006, 3015, 3058, 3115), formulation (emulsions are most toxic, water wettable forms least toxic) (678, 918, 3048, 3110, 3116), size of molecule (for DDT analogs) (2744), and volume of water and shape of receptacle (3005, 3117).

The effect of differing DDT formulations on rainbow trout have been cited as (3005):

DDT in acetone solution—not lethal at 30 mg/l
DDT in fuel oil—not lethal at 20 mg/l
DDT in xylene—toxic at 5 mg/l
DDT in emulsion—toxic at 3 mg/l
DDT in kerosene—toxic at 0.3 mg/l

Owing to these many variables, it is not surprising to find that there is a variation in concentrations of DDT lethal to fish as reported in the literature. The effects of various concentrations of DDT on different fishes encountered in this survey have been tabulated in order of increasing dosage:

	centration DDT mg/l	Type of fish	Resulta	Reference
0.001	[alcohol ]	Common sucker	Killed	3118
0.001	suspension (	Speckled trout	Killed	3118
0.005	{suspension }	Common sucker Speckled trout yearlings	MLC less than this level Killed	3005 3118
0.005	suspension	Creek chub	Killed	3118
0.01	{suspension }	Bluegill	Toxicity threshold	3007. 3048
0.01		Dace	All killed	3005
0.01		Gambusia	Median lethal dose	2744 3007
0.01		Guppies	Toxicity threshold	681
0.01		Bluegill fingerlings	Killed	681
0.01		Bass yearlings	Killed	1144
0.01-1		Bass and shiners, fry	Killed	3058
0.025	0.04 7-0.074	Rainbow trout	96-hour TLm	2199
0.023	1-0.012	Bluegills	Killed	3007, 3058
0.047		Salmon, young	24-hour TLm	3119
0.05		Bass fingerlings	Killed all	681
0.1 /	alcohol }	All fishes	Killed	3118
0.1	solution )	Goldfish	Toxic limit	2962
0.1		Goldfish	Median lethal dose	2744
0.1		Bluegill adults	Killed	681
0.1	ponds )	Goldfish	Killed	681
(	emulsion f	Bluegills	Killed	3058
A 14	powder	Darters	Killed	3058
0.14	powder	Sculpins.	Killed	3058
	powder	Trout	Killed	3058, 3007
0.15	(Downer	Bluegill fingerlings	Killed all	681
0.18		Ricegills and crappies	Killed	3058
0.2		Goldfish	Killed	681 681
0.4	[ponds   powder	Fatheads	Killed	
0.5	(bowder )	Golden shiners	Die	3058
1.6	(ponds	Goldfish	Killed	681
1.0	powder	}		ŀ

It will be noted that the concentrations range from 0.001+ mg/l, an alcohol suspension, to 1.6 mg/l, in a wettable powder formulation. With respect to suspended DDT, Rudd and Genelly (3005) conclude that at 0.1 mg/l all fish will die within 12 hours, at 0.01 mg/l only a few will survive, and at 0.005 mg/l many but not most fish will be killed.

Later work that reports a number of variables is also tabulated in an order of increasing concentration:

Concentration	Tempera				
of DDT mg/l	ture °C	Type of Water	Type of Fish	Results	Reference
0.016	25	(4)	Bluegills	96-hour TLm	3000
0.027	25	(4)	Goldfish	96-hour TLm	3000
0.032	25	(4)	Fatheads	96-hour TLm	3000
0.034	25	(3)	Fatheads	96-hour TLm	3000
0.043	25	(4)	Guppies	96-hour TLm	3000
0.06		(2)	Brook trout	Tolerance limit	3122
0.1	21		Gupples	Distress in 30 min.,	2992
				death in 24 hours	-002
0.12	10-16		Bluegills	Killed all	3123
0.12	10-16		Darters	Killed 22%	3123
0.388	13	(5)	Rainbow trout	96-hour TLm	3124
1.0	21-26	(1)	Mummichog killifish	Toxic symptoms in 4-6 hours, death in 6-12 hours	3014
10.0 (powder)		(2)	Brook trout	Tolerance limit	3122
17.8 (powder)	17	(6)	Chinook salmon	Critical level	2091
50.0 (powder)	17	(6)	Rainbow trout	Critical level	2091

- (1) Brackish water, acetone suspension, 6 liters solution, 5 fish per test.
- (2) pH 7.8-8.2, alkalinity 188-200 mg/l, DDT in kerosene, fish 2.5-5 inches long.
- (3) Hard water, pH 8.2, DO 8.0 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.
- (4) Soft water, pH 7.4, DO 8.0 mg/l, alkalimity 18 mg/l, hardness 20 mg/l.
- (5) Total dissolved solids 113 mg/l, pH 7.1, DO 8 mg/l, total alkalinity and hardness 102.6 mg/l, 10 liters solution, 5 fingerlings per jar.
- (6) Fresh water, aerated, pH 7.7-7.9, D0 6.2-7.4 mg/l, total alkalinity 75.0 mg/l, average size of fish: salmon 90 mm, trout 120 mm, 3 days exposure, 300 liter aquaria, 16 fish per aquaria, concentration given is for the commercial powder, 50 percent wettable. The critical level is defined as the lowest concentration in which obvious deleterious effects were noted.

Other forms of aquatic life are affected in varying degree by DDT. Tarzwell (918) states that crabs, crayfish, and amphipods are more sensitive than fishes for DDT. Aquatic insects and larvae are particularly susceptive to DDT; in fact, it is to control such larvae as those of the anopheline mosquito that DDT is often employed. Amphipods, sowbugs, and bait shrimp are highly susceptible, whereas red mites, snails, and mussels are highly resistant (3125). High sensitivities of many of these forms, however, can reflect upon the fish population since fish have been reported to have starved to death because of the killing of fish-food organisms (3005, 3126). Although DDT is toxic to fish and many fishfood organisms, it does not follow that fish which consume insects killed by DDT will be harmed. Ginsburg (1152) reports that gold fish were not poisoned when they were fed for four consecutive days with larvae of A.egypti which had been killed by 0.05 to 1.0 mg/l DDT. Each fish consumed about 100 larvae during the test. However, snakes and turtles have died from eating DDTkilled fish (3005). The toxicity of DDT to various water organisms other than fish has been reported as follows:

Concentration of DDT mg/l	Tem- pera- ture °C.		1	Results	Reference
0.001 0.0014 0.0014 0.001-0.0015 0.001-0.1 0.01 0.01 0.012 0.025 0.025 0.04 0.1 (for 30 min.) 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	11.5 27.5 11.5 11.5 11.5 11.5	(1) (2) (3) (3) (3) (3) (3) (3) (3)	Culez larvae Daphnia Daphnia A. egypti larvae Daphnia Stonefly (c) Chi onomus Brine shrimp larvae Oyster larvae A. quadrimaculatus larvae Chironomus Simulium Caddis fly (d) Stonefly (b) Dephnia Tadpoles Brine shrimp adults Stonefly (a) Daphnia	64-hour tolerance limit. Immobilized in 50 hours Kills 70-100% in 48 hours. Immobilized 16-32 hours. 96-hour TLm. Infestation controlled. TLm in 5 hours. Did not grow well. Kills all in 48 hours. Kill 50% in 8 hours. Kills. 96-hour TLm. 96-hour TLm. 411 killed (laboratory). All killed (laboratory). TLm in 5 hours. 96-hour TLm. 96-hour TLm.	2744 2699 3255 1131 1150 2699 3127 3128 2515 1131 2531 1148 3055 2699 1144 1144 3128 2699
).25 ).25-0.5			Tadpoles	All killed (field)	1144
).5			Snails	Unaffected	3129, 1144 1144
.0			Oyster tarvae	Death in 4 days	2515
10			Blue crabs	Survived.	3061

The aerial application of DDT has been studied quite intensively. Studies have varied from a single, local application, such as spraying of the Blue Nile to control a green chironomid (at 0.09 mg/l which resulted in a massive fish kill) (3130) to repeated extensive forest applications, such as to the Miramichi Water Shed to control spruce budworm (3005). Reports made from these studies generally cite dosages on an areal basis. Some of the effects of this type of spraying on various water animals has been tabulated as follows:

Applicati	ion.		
of DDT		•	
lbs/acr		Results	
0.01-1.0			Reference
0.01-1.0	Fish	Toxic1136	. 918. 1137
0.025-1.0		Harmless Repeated application, Killed	1146, 920
0.1	Frogs	Repeated application, Killed	3005
0.1	Crayfish	Eliminated	2121
0.25	Snakes	Repeated applications. Killed	3005
0.25	Fiddler crabs	10-20% mortality	3125
0.5	Snakes	rined	2005
0.5 0.5	Toothed herring	Killed in agitated waters	2129
0.5 0.5	Shiners	Killed in agitated waters	919a
0.5	Dace	Killed in agitated waters	2190
0.5	Salmon	Reduction of 80%	9199
0.8	Killifish	Light kills at lesser dosage Nearly complete kill	3125
1.0	Crabs	Nearly complete kill	3125
1.0	Frogs	Killed	3110
1.0	Snakes	nineti	9110
1.0	Mayfly	90% reduction	0017 0100
1.0	Caddisfly	90% reduction	2647, 3133
1.0	Trichoptera	90% reduction Destroyed for 16 months	2647
1.0	Megaloptera		
1.0	Odonata	Resistant	2647
1.0	Frogs	Killed	1197
1.0	Tadpoles	Killed _	1137
1.0	Snakes		1137
1.0	Fish	WEEKIV FOR 211 WOODS do need	*
1.0	TT 5 4	male iiiii cant mortaista	3046
1.0	Hemipterans	Kined	3005
1.0	Coleopterans -	Killed	3005
	Fish-food insects	99% killed	3005
1.0	Amphibians and		3000
1.0	reptiles	Usually not affected	3005
	Surface insects	No appreciable effect	1147
(suspension)	- ·		
	Bottom insects	Many killed	1147
(suspension)	(caddis-fly larvae,		7771
	mayny nymphs)		
2.0	Tubificids,		
3.0	A $e$ $l$ $o$ $o$ $m$ $a$	Not killed	74
	Fish	Totally destructive	3135
7.5	Aquatic organ-	Virtually wiped out	3005
•	isms		0000

For further details of aerial spraying of DDT, the reader is referred to Rudd and Genelly's summary (3005) as well as to the following references (918, 1135, 1147, 2534, 2694, 2695, 3134, 3136, 3137, 3138, 3139, 3140).

Although the presence of aquatic plants reduces the toxicity of DDT toward fish, the plants themselves are unaffected. The alga Scenedesmus has been found thriving in high concentrations of DDT (2744). A laboratory study for 21 days at 22°C showed a 2.0 mg/l concentration to have no effect on any of the tested algae (2041). Applied as a dust or as a solution in fuel oil at concentrations of 0.05 to 0.2 lbs/acre at weekly intervals, DDT had little effect upon the plankton (1151).

It appears that DDT dusts can be applied routinely at 0.1 lb/acre with little or no significant harm to wild-life. Routine treatments with fuel oil solutions at 0.1 lb/acre generally kill large numbers of fish after the 10th treatment. For adequate mosquito control, dusts at 0.1 lb/acre or oil solutions at 0.05 lb/acre are recommended (2611). Rudd and Genelly remark that 0.1 lb/acre as used in mosquito control and 1.0 lb/acre as used in forest insect control are relatively safe levels of application from the standpoint of fish (3005). Another report states that the safe concentration of a formulation of DDT used in budworm control is less than 0.05 mg/l (3141). Some fish and shellfish mortality can be expected after a single application of 0.2 lb DDT/acre to water surfaces (3006).

Oysters that had been kept for 5-8 days in an aquarium treated with DDT at the rate of 5 lbs/acre survived and their shell movements were not affected. Spraying the shells directly with a solution of DDT in kerosene at a rate of 3-5 lb/acre caused a reduction in the setting of spat (1153).

## DEAD - X

(see Aromatic Solvents)

#### DEHYDROABIETYLAMINE ACETATE

(see Rosin Amine Compounds)

#### DELNAB

(see Organic Phosphates-General)

## DELRAD

(see Rosin Amine Compounds)

## DEMETON

(see Systox)

#### DERRIS ROOT

(see Rotenone)

## DIAZINON

C₁₂H₂₁N₂O₃PS

(see also Organic Phosphates—General)

Diazinon is a registered trade name of 0, 0-diethyl 0-(2-isopropyl-6-methyl-4-pyrimidyl) phosphorothioate. Diazinon is a liquid that has a faint ester-like odor. It is miscible with a number of hydrocarbon solvents. Diazinon apparently has very high insecticidal and acaricidal properties (364, 3005).

The estimated fatal dose for a 70 kg man of Diazinon is 25.0 grams (2995). Reports of toxicities to laboratory rats have varied considerably. These reports include an oral  $LD_{50}$  to rats of a 95 percent technical grade formu-

lation as 100 to 150 mg/kg of body weight (3005), 125 mg/kg (3002), and 235 mg/kg (2992). Against male albino rats Diazinon has an LD₅₀ of 435 mg/kg (3142), 408 and 293 mg/kg (3143), and against males and females of 108 and 76 mg/kg (2999). A 23-percent wettable powder had an  $L\bar{D}_{50}$  of 264.5 mg/kg (in terms of active ingredient). No gross effects were observed in rats fed 100 to 1,000 mg/kg of the wettable powder in the diet for 4 weeks (3005). The reported LD₅₀ to mice of technical grade Diazinon is 82 mg/kg in the diet. Levels of 6.5 mg/kg/day of active product fed to dogs inhibited cholinesterase activity, 9.3 mg/kg/day resulted in the usual toxicity signs associated with cholinesterase activity (3144). Concentrations of 0.75 mg/kg fed to dogs produced significant lowering of plasma cholinesterase, but there was no effect at 0.25 mg/kg concentration. Levels of 75.0 mg/kg in the diet produced significant depression of red-cell cholinesterase, but 0.75 ppm produced no effect (3076).

Radeleff et al. (3075) investigated the oral toxicity of Diazinon to livestock. With calves 10.0 mg/kg was lethal, 1.0 mg/kg was toxic, and 0.5 mg/kg non-toxic; with steers 25.0 mg/kg was toxic, and 10.0 mg/kg was non-toxic; and with sheep 30.0 mg/kg was toxic.

Adlung (1992) reports that at temperatures of 20-22°C, Diazinon at a concentration of 4 mg/l caused abnormal behavior in guppies in one hour, death in 24-48 hours. The estimated concentration required to immobilize Daphnia magna in 50 hours at 20°C is 4.3 µg/l (3255).

#### DICAPTHON

(see also Organic Phosphates—General)

Dicapthon is a trade name for 0, 0-dimethyl 0-(2-chloro-4-nitrophenyl) phosphorothicate (2998). The acute oral toxicity of Dicapthon to male rats has been reported as 460 mg/kg of body weight (3142), and against males and females of 400 and 330 mg/kg respectively (2999). The lethal concentration to bivalve larvae is cited as about 2.0 mg/l (2989).

#### DICHLONE

(see Dichloronaphthoquinone)

#### DICHLOROBENZENE

(see Chlorinated Benzenes)

## DICHLORONAPHTHOQUINONE

 $C_{10}H_4Cl_2O_2$ 

3

- 1. General. Also known as Dichlone or Phygon, this is a yellow crystalline substance, soluble to 0.1 mg/l, soluble in xylene and o-dichlorobenzene and moderately soluble in other organic solvents. Its full name is 2,3-dichloro-1,4-naphthoquinone. It is used as a fungicide for seeds, vegetables, and textiles, the application for the former being about one-quarter ounce per 100 lbs of seed (364, 3005, 3067), and as an algacide for ponds and lakes.
  - 2. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. Phygon has a low order of toxicity to man but may cause skin irritation to some persons (2262).

b. Irrigation Waters. Phygon is reported to be non-

injurious to crop plants (2262).

c. Stock and Wildlife Watering. The acute oral LD50 to rats has been noted as 1500 mg/kg of body weight (3005, 3009, 3067). The highest level fed to rats without producing gross effects was 1000 mg/kg of food. Growth was retarded over 1580 mg/kg in food and death oc-

curred at 2500 mg/kg (3005).

d. Fish and Aquatic Life. The 96-hour TL_m values to rainbow trout fingerlings have been reported to range from 0.0237 to 0.074 mg/l (2199). Bond, et al. (2988) report no mortality to coho salmon at concentrations of 0.042 mg/l and less. They mention having a great deal of difficulty in working with Phygon XL because it lost toxicity rapidly. Short exposures had the following effects on coho salmon:

Concentration	on	
of Phygon X	L Exposure	
mg/l	Time	Results
0.1	30 minutes	no mortalities
0.5	15 minutes	20% dead one hour after removal 60% dead 24 hours after removal
0.5	30 minutes	80% dead one hour after removal 100% dead three hours after removal

Studies of the toxicity of Phygon to fish have been summarized as follows:

Concentration of Phygon mg/l	Temperature °C	Type of Water	Type of Fish	Result	Reference
0.07	20	(4)	Largemouth bass	48-hour TLm	2988
0.074	13	(3)	Rainbow trout	96-hour TLm	3124
0.11	21	(1)	Red-sided shiners	96-hour TLm	3011
0.11	21	(2)	Red-sided shiners	96-hour TLm	3011
0.14	19	(5)	Catfish	96-hour TLm	2981
0.15		(6)	Fatheads	96-hour TLm	2987
0.42	20	(4)		48-hour TLm	2988

- (1) Soft water, pH 7.2, D0 9 mg/l, alkalinity 36 mg/l, hardness 18 mg/l, 10 liters solution, 5 fish (6-7 cm) per jar.

  (2) Hard water, pH 8.2, D0 9 mg/l, alkalinity 116 mg/l, hardness 156 mg/l, 10 liters solution, 5 fish (6-7 cm) per jar.

  (3) Water had total dissolved solids content of 113 mg/l, pH 7.1, D0 8 mg/l, alkalinity and hardness 102.6 mg/l, 10 liters solution, 5 fingerlings per aquarium.

  (4) Aerated 15 liter solutions, pH 7.4-7.7, methyl orange alkalinity 41-71 mg/l, 10 fingerlings per annarium.
- fingerlings per aquarium.

  (5) University of Oklahoma tap water, 4-gallon aquaria, 10 fingerlings per aquarium,
- 100 or 200 fish per experiment.

  Soft water, pH 7.2, D0 8.0 mg/l, alkalinity 36 mg/l, hardness 38 mg/l, Pime-phales promelas.

Concentrations of 0.3-0.055 mg/l had no visible effects on fish and zooplankton when applied to a lake for control of algae. Other tests showed 0.1-1.0 mg/l to be toxic to various species of fish (3009). A safe concentration range of 0.05 to 0.6 mg/l has been reported (2988), while another paper mentions that 0.1 mg/l had no injurious effect toward fish (1542).

Observed effects of field applications of Phygon XL to various ponds on fish, algae, and other aquatic plants have been described (3094). Snails, Daphnia, and rotifers seemed to be unaffected by concentrations up to 100

mg/l (3005).

Laboratory tests conducted for 21 days at 22°C with a concentration of 2.0 mg/l showed that 2,3 dichloronaphthoquinone inhibited the growth of 33 percent, and a related compound, beta naphthoquinoline inhibited 50 percent, of the algae tested (2041). Other studies indicated it was lethal to blue-green algae in concentrations as low as 0.002 mg/l. It is selectively toxic to the bloomproducing blue-green algae and nontoxic to most green algae and higher aquatic plants even at concentrations

of 0.1 mg/l. In the dark it is ineffective, but on exposure to sunlight it is highly toxic (1542). A concentration of  $0.5~{
m mg/ar{l}}$  controlled 28 percent of blue-green algae, and no diatoms or green algae. Even 16 mg/l had little or no effect on 50 percent of the green algae (3050).

## DICHLOROPHENOXYACETIC ACID

(see 2,4-D)

## DICHLOROPROPIONIC ACID

(see Dalapon)

## DIELDRIN

C₁₂H₄OCl₆

- General. Dieldrin is the assigned common name for an insecticide containing not less than 85 percent of the endo-exo isomer of 1,2,3,4,10,10-hexachloro-6-7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene. Dieldrin is insoluble in water and moderately soluble in most organic solvents except aliphatic petroleum solvents and methanol. It is stable in the organic and inorganic alkalies and acids commonly used in agriculture. It is affected by strong mineral acids but is compatible with most agricultural chemicals, fertilizers, and economic poisons. It may be formulated as a wettable powder, xylene solutions, or as a dust (364). Dieldrin is similar to aldrin as described hereinbefore.
- 2. Cross References. Chlorinated Hydrocarbons, Endrin, Aldrin, DDT, Benzene Hexachloride.

3. Effects Upon Beneficial Uses.

- a. Domestic Water Supplies. The estimated fatal dose of dieldrin for a man of 70 kg has been estimated as 5 grams (2995). In describing several cases of dieldrin intoxication, it was concluded that contamination of water even with small quantities is very dangerous (3145).
- b. Stock and Wildlife Watering. The acute oral  $LD_{50}$ value of dieldrin for rats has been reported as ranging from 37-87 mg/kg of body weight (3005), 81.3 mg/kg (3002), 87 mg/kg (2992, 3073), 60 mg/kg (3042, 3043) technical grade against males and females of 46 mg/kg (2999). No harm was demonstrated to laboratory rats after feeding on technical grade dieldrin at a level of 25 mg/kg of food for two years (3042, 3146). Rats may be maintained for more than a year without injury on water containing 0.2 mg/l of dieldrin which concentration kills fish in a few hours (3001). Differences in dieldrin toxicities are prescribed to the grade of dieldrin employed and to the nature of the solvents (3005). Ground tobacco stems impregnated with dieldrin and applied at a rate of 0.2 lbs of dieldrin per acre had no immediate detrimental effect on meadow mice or rice rats (3147). Dieldrin ground sprays at 2 lbs/acre, on the other hand, gave complete kills of meadow mice (3148).

The application of dieldrin at 3 lbs/acre caused most losses in wildlife the week following application. Ground squirrels, muskrats, and rabbits were virtually eliminated, short-tailed shrews, fox squirrels, woodchucks, and meadow mice sustained heavy losses, but white-footed mice appeared resistant (2402). Another report cites that aerial applications of 1.5 and 3 lbs of dieldrin in attaclay granules per acre caused no appreciable change in the field mouse population (3149).

Ducks, pheasants, and wading birds were killed when dieldrin was applied at 0.5 lb/acre (3150). Granular dieldrin applied to marshes at 0.2 lbs/acre killed some birds within 3 days (3152). Application of dieldrin at 0.3 pound per acre in granular form to tidal marshes resulted in no apparent injury to birds (3151). Ground tobacco stems impregnated with dieldrin and applied at a rate of 0.2 lb of dieldrin per acre had no observable effect upon adult birds (3147). However, the application of dieldrin at 3 lbs/acre virtually eliminated meadow larks, robins, brown thrashers, starlings, common grackles, and ringneck pheasants. Horned larks sustained heavy losses, although house sparrows and mourning doves appeared resistant (3154, 3155). Dieldrin applied at 4 lbs/acre killed or otherwise affected songbirds and mammals (3153). An application of 0.5 lb/acre killed large numbers of water birds and a smaller number of up-land game birds (3005). In feeding experiments, 10 mg/kg in the diet of breeding pheasants demonstrated no effects on the adult birds but did result in decreased hatchability of eggs and viability of chicks (2945). Inclusion of 1 mg/kg in diet of growing quail resulted in higher mortality rates. Young pheasants failed to survive on a diet containing dieldrin in concentration of 5 mg/kg (3044, 3045). No ill effects were noted when quail were fed winter diets containing one mg/kg (3045). The amount of reproduction decrease in quails caused by 1 mg/kg of dieldrin in the diet has been noted as 40 percent (2996). The amount of dieldrin that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle in mg/kg respectively are 35 and 50 (2994, 2996). Grasshoppers as well as four nestling marsh hens have been killed by 0.2 lb per acre (3147). Earth worms were decimated immediately after application of 1.5 and 3 lbs of dieldrin in attaclay granules per acre but six months later appeared to have recovered (3149).

c. Fish and Other Aquatic Life. Although dieldrin has been said not to persist in soil (3042, 3146), the report that applications of 1 lb of dieldrin per acre continued to kill aquatic beetles for at least ten months (3156) would seem to indicate rather lengthy persistance. A large number of reported lethal figures have been found in the literature with respect to dieldrin toxicity to fish. These are summarized as follows:

Concentration of Dieldrin mg/l	Type of Fish	Result	Reference
0.005-0.042		96-hour TLm	2340
0.006	Bass	Approximate TLm	3005
0.006	Goldfish	Approximate TLm	3005
0.01	Bluegill	Approximate TLm	3005
0.012	Goldfish	17% kill in 96 hours	3047
0.012	Goldfish	Toxicity threshold	3048
0.016	Trout	Toxicity threshold	3007
0.016	4-7" brown	40% dead in 48 hours	3049
0.010	trout		
0.016	Brown trout	Approximate TLm	3005
0.02	4-7" brown	Death in 48 hours	3007
****	trout		
0.02	Goldfish	Toxicity threshold	3007
0.0237-0.074	Rainbow trout	96-hour TLm	2199
	fingerlings		
0.025	Goldfish	60% kill in 96 hours	3047
0.025	Trout	100% dead in 48 hours	3049
0.04	Golden shiners	Approximate TLm	3005
0.050	Mullet, small	100% dead in 5 hours	2423
0.050	Mullet, large	100% dead in 24 hours	2423
0.125	All fish tested	Lethal	1383
0.2	Goldfish	Distress in one hour, death in 12 hours	3073
	a	Distress in one bour.	3073
0.2	Guppies	death in 12 hours	5010
0.25	Goldfish	Approximate TLm	3005

Later studies that report numerous variables associated with the toxicity tests are summarized in the following table:

Concentration of Dieldrin mg/l	Temperature °C	Type of Water	Type of Fish	Result	Reference
0.0079	25	(2)	Bluegills	96-hour TLm	3000
0.016	25	(2) & (4)	Fathead		
*			minnows	96-hour TLm	3000
0.022	25	(2)	Guppies	96-hour TLm	3000
0.0237	13	(3)	Rainbow trout	96-hour TLm	3124
0.037	25	(2)	Goldfish	96-hour TLm	3000
less than 2.5	19	(1)	Catrish,	96-hour TLm	2981

(1) University of Oklahoma tap water, 4-gallon aquaria, 10 fingerlings per aquarlum, 160 or 200 fish per experiment.
(2) Soft water, pH 7.4, DO 8 mg/l, alkalinity 18 mg/l, hardness 20 mg/l, acctone

(2) Soft water, ph 1.7, Do 3 mg/l, pH 7.1, DØ 8 mg/l, total alkalinity and hardness 102.6 as CaCOs, 10 liters solution, five fingerlings per jar.
(4) Hard water, pH 8.2, DØ 8 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.

In landlocked ponds treatments with dieldrin emulsion at a rate of 1 lb of dieldrin per acre is an efficient larvicide but is totally destructive to fish (3135). Granular dieldrin applied to marshes at 0.2 pounds per acre killed many fish (3152). Fish died from 0.1 pound dieldrin per acre applied 20 days previously (3157). From an application of 0.2 pounds dieldrin per acre, there was observed only one dead minnow, no dying fish (3158). An application of 1 pound per acre controlled mosquito larvae for 62-78 weeks, but this concentration was decidedly harmful to fish and other aquatic organisms (1475). Dieldrin was applied as a spray at 0.3 lb/acre. One week later a heavy rain occurred. Two days after the rain, a large but not complete kill of fish occurred (3159). The same rate of application in granule form to tidal marshes killed some killifish and large numbers of small green and blue crabs. Horseshoe crabs, mussels, and snails suffered no apparent injury (3151). Ground tobacco stems impregnated with dieldrin and applied at a rate of 0.2 lb of dieldrin per acre had no immediate detrimental effect on turtles or frogs but blue crabs, fiddler crabs, beetles, flies, and caged killifish were killed. No mortality of killifish under natural conditions was observed (3147). When applied at 1 lb/acre, a fish kill was virtually complete. Mollusks were unharmed, but all crabs except fiddlers were annihilated. The fiddler crabs were apparently spared by uneven coverage (3160). Using two percent granules at the rate of five to ten pounds per acre, three species of *Tilapia* were killed. At 0.2 lb/acre in ponds one to three feet deep, there was a 16 to 40 percent mortality among Tilapia fingerlings over a three-week period (3060). After an area was treated with one pound of dieldrin per acre, repopulation with fish occurred in six weeks. Crab populations were still at a low level 13 weeks after treatment (3161). A concentration of 0.1 mg/l, which had no immediate effect, after two weeks decreased the activity of oysters, reduced the growth of small oysters by one-third to onehalf of normal, and doubled their mortality rate (2423). Application of one pound of dieldrin per acre greatly reduced aquatic insects (3156).

An aerially applied dose of 0.5 pounds per acre was found to be concentrated in the water surface at 0.64 mg/l (3162). Runoff from an area treated with 4.66 pounds per acre was found by fish bioassay to contain 0.13 mg/l; by chemical determination 0.10 mg/l (3024, 3163). Weekly dusting for 20 weeks with 2.5 percent dieldrin dust or 2 percent dieldrin granules caused insignificant fish mortality (3046). An application of 5 lbs/acre of 2.5 percent dust caused a 6.6 percent fish mortality, and 10 lbs/acre a 66.6 percent fish mortality (3046).

The concentration of dieldrin necessary to effect a 50 percent kill in *Chironomus* larvae in eight hours is 0.007 mg/l (2531). The TL_m of larval brine shrimp after 5 hours exposure was 0.595 mg/l, for adults 1.172 mg/l (3128). A dilution of 1:400,000 of 25 percent dieldrin (i.e., about 2.5 mg/l) killed 100 percent of *Lymnaeid* snails in a 24-hour exposure (2993). The estimated concentration of dieldrin required to immobilize *Daphnia magna* in 50 hours at 20°C is 330 µg/l (3255).

Bioassays with different formulations of dieldrin showed the 96-hour  $TL_m$  values to range from 0.0056 to 0.042 mg/l, depending on the formulation, species of fish, and water hardness (3163).

## DILAN

The limits of tolerance of fingerling channel catfish to Dilan have been investigated by Clemens and Sneed (2981) for the Fish and Wildlife Service. At a temperature of 19°C, the 96-hour TL_m was less than 0.5 mg/l.

## DINITRO COMPOUNDS

Dinitro compounds, originally introduced as insecticides, are now widely used as herbicides and as preharvest desiccants. As a crop spray for the control of aphids or mites, they are not used during periods of active plant growth because of their high phytotoxicity. These compounds are toxic to a wide variety of life including microorganisms, plants, arthropods, and higher animals, and as a group are more toxic to mammals than most other herbicides in common use (3005, 3009). Such compounds include 2,4-dinitro-6-sec-butylphenol (DNBP), 2,4-dinitro-6-methylcresol (DNC), 2,4-dinitro-6-cyclohexylphenol (DNCHP), dinitro-ortho-cresol (DNCC), and dinitro carbazole. They are discussed in Chapter VI.

DIPTEREX C₄H₈Cl₃O₄P

1. General. The chemical 0,0-dimethyl-(1-hydroxy-2, 2,2-trichloroethylphosphonate is known by the trade name Dipterex. This crystalline is soluble in water, benzene, chloroform, and ether, and insoluble in oils. Bayer 13/59 is a similar compound the chemical name being 0, 0-dimethyl-2, 2, 2-trichloro-1-hydroxyethyl phosphate (364).

2. Cross References. Organic Phosphates—General.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The estimated fatal dose for a 70 kg man of Dipterex is 25.0 grams (2995).

b. Stock and Wildlife Watering. The acute oral LD₅₀ of Dipterex to rats has been quoted at values of 400 to 1100 mg/kg of body weight (364, 2999, 3002, 3005, 3073, 3143). More than 112 mg/kg fed in the daily diet for a 60-day period was required to produce mortality (3005). Fed to dogs in diet, 500 mg/kg produced significant and 200 mg/kg borderline depression on both plasma and red-cell cholinesterase. There was no effect at 50 mg/kg (3076). Dipterex at 10.0 mg/kg was toxic

and at 5.0 mg/kg was non-toxic against calves (3075). The same authors reported the effects of Bayer 13/59 on sheep, 200 mg/kg being toxic and 100 mg/kg being non-toxic. With cattle, 100 mg/kg was toxic and 50 mg/kg was non-toxic.

c. Fish and Other Aquatic Life. For brook and rainbow trout, 0.01 mg/l of Dipterex was not toxic (3164). Concentrations of 1.0 and 10.0 mg/l caused no damage to fish (3165). Concentrations of Dipterex of 50 mg/l at a temperature of 19-22°C caused goldfish to demonstrate abnormal behavior within two hours and killed them in 30-60 hours (3073). The 96-hour TL_m values to fathead minnows at 25°C were 51.0 mg/l of active ingredient in hard water and 180 mg/l in soft water (3000).

When used to control mosquito larvae at concentrations of 1 and 10 mg/l, no effect on fish was noted (3165). Dipterex has been reported to be effective against *Psorophora* at 0.5 mg/l (2931). Although laboratory tests at rates of 0.0125 to 0.25 mg/l for 24 hours gave 100 percent mortality to *Psorophora*, preflood applications in granular formulation of up to 0.5 lb/acre failed to give satisfactory control of this organism (3082).

## DI - SYSTON

(see also Organic Phosphates-General)

Di-syston is the name by which the chemical 0,0-diethyl S-2-(ethylthio) ethyl phosphorodithioate is known. It is a clear, oily, liquid slightly soluble (1:40,000) in water, but soluble in most organic solvents. The acute oral LD50 to rats has been reported from 2.6 to 12.5 mg/kg of body weight (2997, 3000, 3331), and to guinea pigs of 10.8 mg/kg (3331). With fathead minnows at 25°C, the 96-hour TLm was found to be 2.6 mg/l in hard water and 3.7 mg/l in soft water (3000). Technical grade di-syston 90-percent active in acetone was tested against fish at 25°C in soft water. These tests gave 96-hour TLm values to fatheads of 2.9 and 4.1 mg/l and to bluegills of 0.07 mg/l (3000).

#### DIURON

 $C_9H_{10}Cl_2N_2O$ 

(see also CMU)

Diuron, 3-(3,4-dichlorophenyl)-1-dimethylurea, is a crystalline compound only slightly soluble in water and oils. Its solubility in water at 25°C is 42 mg/l. The acute oral LD₅₀ to rats is 3.4 g/kg of body weight (364, 2997).

Bioassays of diuron conducted at 20°C in aerated water gave 48-hour TL_m values for coho salmon of 16 mg/l. Preliminary experiments indicate that bluegills are resistant but white crappies are killed by concentrations as low as 6 mg/l. Aeration slightly reduced the toxicity of Diuron. Treatment of ponds with 5 and 10 mg/l resulted in the death of bluegills and largemouth bass. The 10 mg/l treatment eradicated all fish and bullfrog tadpoles. However, reduction of dissolved oxygen is thought to have been a contributing factor (2988).

The lethal concentration to bivalve larvae is cited as 5.0 mg/l (2989).

## DOW (ET-14, 15, or 57)

(see Organic Phosphates—General)

## DOWICIDE (A, F, G, 31)

(see Organic Phosphates-General)

#### DOWPON

(see Dalapon)

## ENDOTHAL

 $C_8H_8O_5Na_5$ 

- 1. General. Endothal is the generic name for 3,6-endoxohexahydrophthalic acid disodium salt (364). The common name is disodium endothal and the tradename Aquathol (3166). It is soluble in water and has a selective effect on a number of weed species (3009).
  - 2. Effects Upon Beneficial Uses.
- a. Irrigation Waters. Endothal in a concentration of 100 mg/l killed tomatoes after 15 days but appeared not to have seriously injured cotton. Endothal at 200 mg/l in irrigation water killed tomatoes after 10 days and injured cotton at the end of 41 days (3084).
- b. Stock and Wildlife Watering. The acute oral  $\mathrm{LD}_{50}$  of endothal to rats is 35 mg/kg of body weight (3009). Based upon a 19.2 percent solution of sodium endothal marketed as Aquathol, the  $\mathrm{LD}_{50}$  is 182-198 mg/kg. No internal pathological symptoms developed during 2-year feeding tests with diets containing up to 2500 mg/kg of disodium Endothal (3166).
- c. Fish and Other Aquatic Life. Walker (3167) found that 40 mg/l had no harmful effects on three species of minnows in 96 hours. Other work demonstrates no fish toxicity to endothal in 21 days at a level of 100 mg/l (3168). The lethal dose to bluegills is greater than 100 mg/l but less than 200 mg/l. No mortalities were observed at 10 mg/l on rainbow trout, bass, and fathead minnows (3166).

Bennet (3169) reported that 800 mg/l killed all bluegills in 24 hours. At 400 mg/l about 50 percent of the bluegills were dead after a 48-hour exposure. At 300 mg/l none were killed in 48 hours. Biossays (2988) against largemouth bass and chinook salmon at 20°C gave 24- and 48-hour TL_m values for chinook salmon of 155 and 136 mg/l respectively, whereas the 24- and 48-hour TL_m values for bass were both 200 mg/l. In a 96-hour exposure period in a constant flow apparatus, no bass mortalities were observed at concentrations as high as 135 mg/l. Experimental field studies indicate that endothal controlled a plant species, Potamogeton pusilus, at 0.3 mg/l with no loss of bass or bluegills that were present in the pond.

## ENDRIN

1. General. Endrin is the common name for the chemical 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-endo-endo-dimethano-napthalene (364). It is insoluble in water, acetone, and benzene, and slightly soluble in alcohol (2997). Although endrin is said to have a strong residual toxicity as does its closely related compound, dieldrin (3005), endrin is reported to disappear "relatively rapidly" based upon analyses of water, mud, aquatic vegetation, and surviving fish tissues (3170). Also, another report states that endrin does not persist in soil and presents no accumulation problem,

but this report advises not to contaminate areas frequented by wildlife (3171).

- 2. Cross References. Chlorinated Hydrocarbons, Dieldrin.
  - 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. The acute oral  $\mathrm{LD}_{50}$  value for laboratory rats has been reported at values ranging from 7.3 to 48 mg/kg of body weight (2992, 2999, 3002, 3005, 3172, 3173). Chronic feeding of 100 mg/kg in the diet of males and 25 mg/kg for females gave significant mortality to the same degree. Endrin has been used as a broadcast spray at up to 2.5 lbs/acre to control field rodents (3005). Younger males and older females appear to be more susceptible than their counterparts (3173).

Dogs appear to be more sensitive than rats. Death occurred within six weeks at dietary levels as low as 10 mg/kg, abnormal effects at 4 mg/kg (3005). Oral LD₅₀ values for male and female monkeys were 3 mg/kg of body weight, female rabbits 7-10 mg/kg, and male and female guinea pigs 36 and 16 mg/kg (3173).

Inclusion of endrin at 1 mg/kg in the diet of growing quail resulted in high mortality rates. Young pheasants failed to survive on a diet containing 5 mg/kg of endrin. However, no ill effects were noted when quail were fed winter diets containing 1 mg/kg. Hatchability of eggs and viability of chicks were adversely affected by the inclusion of endrin in the reproduction diet (3044, 3045). The inclusion of 1 mg/kg in the diet will cause a 40 percent or more decrease in the reproduction of quail. The amount of endrin that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 5 and 14 mg/kg, respectively (2994, 2996).

The  $\rm LD_{50}$  values of one-week old chicks is 3.5 mg/kg of body weight. Young chickens, two-months old, incurred a 10 percent mortality at 4.3 mg/kg. In chronic feeding tests with chicks up to seven weeks of age, 95 percent died at 12 mg/kg, 15 percent at 6 mg/kg (3005).

b. Fish and Aquatic Life. Fish are highly sensitive to endrin. Various figures noted in the literature are as follows:

20220			
Concentrat of Endri mg/l 0.0006 0.001	don  Type of  Fish  Bluegills  Guppies	Results 96-hour TLm Abnormal behavior in 5 hours (20°C), death in 24 hours	Reference 3012 2992
0.0015 0.003 0.003 0.005 0.005 0.006 0.051 0.14 0.61 4.2 10.7	Golden shiners Bass Bluegili Goldfish Carp fingerlings Carp fingerlings Salmon Fish Carp fingerlings 5-day carp fry 4-day cary fry 2-day carp larvae Carp eggs	TLon TLon TLon TLon TLon TLon 48-hour TLon 48-hour TLon 48-hour TLon 48-hour TLon 48-hour TLon 48-hour TLon 20°C) Death 48-hour TLon 20°C) 24-hour TLon 20°C) 24-hour TLon 20°C) 24-hour TLon 20°C)	3005 3005 3005 3012 3175 3012 3174 3102 3175 3175 3175

Field applications to rice paddies of one or two lbs/acre remained toxic to fish for over one month (3175). Although laboratory studies indicated a TL_m value for endrin of between 1.0 and 1.5 µg/l, a dose of 1.0 µg/l to a pond gave no results. A second dose of 1.0 µg/l was

administered, but was still without effect. Rapidly lowering temperatures were thought to be inhibiting the lethal effects (3176, 3178). Endrin, used in sugar cane fields to combat borers, has washed into streams during heavy rains, causing fish kills (3177).

The 96-hour  $TL_m$  values of endrin to fathead minnows in hard and soft water at 25°C were, respectively, 1.3 and 1.0  $\mu$ g/l. Tests with bluegills, goldfish, and guppies in soft water at 25°C gave values of 0.60, 1.9, and 1.5  $\mu$ g/l respectively (3000).

In a series of screening tests of a large number of compounds, rainbow trout, bluegill sunfish, and the sea lamprey all died within 14 hours at  $12^{\circ}$ C when exposed to a 5 mg/l concentration of an  $18\frac{1}{2}$  percent emulsion of endrin (2976). The estimated concentration of endrin required to immobilize Daphnia magna in 50 hours at  $20^{\circ}$ C is  $352 \mu g/l$  (3255).

 $\mathbf{EPN} \qquad \qquad \mathbf{C_{14}H_5PSO_5}$ 

- 1. General. EPN is an abbreviation for ethyl p-nitrophenyl thionobenzenephosphate (364). The pure compound occurs as a yellow crystal, the technical material as an amber liquid, insoluble in water, soluble in most organic solvents (2997). Emulsifiable concentrates and wettable powders appear to be preferred formulations. It is used for the control of crop pests and mosquitoes (3005).
- 2. Cross References. Organic Phosphates—General, Malathion.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The estimated fatal dose of EPN for a 70 kg man is 0.3 grams (2995).
- b. Stock and Wildlife Watering. The acute oral LD50 to rats has been reported at values ranging from 7 to 50 mg/kg of body weight (364, 2999, 3002, 3005, 3142). A two-year study, with male rats given up to 450 mg/kg and females up to 225 mg/kg in the diet, showed that amounts of EPN up to 150 mg/kg (males) and 75 mg/kg (females) had no effect on growth; the 450 and 225 mg/ kg levels retarded growth. No other symptoms were noticed. Dogs given up to 2 mg/kg/day for one year showed increased kidney weights with increasing dosage (3179). A marked synergistic effect of up to 50-fold exists for EPN and malathion when administered simultaneously to dogs (3027). Against sheep, a concentration of EPN of 20.0 mg/kg of body weight was lethal, 10 mg/kg was non-toxic; with steers, 10 mg/kg was nontoxic; and with calves, 1.0 mg/kg was toxic, and 0.5 mg/ kg was non-toxic (3075).
- c. Fish and Other Aquatic Life. EPN used as an insect larvacide at 0.1 lb/acre demonstrated little effect on fish (3048). Tests of the toxicity of EPN at 25°C using fathead minnows as the test animal showed 96-hour TL_m values of 0.25 and 0.20 mg/l of active ingredient in hard and soft water respectively (3000). A concentration of EPN of 5 mg/l for 24 hours killed rainbow trout in one hour, bluegill sunfish in 12 hours, and sea lamprey in 12 hours in Lake Huron water at 13°C.

The toxicity of EPN miticide 31.5 percent formulation was tested against Lymnaeid snails. A 24-hour exposure

in a concentration of 10 mg/l gave a 100 percent kill (2993). The estimated concentration of EPN required to immobilize  $Daphnia\ magna\$ at 20°C is 0.1  $\mu$ g/l (3255).

#### ERBON

(see Baron)

F - 98

(see Acrolein)

#### FENURON

This compound (3-phenyl-1,1-dimethylurea) also called phenyldimethylurea, is a substituted urea. It is a crystalline compound of low solubility in water and oils. The acute oral  $\mathrm{LD}_{50}$  to rats is 7500 mg/kg of body weight (2997).

Results of bioassays with Fenuron using coho salmon were extremely variable and no TL_m was estimated. All salmon exposed to 56 mg/l survived for the 96-hour duration of the test, whereas a concentration of 750 mg/l killed all test fish within 24 hours. Ten concentrations between failed to give any consistent trend (2988).

#### FERBAM

 $[(CH_3)_2NCS_2]_3Fe$ 

Ferbam is an organic sulfur compound used as a fungicide. Designated as ferric dimethyl dithiocarbamate, it is also known as Fermate. It is a black powder, insoluble in water, and soluble in chloroform, pyridine, and acetonitrile. The oral LD₅₀ to rats has been reported as about 4 g/kg of body weight (2997) and 17 g/kg (3009, 3056).

In aquaria, fingerling brook trout were killed at concentrations of one and two mg/l, but Ferbam was not lethal to pike, bass, or sunfish in ponds at 0.5 to 4.0 mg/l. However, tissue damage was indicated since all fish had eroded fins and some were completely blind (3009, 3094). The 96-hour TL_m of fingerling channel catfish to Fermate at 19°C was 2.2 mg/l (2981).

## FERMATE

(see Ferbam)

#### GAMMEXANE

(see Benzene Hexachloride)

## **GEIGY 25039**

(see Organic Phosphates—General)

## **GUSATHION**

(see Guthion)

#### **GUTHION**

 $C_{10}H_{12}N_3O_3PS_2$ 

- 1. General. Guthion is designated as 0,0-dimethyl-S-(4-oxobenzotriazino-3-methyl) phosphorodithioate. Other names for this compound are DBD, Gusathion, and Bayer 17147. Guthion is a brown waxy solid, insoluble in water, soluble in most organic solvents (364, 2997). The half-life of Guthion spray and dust on cotton leaves has been reported as 2-4 days (3180).
  - 2. Cross References. Organic Phosphates-General.

- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The estimated fatal dose of Guthion for a 70 kg man is 0.2 grams (2995).
- b. Stock and Wildlife Watering. The acute oral LD₅₀ to rats is reported as 11 to 80 mg/kg of body weight (2997, 2999, 3002, 3142), and to mice 20 mg/kg (364). The oral toxicity to calves is cited as: 25 mg/kg of body weight lethal, 0.5 mg/kg toxic, and 0.1 mg/kg non-toxic (3075). The amounts of Guthion that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 5000 and 6000 mg/kg respectively (2994, 2996). Oral administration of Bayer 17147 at 25 mg/kg to sheep was toxic, 12.5 mg/kg non-toxic (3075).
- c. Fish and Other Aquatic Life. The toxicity of Guthion to fathead minnows in hard and soft waters has been investigated. The 96-hour TL_m values at 25°C for hard and soft waters, respectively, were 0.16 and 0.093 mg/l of active ingredient. These values were obtained with acetone solutions. The 96-hour TLm of a similar solution to bluegills in soft water was 0.0052 mg/l. For an emulsifiable concentrate under the same conditions, the value was 0.0048 mg/l. The toxicity of a commercial preparation of Guthion, 18.3 percent emulsifiable concentrate, was investigated in both waters against several species of fish. The 96-hour TLm values of this formulation were reported as follows (3000):

Fish	Type of Water	96-hour $TL_m$ , $mg/l$
Fathead minnows	Hard	0.92
Fathead minnows	Soft	0.68
Bluegills	Hard	0.032
Bluegills	Soft	0.030
Guppies	Soft	0.63

## HEPTACHLOR

C₁₀H₅Cl₇

- 1. General. Heptachlor is a refined ingredient of the well-known insecticide chlordane. Its uses and chemical characteristics, therefore, parallel those of chlordane. Heptachlor is formulated in dusts, wettable powders, emulsifiable concentrates, and granules (2997). No heptachlor could be found 42 days after application to soil (3071).
- 2. Cross References. See Chlordane, Chlorinated Hydrocarbons.
  - 3. Effects Upon Beneficial Uses.
- a. Stock and Wildlife Watering. The acute oral LD₅₀ value for rats is given as 90 mg/kg of body weight (2992, 3002). Against male and female rats,  $LD_{50}$  values were 100 and 162 mg/kg respectively (2999). Daily doses of heptachlor of 5 mg/kg killed dogs after about one year of exposure. The amount of heptachlor that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 125 and 150-400 mg/kg respectively (2994, 2996). A concentration of 10 mg/kg in the diet will cause a 40 percent or more decrease in the reproduction of quail (2996). The use of 0.3 lb/acre for mosquito control resulted in no ill effects to mammals, birds, reptiles, or amphibians (3112). Airplane spraying of 0.25 lb/acre to a marsh had no effect on birds (3181). Cows fed hay

from forage sprayed with heptachlor in amounts up to 8 oz/acre did not show toxic effects (3005).

b. Fish and Aquatic Life. Heptachlor concentrations of 7.9-19 µg/l were found lethal to bluegills (2996). In aquaria tests, 0.1 mg/l caused 80 percent mortality in 24 hours to rainbow trout (3182). Tests conducted at 21°C using guppies showed that a concentration of heptachlor of 0.5 mg/l caused abnormal behavior in 30 minutes, death in 24 hours (2992). Heptachlor is much less toxic to fish as a dust or wettable powder (3005).

Later toxicity studies reporting numerous variables are summarized in the following table:

Concentration of Heptachlor mg/l	Temperature °C	Type of Water	Type of Fish	Results	Reference
0.019	25	(5)	Bluegills	96-hour TLm	-3000
0.056	25	( <u>4</u> )	Fatheads	96-hour TLm	3000
0.094	25	(5)	Fatheads	96-hour TLm	3000
0.096	21	(1)	Red-sided shiners	96-hour TLm	3011
0.107	25	(5)	Guppies	96-hour TLm	3000
0.11	21	(2)	Red-sided shiners	96-hour TLm	3011
0.175	19	(3)	Catfish	96-hour TLm	2981
0.230	25	(5)	Goldfish	96-hour TLm	3000

- Soft water, pH 7.6, DO 9 mg/l, alkalinity 36 mg/l, hardness 18 mg/l, 10 liters solution, five fish (6-7 cm) per jar.
   Hard water, pH 8.2, DO 9 mg/l, alkalinity 116 mg/l, hardness 156 mg/l, same
- (2) Hard water, pH 8.2, D0 9 mg/l, alkalmity 116 mg/l, hardness 106 mg/l, same remaining conditions as (1) above.

  (3) Tap water from the University of Oklahoma, 4-gallon aquaria, 10 fingerling channel catfish per aquarium, 100 or 200 fish per concentration.

  (4) Hard water, pH 8.2, D0 6 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.

  (5) Soft water, pH 7.4, D0 8 mg/l, alkalinity 18 mg/l, hardness 20 mg/l.

Airplane spraying of 0.25 lb/acre to a marsh killed many small crayfish and aquatic insects (3181). Heptachlor at 0.16 lb/acre killed 50 percent of bluegills. Where 0.25 lb/acre was used, both bluegills and blackbass were killed (2996). Post-larval brown shrimp about ½ inch long showed 100 percent mortality in less than 24 hours at concentrations of 25  $\mu$ g/l (2423). A spraying of 0.25 lb of heptachlor per acre killed 131 small game fish (3158). Twenty pounds of 10 percent heptachlor per acre were applied to a farm near a lake. A fish kill resulted, the young fish dying first. The few survivors were large and, except for shad and mosquite fish, thin (3184). A concentration of 0.033 mg/l killed mosquito larvae but did not injure trout (3184). The estimated concentration of heptachlor required to immobilize Daphnia magna in 50 hours at 20°C is 57.7 μg/l (3255).

## HETP

(see TEPP)

## HEXACHLORAN

(see Chlorinated Hydrocarbons-General)

## HEXACHLOROCYCLOHEXANE

(see Benzene Hexachloride)

## IPC

IPC has the chemical name isopropyl N-phenylcarbamate. Chloro IPC is a closely related chemical, the full name being isopropyl N-(3-chlorophenyl) carbamate. IPC is a selective pre-emergence herbicide, used at 2 to 5 pounds per acre which is then washed into soil. Its effect in soil is particularly strong on germinating grass seedlings (3005).

The acute oral LD₅₀ to rats is 1,000 mg/kg of body weight (3005, 3009). Chloro-IPC is less toxic, the acute oral LD₅₀ being 1,500 mg/kg (3005). The 96-hour TL_m value of IPC at 20°C for fingerling channel catish is reported at 86.5 mg/l (a 50% formulation) (2981). A concentration of 56 mg/l of a wettable formulation and 1.8 mg/l of an unnamed preparation of IPC caused mortalities of 40 percent among white crappies (3009).

## ISODRIN

(see also Aldrin, Chlorinated Hydrocarbons-General)

Isodrin is a common name for the insecticide 1,2,3,4,10, 10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-endo-endo dimethanonaphthalene (364). It is a stereoisomer of aldrin and is formulated as dusts, wettable powders, and emulsifiable concentrates. This crystalline compound according to Frear (2997) is no longer manufactured. The acute oral LD₅₀ values for rats have been reported as 7 to 42 mg/kg of body weight (2999, 3005, 3073). The acute oral LD₅₀ to rabbits lies between 5 and 7 mg/kg. The oral LD₅₀ for 7-day-old chicks is 2.7 mg/kg. Chronic feeding tests with chicks at 12 mg/kg in the diet produced 92.5 percent mortality in 7 weeks; but there was no mortality at a 6 mg/kg level for the same period (3005).

Adlung tested isodrin against guppies and goldfish at  $19-22^{\circ}$ C and found that 0.05 mg/l produced abnormal behavior in 4 hours, and killed the fish in 12 hours (3073). The  $TL_m$  values for several common species of fish has been given as 0.0025 mg/l for bluegill and golden shiners, and 0.0015 mg/l for goldfish (3005).

## **ISOLAN**

Isolan, a tradename of dimethyl 5-(1-isopropyl-3-methyl-pyrazolyl) carbamate, has an acute oral  $LD_{50}$  against male and female laboratory rats of 23 and 13 mg/kg respectively (2998, 2999).

Used against Mummichog killifish at 20-21°C, 1.0 mg/l caused loss of equilibrium within 30 minutes and 5 mg/l caused death in 15 minutes (3014).

## KARMEX

(see CMU, Diuron)

## KELTHANE

Kelthane is a tradename for the miticide 1,1-bis (p-chlorophenyl)-2,2,2-trichloroethanol. It is a solid with a melting point of 77-78°C. The acute oral toxicity to rats has been cited as 575 to 1100 mg/kg of body weight (364, 2992, 2997, 2999). Toxicity tests with guppies at temperatures of 21°C showed that a level of concentration of 0.5 mg/l caused abnormal behavior in 30 minutes, and killed the fish in 48 hours (2992).

## KURON

The chemical name of Kuron is 2-(2,4,5-trichlorophenoxy) propionic acid, propylene glycol butyl ether es-

ter. It is insoluble in water, and irritating to eyes and hands. It has an LD₅₀ to rats of 500 mg/kg of body weight (364).

The 48-hour  $TL_m$  value for chinook salmon at 20°C was 1.23 mg/l; the 24-hour  $TL_m$  value for largemouth bass was 3.5 mg/l. In open plot experiments, bass fingerlings were killed by a concentration of about 5 mg/l. Lawrence cites a safe concentration of 3 mg/l. Short term immersion tests with coho salmon after 15 and 30 minutes exposure to Kuron concentrations of 5 and 10 mg/l demonstrated no mortalities in a 24-hour period following removal (2988).

## LEAD ARSENATE

(see Chapter VI)

#### LINDANE

(see Benzene Hexachloride)

## MALATHION

C10H19O6PS2

- 1. General. Malathion (or malathon as it was originally called) is a generic name for S-(1,2-dicarbethoxyethyl)-0,0-dimethyldithiophosphate. It is a deep brownyellow liquid soluble in water to the extent of 145 mg/l. As an insecticide, it appears to be about 100 times less toxic to warm-blooded animals than parathion and two to four times less toxic to insects (364).
- 2. Cross References. Organic Phosphates-General, Parathion, EPN.
  - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The estimated fatal dose of malathion for a 70 kg man is 60 grams (2995).

b. Stock and Wildlife Watering. Acute oral LD₅₀ values to rats have been reported as 1000 to 2830 mg/kg of body weight (2999, 3002, 3074, 3142). Acute oral MLD concentrations of the 90 percent technical compound administered in vegetable oil were 885 mg/kg for male mice and 430 mg/kg for male rats. Male and female rats on chronic toxicity studies have satisfactorily tolerated 1,000 mg/kg in diets for six months (1536). A 99-percent pure material in vegetable oil had an LD₅₀ to male mice of 3321 mg/kg of body weight, and to male rats of 1845 mg/kg (3185). No effects were noted on rats fed 5000 mg/kg of diet for 63 consecutive days (3186).

The toxicity of malathion to livestock was investigated (3075). With sheep, 150 mg/kg of body weight was lethal, 100 mg/kg was toxic, and 50 mg/kg was nontoxic; with cattle 200 mg/kg was lethal, 100 mg/kg toxic, and 50 mg/kg non-toxic; and with calves, 20 mg/kg was toxic and 10 mg/kg was non-toxic. A marked synergistic effect of up to 50-fold exists for EPN and malathion when administered simultaneously to dogs (3027). The amounts of malathion that will produce at least a 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 400 and 1600 mg/kg of body weight respectively (2994, 2996).

The use of 0.1 lb/acre of malathion for mosquito larvaciding resulted in no ill effects to mammals, birds, reptiles, or amphibians (3112).

c. Fish and Other Aquatic Life. Toxicities of malathion to fish have been summarized in the following tabulation:

Concentration of Malathion mg/l	Tempera- ture °C.	Type of water	Type of fish	Results	Refer- ence
0.05 0.033 0.1 0.12 2.0 5.0 5.0 5.0 5.0 9.6 12.5 25.0 (25%) Malathion)	25 25 25 25 26	(5) (4) (2) & (3)	Gambusia Young salmon Salmon fingerlings Salmon fingerlings Guppies Bluegill Goldfish Rainbow trout Sunfish Yellow perch Red-sided shiners (6-7 cm long) Red-sided shiners (6-7 cm long) Fatheads Fatheads Catfish	40 percent killed24-hour TL_m	3008 3121 3008 3188 2992 3008 3008 3008 3011 3011 3000 3008

- Tap water from the University of Oklahoma, 4-gallon aquaria, 10 fingerling channel catâsh per tank, 100 or 200 fish per experiment.
   Hard water, pH 2.2, DO 8.0 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.
   Soft water, pH 7.4, DO 8.0 mg/l, alkalinity 18 mg/l, hardness 20 mg/l.
   Hard water, pH 8.2, DO 9 mg/l, alkalinity 116 mg/l, hardness 156 mg/l.
   Soft water, pH 7.6, DO 9 mg/l, alkalinity 36 mg/l, hardness 18 mg/l.

Malathion applications at the rate of 0.2-0.75 lb/acre in either granular or emulsion form gave an extensive kill of killifish. Rates of 0.2-0.25 lb/acre also gave complete kills (3156). At 0.5 lb/acre in tidal marshes 26 percent of killifish died in four hours, and 42 percent were sublethally poisoned (3008, 3189). Two lbs/acre resulted in a complete mortality of killifish (3048). Malathion at 21 pounds per acre allowed 95 percent survival of fathead minnows (3008). Gaufin (2699) quotes Anderson's report (3255) that the tolerance limits of Daphmagna in 48 or 64 hours is less than 0.9 μg/l.

Laboratory tests at concentrations of 0.0125 to 0.25 mg/l for 24 hours gave 100 percent kill of Psorophora. Applied as a preflood application to soil test plots, rates of 0.2, 0.4, and 0.5 lb/acre of granular formulation failed to give satisfactory control (3082).

The toxicity of malathion in hard water at 11.5°C was tested against several aquatic insects the results being reported as 96-hour TLm values in µg/l of active agent (2699). For Acroneuria pacifica the 96-hour TLm was 5.6 µg/l, for Pteronarcys californica 100 µg/l, Claassenia sabulosa 56 µg/l (all stoneflies), and Arctopsyche grandis 32 µg/l (a caddis fly).

## MCP

(see also TBA, 2,4-D, 2,4,5,-T)

This chemical, 2-methyl-4-chlorophenoxyacetic acid, is generally compounded along with other chemicals, the mixture resulting in a better herbicide than any one constituent would be by itself. Marini (1726) reports that pure MCP was not toxic to carp in a concentration of 130 mg/l; however, 650 mg/l of Agroxone (10 percent MCP) was lethel. Screening tests of a large number of compounds at a concentration of 5 mg/l in Lake Huron water at 12°C showed that MCP had no effect on trout, bluegill, or the sea lamprey in a 24-hour exposure (2976).

## MERCURIC COMPOUNDS

(see Chapter VI)

## METADICHLOROBENZENE

(see Chlorinated Benzenes)

## METASYSTOX

(see Systox, Organic Phosphates-General)

Metasystox is a mixture of 0,0-dimethyl 0-(2-ethylthio) ethyl phosphorothioate (A) and 0,0-dimethyl S-(2ethylthio) ethyl phosphorothioate (B). Both isomers are liquid in pure form, both are very slightly soluble in water but soluble in most organic solvents. The acute oral LD50 to rats of (A) is 180 mg/kg of body weight, and of (B) 40 mg/kg (2997). The oral LD50 to rats has also been cited as 138 mg/kg (2992).

By analogy with systox, it appears that the toxic action of metasystox would be due mainly to sulfoxide and sulfones of the thiolate produced metabolically in both plants and animals. Both isomers, however, also undergo reactions in water and on storage that yield small amounts of sulfonium compounds of very high intravenous toxicity. Oral toxicity is hardly affected (3190).

The toxicity of metasystox to guppies of 21°C has been studied (2992). A concentration of 5 mg/l caused abnormal behavior in 24-30 hours, death in 8-12 days.

## METHOXYCHLOR

 $C_{16}H_{15}Cl_3O_2$ 

- 1. General. This compound is slightly soluble in water, soluble in xylene, very soluble in alcohol. Sodium and dimethylamine salts are freely soluble in water (2997). Methoxychlor has lower toxicity to warmblooded animals than DDT and little accumulation in animal tissue. Concentrations used for sprays or dips usually range from 0.5-1.5 percent. When sprayed on crops dosages of 1 to 3 lbs/acre are required. Dusts and wettable powders are the preferred formulation.
- 2. Cross References. DDT, Chlorinated Hydrocarbons.
  - 3. Effects Upon Beneficial Uses.
- The estimated fatal a. Domestic Water Supplies. dose of methoxychlor for a 70 kg man is 350 grams (2995).
- b. Stock and Wildlife Watering. The oral LD50 to rats has been reported as 5000-7000 mg/kg of body weight (3002, 3003, 3005, 3055, 3056, 3073). Chronic oral toxicity to rats fed daily for 2 years was 10 mg/kg of body weight (3003). The amount of methoxychlor that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle, are 22,000 and 25,000 mg/kg of body weight respectively (2994, 2996). Oral feeding of 1000 mg/kg in the diet will cause a 40 percent or more decrease in the reproduction of quail (2996). Cows eating alfalfa hay with a residue of 14 mg/kg of methoxychlor showed no toxic effects (3005). Methoxychlor in oil applied at 2 lbs/acre did not adversely affect terrestrial vertebrates (3005).
- c. Fish and Other Aquatic Life. The toxicities of methoxychlor to various fish as noted from the literature are summarized in the following table:

of Me	centration thoxychlor mg/l	Temperature °C	Type of Water	Type of Fish	Results	D. e.
(	0.025			Bluegill	A few survived	Reference
C	0.03			fingerlings Bluegill	Toxicity threshold	3007 3007
	.035	25	(1)	fingeriings Fatheads	96-hour TLm	
	.05	:		Bluegill fingerlings	All died	3000 3007
	.056	25	(2)	Goldfish	OC home mr	
	.062	25	(2)	Bluegills	96-hour TLm	3000
	.063		(2)		96-hour TLm	3000
0	.064	25	$(\overline{2})$	Goldfish	TL _m	3005
0.	.120	25		Fatheads	96-hour TLm	3000
	.125	20	(2)	Guppies	96-hour TLm	3000
	.2		4==	Goldfish	90% killed	3005
-		<del></del>	(3)	Large	Killed	681
				bluegills	77/1× 4	_
0.	250			Bass	Killed	681
1.	0	19-22		Goldfish	100% killed	3005
		TO-02		Guppies	Distress in 30 min.	3073
(1) H	ard water	nu ce no e		Goldfish	Death in 14 hours	3073

Hard water, pH 8.2, D0 8 mg/1, alkalinity 360 mg/1, hardness 400 mg/1.
 Soft water, pH 7.4, D0 3 mg/1, alkalinity 18 mg/1, hardness 20 mg/1.
 Outdoor ponds, some of loss may have been due to DDT (3005).

Methoxychlor in oil applied at 2 lbs/acre killed all sunfish in a small pool within 24 hours. Black bullheads although slightly more resistant were also killed. Some catfish were killed but the entire population was not removed (3005). Clemens and Sneed (2981) subjected a mixture of 3 percent lindane and 50 percent methoxychlor to a toxicity test using fingerling channel catfish at 19°C. The 48-hour TL_m to this formulation was 1.0

The estimated concentration of methoxychlor required to immobilize Daphnia magna in 50 hours at 20°C is 3.6  $\mu g/I (3255)$ .

## METHYL PARATHION

(see Parathion, Phosdrin, TEPP)

Methyl parathion, 0,0-dimethyl-0-p-nitrophenyl thiophosphate, is an organo-phosphorus similar in physiological action to parathion, Phosdrin, and TEPP, and has about the same toxicity (3191, 3192). The half-life of methyl parathion on cotton leaves is less than one hour (3180). The estimated fatal dose for a 70 kg man is 0.15 grams (2995). Methyl parathion has an acute oral  ${
m LD_{50}}$ for rats of 9 to 25 mg/kg of body weight (2999, 3191). Sublethal doses of methyl parathion lower cholinesterase levels. Methyl parathion at 50 mg/kg in the diet of dogs induced significant depression in plasma and erythrocyte cholinesterase, and at 20 mg/kg induced significant depression of erythrocyte and questionable depression of plasma (3076, 3191).

The 96-hour TL_m values of methyl parathion to fathead minnows in hard and soft waters were at 25°C determined respectively as 7.5 and 8.3 mg/l of active ingredient (3000).

## MONOCHLOROBENZENE

(see Chlorinated Benzenes)

## MONURON

(see CMU)

## MUSCATOX

(See Co-Ral)

## NABAM

C₄H₆N₂Na₂S₄

Nabam, disodium ethylene bis dithiocarbamate, is a fungicide used for vegetables, ornamentals, and tobacco. It is described as being moderately toxic, the acute oral

LD₅₀ for rats being 395 mg/kg of body weight (364, 3009, 3056, 3067). However, in a discussion of bivalve larvae as a bioassay tool, Woelke notes that the lethal concentration of Nabam was 0.50 mg/l (2989).

## NEOMYCIN

(see Antibiotics)

## NEOTRAN

 $C_{13}H_2Cl_2O_2$ 

Neotran, bis (p-chlorophenoxy) methane, is a proprietary product containing 40 percent of the active chemical. It is a solid, insoluble in water and oils but soluble in ether and acetone. Neotran is used as a persistent acaricide and ovicide. There is no record of harm stemming from the use of Neotran. The acute oral  $\mathrm{LD}_{50}$  to rats is 5,800 mg/kg of body weight. Rats on a diet containing 1,000 mg/kg of the pure chemical in food showed no effects after 50 days; 3,000 mg/kg produced a pronounced histopathology (3005).

Surber (3007) reported that 0.2 mg/l killed all bluegills at 17.5°C. According to Clemens and Sneed (2981) the 96-hour TLm for fingerling channel catfish at 19°C was 21.8 mg/l.

## NICOTINE

 $C_{10}H_{14}N_2$ 

- 1. General. This agricultural insecticide is commonly used in the U.S. as a 40-percent solution of nicotine sulfate (Black Leaf 40). It is a pale-yellow oily liquid, highly miscible with water below 60°C (364). Nicotine is available in low-percentage sprays and dusts. Nicotine alkaloid presents no residue problem because it is highly volatile; the sulfate, however, offers some residue hazard
  - 2. Cross References. Pyrethrum, Rotenone.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. Rapidly poisonous to man and animal, as well as insects, nicotine has a minimum lethal oral dose for man of 40 mg (364) to 60 mg (677). According to Smith (922), adults may safely drink daily one-half gallon of water containing 10 mg/l of nicotine (about 19 mg) but over 1 gallon per day would be fatal. The lethal oral dose for most animals is about 10 mg/kg of body weight.

b. Irrigation Water. Being of plant origin, nicotine is not phytotoxic (677); consequently, its pollution of irrigation water should not be detrimental.

c. Stock and Wildlife Watering. The acute oral  $\mathrm{LD}_{50}$ of nicotine to laboratory rats is 55.2 mg/kg of body weight (3002), of nicotine sulfate to female rats, 83

mg/kg (2999)

d. Fish and Other Aquatic Life. The toxicity of nicotine increases with the nervous complexity of the aquatic species. Since it is less toxic to mosquito larvae than to fish, it is not used as a larvicide. The toxicity of nicotine to fish is evident in concentrations of 3 to 29 mg/l and is greater in alkaline than acid solutions. Fish can endure weak solutions for many days (3005).

## OCTA - KLOR

(see Chlordane)

## **OMAZENE**

The toxicity of omazene (copper dihydrazinium sulfate) has been studied with chinook salmon. The 48-hour  $TL_m$  value at 20°C was 0.83 mg/l. A concentration of 1.8 mg/l killed all salmon in 48 hours (2988).

#### OMPA

(see Schradan)

## ORGANIC PHOSPHATES - GENERAL

(see also TEPP, Guthion, Parathion, Para-oxon, Malathion, EPN, Systox, Metasystox, Dipterex, Chlorthion, Co-Ral, Diazinon, Dicapthon, Di-Syston)

The organic phosphorus compounds vary greatly in toxicity to different species of organisms, e.g., Delnab is 940 times more toxic to bluegills than to goldfish, and malathion is 500 times more toxic to salmon and 250 times more toxic to bluegills than it is to fathead minnows (3259). The *in vivo* inactivation of fish brain acetylcholinesterase by organic phosphorus insecticides has been studied as a means of assaying water for previous or concurrent pollution by these compounds (3030). This test was remarkably demonstrative of the synergistic effect of malathion and EPN in combination. As a group, the organic phosphates have been rejected as fish poisons since they are not toxic enough (3260).

The Russians have published water quality studies on two organic phosphate insecticides, metaphos and thiophos. Although these compounds are not likely to be used in the U. S., some aspects of this work may be of interest to water pollution control workers. The recommended limit in water for metaphos is 0.02 mg/l. The lowest concentration detectable by odor is 0.02-0.05mg/l. A concentration of 1 mg/l hinders nitrification and 20 mg/l hinders BOD (3261). Thiophos (NIUIF-100) has an odor perception threshold of 1 to 5 μg/l, and a taste threshold of 20-125 μg/l. Feeding of 0.01 and 0.0005 mg/l/kg body weight to rabbits and rats did not result in toxic symptoms. Concentrations of 50 mg/l do not affect pH, oxygen content, or BOD, although some bacteriostatic activity is evident during the first days (3262).

The acute oral toxicities of various organic phosphate insecticides noted in the literature are summed in the following table:

Name of Chemical	Concentration mg/kg	Animal	Result	Reference
American Cyanami	1 25	Calves	Toxic	3075
4124	5	Calves	Non-texic	3075
American Cyanamic	10	Sheep	Lethal	3075
12009	5	Sheep	Toxic	3075
Bayer	211	Male rats	LD ₅₀	2999
29493	245	Female rats	LD50	2999
DOW ET-14	100	Sheep	Non-toxic	3075
24//	100	Calves	Toxic	3075
	50	Calves	Non-toxic	3075
DOW ET-15	100	Sheep	Non-texic	3075
2011 22 20	100	Cattle	Toxic	3075
	25	Calves	Toxic	3075
DOW ET-57	400	Sheep	Toxie	3075
(Ronnel or	100	Sheep	Non-toxic	3075
Trolene)	125	Cattle	Toxic	3075
2. 0.000,	100	Cattle	Non-toxic	3075
	310	Lamb	Injured	2809
	1250	Male rats	$LD_{50}$	2999
	2630	Female rats	LDso	2999
	1750	Male rats	LD50	3263
	3140	Male guinea pigs	LD50	3263
	640	Rabbits	LD50	3263
	2140	Female mice	LD50	3263
	500	Dogs	LDsc	3263
	5000	Ducks	LD ₅₀	3263
	5000	Chickens	$LD_{50}$	3263
,	500	Turkeys	$LD_{50}$	3263
(For toxicities of	mixtures of	Ronnel with other	erganic phosphates,	
Geigy 25039	25	Sheep	Non-texic	3075
	25	Calves	Non-toxic	3075

In chronic toxicity studies of Ronnel, no morphological changes resulted from long-term feeding of rats at 15 mg/kg/day or in dogs at 25 mg/kg/day (3263).

The effects of several Dow Chemical Company organic phosphate formulations on various aquatic life forms are

summarized as follows:

Result Lethal 100% kill in 24 hours Lethal Inhibited	_ 2989 _ 2986 _ 2986 _ 2986 _ 2986 _ 2986
	ethal 00% kill in 24 hour: ethal inhibited inhibited inhibited inhibited inhibited

## ORTHO AQUATIC WEED KILLER

(see Aromatic Solvents)

## ORTHOCIDE

(see Captan)

## ORTHODICHLOROBENZENE

(see Chlorinated Benzenes)

## OVOTRAN

 $\mathrm{C_{12}H_8Cl_2O_3S}$ 

Ovotran is a white solid, soluble in acetone and aromatic solvents, and moderately soluble in alcohol and oils. It is insoluble in water and is designated as p-chlorophenyl-p-chlorobenzene sulfonate (2997, 2998).

Ovotran has a pronounced residual ovicidal action. It may be considered nonhazardous to warm-blooded animals. The acute oral LD₅₀ to rats of the active material is about 2,000 mg/kg (2992, 3005). Minimal liver damage appeared at 1,000 mg/kg in the diet, and at 10,000 mg/kg adverse growth and pronounced liver and kidney damage were manifest (3005).

Ovotran at 10 mg/l and 21°C caused injury to gup-

pies in 2 hours and death in 5 hours (2992).

## PARADICHLOROBENZENE

(see Chlorinated Benzenes)

## PARA - OXON

(see also Parathion)

Para-oxon is an oxygen analog of parathion. It is designated 0,0-diethyl 0-p-nitrophenyl phosphate. This brown liquid is soluble in most organic solvents and of low solubility in water and oils. The acute oral LD₅₀ to rats is 3.5 mg/kg of body weight (2997).

In soft water, the 96-hour TL_m to fathead minnows at 25°C was 0.33 mg/l; in hard water it was 0.25 mg/l

(3000).

## PARATHION

 $C_{10}H_{14}O_5$  NPS

1. General. Parathion, 0,0-diethyl-0-p-nitrophenyl thiophosphate, is a phosphate ester insecticide. It is a yellow liquid, freely soluble in alcohols and aromatic hydrocarbons, but insoluble (20 mg/l) in water or kerosene. Parathion is incompatible with any substance having a pH higher than 7.5 (364). Parathion is most commonly applied to row and orchard crops (3005).

It has been noted that the chronic hazard from parathion appears slight. Among other reasons, residues disappear quickly (3005). However, Hayes (3193) reports a case of parathion poisoning in a child that demonstrated the persistence of parathion in soil. The child had eaten some of the soil which still contained nearly one percent of parathion six months after the insecticide had been spilled. Another illustration of the persistence of parathion is mentioned by Nicholson (3086). Parathion contamination of pond water, 0.02 µg/l, and mud, 1.9 mg/l, was found in the spring before any use of parathion that year. The contamination probably occurred in March the previous year during a period of accelerated soil erosion when orchard soil apparently washed into the pond.

- 2. Cross References. Organic Phosphates—General, Para-Oxon, Methyl Parathion.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The estimated fatal dose of parathion for a 70 kg man is 0.1 gram (2995). Absorption of 5 mg of parathion will produce symptoms, and minor physiologic response can be expected from even smaller doses if repeated. Such absorption can possibly come from a water supply that received a strong spray load or waste water from the cleaning of parathion-contaminated equipment (3194).
- b. Stock and Wildlife Watering. The acute oral LD₅₀ of parathion to rats has been cited as 3 to 15 mg/kg of body weight (2992, 2999, 3002, 3142, 3143, 3195). There is considerable difference in species and sex susceptibility. The extreme LD₅₀ range seems to be 2 to 30 mg/kg. Rats fed diets containing parathion up to 100 mg/kg in their diet showed normal weight gains, survival, and food consumption (3005). At 10 to 20 mg/kg, second generation rats produced many dead in their litters (3186).

Cattle fed alfalfa contaminated at the excessive value of 14 mg/kg of feed showed no adverse effects (3005). Studies of parathion oral toxicity to steers showed 75 mg/kg to be lethal, 50 mg/kg toxic, and 25 mg/kg nontoxic; with calves, 1.5 mg/kg was lethal, 0.5 mg/kg toxic, and 0.25 mg/kg non-toxic; and with sheep, 20 mg/kg was lethal, and 10 mg/kg non-toxic (3075).

As little parathion as 1 mg/kg in the diet of dogs causes significant plasma cholinesterase inhibition, 2 mg/kg causes erythrocyte enzyme inhibition (3196). The use of 0.05 lb/acre for mosquito larvaciding resulted in no ill effects to mammals or birds (3112).

c. Fish and Aquatic Life. Numerous reports of the toxic effects of parathion on fish have been summarized as follows:

Concentration of Parathion mg/l	Temperature °C	Type of Fish	Results	Defense
0.01		Trout		Reference
0.04			Not toxic	3164
0.063		Bluegills	Heavy mortality	8005
		Bluegills	Killed	3058
0.19	18	Bluegills	75% died	
		2.7" long	70 70 2202	3007
0.2 (powder)	18	Bluegills I" long	33% died	3007
0.2	13	T TOOK		
0.20	19	Bluegills	Several died	3007
0.38		Bluegills	Toxicity threshold	679, 3007, 3048
9.00		Rainbow	Survived	3005
0.00		trout		9903
0.38		Brook trout	Survived	3005
0.4	13	Bluegills 2.7" long	67% died	3007

Concentration of Parathion mg/l 0.5	Temperature °C 21	Type of Fish Guppies	Results Distress in 1 hour,	Reference 2992
1.0	_	Brook	death in several days No damage	3165
1.0		trout Rainbow	No damage	3165
1.5 2.0		trout Goldfish Goldfish	TLm All died	3005 8005

Tests of parathion no. 1 (99 percent active ingredient) and parathion no. 2 (96.5 percent active ingredient) were made with fathead minnows in hard and soft water at 25°C. For parathion no. 1, the 96-hour TL_m in hard water was 1.6 mg/l of active ingredient, and in soft water 1.4 mg/l. For parathion no. 2, the corresponding values were 3.6 and 2.7 mg/l (3000).

The tolerance limits of Daphnia magna to parathion for 48 to 64 hours is less than 0.8 µg/l (2699, 3255). Concentrations of 0.5 and 1.0 mg/l applied for 5 minutes eliminated all black-fly larvae in 1.6 miles of slowly moving water. A 24-minute application failed to control an area 2-3 miles downstream (3197). Parathion at concentrations of 0.01 to 0.1 mg/l controlled Aedes spp., and 0.5 mg/l controlled Psorophora (2931).

The concentration of parathion necessary to kill 50 percent of *Chironomus* larvae in eight hours is 0.008 mg/l (2531). The 96-hour  $TL_m$  values at 11.5°C, based on active ingredient, were *Acroneuria pacifica* 0.1  $\mu$ g/l, and *Pteronarcys californica* 3.2  $\mu$ g/l; and for the caddis fly, 1  $\mu$ g/l (2699).

The use of 0.05 lb/acre of parathion for mosquito larvaciding killed frogs (3112). A concentration of 0.325 mg/l of parathion killed all Lymnaeid snails in a 24-hour exposure (2993). The TL_m values for brine shrimp at a 5-hour exposure was 0.320 mg/l for the larva and 0.430 mg/l for the adult (3128).

A concluding test that expresses no finite values may be worth citing. Goldfish and Japanese killifish kept one month in a concentration of one-thirtieth of the 48-hour TL_m experienced retarded growth and consumed less food. The study concludes that the arbitrary concentration of one-tenth the 48-hour TL_m sometimes used as a limiting value is too toxic (3198).

#### PARIS GREEN

 $3\mathrm{Cu}(\mathrm{AsO_2})_2 \cdot \mathrm{Cu}(\mathrm{C_2H_3O_2})_2$ 

Paris green, copper aceto-arsenate, has been reported to have  $\mathrm{LD}_{50}$  values to rats of 21.9 mg/kg of body weight (3002) and 100 mg/kg (females) (2999). A dose of 1.5 lb/acre is effective against the mosquito larvae Aedes, Psorophora, and Culex. A few dead tadpoles were also observed. Paris green does not persist in water (3199).

#### PENICILLIN

(see Antibiotics)

## PENTACHLOROPHENOL AND PENTACHLOROPHENATES

C₆Cl₅OH

1. General. Pentachlorophenol is a crystalline material that is almost insoluble in water but freely soluble in alcohol, ether, and benzene. Its sodium salt, however, is highly soluble in water. Pentachlorophenol, also known as Penta, possesses bactericidal, herbicidal, insecticidal,

fungicidal and molluscacidal properties (364). Its toxicity is strongly conditioned by the vehicle in which it is administered. The sodium salt is much less toxic than pentachlorophenol (3005).

2. Cross References. Acrolein, Phenol, Halogenated Phenols.

3. Effects Upon Beneficial Uses.

- a. Domestic Water Supplies. Concentrated doses cause lung, liver, and kidney damage (364). Two fatal cases among foresters have been reported (3200). According to Gelfand (971), the smallest lethal dose of sodium pentachlorophenate taken internally for a 70-kg man is estimated to be 18 grams. Contact with solutions stronger than 1.0 percent produces dermatitis (3005).
- b. Industrial Water Supplies. Turner et al. (976) report that a concentration of 1.0 mg/l of sodium pentachlorophenate in sea water prevented entirely the attachment of marine fouling organisms in pipe and conduit.
- c. Stock and Wildlife Watering. The acute oral LD₅₀ of undiluted Penta to laboratory rats has been cited as 78 mg/kg of body weight (3002, 3005, 3009). The oral LD₅₀ of 5 percent Penta in fuel oil is 27.3 mg/kg, and of a 2 percent aqueous solution of sodium pentachlorophenate 210.6 mg/kg (3005). Chronic toxicity of Penta is not serious because it is rapidly eliminated from the body. Rats and dogs fed for 3 or 4 months on daily amounts up to 10 mg per animal showed no fatalities (3005).

To determine if these substances might harm livestock drinking treated waters, calves were fed drinking water as follows: calf A received water containing 60 mg/l of sodium pentachlorophenate for seven weeks, calf B received water with 51 mg/l of copper pentachlorophenate for five weeks, and calf C got 46.5 mg/l of pentabromophenol for six weeks. Postmortem examinations of all calves showed no significant changes except for slight enteritis. Such exposure did not affect the taste or quality of the meat. It was concluded that these chemicals have an adequate margin of safety toward livestock when used as molluscacides (1631).

A rhesus monkey was given 200 ml of water containing 20 mg/l of sodium pentachlorophenate without symptoms of toxicity, and a calf drank 40 gallons of such water over a period of four days without ill effect (1631).

Penta apparently is repellent to animals. Livestock avoided treated pasture and in general showed no effects from exposure to Penta (3005).

d. Fish and Other Aquatic Life. As a result of his studies of 19 varieties of fish in open jars, Goodknight (247, 973) showed that 0.2 to 0.6 mg/l of sodium pentachlorophenate and pentachlorophenol was lethal to fish. Between 9° and 24°C, temperature was not a factor but toxicity increased at pH values lower than 6.6. Another paper cites the 24-hour TL_m value for sodium pentachlorophenate to fathead minnows as being between 0.32 and 0.35 mg/l. All fish were killed at 0.4 mg/l. As the pH was lowered and as the temperature was raised the solution became more toxic (3201).

Sodium pentachlorophenate caused losses of white crappies at concentrations of 0.056-0.075 mg/l in laboratory tests and of guppies at 1 mg/l in field trials. A 9.5 mg/l concentration killed catfish, guppies, and eels in a small creek, but crayfish appeared unharmed. Guppies returned 24 hours after application (3009).

Van Horn (974) reports the survival times of several fish in solutions containing Santobrite, a commercial sodium pentachlorophenate. A concentration of 5 mg/l allowed fish to live from 16 to 21 minutes, 1 mg/l from 74 to 87 minutes, and 0.4 mg/l from 234 to 418 minutes. Fish used in his test are described as steel-colored minnows, blunt-nosed minnows, and Lake Emerald shiners. The limits of tolerance of fingerling channel catfish to sodium pentachlorophenate at 25° C were studied by Clemens and Sneed (2981). The 96-hour LD50 was reported as 0.46 ppm by volume.

Santobrite was tested against the bluegill in carbonfiltered, Philadelphia tap water at 20°C. The 48-hour  $TL_m$  value was 0.35 mg/l, and the safe concentration 0.10 mg/l (2093).

Fleming (210) reports that 0.2 mg/l of sodium pentachlorophenate is toxic to fish. Invertebrates such as Daphnia are less sensitive than fish and nearly all such organisms can survive concentrations of 5 mg/l. An 88percent solution of sodium pentachlorophenate in a dilution of 1:400,000 affected a 100-percent kill in 24 hours to Lymnaeid snails (2993). According to Berry et al. (975), sodium and copper pentachlorophenates at concentrations of 10 mg/l killed 95 to 100 percent of snails (Australorbis glabratus). In a flowing stream the addition of 9.5 mg/l of sodium pentachlorophenate destroyed all snails for 1.5 miles downstream. In Egyptian irrigation waters, concentrations of 15 to 20 mg/l of sodium pentachlorophenate were necessary to control molluscan schistosome vectors. In these field studies, sodium pentachlorophenate was toxic to centrachid fishes at 6 mg/l. Violent reactions began in 10 to 20 minutes after application. Catfish were also affected but surfaced only after the majority of other fish had succumbed. No ill effects were reported by persons who collected and ate considerable quantities of the fish. Some aquatic insects were killed in water treated at 15 mg/l but on no occasion was the arthropod population depleted. There was no serious damage to aquatic plants (3005). Santobrite at 1 mg/l killed 94 percent of Australorbis snails in 48 hours, 2.5 mg/l killed 100 percent (2042).

According to Hirsch (972), a concentration of 5.0 mg/l of Santobrite retards the growth of water hyacinth without harming aquatic organisms, but a concentration of 80 mg/l is required for complete elimination of water hyacinth. Pentachlorophenol at 2.66 mg/l eliminated all photosynthesis by kelp (Macrocystis pyrifera) in 4 days and gave weak, flaccid blades. A concentration of 1.0 mg/l eliminated photosynthesis in 48 hours (2867). These studies also utilized the commercial product Santobrite. The concentration causing 50-percent inactivation of photosynthesis in bottom kelp fronds during a fourday exposure had been reported as 0.3 mg/l (2106).

A solution of 75 percent pentachlorophenate plus sodium salts of other phenols at a concentration of 2.0 mg/l in a 21-day laboratory incubation test at 22°C inhibited 50 percent of the test algae. Sodium pentachlorophenate at 75 percent plus sodium salts of other phenols at 13 percent at the same concentration inhibited 17 percent of the test algae (2041). The growth of algae in filtered

water from a spray pond was prevented by 15 mg/l of sodium pentachlorophenate, and in a pond containing living algae all growth was stopped in seven days (971). Algae stopped growing immediately in water containing a concentration of 20 mg/l. Horn and Balch (2986) studied the inhibiting concentration of Santobrite towards a number of organisms. Temperature, time. DO. pH, and alkalinity are given in the paper. The inhibiting concentration for Aerobacter aerogenes was 225.0 mg/l; Bacillus mycoides 4.0 mg/l; Aspergillis niger 35.0 mg/l; Pencillium expansum 30.0 mg/l; and for the fish Notropis atherinoides 0.2 mg/l was the MLD.

## PERTHANE

C18H20Cl2

This crystalline compound, designated as 1,1-dichloro-2,2-bis (p-ethylphenyl)-ethane, is soluble in acetone and petroleum oils. The acute oral LD50 to rats has been cited as 8,200 mg/kg of body weight (364, 2997), and 8,500 mg/kg (2992). The amount of perthane that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle is 9,000 and greater than 9,000 mg/kg respectively (2994, 2996). At a temperature of 21°C, a concentration of 0.1 mg/l distressed guppies in 4 days and killed them in 5 days (2992).

## PHENYLDIMETHYLUREA

(see Fenuron)

## PHOSDRIN

(see also Organic Phosphates-General, Parathion, Methyl Parathion, TEPP)

Phosdrin is designated as 2-carbomethoxy-1-methylvinyldimethyl phosphate. The commercial product is a liquid miscible in water, benzene, and acetone (364, 2997, 3202). The acute oral LD50 to laboratory rats has been cited as 6 to 13.1 mg/kg of body weight (2999, 3002, 3142, 3202). The amount of Phosdrin that will produce at least 50 percent mortality in bobwhite quail considering all stages of the life cycle is 90 mg/kg (2994, 2996). The physiological action of Phosdrin is similar to that of parathion and TEPP (3203). Chronic studies with rats show 100-200 mg/kg in the diet to be lethal

Concentrations of phosdrin of 0.25 mg/l controlled the mosquito larvae Psorophora (2931). Concentrations of 0.05 mg/l destroyed trout. Even 0.01 mg/l for 180 hours caused symptoms of poisoning (3165).

## **PHYGON**

(see Dichloronaphthoquinone)

### POLYMYXIN B

(see Antibiotics)

### PRO - NOXFISH

(see Rotenone, Sulfox-Cide)

## **PYRETHRUM**

1. General. This insecticide is a combination of pyrethrin compounds obtained from the dried flower heads of Chrysanthemum cinerariaefolium (364, 677).

The ground pyrethrum flowers containing between 0.5 and 3.0 percent of active ingredients may be used directly as insect powder, or the pyrethrins and cinerins may be extracted in kerosene and concentrated. In commercial preparations, various synergists and activators are added to enhance the insecticidal activity of pyrethrum formulations (3005).

2. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The estimated fatal dose for a 70 kg man is  $\hat{50}$  grams. Allethrin, the allyl homolgue of cinerin I, is even less toxic (2995). Pyrethrins have been used as anthelminthics.

b. Stock and Wildlife Watering. The acute oral LD₅₀ of pyrethrum to rats has been cited as 200 mg/kg of body weight (2992, 3003). That of allethrin has been cited as 680 mg/kg (3002), and 920 mg/kg (3005). The chronic oral toxicity to rats fed daily for two years is cited as 250 mg/kg of body weight (3003). Neither rats nor their offspring suffered from intake of 0.2 percent in their diet for 24 weeks (3005). The acute oral  $LD_{50}$ of the cyclopentenyl analogue of allethrin to rats ranges from 1,400 to 2,800 mg/kg of body weight and is less toxic in dilutions (3005).

c. Fish and Other Aquatic Life. The toxic effects of pyrethrum against carp begin at 2 mg/l. The median lethal limit is between 5 and 10 mg/l (2977). In a test at 21°C, a level of 1 mg/l caused distress in guppies in 20 minutes and death in five hours (2992). Fish were poisoned at a water works in Germany by water containing up to 20 mg/l of pyrethrum (about 0.2 mg/l of pyrethrins). Thereafter, aquarium experiments showed that 2.0 mg/l affected movements of carp and 5 to 10 mg/l caused paralysis and death (313, 754). According to Ginsburg (756), pyrethrum in an insecticide spray does not remain toxic after 48 hours. Fish are more sensitive to pyrethrum in an emulsifiable formulation. At 0.33 mg/l, death occurred in 3 or 4 hours; at 10 to 20 mg/l death occurred in 15 to 20 minutes. Rainbow trout were distressed by concentrations of 0.1 mg/l in Alaskan streams (3005).

Turner (2612) notes that 0.005 mg/l of pyrethrum will destroy the crustacean Asellus aquaticus in water distribution systems. Another report notes that the concentration is not critical, anything between 0.0001 and 0.1 mg/l would be effective. This report cites the use of a concentration of pyrethrum of 0.01 mg/l as eliminating Asellus from water mains, and notes that this level was not injurious to humans (3204).

(see Rosin Amine Compounds)

#### RADS

(see Rosin Amine Compounds)

## RHOTHANE

(see DDD)

#### RONNEL

(see Organic Phosphates—General)

## ROSIN AMINE COMPOUNDS

1. General. Several rosin amine compounds have been used as algicides. Delrad is a proprietary name of rosin amine D acetate, also known as RADA or dehydroabietylamine acetate. Other rosin amines include rosin amine D sulfate or RADS, rosin amine D pentachlorophenate, sodium carboxyethyl rosin amine, and N(3aminopropyl) rosin amine D diacetate. Different formulations are available, i.e., Delrad 50 S is a liquid form, and Delrad 70 is a paste form.

2. Effects Upon Beneficial Uses.

a. Irrigation Waters. RADA at a concentration of 66.3 mg/l in irrigation water did not injure tomatoes but did injure cotton after 41 days (3084).

The acute oral  $LD_{50}$ b. Stock and Wildlife Watering. value of Delrad to laboratory rats is 850 mg/kg of body

weight (3009).

c. Fish and Other Aquatic Life. Springer notes that Delrad is toxic to various fish species at 0.4-0.7 mg/l, although two to four applications at 0.25 mg/l during the bass and bluegill spawning seasons had no effect on production of young. Fish-food organisms, unaffected in the spring, were reduced in number during the summer (3009). As many as three applications at 0.3 mg/l in bass brood ponds did not affect spawning of bass, hatching of eggs, or survival of fry and fingerlings (3264). Short-term exposures of coho salmon, viz 15 and 30 minutes to 0.5 and 1.0 mg Delrad/liter, had no effect for 24 hours (2988).

Eipper (3094) has published the results of extensive field application of Delrad to various ponds on fish, algae, and other aquatic plants (3094). Results of other tests of rosin amine compounds on fish are as follows:

Concentration mg/l*	Test Conditio	Type of ns Fish	Results	Reference
0.16 (RADS) 0.23	(3) (2)	Fatheads Fatheads	96-hour TL _m 96-hour TL _m	2987 2987
0.50	(4)	Trout	No deleterious effect MLC**	3095 3264
0.65 0.65		Bluegills Bass	MLC**	3264
0.67	(1)	Catfish	96-hour TL _m	2981

Four rosin amine compounds were screened for effectiveness against the sea lamprey, rainbow trout, and bluegill sunfish at 13°C. The following results were - 4-3 (9076)

noted (2976):			
Con	centrati	on	
Compound	mg/l	Animal	Result
Rosin amine D	5	Trout	Killed in 4 hours
	5	Bluegill	Killed in 6 hours
	5	Lamprey	Killed in 9 hours
Rosin amine D	5	Trout	Killed in 2 hours
acetate, 70 % paste	5	Bluegill	Killed in 3 hours
2002201, 70 70 2	5	Lamprey	Killed in 12 hours
N (3-aminopropyl)	5	Trout	Killed in 2 hours
rosin amine	5	Bluegill	Killed in 8 hours
D diacetate	5	Lamprey	Killed in 12 hours
Rosin amine D	5	Trout	Killed in 1 hour
pentachlorophenate	5	Bluegill	Killed in 2 hours
pontacino	5	Lamprey	Killed in 4 hours
	1	Trout	Survived 24 hours
	1	Bluegill	Killed in 12 hours
*	1	Lamprey	Survived 24 hours
	0.1	Trout	Survived 24 hours
	0.1	Bluegill	Survived 24 hours
	0.1	Lamprey	Survived 24 hours

Toxicity studies of a large number of rosin amine compounds against algae have been summarized in the following tabulation:

Compound	Concen- tration mg/l	Results	Refer- ence
RADA	2.0	Controlled 90% algae species	2987
RADA	0.25	Controlled 20% algae species	2987
RADS	2.0	Controlled 70% algae species	2987
RADS	0.25	Controlled 13% algae species	2987
RADA	2.0	Inhibited 83% algae species.	2041
RADS, powder	2.0	Inhibited 100% algae species	2041
Diethanol RADA	2.0	Inhibited 83% algae species	2041
Emulsifiable RAD pentachloro-			İ
phenate	2.0	Inhibited 17% of algae species	2041
Sodium carboxyethyl rosin amine.	2.0	Inhibited 0% of algae species	2041
N(3-aminopropyl) rosin amine D	]		
diacetate	2.0	Inhibited 100% of algae species	2041
Delrad 70	0.25	Killed Ulothrix in 6 hours	3095
Delrad	0.25	Killed Pithophora	3264

Springer (3009) notes that although Delrad may be used to control certain pond algae at less than 0.5 mg/l, a concentration of 1.0 mg/l is toxic to small crustaceans (copepods).

## ROTENONE

 $C_{23}H_{22}O_6$ 

1. General. Normally obtained from the roots of Derris elliptica, rotenone is a white crystalline solid that is almost completely insoluble in water (0.17 mg/l at 18°C) but soluble in many organic solvents (364). Dried derris roots have an average rotenone content of about 5 percent. It is also found in some weeds in the eastern U. S. (362) and is widely used as a fish poison and insecticide. When exposed to air, rotenone undergoes decomposition to non-toxic substances. It is more effective than DDT against a few crop insects although historically rotenone is best known as a fish poison. Natives in all tropical regions of the world have employed this or similar plant poisons for centuries to obtain fish for food. As a tool in fish management, its use has expanded to such an extent that few fishery departments have failed to employ it in practical fish population control. The chief aim in such control is the improvement of sport fisheries (3005).

Since weathering breaks rotenone down rapidly, chronic effects appear to be unlikely. The main hazard concerns the contamination of water. Because of the extreme sensitivity of rotenone to fish and some small crustaceans, damage to these organisms will almost inevitably result from water pollution (3005).

- 2. Cross References. Toxaphene, Sulfoxide.
- 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. For humans, the lethal oral dose of rotenone has been estimated as 0.2 grams (364). It has been used for animals and humans as an anthelminthic.

Bonn and Holbert (3205) have reported on the effects of rotenone products in water supplies. Turbidity decreased and plankton and bacterial counts increased. The most important change was in taste and odor. A temporary taste and odor problem can result from the decomposition of the fish killed. However, laboratory tests showed that these conditions can be easily controlled (see also 3206). Another report describes the use of rotenone to eliminate fish from a water supply reservoir.

^{*} Rosin amine D acetate unless otherwise indicated.

** Minimum Lethal Concentration—approximate value.

(1) University of Oklahoma tap water, temperature 25°C, 4-gallon aquaria, 10 fingerling channel catfish per aquarium, 100 or 200 fish per experiment, Delrad 70.

(2) Soft water, pH 7.7, DO 8.0 mg/l, alkalinity 34 mg/l, hardness 37 mg/l, fish Pimephales

promelas.
(3) Soft water, pH 7.4, DO 7.5 mg/l, alkalinity 20 mg/l, hardness 23 mg/l, fish Pimephales

⁽⁴⁾ Hatchery water, brook trout fingerlings, temperature 10°C, total alkalinity 127 mg/l.

A safe and palatable water was produced by the water treatment plant, the finished water demonstrating no fish toxicity and a threshold odor number of one (3207).

The threshold odor values of various rotenone formulations have been reported (2984). For rotenone, it was 13.8 mg/l; cube powder, 30.6 mg/l; and for two formulations comprising rotenone, rotenoids, solvent, and emulsifier, 0.018 and 0.023 mg/l.

b. Stock and Wildlife Watering. The acute oral LD₅₀ to rats has been cited as 132 mg/kg of body weight (2992, 3208, 3209). The chronic oral toxicity to rats fed daily for two years is 0.25 mg/kg of body weight (3003). A level of 5 mg/kg in the diet produced necrosis of the liver (3215). Cattle were slightly affected by an acute dose of 18 mg/kg in the feed but pigs were killed by 3.7 mg/kg in four hours (3209). Livestock are ordinarily not harmed by drinking rotenone-treated water (3210).

Pro-Noxfish, a proprietary product containing 2.5 percent each of rotenone and sulfoxide (a synergist) was fed to rats in drinking water at a level of 100 mg/l for 70 weeks after which the average weight was less than that of controls. A similar formulation was exposed to light and air until no test for rotenone could be established, then was fed to rats in drinking water at a level of 100 mg/l for one year. A slight difference in weight was observed compared to controls (3211).

c. Fish and Aquatic Life. There is a great deal of information in the literature on the toxicity of rotenone and related products to various fish since rotenone has been used so extensively as a piscicide. It has been reported to persist for 5-6 days in the spring and 2-3 days in the summer. The rate of detoxification and hence the toxicity is proportional to the light energy (3215), alkalinity, temperature, ice cover (3068, 3215), pH, species of fish, time of exposure, depth of animals, volume of water (3212), turbidity, and vertical dissipation of the distribution of rotenone (2916). Other reports cite duration of toxicities of a maximum of five months but generally less than one month (606, 913, 3213, 3215).

Gersdorff's work of three decades ago compared the theoretical threshold of toxicity, i.e., the concentration just necessary to kill goldfish. For rotenone it was 0.125 mg/l, and for two derivatives, isorotenone-0.055 mg/l, and dihydrorotenone-0.005 mg/l (3214). Concentrations of 0.5 mg/l of powdered derris root (five-percent rotenone) killed bluegill, sunfish, sucker, shiners, stickleback, mud-minnow, and goldfish, but 0.25 mg/l was nontoxic (3212). Rotenone toxicity to small fish starts in the range 0.01 to 0.1 mg/l (2977). A summary of toxicities against different fish follows:

Concentration of Rotenone mg/l	Temperature °C	Type of Fish	Results	Reference
0.006 0.066 (cube root)		Fatheads Fatheads	96-hour TLm 96-hour TLm	3215 3215
0.1 0.2 0.2	21 13	Trout Trout Trout	Toxicity limit Death in 22 minutes Death in 100 minutes	2977 2197
0.25 (derris root) 0.4	21	Bluegills Trout	Toxicity threshold Death in 15 minutes	2197 3048 2197
0.4 0.47 *	13 25	Trout Catfish	Death in 70 minutes 96-hour TLm	2197 2981
0.5	21	Guppies	Distress in 30 minutes, death in 5 hours	2992

Cube powder, in tap water of the University of Oklahoma, 4-gallon aquaria, 10 finger-ling channel catfish per aquarium, 100 or 200 fish per experiment.

For more complete information the reader is referred to the work of Burdick (3212, 3216) and others (3218).

Rotenone is non-injurious to humans when eating fish killed by it (3210). However, Cohen et al. (3215) note that because of the peculiar injury of rotenone to the gills of fish it is doubtful that any significant amount would enter the fleshy part of the fish.

A variety of insects, crustacea, and snails were not affected by 0.05 mg/l of rotenone but 1.0 mg/l killed Chironomus larvae in one hour and 0.25 mg/l killed Daphnia in 1.5 to 4.0 hours (913). Powdered derris root at 2 mg/l greatly reduced numbers of Corethra (insects), Daphnia, and diaptomus (copepoda). Tadpoles, leeches, and dragonflies were also greatly affected by a first poisoning, but less so by a second poisoning. Phytoplankton were not affected (2613).

A concentration of derris root of 5 mg/l killed Daphnia in 1.5 hours while 2 mg/l killed snails after several days and Chironomus and Gammarus in several hours. However, older fly larvae and Hemiptera of the Corixidae family can sustain concentrations of 10 mg/l for 48 hours (2977).

An application of rotenone of 1 mg/l to a reservoir did not affect the chironomid population but oligochaetes showed an initial increase that soon became stable (3219).

## SANTOBRITE

(see Pentachlorophenol and Pentachlorophenates)

#### SARIN

(CH₃)₂CHOOPCH₃F

(see also Parathion, TEPP)

Sarin is one of the nerve gases, used as an insecticide, described as isopropoxymethyl phosphoryl fluoride or isopropyl methylphosphonofluoridate. It is the most toxic of the three nerve gases, Tabun, Saman, and Sarin. It is a liquid that is miscible with and hydrolyzed by water. The lethal dose to man may be as low as 0.01 mg/kg (364). At concentrations of 0.01 mg/l and a temperature of 24°C, the time in minutes for the LD₅₀ to minnows is 360, sunfish 320, and goldfish 2,000. At 1.0 mg/l, LD₅₀ times are 3.25, 5.8, and 7.5 minutes respectively. At 12°C and 1.0 mg/l, the values are 11.0, 14.0, and 19.0 minutes respectively (3290).

### SCHRADAN

- 1. General. Schradan is the accepted common name of a systemic insecticide also known as OMPA (octamethyl pyrophosphoramid). Applied to plants, it is absorbed and distributed to all parts, the plant sap thereby being rendered toxic. Normally it is used in water sprays at the rate of 1-2 lbs/acre (3005).
  - 2. Cross References. Parathion.
  - 3. Effects Upon Beneficial Uses.
- a. Irrigation Waters. Concentrations of Schradan of 10 and 100 mg/l in nutrient solution stimulated cotton plant growth, but 1000 mg/l was phytotoxic. However, all levels were antagonistic to fruiting activity and reduced yields of seed. Concentrations of chlorophyll and carotenoids in the leaves correlated with the concentration of Schradan in the nutrient solution (3220).
- b. Stock and Wildlife Watering. This compound is toxic in any form and by all routes of entry, being about

as toxic as parathion. The acute oral LD50 to rats has been cited as 9.1 to 42 mg/kg of body weight (2999, 3002, 3005). Male and female rats fed diets of 50 mg/kg of feed showed signs of poisoning and diminished growth in the males but not the females. Although cholinesterase was not affected greatly even in the rats with retarded growth, some inhibition was noted as low as the 1 mg/kg dietary level (3221).

c. Fish and Other Aquatic Life. The 96-hour  $\mathrm{LD}_{50}$ value for Schradan against fingerling channel catfish at a temperature of 20°C has been reported to be 8150 mg/l (2981). Another study, utilizing OMPA in hard and soft waters, and fathead minnows at a temperature of 25°C reported 96-hour  $TL_m$  values of 135.0 and 121.0 mg/l respectively (3000).

#### SESONE

Sesone, a herbicide, is reported to have a single-dose  $\mathrm{LD}_{50}$  to 90-120 gram rats of 640-1330 mg/kg of body weight when administered in drinking water. Capsular feeding to dogs equivalent to 360 mg/kg in diet for five days a week for one year was tolerated without ill effect. Rats tolerated 200 mg/kg for the same time but 600 mg/kg injured them slightly (3222).

#### SEVIN

1. General. Sevin, 1-naphthyl-N-methylcarbamate, is slightly soluble in water, sparingly soluble in most organic solvents, but freely soluble in amides such as dimethylformamide. It is used as an insecticide and has low mammalian toxicity (364, 2997, 3029, 3223, 3291).

2. Effects Upon Beneficial Uses.

a. Stock and Wildlife Watering. The acute oral LD50 of Sevin to laboratory rats has been reported as 500 to 2190 mg/kg of body weight (2999, 3002), and to cats, dogs, and rabbits as 125-250, 250-795, and 710 mg/kg respectively (3029). A paper that studied the toxicity of Sevin mixtures with other insecticides indicated oral  $\mathrm{LD}_{50}$  values to rats varying from 390 to 750 mg/kg (3029). The amount of Sevin required to produce a 50 percent mortality in ringneck pheasant considering all stages of the life cycle is over 40 gms/kg (2994, 2996).

b. Fish and Other Aquatic Life. Toxicity values of Sevin toward various fish species are as follows:

Concentration of Sevin mg/l	Temperature °C	Type of Water	Type of Fish	Results	Reference
4.0 (d)			Goldfish	TLm value (no time	3291
5.0	21-26	(1)	Killifish	Loss of equilibrium 5 hours but recovery	in 3014
5.6 (b)	25	(0)	707	10 hours	
		(3)	Bluegfils	96-hour TLm	3000
6.7	25	(2)	Fatheads	96-bour TLm	3000
7.0 (b)	25	(3)	Fatheads	96-hour TLm	3000
11.0 (a)	25	(3)	Bluegills	96-hour TLm	3000
12.0	25	(3)	Fatheads	96-hour TLm	3000
13.0 (b)	25	(3)	Fatheads	96-hour TLm	3000
28.0 (c)		(0)	Goldfish	TLm value (no time	
41.0 (a)	25	(3)	Fatheads		
(u)	49	19)	ranteaus	96-hour TLm	3000

Brackish water, 2-gallon aquaria, 5 Mummlehog kililish per aquarium.
 Hard water, pH 8.2, DO 8.0 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.
 Soft water, pH 7.4, DO 8.0 mg/l, alkalinity 18 mg/l, hardness 20 mg/l.
 Commercial Sevin, 50 percent wettable powder.
 Technical Sevin, 95 percent active in acetone.

(e) Ethanol solution.(d) Wettable powder.

Sevin applied at a rate of 1.25 lb/acre in fuel oil with a paraffin oil sticker effected reductions in weight of invertebrate fish food of 48.9 to 97.2 percent. On one

stream, little recovery was observed up to one month later. No fish mortality was noted (3223). In a discussion of bivalve larvae as a bioassay tool, the lethal concentration of Sevin was reported to be 5.0 mg/l (2989).

#### SILVEX

(see also 2,4-D, 2,4,5-T)

Silvex, 2 (2,4,5-trichlorophenoxy) propionic acid, is slightly soluble in water, freely soluble in acetone and methyl alcohol. It is used as a herbicide and is reported to be slightly less toxic than 2,4-D and 2,4,5-T type materials (3091). Its acute oral LD₅₀ to rats is 650 mg/kg of body weight (2997) and to rats, guinea pigs, rabbits, mice, and chicks ranges from 500-2000 mg/kg (2424).

Concentrations of Silvex of 0.5-1.0 mg/l have proved satisfactory for control of some species of watermilfoils in still waters. A level of 2 mg/l added to a section of a lake reduced the number of plankton therein for two weeks (2424). It is reported that concentrations of 2.5 mg/l have failed to kill fish (3010) and also that concentrations of 4-5 mg/l water of the emulsifiable ester are safe for fish. However, 5 mg/l is reported to be a threshold of toxicity to emerald shiners, the TLm value in 72 hours being 7 mg/l. Three fish kills at concentrations of 1.5 to 3 mg/l have been reported but it is not known if these were due to toxicological effects or to a temporary oxygen depletion caused by decomposition of the treated plants. In some instances, fish have acquired an unpleasant, oily taste following exposure to Silvex (2424, 3224).

## SIMAZINE

C₇H₁₂Cl N₅

Simazine, 2-chloro-4, 6-bis (ethylamino)-5-triazine, is a crystalline that is insoluble in water and usually formulated as a 50-percent wettable powder. The acute oral LD₅₀ to mice is about 5 g/kg (364, 3038) of body weight. Toxicity studies at 20°C using chinook salmon showed that the 48-hour TLm value was 6.6 mg/l. In a constant flow apparatus, the value was 7.7 mg/l (2988).

## SINOX

The 96-hour TLm value for Sinox using red-sided shiners in hard and soft waters at 21°C was 0.24 and 0.13 mg/l respectively (3011).

## SOCAL #3

(see Aromatic Solvents)

## SODIUM ARSENATE AND SODIUM ARSENITE

(see Chapter VI)

## SODIUM BORATE

(see Chapter VI)

## SODIUM CHLORATE

(see Chapter VI)

## SODIUM CYANIDE

(see Chapter VI)

## SODIUM PENTACHLOROPHENATE

(see Pentachlorophenol and Pentachlorophenates)

#### SR - 406

(see Captan)

## STREPTOMYCIN

(see Antibiotics)

#### SULFOXIDE

(see also Rotenone)

Sulfoxide is said to have a synergistic effect on rotenone, and a formulation (Pro-Noxfish) of 2.5 percent rotenone, 2.5 percent sulfoxide, and 5 percent other cube extracts is designed to be as effective as preparations containing 5 percent rotenone. However, one investigator found it to be less effective against seven fish species than Noxfish which contains 5 percent rotenone (2685).

The threshold odor of sulfoxide has been reported as 0.091 mg/l. A formulation of sulfoxide, rotenone, rotenoids, solvent, and emulsifier had a threshold odor concentration of 0.007 mg/l (2984).

The 96-hour TLm value for sulfoxide using fathead minnows is reported to be 0.75 mg/l (3215).

#### SYSTOX

 $C_8H_{19}O_3PS_2$ 

- 1. General. Systox, also known as Demeton, is designated as beta-ethylmercaptoethyl diethyl thionophosphate. Commercial systox is a mixture of isomers with varying toxicities. It is insoluble in water, soluble in alcohol (2997, 3005).
  - 2. Cross References. Metasystox.

3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The estimated fatal dose of systox for a 70 kg man is 0.1 grams (2995).

- b. Stock and Wildlife Watering. The acute oral LD₅₀ to rats has been cited as 2.5 to 40 mg/kg of body weight (2992, 2997, 2999, 3142). No signs of intoxification were observed in rabbits fed 98 days on 1 mg/kg (3225). Significant plasma cholinesterase inhibition in dogs occurs with 2 mg/kg in the diet, and erythrocyte enzyme inhibition occurs with 5 mg/kg (3196). Technical grade demeton was fed in capsules to cows at a rate of 0.1 mg/kg for three consecutive days. The cows exhibited severe symptoms of organic phosphate poisoning, milk production dropped sharply, and fat percentage increased. Systox fed with hay at 51 mg/kg for 49 days caused mildly adverse effects on weight gains and red blood cell cholinesterase activity. At 41 mg/kg for 56 days, no adverse effects were observed, but red blood cell cholinesterase activity decreased gradually during the last 6 weeks of feeding (3226).
- c. Fish and Other Aquatic Life. The toxicity of systox to guppies at 21°C was studied, demonstrating that a level of 0.5 mg/1 caused distress in 90 minutes and death in 8-12 days (2992). The 96-hour TL_m value of systox to fathead minnows in hard and soft water at 25°C was 4.2 and 3.6 mg/l of active ingredient respec-

tively.

## 2, 4, 5 - T

C₈H₅Cl₃O₃

(see also 2,4-D, CMU, MCPA, Silvex)

This compound, 2,4,5-trichlorophenoxyacetic acid, consists of crystals that are almost insoluble in water, solu-

ble in alcohol. It is a plant hormone with an estimated human toxicity for a 90 kg man of 54 grams (364, 1723). The acute oral LD50 to rats is given as 300 mg/kg of body weight (364, 3009). 2,4,5-T forms phenol as a breakdown product, similar to 2,4-D and CMU (1723). 2,4,5-T was ineffective against algae at 2 mg/l for the species and test conditions utilized in this screening study (2041).

A commercial weed killer that combines 6.25 percent 2,4-D and 6.25 percent 2,4,5-T with propylene glycol, butyl ether esters, and inert ingredients, in concentrations of 50 mg/l or more caused the test fish to become immediately distressed. In a 72-hour period, a 25-percent kill occurred at 10 mg/l, but no fish died at 5 mg/l (2091).

The threshold value of toxicity of 2,4,5-T for perch is 55 mg/l, and for bleak 60 mg/l (2977).

## TBA (TRICHLOROBENZOIC ACID)

(see also MCPA)

TBA, a herbicide, is very effective when used with MCPA (2-methyl-4-chlorophenoxyacetic acid). It exists in several isomeric forms of varying toxicity. The most herbicidal isomers are least toxic to mammals. The acute oral LD₅₀ values to laboratory animals range from 300-1500 mg/kg of body weight depending upon species. A diet containing 10,000 mg/kg caused no mortality or obvious toxic effect to rats, but there was histological evidence of cellular injury to the liver and kidneys (3227). The 24-hour TL_m for both largemouth bass and bluegill sunfish was 1500 mg/l for the isomer 2,3,6-trichlorobenzoic acid, and 150 mg/l for 2,3,5-trichlorobenzoic acid (3092).

#### TCA (TRICHLOROACETIC ACID) CCl₃·COOH

(see also 2,4-D, Dalapon)

Trichloroacetic acid (TCA) is a crystalline substance with a slight characteristic odor. It is soluble in 0.1 part water, and very soluble in alcohol (364). It is useful for the control of tough, deep-rooted emergent plants such as Phragmites and Typha. TCA is used in combination with 2,4-D (3010). The acute oral  $LD_{50}$  to laboratory rats has been cited as 3,300 to 3,370 mg/kg of body weight (364, 3005, 3009). Growth in rats was inhibited on consuming 0.3 percent TCA for four months but there was no mortality (3005). There appears to be no danger to livestock and man from normal application (2861). The lethal dose of sodium trichloroacetate for an average 90 kg man is 300 grams (1723).

Fish and the organisms on which they feed are reported to tolerate TCA at concentrations of 1.15 percent (2861). The 96-hour TL_m at 20°C to fingerling channel catfish is greater than 2,000 mg/l (2981, 3228). No mortalities of chinook salmon were sustained during 48-hour exposure to concentrations ranging up to 870 mg/l (2988). However, although the sodium salt of TCA was reported to have no effect on fingerling largemouth bass at 102 mg/l, a concentration of 56 mg/l caused a 40 per-

cent loss of white crappies (3009).

#### TDE

(see DDD)

#### TEDION

 $C_{12}H_{16}Cl_4O_2S$ 

Tedion, designated as 2, 4, 5, 4'-tetrachlorodiphenyl sulfone, is insoluble in water, slightly soluble in polar organic solvents, soluble in chloroform, and aromatic hydrocarbons. The mammalian toxicity is low, there were no deaths among rats fed 14.7 g/kg. Tedion, at 1 mg/l and 21°C caused injury to guppies in 5 hours, after which recovery followed (2992).

## $\mathbf{TEPP} \qquad \qquad \mathbf{C_8H_{20}P_2O_7}$

- 1. General. TEPP, tetraethyl pyrophosphate, is a hygroscopic, mobile liquid that hydrolizes in water; it is miscible with water and xylene but not with kerosene or other petroleum oils (364). TEPP was originally synthesized prior to 1938, being the much-publicized German nerve gas "bladan" of World War II. It was marketed as an insecticide after the war as HETP. This material contained varying amounts of TEPP and since 1948 has not been used (3005, 3229). Like the other organic phosphates, TEPP was particularly useful in the control of aphids, spider mites, and thrips. Although it possesses an initial high lethality, its toxicity declines very rapidly so that within one or two days residues may be considered nontoxic.
- 2. Cross References. Organic Phosphates-General, Methyl Parathion, Sarin.
  - 3. Effects Upon Beneficial Uses.
- a. Domestic Water Supplies. The estimated fatal dose of TEPP for a 70 kg man is 0.05 grams (2995). Another source cites 100 mg of TEPP orally in a single dose as being lethal and 25 mg as causing severe nervous symptoms in man (3230, 3231).
- b. Stock and Wildlife Watering. The acute oral  $\rm LD_{50}$  of TEPP to laboratory rats has been cited as 1.2 to 2.0 mg/kg of body weight (3002, 3005, 3055, 3232). When food contaminated with TEPP was allowed to stand 24 hours before being fed to rats, the toxic  $\rm LD_{50}$  value declined. Toxicity essentially disappeared in three days. There is no problem of residual toxicity for TEPP (3005).
- e. Fish and Other Aquatic Life. TEPP is reported to be comparable to DDT in toxicity (3059). Toxicity figures noted in the literature for various fish have been summarized in the following table:

Concentration of TEPP mg/l	Temperature °C	Type of Water	Type of Fish	Results	Reference
0.25	17		Bluegill fingerlings	Killed	3007
0.25			Bluegills	Toxicity threshold	3007, 3048
1,0	25	(1)	Fatheads	96-hour TLm	3000
1.2	22-26		Bluegills	Killed	3007
1.2	22-26		Bass	Killed	3007
1.6	19	(3)	Catifish	96-hour TLm	2981
1.7	25	(2)	Fatheads	96-hour TLm	3000
(3) 37-4-4-	T 00 D0	~ ~ 7	4716-16-1644 O	en - A bordroom	400 mg/l

Hard water, pH 8.2, D0 8.0 mg/l, alkalinity 380 mg/l, hardness 400 mg/l.
 Soft water, pH 7.4, D0 8.0 mg/l, alkalinity 18 mg/l, hardness 20 mg/l.
 Tap water of the University of Oklahoma, 4-gallon aquaria, 10 fingerling channel catfish per aquarium, 100 or 200 fish per experiment.

In aquarium tests, TEPP at an initial toxic concentration of 1.2 mg/l became safe for bluegills in 43 hours; 1.8 mg/l in 59 hours; and 3.5 mg/l in 70 hours. Temperature during this work averaged 17°C (3007). The concentration of TEPP required to kill 50 percent *Chironomus* larvae in eight hours is 0.008 mg/l (2531).

#### TERRAMYCIN

(see Antibiotics)

### THIODAN

 $C_9H_6Cl_6O_3S$ 

Thiodan is an odorless crystalline compound that is stable toward water and dilute mineral acids. It is insoluble in water but soluble in alcohol and most organic solvents. The commercial product is a mixture of two isomers (364, 2997).

The acute oral LD₅₀ to rats has been cited as 90 and 110 mg/kg of body weight (3002, 3073). Experiments on guppies and goldfish at  $19^{\circ}-22^{\circ}$ C report that 0.01 mg/l caused distress in 30 minutes and death in 20 hours (3073).

#### THIRAM

 $C_6H_{12}N_2S_4$ 

Thiram (tetramethylthiuram disulfide) crystals are insoluble in water, soluble in alcohol, and partially soluble in acetone, benzene, and chloroform. It is used as a seed disinfectant, turf fungicide, and as a bacteriostat in soap (364, 3067). Thiram has an acute oral LD₅₀ to laboratory rats of 350 mg/kg of body weight (3067) and 865 mg/kg (3009). The toxicity to rabbits is 350 mg/kg (364).

A toxicity test was made using fingerling channel catfish; at 19°C, the 96-hour TL_m was 0.79 mg/l (2981).

### THURICIDE

(see also Chapter VII, Bacteria-General)

Thuricide is the world's first commercial biological insecticide. Although the bacterium, Bacillus thuringiensis, that produces the toxic component has been known for years (it was first isolated from a diseased moth in 1911), it was not until 1956 that industrial concerns began to show an interest in production (2527, 3085). The bacillus grown on an artificial media forms crystallike inclusions upon sporulating. These crystals are harmless to mammals, fish, and plants as well as to insect predators and bees (3085). Eighteen human subjects ingested one gram of Thuricide capsules daily for five days with no toxic symptoms developing. A 33-percent suspension in water containing one percent carboxymethly cellulose was administered to rats by stomach tube at doses up to 24 grams of Thuricide per kilogram of body weight without any toxic symptoms developing.

## TOXAPHENE

 $\mathrm{C_{10}H_{10}Cl_8}$ 

- 1. General. Toxaphene is a chlorinated camphene containing about 68 percent chlorine. Insoluble in water but highly soluble in organic solvents and oils, it is widely used in the control of insects. When used against agricultural crops, the normal dosage is in the range 1-3 lbs/acre. Dusts, emulsifiable concentrates, and wettable powders are available commercially. Because of its persistence and particularly high toxicity to fish, drifting sprays and dusts are hazardous near water courses (364, 3005).
- 2. Cross References. Chlorinated Hydrocarbons, Rotenone, DDT, Benzene Hexachloride.
  - 3. Effects Upon Beneficial Uses.

a. Domestic Water Supplies. The estimated fatal dose of toxaphene for a 70 kg man has been cited as 5 grams (2995). Another report cites a slightly lower figure, 60 mg/kg (3233). Owing to the turpene odor, it is unlikely that toxic concentrations will be consumed by man or animals (677). The threshold odor of toxaphene has been reported as 0.0052 mg/l (2984). The threshold odor of a formulation containing rotenone, rotenoids, toxaphene, solvent, emulsifier, and clay has been reported as 0.020 mg/l (2984). In most cases, toxaphene treatments will result in concentrations of toxaphene of less than 25 µg/l (3208). However, water that is to be used for domestic purposes should not be treated with toxaphene (3024, 3233).

b. Irrigation Waters. Although it has been reported that toxaphene at low concentration may depress the growth of seedlings (677), no specific reference to the effect of toxaphene in irrigation water was noted in this

survey.

c. Stock and Wildlife Watering. The acute oral LD₅₀ value of toxaphene to rats has been reported at 69 to 90 mg/kg of body weight (2992, 2999, 3002, 3073). The chronic oral toxicity to rats fed daily for two years was 5.0 mg/kg of body weight (3003). The highest level fed to rats without gross effects was 100 mg/kg in the diet (3005). Dogs are considerably more sensitive to toxaphene than rats. Death in dogs occurred at chronic levels as low as 10 mg/kg in the diet per day. Dogs fed toxaphene at levels of 4 mg/kg/day lost weight and exhibited abnormal behavior in the first few days (3005). Toxaphene at 313 mg/kg in the diet killed dogs in 33 days. For cattle, sublethal doses are between 35 and 110 mg/kg. The lowest lethal dose was 144 mg/kg (3070). It is estimated that a cow would have to drink 18,000 gallons of water a day which had been treated with toxaphene at 0.1 mg/l to produce toxic symptoms (3233).

Toxaphene and oil caused a heavy mortality to young birds (3069). It has been implicated in the poisoning of fish-eating birds (3100). Ducks and other waterfowl have suffered significant losses from single sprayings of toxaphene at 1.5 lb/acre (3006). The amount of toxaphene that will produce at least 50 percent mortality in bobwhite quail and ringneck pheasant considering all stages of the life cycle are 500 and 450 mg/kg respectively (2994, 2996). For a rather complete discussion of the effects of toxaphene on wildlife see Rudd and Genelly

(3005), and also Von Oettingen (3292).

d. Fish and Other Aquatic Life. During the past few years, toxaphene has been gaining widespread use in fish eradication. Although it is advantageous from the aspects of cost and ease of application, its principal disadvantage is its stability which often results in long periods of toxicity (3213). Some lakes treated with toxaphene have retained toxicity for 3-4 years (3208). It appears that the breakdown in toxicity is much more rapid in highly turbid lakes (3234). Laboratory studies have indicated that hard water detoxifies toxaphene more rapidly than soft water, that autoclaving hinders detoxifying, and that stirring increases detoxifying (3239). All these variables result in a broad range of toxicity figures cited in the literature. The reader is referred to (3235) for a more complete discussion of the duration of toxicity of toxaphene treated lakes and to

(3033) for a discussion of variation in results.

The numerous finite values of toxaphene concentrations and their effects on various fish as obtained from the literature are summarized in the following tabula-

Concentration of Toxaphene mg/l	Type of Fish	Results	Reference
0.005	Trout	Killed	679
0.005	Goldfish	TLm in 10 days	680
0.025	Coldfish	Loss of equilibrium in 24 hour	
0.05	Bass fingerlings	Killed	681
0.05	Bluegill fingerlings	Killed	681
0.05	Goldfish	Toxic	681
0.013	Fatheads	96-hour TLm	3215
0135-0165	Trout fingerlings	96-hour TLm	2199
0.1	Carp	Total kill in 72 hours (18°C)	3233
0.01	Bluegili	Toxicity threshold	3007. 3048
0.005	Trout, rainbow	Texicity threshold (1" long)	3048
	and brown	,,-	
0.025	Brown trout	Killed 70% in 24 hours	3049
	(4-7" long)		
0.1	Carp	Killed	3005
0.1	Bonefish	Killed	3005
0.1	Largemouth bass	Killed	3005
0.1	Bullhead catfish	Killed	3005
0.1	Yellow perch	Killed	3005
0.1	Brown trout	Killed	3005
0.125	Carp	Toxic	3236
0.125	Rainbow trout	Toxic	3236
0.02	Bluegills	Killed	3007
0.02	Creek chubs	Killed	3007
0.02	Blacknose dace	Killed	3007
0.02	Shiners	Killed	3007
0.02	Fallfish	Killed	3007
0.02	Minnows	Killed	3007
0.02	Sculpins	Killed	3007
0.02	Darters	Killed	3007
0.04	Goldfish	Killed	3007

Other toxic values of toxaphene toward fish are as follows:

Concentration of Toxaphene mg/l	Result	Reference
0.006	Lethal in 10 days	3004
0.036	Complete kills	918, 920
0.04	Lethal	679
1.0-10.0	Toxic	919

Later studies are summarized in the following tabulation:

Concentration of Toxaphene mg/l	Temperature °C	Type of Water	Type of Fish	Result	Reference
0.0035	25	(3)	Bluegills	96-hour TLm	3000
0.005	19–22		Gupoies	Distress in 12 hours, death in 30 hours	3073
0.005	19–22		Goldfish	Distress in 12 hours, death in 30 hours	3073
0.0051	25	(2)	Fathead minnows	96-hour TLm	3000
0.0056	25	(3)	Goldfish	96-hour TLm	3000
0.0075	25	(3)	Fathead minnows	96-hour TLm	3000
0.01	13		Bluegill fingerlings	50-75% died	3007
0.0135	13	(4)	Rainbow trout	96-hour TLm	3124
0.0145	13	(5)	Rainbow trout	96-hour TLm	3124
0.0165	13	(6)	Rainbow trout	96-hour TLm	3124
0.02	17	_	Bluegill fingerlings	Killed all	3007
0.020	25	(3)	Guppies	96-hour TLm	3000
0-05	21	`	Guppies	Distress in 5 hours, death in 24 hours	2992
0.05	19–22		Gupples	Distress in 30 minutes death in 20 hours	, 3073
0.05	19-22		Goldfish	Distress in 30 minutes, death in 20 hours	3073
1.9 *	20	(1)	Catfish	96-hour TLm	2981

*ppm by volume

(1) Tap water of the University of Oklahoma, 4-gallon aquaria, 10 fingerling channel catfish per aquarium, 100 or 200 fish per experiment.

(2) Hard water, pH 3.2, D0 8.0 mg/l, alkalinity 360 mg/l, hardness 400 mg/l.

(3) Soft water, pH 7.4, D0 8.0 mg/l, alkalinity 18 mg/l, hardness 20 mg/l.

(4) Dissolved solids 190 mg/l, pH 7.9, D0 9 mg/l, total alkalinity 225 mg/l, total hardness 154 mg/l, 5 fingerlings per 10 liters.

(5) Dissolved solids 115 mg/l, pH 7.5, D0 8 mg/l, total alkalinity 96 mg/l, total hardness 85 5 mg/l

hardness 85.5 mg/l.

(6) Dissolved solide 25 mg/l, pH 7.2, DO 10 mg/l, total alkalinity 51 mg/l, total hardness 34 mg/l.

Fish that have been killed by toxaphene have not been found to be off-flavor (3208). Frogs and water snakes have exhibited toxic effects (3233). The 24-hour TL_m values of toxaphene for aquatic sow bugs (Asellus), scuds (Gammarus), Daphnia, and mayflies (Ephemera) are greater than for fish (3208). Applications of toxaphene of about 0.1 mg/l killed chironomids within three weeks but the lake was completely repopulated again after nine months. Chaoborus larvae showed no immediate effects from toxaphene although larvae were absent from a sample taken six months later and had not reappeared by the end of the study. Oligochaetes increased in numbers during these studies (3219). Eight alkaline lakes in British Columbia were treated with toxaphene at concentrations of 0.01-0.10 mg/l. Most of the fish which were killed died within 120 hours. All fish were killed and the lakes were still toxic to fish eight or nine months later. Amphipods were eliminated at all concentrations and were still absent nine months later. Dragon flies, damselflies, and midge larvae were killed at a concentration of 0.03 mg/l (3237). Toxaphene at a concentration of 5 µg/l can reduce the population of small fish in hard-water lakes without greatly affecting the population of larger fish (3238). Toxaphene, used to control field mice, has been washed by rain into a stream thereby causing the death of fish (3236). Frogs and water snakes are the only vertebrates, other than fish, that have exhibited toxic symptoms in toxaphene-treated waters. Insect life is severely affected but not eliminated (3233). In earthen ponds, toxaphene at 0.2 mg/l remained toxic to bluegills for more than ten weeks, but a concentration of 0.05 mg/I did not kill fingerlings in a 5-week period. Trout fingerlings were disabled by concentrations of toxaphene ranging from 2.0 mg/l in Velsicol solution to 8.0 mg/l in acetone solution (755).

Doudoroff et al. (1449) tested the toxicity at 20°C to goldfish of a dust containing 20 percent toxaphene and 80 percent inert compounds. Goldfish survived 10 days at a concentration of 0.0032 mg/l as toxaphene, but most were killed within 10 days by 0.0056 mg/l, and all were killed by 0.01 mg/l. About 0.025 mg/l caused half of the fish to turn over in less than 24 hours. In earthen ponds, 0.2 mg/l killed bluegills and bass (681). In aquaria, goldfish were killed by 0.05 mg/l; in earthen ponds by 0.2 mg/l. Toxaphene at 0.2 mg/l remained toxic to bluegills for over 10 weeks in earthen ponds (681). A concentration of 10.0 mg/l has been reported lethal to bivalve larvae (2989). A solution of toxaphene (60 percent) at 2.0 mg/l inhibited the growth of 50 percent of the test algae during a 21-day, 22°C incubation period in laboratory tests (2041).

It does not appear that important hazards will arise from the addition of toxaphene in the quantity required for fish eradication to waters not used as drinking water supplies. Even overdosages would not appear to be dangerous. The amount of chemical absorbed by fish at the time of death appears to be very small and there is little chance of acquiring a dangerous dosage from fish flesh.

Nevertheless, toxaphene has the greatest toxicity to fish of any of the chlorinated hydrocarbons except endrin.

See Applegate et al. (2976) for the results of screening tests of a number of toxaphene formulations on trout, bluegill, and the sea lamprey.

## TOXICHLOR

(see Chlordane)

## TRICHLOROACETIC ACID

(see TCA)

## TRICHLOROBENZENE

(see Chlorinated Benzenes)

## TRICHLOROBENZOIC ACID

(see TBA)

## 2. 4. 5 - TRICHLOROPHENOXYACETIC ACID

(see 2,4,5-T)

#### TROLENE

(see Organic Phosphates-General)

## VANCIDE

(see Captan)

## VAPAM

 $C_2H_4NNaS_2 \cdot 2H_2O$ 

This crystalline compound, sodium N-methylodithio-carbamate, has an unpleasant odor, is soluble in water to 72.2 g/100 ml at 20°C, moderately soluble in alcohol, and sparingly soluble in other solvents. It disappears from soil in about two weeks (364). The acute oral LD₅₀ to rats is 800 mg/kg of body weight (2992), and mice 285 mg/kg (364).

Vapam at a concentration of 1 mg/l at 21°C caused distress in guppies in six hours, death in 30 hours (2992).

## VELSICOL 1068

(see Chlordane)

## WS - 1492

(see Aromatic Solvents)

## ZDD

ZDD, zinc dimethyl dithiocarbamate, was tested as an algicide at a concentration of 2 mg/l, temperature 22°C, for a laboratory incubation period of 21 days. A 65 percent solution controlled 17 percent, and a 100 percent solution controlled 100 percent, of the algae tested (2041). Concentrations of 0.004 mg/l inhibited Microcystis, 0.25 mg/l controlled all diatoms tested, 43 percent of blue-green algae, and 18 percent of green algae (3050). In soft water the 96-hour TL_m value to the fathead minnow was 0.008 mg/l (2987).

#### CHAPTER X

## SURFACE ACTIVE AGENTS

by Jack Patton *

This chapter deals exclusively with surface-active agents including their presence in commercial synthetic detergents. Phosphorus compounds and other "builders," which may constitute from 60 to 80 percent of a commercial synthetic detergent, are covered in Chapter VI, Potential Pollutants.

Certain solutes, even when present in low concentrations, have the remarkable property of lowering the surface tension or other interfacial properties of their solvents. Such solutes are known as surface-active agents and their unique effect is called surface activity (24). The surface-active agents include soaps, detergents, emulsifiers, wetting agents, and penetrants. Of these substances, the synthetic detergents are economically most important and are used in the greatest amounts (2115).

#### **GENERAL**

Synthetic surface-active agents were developed primarily to overcome the disadvantages of soaps in hard water. Unfortunately, soap is a softening agent and in hard water some of it must combine with the calcium. magnesium, and certain other metallic ions of the solution before the remainder can become an effective detergent. This combination requires that a greater amount of soap be used than actually goes into cleaning. Indeed, Aultman (34) has shown that the annual cost for a family of 5 using water with a total CaCO3 hardness of about 300 mg/l (as contained by the water in Indianapolis, Indiana) (43) will be about \$18 more if the family uses ordinary soap instead of a synthetic detergent. The majority of soaps are sodium or potassium salts of fatty acids. The calcium, magnesium, and ferric cations in hard water form insoluble compounds with the fatty acid anions. The resulting water "scum" often causes clothes washed in such a solution to appear dingy.

The history of synthetic surface-active agents dates back considerably further than is commonly known. Frémy sulfonated olive and almond oils as early as 1831. In 1897, mention was made of the sulfonation of cetyl alcohol from sperm oil as a scouring agent. Twitchell's American patent 601,603 of 1898 made use of sodium sulfonate from petroleum oils, and the German patent 336,558 taken out in 1916 described the production of disopropyl naphthalene solium sulfonate (44).

The critical soap shortage in Germany during World War I led to the development of modern surface-active agents (24). It was not until 1933, however, that serious production of these compounds was undertaken in the United States. In that year "Dreft" appeared as this nation's first packaged household synthetic-detergent washing product, intended primarily for silks and woolens; and the first synthetic surface-active shampoo, "Dreen," was also marketed (2113).

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For over ten years after their introduction, synthetic detergents made no phenomenal gains. In 1940, only three percent of the total soap and detergent sales were synthetic detergents (48). In 1946, however, with the introduction of "Tide," a product designed to do the "whole family wash," synthetic detergent sales began to skyrocket. In 1948, the synthetic detergents constituted 16 percent of the annual soap and detergent sales (49) and in 1957 the figure had grown to over 75 percent (48). Ward (48) reported an estimate that synthetic detergent sales will level off at about 85 percent of the total market for soaps and detergents. Earlier, however, McKinney and Symons indicated that within twenty years synthetic detergents would replace 98-99 percent of the soap sales (50).

## CHEMICAL CONSIDERATIONS

The molecules of surface-active agents are essentially dipolar, and the characteristics of the end groups provide a natural system of division. Chemically, there are two classes of surface-active agents: the nonionic and the ionic or ionogenic (24). The nonionic class has high affinity, nonionizable end groups. Hence it does not ionize in aqueous solution. Nonionic surface-active agents are a ripidly growing class. In the last two years, sales of these products have risen from ten percent of the domestic market to 26 percent (1902).

The ionogenic class of surface-active agents has two main divisions based again upon the end groups of the dipolar molecule, which in this class has an elongated portion of low residual affinity and one end of high residual affinity. If the elongated, low-affinity group is included in the cation in aqueous solution, the agent is termed cationic or cation active (24). These substances are more bactericidal than soaps or other synthetic detergents and are used as sanitizing agents in connection with dishwashing and laundering. The production of cationic surface-active agents is relatively small and they probably present few problems from a water treatment or pollution standpoint (43). Flynn, et al. (49) attribute this low acceptance primarily to the effect of cationics on the protein of the skin. If the surface-active agent ionizes in aqueous solution to give a negatively charged group or anion that contains the low-affinity portion of the molecule, the substance is called anion active or anionic. Presently, about 80 percent of all synthetic detergents in this country (53) are of the anionic type. Most of these anionics are cyclic, with dodecylbenzene sulfonates representing about three-quarters of the total anionic. production (49).

Based on the preceding three divisions, the following classification of surface-active agents is quoted from Woodard and Calvery (1895):

- "I. Anionic: Ionizing so that the major part of the molecule is the anion.
  - A. Sulfates: Compounds with carbon-oxygen sulfur linkages
    - 1. Alkyl sulfates—alcohol sulfates
    - 2. Sulfated esters—sulfated monoglycerides
    - 3. Sulfate-substituted amides
  - B. Sulfonates: Compounds with carbon-sulfur linkages
    - 1. Alkyl sulfonates—aliphatic sulfonates
    - Alkyl aryl sulfonates—aliphatic aromatic sulfonates
    - 3. Sulfonated esters
    - 4. Sulfonated amides
- "II. Cationic: Ionizing so that the major portion of the molecule is the cation.
  - A. Substituted ammonium compounds: Alkyl aryl ammonium compounds
  - B. Cyclic quaternary ammonium compounds
- "III. Nonionic: Compounds not ionizing when dissolved in water.
  - A. Polyethylene glycol fatty acid esters
  - B. Ethers
    - 1. Alkyl aryl polyether alcohols
    - Polyoxalkylene derivatives of hexitol anhydride fatty acid esters"

Although the fundamental ingredient of all commercial synthetic detergents is a surface-active agent, they also contain a variety of other components. In fact, the over-all composition of synthetic detergents is quite variable. The amount of surface-active agent used as the active part may range from 20 to 40 percent (49). In addition to this active ingredient, 30 to 50 percent of the product is made up of a molecularly dehydrated phosphate (49) which assists in suspension, dispersion, and emulsification of soil (48). Synthetic detergents also contain about 20 percent (2056) of sodium sulfate which acts as an additional electrolyte to aid in wetting and dispersion, and a maximum of 10 percent of sodium silicate which controls the corrosion of metals, particularly aluminum (49). The remainder of the composition of the detergent comprises fatty acids to stabilize foam (48), a bleaching agent (such as sodium perborate) (48), and a fraction of one percent of sodium carboxymethyl cellulose (2056) to prevent redeposition of soil on the fabrics (49). After a packaged product—whatever type of surface-active agent and other component it may represent-is used for laundering or cleaning and released down the drain, however, it loses its individual identity and must be considered on the basis of its separate components.

The specific surface-active material most widely used today in the bulk of synthetic detergents is the group of anionic alkyl benzene sulfonates, generally termed ABS (48). Derived from polypropylene (55), the ABS molecules are saturated, highly branched hydrocarbons that terminate with a quaternary carbon to which the benzene ring is attached (57). McKinney and Symons (58) maintain that the quaternary carbon of the ABS molecule prevents its bacterial degradation. Hence, some

ABS compounds persist in sewage and streams in biologically active solutions without appreciable decomposition from either treatment processes or natural purification. The facts that almost the entire annual production of over 3.8 billion pounds (57) of synthetic detergent is discharged to a ground or surface water and that ABS, the most common ingredient, is resistant to biological metabolism, account for the rising incidence of surface-active materials as water-quality problems.

### SURFACE WATER POLLUTION

The concentration of surface-active agents (in mg/l of Manoxol OT) at Raleham on the River Thames grew from 0.24 in 1954 to 0.38 in 1956 (2056). The Orsanco monitoring program has disclosed that the average ABS content of the Ohio River has mounted to about 0.2 mg/l (59). The surface-active agents that reach rivers in the effluents of complete sewage treatment plants have resisted the rigors of intense biological activity in secondary sewage treatment processes, and consequently they are not likely to be metabolized quickly in river water (57).

Hammerton (60) maintains that the rates at which different surface-active agents decompose in river water is dependent on the particular configuration of the alkyl group in the molecule. If the alkyl group has a straight chain, the material will be susceptible to biochemical oxidation; but if the alkyl group is branched, bacterial degradation will either be delayed or greatly resisted, according to the degree of branching (63). As a result, sodium n-decyl sulfate is biologically decomposed after two days in river water, sodium p-n-decyl benzene sulfonate after four days, but sodium kerylbenzene sulfonate and sodium tetrapropylene benzene sulfonate persist longer than twenty days. Sawyer (64), however, reports ABS to have a half-life of about fifteen days, and hence it has been observed (66) that only 37 percent removal of ABS occurred in the Illinois River over a distance of 114 miles during about eight days of travel time.

Sodium lauryl sulfate, an anionic compound, in a concentration of 150 mg/l, was found to increase the BOD of sewage considerably, and to cause an increase in the reduction of nitrate to nitrite (68). The presence of 50-75 mg/l of secondary sodium alkyl sulfate (under the trade name Teepol) had no perceptible effect on biological sewage treatment but it has been estimated that 100-200 mg/l would cause difficulties. Leclerc and Beaujean (68) found that the presence of 300 mg/I of sodium dodecyl benzene sulfonate caused the development of reducing flora, resulting in the formation of sulfides, 60 mg/l retarded the development of proteolytic bacteria, 15-60 mg/l retarded the growth of aerobic bacteria, and 150 mg/l retarded the growth of denitrifying bacteria. The inhibitory effect of this compound on aerobic organisms is attributed to its interference with the uptake of oxygen.

Fischer (70) studied the effects of ABS on the oxygen uptake of several bacteria in two different media at 38°C. The results are presented in a series of sigmoidally shaped curves. Since it is difficult to pin-point a concentration of initial or final effect, the approximate concentrations for 50 percent inhibition of oxygen uptake were as follows (Puffer's Medium is a buffer):

ABS Concentration

		% Inhibition of Or Uptake
$Test\ Organism$	Medium (Appr	oximate mg/l)
Proteus vulgaris	Dextrose-Bouillion	2,500
	M/20 Puffer's Medium + Glucose	220
Staphylococcus	Dextrose-Bouillion	40
aureus	M/20 Puffer's Medium + Glucose	200
Mycobacterium	Dextrose-Bouillion	40
phlei	M/20 Puffer's Medium + Glucose	250

Another report states that anionic surface-active agents slightly increased the oxygen uptake of *Pseudomonas fluorescens* and accelerated the respiration of fungal spores (71), but the concentrations that effected these results were not available in the abstract. In another experiment, however, Van Beneden (69) observed that proteolytic bacteria were not affected by the presence of anionic detergents in concentrations of 500-2000 mg/l (85% active product).

Cationic detergents inhibited the development of proteolytic bacteria considerably even in extremely low concentrations, but in the presence of nonionic detergents there was a large increase in the numbers of bacteria. Cationic detergents in concentrations of 1-100 mg/l completely inhibited the development of nitrifying bacteria and algae, and in a concentration of 0.01 mg/l retarded growth for 6-10 days. Anionic detergents in concentrations of 50-600 mg/l completely inhibited the growth of nitrifying bacteria. Detergents of the alkyl sulfate type in a concentration of 5 mg/l did not interfere with the growth of algae but in higher concentrations growth was affected; detergents of the alkyl aryl sulfonate type in concentrations up to 60 mg/l did not inhibit growth of algae but in concentrations of 120-260 mg/l growth was completely stopped. Nonionic detergents had little effect on nitrifying bacteria in low concentrations and growth was only inhibited with a concentration of 50,000 mg/l. Growth of algae was inhibited by nonionic detergents in a concentration of 500 mg/l (69).

Another report (72) investigated effects of 10 to 100 mg/l concentrations of an anionic, a nonionic, and a cationic detergent upon slime growth. At concentrations that can be expected in sewers, the anionic and nonionic types were reported to stimulate slime growth significantly. The same report states that the anionic and nonionic detergents in the 10 to 100 mg/l range had no marked effect on the number of coliforms and did not increase the bactericidal efficiency of chlorine (in sewage). The cationic compounds, however, caused a considerable decrease in the number of coliforms.

There have been numerous reports of foaming in rivers, especially in turbulent reaches and at points where sewage-treatment-plant effluents flow into receiving waters (48). Indeed, it is reported that foaming caused by surface-active agents in the River Lee, in England, is now a normal occurrence (74). On one occasion froth covered an area of 1500 square yards and was built up to a height of 12 feet (48). ABS compounds are the principal surface-active agents causing foam. Under favorable conditions a concentration of 1 mg/l of ABS will cause a light froth (76) and there have been reports of foaming at concentrations as low as 0.5 mg/l (1745).

Even when foaming does not occur, a detergent-containing film may form over the surface of the water, delaying the gas exchange with the atmosphere (78). Gameson et al. (80) have shown that the presence of detergents will reduce many times the rate of re-aeration in a stream. When the "exit coefficient" in the absence of detergents was 30 cm per hour, the addition of sodium dodecyl benzene sulfonate reduced the rate of entry of oxygen by about 50 percent. When the exit coefficient in the absence of detergent was 100 cm per hour, the addition of detergents had no apparent effect. Between these two extremes, the effect of surface-active agents on re-aeration changed approximately linearly. In general, it has been stated (82) that the presence of 1 mg/l of detergent in river water reduces its capacity for reoxygenation by about 60 percent. Observations on the River Thames (1950) report that the introduction of detergents was followed by a marked lengthening of the zone devoid of oxygen.

Baars (85) stated that although the addition of synthetic detergents decreased the rate of oxygenation in diffused-air activated-sludge systems, there is evidence that oxygenation was increased with the brush-aeration method. For further information, including the aeration of mixed detergents in clean water, see Downing et al. (86).

British investigators (88) studied the effects that residual surface-active matter in an estuary may have on the rate of settling of suspended matter. Their preliminary results show that the effect of 1 mg/l of ABS is to decrease the rate of settling of the mud for any given mud concentration. In one experiment in which the detergent concentration was increased ten-fold, the effect on solids in suspension was roughly doubled.

## GROUND WATER POLLUTION

Various cities have recently reported the average value of total synthetic detergents in their raw sewage to be over 40 mg/1 (92, 93, 94). Many of the constituents of these detergents are not removed appreciably by treatment processes (2112). If the sewage disposal system involves a method whereby the treated or untreated effluent is released into intimate contact with the soil, ground-water pollution may result. ABS compounds are not precipitated by the calcium, magnesium, or ferric ions of the soil. Moreover, they are resistant to biological degradation in saturated ground-water flow (96). Preliminary evidence indicates, however, that some ABS can be decomposed biochemically in percolation through the zone of aeration under special conditions of intermittent application. Nevertheless, large quantities of synthetic detergents ultimately reach ground water and various cases of pollution have been reported. A survey of individual wells in a Minnesota community of 10,000 (97) indicated that 23.6 percent of the supplies contained surfactants.

After about a year of operation of an experimental sewage lagoon at Kearney, Nebraska, nearby wells were observed to have been polluted by detergents. In a study of the area, Neal et al. (99) found that in 14 months synthetic detergents had contaminated ground water within a radius of  $\frac{3}{4}$  of a mile around the lagoon. An

irrigation well 800 feet away was found to contain an ABS concentration of 2.0 mg/l, and a domestic well

1,000 feet away, 1.5 mg/l.

In a rural German town, Netsch (100) reported that the waste water from a laundry was let into a village pond that had no outflow. After about 10 months of operation, changes began to occur in the water of nearby wells. Water foamed in buckets on pumping, had an unpleasant taste and odor, was refused by livestock, and finally became almost unusable. In a study of the area, it was found that synthetic detergents had polluted ground water for over 600 feet around the pond and the effect was still spreading.

In 1960, a water-quality study of the Mojave River Valley in California (102) revealed that ground water to a depth of 100 feet and extending over a distance of about 2 miles was affected by tastes, odors, and ABS. Water from some of the wells of the area frothed. The observed pollution was attributed to effluents from a municipal treatment plant and from a railroad shop dis-

posal system.

A most famous and thoroughly studied case of ground-water pollution occurred in Suffolk County, New York (49, 96, 111, 112, 117). Here, during investigations of unusual tastes and odors in well water, synthetic detergents were found in one-third of the wells tested in concentrations up to 1.4 mg/l. The Federal Housing Administration refused to approve mortgages in this and surrounding areas when a well and sewage disposal system were to be located on the same lot, unless certain strict conditions were met (117). In a study of the area (111), it was found that pollution by synthetic detergents followed the general direction of ground-water flow, and that some of the detergents from test wells had probably been in the ground water for 1 to 3 years.

The significance of synthetic detergents as vehicles to transport bacteria, viruses, or other biological pollutants greater distances than they might normally travel in ground water has become an area of great concern (49). In this vein, Nichols and Koepp (121) maintain that the presence of ABS-type detergents is a better indicator of possible intestinal virus contamination of drinking water than is the presence of coliform organisms. In their work, they found that water samples with 3 to 10 mg/l of detergents represented nearly five times as many bacteriologically unsafe waters as the group free of detergents. In recent studies with Ohio sands, however, Robeck et al. (122) have shown that ABS at 1-10 mg/l did not have a significant influence on the movement of coliform organisms through soils that were saturated with water.

Much remains to be learned about the fate of ABS and other constituents of commercial synthetic detergents in saturated soil and the zone of aeration. Current research at the Robert A. Taft Sanitary Engineering Center (123), California Institute of Technology (124), University of Illinois (2029), University of California at Berkeley (2022), Manhattan College (111), and elsewhere should provide additional information on this subject.

## DOMESTIC WATER SUPPLIES

Difficulties caused by detergents in domestic water supplies include dramatic foaming, turbidity, interference

with coagulation, and production of taste and odor (1755). Among the more spectacular effects of detergents in water is the foaming phenomenon. Such a demonstration of frothing occurred in 1957 at Chanute, Kansas (125, 2119). During a drought the city officials decided to reutilize sewage effluent after circulation through a natural reservoir. Although this emergency operation was successfully conducted for five months without hazard to health, the increase of surface-active material caused the water to foam at the plant in waves accumulating to a height of 15 feet at the recarbonation basin, and in the filters during backwashing.

Foaming of ABS is reported to occur at a concentration as low as 0.5 mg/l (1745). Another paper reports laboratory work that produced a stable foam on aeration of a good quality water containing as little as 0.7 mg/l of surface-active material (2120). Truesdale (129) showed that the amount of foam produced increased linearly with the concentration of surface-active agent and the tendency to foam was greatest in clean water, decreasing progressively as the pollution was increased. Edwards et al. (136) studied the frothing of surface-active agents in the presence of common food types. This work indicated that low concentrations of casein are effective in preventing frothing of alkyl aryl sulfonates.

The foaming power of alkyl aryl sulfonates and the stability of the foam produced are greater at pH values of 3 and 9 than at 7 (138). Although the presence of surface-active agents reduces the oxygenation capacity of water, the only probable effect in a water-treatment plant aeration system would probably be the foaming

that can result.

Synthetic detergents in concentrations exceeding 3.0 to 5.0 mg/l may interfere with coagulation and floc formation (818). Also, Smith et al. (2047) found that dodecyl benzene sulfonates interfered with water softening by coagulation at 8 mg/l. For the most part, however, recent research seems to indicate that the major detriment to coagulation is not the surface-active agents but the complex phosphates that are used as builder compounds in synthetic detergents (57, 2048, 2049, 2050, 2051). The Water Research Association of England investigated these findings. The surface-active alkyl aryl sulfonates were removed from a commercial product by extraction with alcohol and evaporating to an organic residue. Coagulation tests were carried out with the original packaged product, the organic fraction, and the inorganic fraction. It was found that small concentrations, 2 mg/l, of the inorganic fraction caused noticeable deterioration in results, whereas the organic fraction and the original product produced similar effects at 7 mg/l.

In the subsequent settling process, some workers have shown that common synthetic detergents in concentrations up to 100 mg/l have little effect (1704, 2052). However, it might be pointed out that with respect to the sedimentation of sewage, an increased amount of sludge is obtained after addition of detergent. It is noted that this phenomenon is a function also of the purity of the

detergent, the hardness, and the pH (2053).

One of the common properties of surface-active agents is their ability to disperse colloidal particles, thus achieving the opposite of flocculation. Langelier et al. (2054) found that an alkyl aryl sulfonate at a level of 17 mg/l

had no effect on floc formation. But greater concentrations-up to 40 mg/l-showed increasing interference. One nonionic detergent at 40 mg/l and a cationic quaternary compound at 20 mg/l caused complete dispersion in a system that otherwise would have developed a good

Alkyl benzene sulfonate is reported to have caused a marked head loss in the performance of rapid sand filters at concentrations greater than 5 mg/l (2055).

The bactericidal efficiency of chlorine in water treatment processes is not affected by a concentration of surface-active materials of 4 mg/l or below (2056). There is some evidence, however, that the chlorination of detergent-containing waters may produce unpleasant tastes and odors. Filicky (819) reports that 5.0 mg/l of detergents in odor-free water caused both tastes and odors. Hammerton (2056) found that the lowest concentration of mixed anionic detergents (Omo, Fab, Surf, Tide, and Wisk) that will cause a soapy taste in clean water is 4 mg/l. At a water treatment plant in Wheeling, West Virginia, Todd (2057) reported that raw water having a daily average of sythentic detergent concentration of 4 mg/l (with peaks of 12 mg/l) caused an intense fishy odor.

Threshold levels at which ABS will cause an off-taste in clean water have been reported to range from 1 mg/l (49, 1745) to higher than 40 mg/l (76, 2058). The threshold value seems to be dependent upon the purity of the compound. Tests made at the Robert A. Taft Sanitary Engineering Center at Cincinnati, Ohio, showed that the odor of purified ABS is rarely detectable at concentrations less than 1,000 mg/l and that only very sensitive individuals can taste it in water as high as 16 mg/l. In similar tests with a common household detergent containing ABS, however, an off-taste in water occurred at 2 mg/l or more of synthetic detergents (49, 1901). In another test also using the entire detergent, Campbell et al. (2059) reported the taste threshold in redistilled water for the familiar anionic "Tide" to be 12 mg/I.

Filicky et al. (2040) conducted numerous tests on odors and tastes resulting from surface-active agents. The minimum concentrations of several detergents required to produce a perceptible taste and odor in water and also the taste and odor threshold values of a 5 mg/l concentration of the compounds are presented in Table 10-1. In this work, solutions were prepared with adorfree water having a total hardness of 100 mg/l and pH of 8.3. Odor tests were conducted at 60°C, taste tests at 20° C. The same authors found that when hydrochloric acid was used to adjust the pH of the surface-active solutions from 8.3 to 5.0, the taste and odor of the alkyl sulfate was greatly intensified. The other surface-active agents showed little change in taste and odor values (see also 2984).

The increasing concentrations of surface-active agents in water supplies have led to many questions concerning the possible detrimental effects or toxicity that may be caused by these compounds. From a review of the available literature, it has been found that the degree of toxicity exhibited by surface-active agents is extremely variable. For instance, some surface-active agents have

very low oral LD50 values, while others have proved to be excellent food supplements (2060).

As a rule, the cationic surface-active agents exhibit the greatest toxicity. However, those cationics that are effective germicides are not compatible with the anionies; they cannot exist in the same solution in any appreciable amounts and keep their identity (2061). Therefore, as long as there are anion active agents in waterand anionics are the main class causing water pollution-there should not be any reason to worry about the effects of cationics, for they will be neutralized.

Numerous authors have advanced the opinion that neither present nor future expected concentrations of surface-active agents in water supplies present any reason for alarm from a toxicological standpoint. Indeed, the British government committee on synthetic detergents has concluded that there is no evidence pointing to any serious toxic effects from anionic or nonionic detergents (1902, 2120). It may be of interest to note that Schwartz et al. (2044) claim that there is no doubt that dermatitis of the hands is on the increase since the advent of surfactants (see also 2045). However, Coughlin (2046) estimates that a housewife uses about 3000 mg/l of detergent (about 600 mg/l of ABS) in a dishpan to obtain "proper suds."

### TABLE 10-1

Minimum Concentration of a Detergent Required to Produce a Perceptible Taste and Odor. Also, Taste and Odor Threshold Values of a 5 mg/l Detergent Concentration

(After Filicky, et al.) (2040)

Surface-Active Agent	Minimum Concentration Perceptible (mg/l)	Threshold Value of 5 mg/l Concentration	Type of Taste or 1 Odor
	Taste R	esults	
Alkyl aryl sulfonate Alkyl aryl sulfonate Alkyl sulfate Alkyl sulfonate Sulfonated amide	0.6 0.4 3.0 1.4 2.5 Odor Re	8 13 2 4 2	Limey, chemical Chemical, soapy Solvent Bitter, soapy Chemical, soapy
Alkyl aryl sulfonate Alkyl aryl sulfonate Alkyl sulfate Alkyl sulfonate Sulfonated smide	0.7 0.3 0.2 0.3 2.0	7 17 25 21 3	Limey, chemical Soapy Aromatic, solvent Kerosene, soapy Chemical, soapy

Because reports of contamination of drinking water by surface-active agents are becoming more common, recognition of this contaminant seemed necessary for the recent revision of the Public Health Service Drinking Water Standards (see Chapter V, Quality Criteria for the Major Beneficial Uses of Water). Since the bulk of detergent sales are anionic, with ABS being the principal agent, the maximum permissible concentration was established in terms of ABS (2062). However, the adopted limit of 0.5 mg/l appears to have been based on esthetic rather than toxicological consideration (2063). ABS will not be toxic at this concentration, but it may cause foaming at the tap. Moreover, this concentration acts as an indicator that at least 5 percent of the water is of sewage origin (2062). Jente, et al. (2064) in a recent survey found the average concentration of ABS in

TABLE 10-2

## SINGLE ORAL DOSE TOXICITIES (TOWARD MAMMALS) OF SOME SURFACE-ACTIVE AGENTS

	Surface-Active Agent or	Test	Approximate	Refer-
Trade Name	Chemical Form	Animal	$\mathrm{LD}_{50}$	ence
	Anionic	5		
Aerosol O.T	Sodium di(2-ethylhexyl) sulfosuc- cinate*	Mice	4.80 gm/kg	1894
	Sodium di(2-ethylhexyl) sulfosuc- cinate*	Mice	1.5 gm/kg	1895
Areskap 100	Alkyl aryl amine sulfonate Sodium monobutyl phenylphenol monosulfonate*	Mice	2.8 gm/kg 3.80 gm/kg	1895 1894
Areaket 300	Sodium monobutyldiphenyl sulfon- ate*	Mice	3.50 gm/kg	1894
Aresklene 400 _	Disodium salt of dibutyl phenyl- phenol disulfonate*	Mice	$2.20~\mathrm{gm/kg}$	1894
Igepon T	A substituted amide C ₁₇ H ₂₃ CON (CH ₂ )C ₂ H ₄ SO ₂ Na	Mice	6.63 gm/kg	1894
Ivory Snow	Soap	Albino Rat	> 15 ml/kg >25.00 gm/kg	1897
Monosulph	Highly sulfonated castor oil	Mice	>25.00 gm/kg	1894 1893
Nacconol NRSF	Alkyl aryl sulfonate	Rat	1.4 gm/kg 1.5 gm/kg	1895
MIND		Mice	2.8  gm/kg	1895
Nopco 2272-R_	Sulfated fatty ester	Mice	8.75 gm/kg	1894
	N-(sodium sulfoethyl) oleamide	Rat	> 4.0 gm/kg	1895
		Mice	6.3 gm/kg	1895
Santomerse D	Sodium decylbenzene sulfonate*	Mice Rat	2.0 gm/kg 2.0 gm/kg	1895 1893
		Mice	2.10 gm/kg	1894
Santomerse 3	Sodium dodecylbenzene sulfonate*	Rat	2.0 gm/kg	1893
				1894
	Sodium aryl alkyl polyether sul- fonate	Mice	12.6 gm/kg (comm. sol. not 100%)	1895
	Sodium hydrocarbon sulfonate	Rat	> 4.0 gm/kg	1895
	Sodium lauryl and myristyl col-	Mice	2.0 gm/kg	1895
	lamide sulfonate	Rat	3.5 gm./kg	1895
	Sodium lauryl sulfate	Rat	2.7 gm/kg	1895
	Sodium lauryl sulfate (30 percent solution)	Albino Rat	1.0 gm/kg 9.1 ml/kg	1895 1897
:	Sodium monoethyl phenylphenol monosulfonate	Rat	2.0 gm/kg	1895
Sulfatex Tergitol 4	Sulfated amine Sodium sec-tetradecyl sulfate* (25 percent aqueous solution)	MiceAlbino Rat	>25.00 gm/kg 5.0 ml/kg 1.3 gm/kg	1894 1897 1893
	(20 percent aqueous solution)		7.9 ml/kg (purified)	1897
		Guinea Pig	2.6 ml/kg	1897
Tergitol 7	Sodium sec-heptadecyl sulfate*	Albino Rat	5.7 ml/kg	1897
	(25 percent aqueous solution)	G Bt.	1.3 gm/kg 1.7 ml/kg	1893
Thereital AO	Sodium 2-ethylhexyl sulfate*	Guinea Pig Guinea Pig	1.7 ml/kg 3.8 ml/kg	1897 1897
Tergitol 08	(40 percent aqueous solution)	Albino Rat	10.3 ml/kg	1897
	Cationic	s		
Emcol 888	Polyalkylnaphthalene methyl pyr-	Rat	0.47 gm/kg	1893
Hyamine 1622_	idinium chloride (Diisobutylphenoxyethoxyethyl)	Rat	0.42 gm/kg	1894 1896
Hyamine 2389.	dimethyl benzylammonium cbloride* Methyldodecylbenzyl trimethyl-	Rat	0.39 gm/kg	1896
	ammonium chloride and methyl- dodecylxylene bis (trimethyl- ammonium chloride)*			
	Methyldodecylbenzyl trimethyl- ammonium chloride (10 percent	Human	28.3 grams	1898
Roccal	aqueous solution) Alkyl dimethyl benzyl ammonium chloride	Rat	0.34 gm/kg	1893 1894
Tetrosan	Alkyl dimethyl 3:4-dichlorobenzyl	Mîce	0.35 gm/kg 2.00 gm/kg	1895 1894
	ammonium chloride also contains alkenyl dimethyl ethyl ammon-		1	}
	ium bromide	1		l .

#### Nonionics

Igepal CA	Cottonseed oil monoglyceride Glycerol monolaurate Polyoxyethylated tert-octylphenol*_	Rat Rat Mice	>90.0 ml/kg 53.4 ml/kg 3.50 gm/kg	1899 1899 1894
Nopalco 4-0	Polyethylene Glycol 400 mono- oleate*	Mice	>25.00 gm/kg	1894
Nopalco 6-0	Polyethylene Glycol 600 mono- oleate*	Mice	>25.00 gm/kg	1894
Nopalco 6-L	Polyethylene Glycol 600 mono- laurate*	Mice	>25.00 gm/kg	1894
Nopcogen 14-L	Fatty amino compound	Mice	9.65 gm/kg	1894
	Polyoxyethylene monostearate	Hamster	19.5 ml/kg	1899
		Rat	53.0 ml/kg	1899
		Rabbit	>15.0 ml/kg	1899
	Polyoxyethylene-8-monostearate	Hamster	27.0 ml/kg	1899
	100,000,0000,000	Rat	64.0 ml/kg	1899
		Rabbit	>12.0 ml/kg	1899
	Polyoxyethylene-20-sorbitan mono-		18.0 ml/kg	1899
	lanrate	Rat	36.7 ml/kg	1899
	Polyoxyethylene-40-sorbitan mono-	Rat	>60.0 ml/kg	1899
	stearate			
Span 60	Sorbitan monostearate	Rat	31.0 ml/kg	1899
Tween 80	Polyoxyethylated sorbitan mono-	Mice	>25.00 gm/kg	1894
I #CCH CO	oleate (20 moles EtO)*	Rat	54.5 ml/kg	1899
	(20 mores 1100)			

^{*} Chemical form according to Rosen and Galdsmith (1900).

the drinking waters of the United States to be 0.024 mg/l ABS, with a range of 0.00 to 0.14 mg/l.

Another important aspect of surface-active agents in drinking water as a menace to public health has been pointed out by Borneff (2065). He has found that water supplies containing synthetic detergents are capable of solubilizing carcinogenic compounds such as 3,4-benzo-pyrene. From his study Borneff concludes: "Drinking water obtained from rivers subject to contamination with waste waters containing detergents must be considered injurious to health."

The available existing information on the toxicological properties of surface-active agents by oral administration has been summarized in Table 10-2 showing single dose (acute) toxicities, and Table 10-3, presenting toxicities from repeated doses (chronic).

Today, although a great amount of research work is being conducted, one must still agree with the statement of Woodard and Calvery (1895): "We are appalled by the many unanswered questions concerning the toxicological properties of surface-active agents."

Since water treatment processes generally remove very little of the surface-active material, the corrosive properties of syndets are deserving of mention. The corrosion of domestic equipment and plumbing, attributable to syndets uncovering the protective, greasy film on surfaces, has been mentioned as an undesirable consequence of syndets by the British Ministry of Housing (2045). This action would not be in reference to potable water lines. The major studies on the corrosive effect of these compounds have involved solutions of 0.1 to 5.0 percent (1,000 to 50,000 mg/l), and these concentrations are certainly not likely to be encountered even in polluted waters (2066, 2067, 2068, 2069, 2070, 2071, 2072). Briefly these studies indicate that temperature, pH, dissolved

# WATER QUALITY CRITERIA TABLE 10-3

# REPEATED DOSE ORAL TOXICITIES (TOWARD MAMMALS) OF SOME SURFACE-ACTIVE AGENTS

Trade name	Surface-active agent	Test anima	d Medium	Level	Duration	Effects	Referen
			Al	NIONICS	<del></del>		<u>.I</u>
Aerosol O.T	Sodium di(2-ethylhexyl) sulfosuccinate*	Rats	Diet	.25 gm/kg per day	160 days	N	T
				.5 gm/kg per day	. 160 davs	No effect.	1895 1895
		1		.75 gm/kg per day	160 days	Occasional diarrhea	1895
		1	1	.87 gm/kg per day	.   160 days	_ 50 rats, occasional diarrhea	l 1907
	i	i		1.0%	160 dave	Retardation of growth No effect	. 1904
			ł	1 1.25%	160 days	No effect	. 1895 . 1895
	1	Rabbits	C	1 5.0%	< 4 months	.! All animals dead	1904
		Monkeys_	Gavage Gavage	1 - 8 KM/KK DEL GRV	6 months_	. 3 out of 5 animals dead	. 1907
		Dogs		1 gm/kg per day_	6 months_	3 monkeys no effect, larger doses vomited 3 dogs no effect	1907 1907
	1	Cuiusa min		.1 gm/kg per day .25 gm/kg per day 2000 mg/l	6 months	_∤ o dogs no euecl. larger doges vormited	1907
	Alkyl aryl sulfonate	Guinea pig		100 mg/i 100 mg per day	180 days	Slight toxic effect	1895
	Alkyl benzene sulfonate	Humans	! Orai	100 mg per day	4 months	No toxic effect on six men No effect	1902 1901
		Dogs	Diet	I gm per day	- 6 months	No effect	1902
		Guinea pig Young pigs	8 Water Diet			No effect	1902
	1	1	- 2000	0.2%	79 days 79 days	No effect	1903 1903
		l.,	l	0.2%_ 0.4%_ 0.5%_ up to 0.5%_	_ 79 days	. No effect	1903
		Rats	Diet	0.5%	_ 65 days	No effect	1902
l		ł	Water	500 mg/l	2 years 2 years	No effect	1909
Areskap 100	Sodium monobutyl phenylphenol monosulfon- ate*	Guinea pig	Water	2000 mg/l	180 days	Slight toxic effect	1909 1895
	Lorol meta sodium sulfobenzoate	Guinea pig	Water	i -		Í	
<b></b> .	N-(sodium sulfoethyl) oleamide	Guines nim	Water Water		- 180 days 180 days	Slight toxic effect	1895
	ocium alkyi arvi sulionate	Curnes pier	Water	2000 mg/l_	ISO dave	Slight toxic effect	1895 1895
	Sedium alkyl sulfate	Rats	- Water	1000 mg/l	_ 160 days	No effect	1895
	1	1	ı	2500 mg/l 5000 mg/l		Diminished growth intectinal ignitation	1895
		1	1	10,000 mg/l	_ 160 days _ 160 days	Diminished growth, intestinal irritation 4 of 11 animals survived	1895
		i	1	50,000 mg/l	_ 5 days	All animals dead	1895 1895
		Guinea pigs	Water	100,000 mg/l 2000 mg/l	5 days	All animals dead	1895
	Sodium decyl benzene sulfonate	Guinea pigs	Water	2000 mg/l	180 days	Slight toxic effect	1895
-	Sodium isopropyl naphthylene sulfonate Sodium lauryl sulfate		Water	2000 mg/l	180 days	Slight toxic effect	1895 1895
	Locatini izanyi sanane	Rats	_ Diet		2 years	No effect	1904
	Į.	1	1 .	8.0%	4 months	Decreased growth	1904
	Suffered with 12 12 12	1	Oral	8.0% 0.1 gm/kg per day	continued ?	All animals dead	1904 1908
	Sulfoethyl methyl olylamide	Rats	_ Diet	2.0%	4 months	Retardation of growth	1904
ergitol 4	Sodium sec-tetradecyl sulfate*	Rats	Water	8.0% up to 40,000 mg/l	4 months 30 days	3 of 5 animals survived	1904
ergitol 7	i Sodium sec-heptadeevi sulfate*	Rats	Water	up to 40,000 mg/l	30 days	Possible slight toxic effect Possible slight toxic effect	1895
ergitol 08	Sodium 2-ethylhexyl sulfate*	Rats	Water	_ up to 40,000 mg/l	30 days	Possible slight toxic effect	1895 1895
		<u> </u>	CA-	FIONICS	<u> </u>		
·		<b>_</b>	- UA	IONICS			
	Alkyl dimethyl benzyl ammonium chloride	Rats	Diet	0.063%	2 years	Some toxic symptoms	1904
yamine 1622	(Diisobutylphenoxy-ethoxyethyl)dimethyl	D	D: .	0.5%	10 weeks	All animals dead	1904
	benzylammonium chloride*	Dogs	Diet	up to 500 mg/l	1 year	No effect	1896
		Rats	Diet	<2500 ppm	2 years	Mortality not affected	1004
yamine 2389	Watheldadamilaanilaanilaanilaanilaanilaanilaanila	_		>2500 ppm	2 years	Increased mortality in 10 to 30 weeks	1896 1896
, warmer 2009	Methyldodecylbenzyl trimethyl ammonium chloride and methyldodecylxylene bis(tri-	Dogs	Diet	. 500 mg/l	1 year	No effect	1896
	methyl) ammonium chloride*		!		l i		
i		Rats	Diet	. <2500 ppm	2 years	Mortality not affected	1896
occal	Alkyl dimethyl bensyl ammonium chloride			>2500 ppm	2 years	Increased in 5 weeks	1896
		Guinea piga	Water	. 2000 mg/l	40 days	All of 12 animals dead	1895
			NON	IIONICS	· · · · · ·		
	Aryl alkyl polyether alcohol	0			1		
2125	Polyoxyethylene (4) laurate	Guinea pigs Cockerel	Water Diet	2000 mg/l up to 2.0%	180 days	Slight toxic effect	1895
2107	1	chicks			10 weeks	No effect	1906
2127	Polyoxyethylene (8) laurate	Cockerel	Diet	up to 2.0%	10 weeks	No effect	1906
2129	Polyoxyethylene (20) laurate	chicks Cockerel	Diet	up to 2.0%		No effect	1906
nj 45	Polyoxyethylated stearic acid (8 moles EtO)*_	chicks Cockerel	Diet	up to 2.0%	.	No effect	1906
rj 52	Polyoxyethylated stearic acid (40 moles EtO)*	chicks Cockerel	Diet	up to 2.0%	- 1	No effect	1906
-	Oleylpolyoxyethylene glycol ether	chicks Rats	Water	1000 mg/l	6 months	No effect	1905
Į	İ	I		2500 mg/l	6 months	No effect	1905
S No. 1	Polyoxyethylene monostearate	Hamsters	Oral	5000 mg/l 0.5 ml per day	6 months 8 days	Slight growth retardation	1905
1				1.0 ml per day	8 days	4 out of 18 dead within 4 days	1899 1899
ŀ		ļ		2.0 ml per day	8 days	8 out of 8 dead in 3 days	18 <del>99</del>
8 No. 2	Polyoxyethylene-8-monostearate	Hamsters	Oral	4.0 ml per day 1.0 ml per day	I day	All dead after I dose	1899
	i			2.0 ml per day		All survived All dead after 8 days	1899 1899
- 1	Polyethylene glycol monoisooctyl phenol ether	Rats	Diet	2%	4 months	Retardation of growth	1904
n 20	Sorbitan monolaurate*	Cockerel	Diet		ľ		
		chicks			1	No effect	1906
	Polyoxyethylated sorbites manalageata	( 'contrare)					4000
еп 20	Polyoxyethylated sorbitan monolaurate*	Cockerel chicks	Diet	1	J	No effect	1906
en 20	Polyoxyethylated sorbitan monolaurate*  Polyoxyethylated sorbitan monostearate (20 mois Etc))*	chicks	Diet	1	- 1	No effect	1906

Chemical form according to Rosen and Goldsmith (1900).

oxygen, surface roughness, and dissolved solids may be among the important variables, depending upon the agent and concentration as well as the metal. The above references include studies on aluminum, copper, mild steel, nickel, and tin.

The use of natural surface-active agents, such as soaps, for disinfectant purposes has long been established. The work of Valko and Domagk, around 1935, however, stimulated widespread interest in the possible bactericidal potentials of the whole expanding range of synthetic surface-active agents (2044). Since that time the disinfecting power of surface-active agents has been investigated by numerous authors.

Pinsky (71) found that cation-active materials in high concentrations caused agglutination of *Pseudomonas fluorescens*. The effect was neutralized if an anionic detergent was added before or together with the cationic, but the cationic affect was irreversible if the anionic was added after 15 seconds. Cationics also appear to be bactericidal to *Escherichia coli* because they affect a specific enzyme system and not because they alter cell structure (820). Cousins and Clegg (2073) found that the mineral content of the water greatly influenced the action of

quaternary ammonium compounds. Indeed, the efficiencies of all the agents tested at 200 mg/l in hard water were less than at 50 mg/l in distilled water against E. coli. Chambers et al. (2074) had previously indicated the interfering minerals causing primary interference to be bicarbonates, sulfates, and chlorides of calcium and magnesium. However, in experiments on the effect of minerals and other elements on the disinfection of water by benzalkonium chloride, Klimek and Bailey (2075) found that hardness up to 450 mg/l or the presence of 5 mg/l of iron or aluminum did not reduce the effectiveness of the disinfectant against bacteria exposed to it for 2 minutes, but did tend to reduce its effectiveness over shorter periods of time. Kravitz and Stedman (2076) found no effect attributable to hardness in their testing procedures. Klimek (2077) claims the "hard water effect" is a laboratory phenomenon of questionable significance.

None of the anionic detergents were effective against cysts of Entamoeba histolytica in concentrations up to 1000 mg/l (742, 744), but the best cationic detergents were cysticidal at concentrations of 30 mg/l for 10 minutes or 10 mg/l for 2 hours. A neutral detergent (hexylresorcinol) was much less effective. Fair et al. (744) suggest that the use of detergents in drinking water should remain experimental until psychological and physiological factors are better known. Smith et al. (822) state that detergents are not good bactericidal agents against tubercle bacteria. For results of tests of a large number of surface-active compounds against Mycobacterium tuberculosis see Smith, et al. (2078).

#### INDUSTRIAL WATER SUPPLIES

Reports of detergents in a water supply that interfered indirectly with commercial laundry operations have been published (2079). "Blackish" water found in the distribution system was attributed to iron and manganese that may have been loosened from pipes by detergents. Also, the back-washing of water softening systems was considerably hindered.

The addition of surface-active agents to coal-washing waters prior to vacuum filtration was studied. In the abstract available, no concentrations are given. However, the effect of the detergent additions was to decrease the water content of the filter cake and double or triple the time required for filtration of a one-liter sample. In the presence of surface-active agents, filtration was claimed not to obey Poiseuille's law (2080).

#### **IRRIGATION WATERS**

With the concentration of surface-active agents continuing to increase in surface waters, a natural concern arises over the effect that these materials may have on irrigated crops. A review of the available literature, however, revealed only sparse information.

Halevy and Cathey (2081) found that the quaternary Amo-1618 (2-isopropyl-4-dimethylamino-5-methylphenyl-1-piperidine carboxylate methyl chloride) retarded the growth of the seeds of the cucumber (Cucumis sativus L.) in concentrations greater than  $3x10^{-6}$  Molar.

Den Dulk (2082) reported that a dressing of alkyl aryl sulfonate had a harmful effect on the development of spinach, carrots, endive, lettuce, and tomatoes. It seems that the harmful effect is based on the disturbance of the balance of humidity in the soil, the moisture draining too rapidly. Yet, the use of syndets as a soil additive has been suggested to promote water penetration and retention (2083).

Day and Tucker (2118) attributed lower yields of hay in a plot irrigated with sewage effluent to the detergents and soluble salts. They also state that oats and wheat are less sensitive to detergents and soluble salts than barley or hay.

See also Chapter IX—Aromatic Solvents.

#### STOCK AND WILDLIFE WATERING

The toxicological information available on animals for surface-active agents has been included in Tables 10-2 and 10-3.

An unexpected result of the pollution of waters by surface-active agents has been reported by Chase (2084). It seems the normal protective oily coating on duck feathers tends to be dissolved by synthetic detergents, thus causing the feathers to become waterlogged and the ducks to be drowned.

Wells polluted by detergents from a pond into which laundry wastes drained contained water that was "refused by livestock" (100).

It has been suggested (2083) that small amounts of alkyl aryl sulfonates added to poultry foods might result in increased weights. Results indicate that there may be weight gain, no growth response, or even weight loss. Sodium oronite at 5 mg/l in the diet was reported to have given a five percent increase in weight for chicks (2085).

#### FISH AND OTHER AQUATIC LIFE

The concentrations of surface-active materials normally found in American rivers (0.0-0.14 mg/l) (2064) are not generally toxic to fish or other aquatic life over short periods of time (2086). There is a possibility, however, that toxicity to aquatic organisms might result if

the organisms are exposed to these materials over a long period of time or at greater concentrations. Although there is a considerable amount of information with respect to the toxicities of detergents to various aquatic life, it is still almost impossible to compare the work of different investigators. Many variables have been noted that are of considerable importance, and unless standardized techniques are agreed upon and used, there appears to be little hope that comparisons can often be made. Investigators are generally more interested in toxicities under a specific set of conditions than in theoretical or comparative toxicities.

It has been reported by Schmassman (753) that solutions of 10 mg/l of a Swiss detergent (containing pyridin) affected the respiration of fish and 20 mg/l of a German detergent killed fish in 12 hours, but fish immersed for a short time in 100 mg/l recovered completely when transferred to fresh water. He suggested that the strong wetting action of the detergents adversely affected the exchange of gas at respiratory surfaces. An American report (2087) possibly attributes a fish kill to an 8 mg/l ABS concentration from a sewage treatment plant effluent.

Degens et al. (821) show that concentrations of 5.0 mg/l of various detergents had a lethal effect on tadpoles. sticklebacks, roach, carp, and Daphnia after 5 to 100 hours, depending on the detergent and organism. Fish can become acclimatized to concentrations of 9 to 36 mg/l if the build-up is gradual from 3.0 mg/l. The limiting concentrations tolerated under acclimatized conditions were reported by Degens et al. as follows:

	Limiting	Concentra	tion in	mg/l for
Detergent **	Roach	Rhodeus	Idus	Carp
Sodium secondary alkyl sulfat	e 9	9	9	18
Alkyl aryl sulfonate	18	18	36	36
Sodium primary alkyl sulfate	9	9	9	18
Polyglycol ether of alkyl pheno	1 21	21	21	21

Experiments have shown that roach will normally die in waters containing 5 mg/l of detergent, but that this fish may gradually be acclimatized to live in waters containing 20 mg/l (2088). Herbert et al. (2086) observe that concentrations of 3 mg/l of alkyl aryl sulfonate in well-oxygenated, clean water produced a 50 percent mortality among rainbow trout in 12 weeks. This concentration would constitute an immediate danger to the fish if the dissolved-oxygen levels were at or near the lethal point. The work showed that the toxicity to fish of synthetic detergents is due to the surface-active material and not to the builder portions. Also, the paper points out that after sewage treatment the residues of the detergents that remain are much less toxic than the original detergents.

In a similar study, using both alkyl sulfate and alkyl aryl sulfonate, in aerated, 15-liter aquaria, and presumably at room temperature, Sierp and Thiele (2089) reported the following influences on goldfish:

Surface-Active Agent	Concentration mg/l	Mortality, in percent	Time of Exposure
None	0	0	14 days
Alkyl sulfate	5	0	10 days
-	10	30	4 days
	15	100	20 hours
Alkyl aryl sulfonate	5	0	14 days
•	10	30	2 days
	15	100	6 hours

Mann (2116) states that the characteristics of the toxic effects of surface-active agents on fish include the strong sliming of skin and gills, disturbance of equilibrium, turning to a side position, and finally, death. Mann's studies showed that the action of the toxic mechanism was on the epithelium of the gills and skin. Fish soaked in solutions of 100 mg/l or more prior to being cooked caused a burning feeling on the tongue. Lesser concentrations had no effect on the appearance or taste of the flesh. Even injecting detergents into the intestine of the fish had no effect on flesh taste. Experiments on Tubifex, Chironomus, Carinogammus, and Asellus demonstrated limiting concentrations for fishfood animals in the range of 5 to 10 mg/l. Later work (2117) showed limiting concentrations for fish of between 10 and 50 mg/l, but with Daphnia the first damage was observed at 5 mg/l.

The relative hardness of the water solution seems to have a definite effect upon the toxicity of surface-active agents to fish. Indeed, because of their precipitation as insoluble calcium salts, natural surface-active compounds exhibit a very greatly reduced effect in hard water (1756). Leclerc and Devlaminck (2090) reported the following toxicities to fish of synthetic and natural compounds in hard and soft water:

•	Minimum Lethal Concentration (mg/l active product)					
	Distilled Water		Hard Water (2 mg/l CaCOs)			
Surface-Active Compound	Dose	Temper- ature °C		Temper- ature °C		
Synthetic:						
Sodium lauryl sulfate (anionic) Sodium dodecyl benzene sulfonate	6-7	18°	6-7	23°		
(anionic)	6-7	18°	6-7	23°		
Polyglycol ether (nonionic)	2-3	18°	2-3	23°		
Natural		·				
Sodium palmitate	10-11	20°	900-950	21°		
Sodium oleate	11-12	20°	1000	21°		
Sodium stearate	10-12	20°	250-300			

Henderson et al. (1910) determined the median tolerance limits of various surface-active agents, largely with different percentages of ABS as the active ingredient. The results for both hard and soft waters have been summarized in Table 10-4. The same paper also studied the toxicities of soaps, using Lux Flakes, Ivory Snow, and Fels Naptha. The 96-hour TL_m values in soft water for the soaps varied from 29 to 42 mg/l (34 mg/l average), and in hard water from 920 to 1800 mg/l (1470 mg/l average). The same results for the five commercial synthetic detergents, Cheer, Tide, Dreft, Felso, and Vel, in soft water were 10.6 to 19.0 mg/l (15.1 mg/l average) and in hard water 4.5 to 15.6 mg/l (8.5 mg/l average) expressed in terms of 100 percent surfactant basis.

The State of Washington's Department of Fisheries has published an extensive work on toxicity studies of various pollutants to salmon and trout (2091). These studies included detergents known commercially as Blast, Santomerse D, Santomerse 3, Sterox SE, Sterox SK, and Gamlen CW. Results are presented in extensive tables that cite the fish stock, age, weight, numbers, source of water, analyses, volume, etc. Different parameters are used to express the results, but generally it was attempted to express them as a critical level (in mg/l) at which concentration obvious deleterious effects were observed. Hence, the critical level is recorded as "less than" this observed value. A brief summary of these data is presented on the following page.

Detergent Fish Santomerse D Silver Salmon Santomerse 3 Silver Salmon Sterox SE Silver Salmon Sterox SK Silver Salmon Chinook Salmon Blast Rainbow Trout	Lake, aerated Lake, aerated Lake, aerated Ground, aerated G Sea, aerated Lake, aerated	Critical Level in mg/l of Total Compound  < 5.6 < 5.6 < 20.0 < 5.6 < 17.8 < 53.2 <112.5 (67 mm fish) < 150.0 (118 mm fish)
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#### TABLE 10-4

## MEDIAN TOLERANCE LIMITS OF SURFACE-ACTIVE AGENTS TO FATHEAD MINNOWS AT 25°C

(After Henderson et al.) (1910)

<b>\</b> —-						
	л	fedian	Tolerance Limit (mg/l)			
	Sof	t Water	r *	Har	d Wate	· *
			96 hr			
Surface-Active Compound	z4 nr	48 167	90 147	24 161	40 101	20
Alkyl benzene sulfonates:						0.7
1. 100% ABS	4.8	4.5		4.0	3.5	3.5
2. 100% ABS**	8.2	7.5	5.6			
3 85% ABS: 15% inert						
(mostly sodium sul-	4.5	4.2	4.2	4.4	4.4	4.4
fate) 4. 60% ABS; 40% inert	1.0					
(mostly sodium sul-						0 =
fate)	15	15	15	8.5	8.5	8.5
5. 40% ABS: 60% inert						
(mostly sodium sul-	23	23	23	12	12	12
fate) 6. 31% ABS; 57% so-	43	20	20			
dium tripolyphos-						
phate	63	61	61	21	21	17
7. 30% ABS: 27% so-						
dium tripolyphos- phate; 20% sodium						
phate; 20% sodium	46	44	41	20	16	15
sulfate	40	**	11	20 .		
8. 22% ABS; 8% Alkyl sulfate; 65% sodium						
sulfate	64	62	61	28	28	28
9, 18% ABS; 47% so-						
dium tripolyphos-						
phate; 25% sodium	85	85	85	51	51	48
sulfate 10. 9% ABS; 9% alkyl	99	00	00	0.1	• •	
sulfate; 50% sodium						
tripolyphosphate;					• •	87
20% sodium sulfate_	59	59	59	100	90	5.9
Alkyl sulfate	5.9	5. l	59 5.1 37	56	42	38
Polyoxyethylene ester	- 14	$\begin{array}{c} 37 \\ 100 \end{array}$		,800 >1		
Sodium stearate	100	TOO	100 /1	,,,,,,	-,	

<ul> <li>Soft-water analysis:</li> <li>Hard-water analysis:</li> </ul>	EDTA Hardness	Alkalinity	Dissolved Oxygen	pH
	20 mg/l	18 mg/l	8.0 mg/l	7.4
	400 mg/l	360 mg/l	8.0 mg/l	8.2

** Bluegills were the test fish here

Wurtz-Arlet (2092) published a series of experiments on the toxicity of detergents to rainbow trout (Salmo gairdnerii). He used trout of 10 and 65 days age, and 4 and 8 cm length in groups of 10, and of 15 cm length in groups of 2 or 5. The test water was the same in which the fish had been raised: pH 6.9 ± 0.2, alkalinity (as CaO, to methyl orange) 22 mg/l, DO 75% ± 5% of saturation, temperature 9° and 14° C. He defined the dilution limit as being the highest concentration that does not cause any apparent trouble in the fish during the experiment nor during a 24-hour follow-up observation period in which the fish had been removed to uncontaminated water. In this study, he used one-and six-hour experimental periods. Results were as follows in mg/l of active product:

### Dilution Limits (After Wurtz-Arlet) (2092)

	Sodiu Arul Sulfo	m Alkyl nate (mg/l)	Octophenol (no	nionic) $(mg/l)$
Trout  10 days old 65 days old 4 cm long 8 cm long 15 cm long	1 Hour Exposure 10 12 12	6 Hours Exposure  5 7 7 7 7	1 Hour Exposure 10 15 25 25 25	s Hours Exposure 5 7 5 5 5 5

Wurtz-Arlet then defines "minimum lethal dose" as that concentration which causes the death of the fish during the period of the experiment. In this study he used similar one- and six-hour periods. The results:

## Minimum Lethal Dose (After Wurtz-Arlet) (2092)

	Sodiu Aryl Sulfo	m Alkyl nate (mg/l)	Octophenol (no	
Trout  10 days old 65 days old 4 cm long 8 cm long 15 cm long	1 Hour Exposure 20 20 15 20	6 Hours Exposure 12 10 12 12 12	1 Hour Exposure 30 30 35 35 35	6 Hours Exposure 15 15 10 12 12

In a study of the time required to kill all of the fish, a concentration of 5 mg/l of the anionic killed all fish in 26 to 30 hours, whereas a similar concentration of the nonionic took from one to three days. At 30 mg/l, the anionic killed in 35 to 45 minutes whereas the nonionic took 60 to 135 minutes.

The fourth method used by Wurtz-Arlet was that of average tolerance limit, or that concentration effective in killing 50 percent of the fish in 24 hours. These tests showed values of 3 to 7 mg/l for the anionic and 3 to 10 mg/l for the nonionic.

Turnbull et al. (2093) tested the toxicity of several commercial detergents against Lepomis machrochirus in carbon-filtered, Philadelphia tap water of the following characteristics. Total alkalinity to methyl orange, as CaCO₃, was 33.0-81.0 mg/l, pH 6.9-7.5, total hardness as  $CaCO_3$  84.0-163.0 mg/ $\overline{l}$ , specific conductance 228-301 micromhos, dissolved solids 154-210 mg/l, sulfates as SO₄ 56.0-98.0 mg/l, and chlorides as Cl 3.0-26.0 mg/l. Using the oxygenation interface method, and reporting values in terms of the commercial product, the 24- and 48-hour TLm values and the safe concentration in mg/l for Nalco 21 were 1.5, 1.4, and 0.37, and for alkyl aryl sulfonate were 4.2, 3.7, and 0.86, respectively. Other variables in these tests included: fish size 7 cm, fish weight 5 gms, temperature 20°C, 10 day acclimatization, DÖ 5 mg/l, and 10 fish per test.

A number of slime-control agents were studied using two bacteria, two molds, and a fish, the emerald shiner. The reader is referred to the original paper (2986) for the variables; the inhibiting concentration in mg/l for each agent was reported as follows:

Nalco	21 Nalco 23	Pyridyl- mercurio acetate	Pyridyl- mercuri chloride	c
Aerobacter aerogenes 750.  Bacillus mycoides 8.  Aspergillis niger 2000.  Penicillium expansum 95.  Emerald shiner 0.	0 450.0 0 10.0 0 35.0 0 40.0	1.0 0.15 95.0 25.0 0.15	1.0 .4.0 40.0 -0.04	200.0 7.0 3000, 3000. 10.0

Roccal, or alkyl dimethyl benzyl ammonium chloride, was tested against silver salmon (2091) and common shiner (2986). The 72-hour TL_m with salmon was 17.8 mg/l, and the TL_m in an unspecified time with shiner was between 15 and 17.5 mg/l. Although the salmon were unaffected by 10 mg/l for 72 hours, Woelke states that a concentration of 1.0 mg/l is lethal to bivalve larvae (2989).

Cairns and Scheier (2094), in an interesting, remarkably illustrated paper, show the extensive damage that is inflicted upon fish gills in relatively dilute solutions of

sodium alkyl benzene sulfonate. Acute tests with the bluegill sunfish at  $20^{\circ} \pm 1^{\circ}\mathrm{C}$  in both hard and soft synthetic dilution waters, using both batch and continuous flow, indicated 24-, 48-, and 96-hour  $\mathrm{TL_m}$  values of 17.15 to 17.44 mg/l for all test conditions. This test indicated a biologically safe concentration of 5.15 to 5.23 mg/l. Subsequent chronic studies (3 months exposure to 5.6 mg/l ABS) was reflected in severe gill damage, even though the fish's cruising-speed ability was not affected. The exposed fish also had higher oxygen consumption rates, increased erythrocyte counts, and increased parasitism in the mucous laden gill area by lower invertebrates (protozoans, rotifers, etc.) as compared to controls.

As the result of a proposal to use Tricon Oil Spill Eradicator in the San Francisco Bay area, Chadwick (2095) reported on toxicity studies of this proprietary product against striped bass which inhabit these waters. The product is an emulsifier consisting of 20 percent petroleum sulfonate, 5 percent fatty acid esters, 10 percent polyethylene glycol ether, 63 percent petroleum solvents and 2 percent alcohol, according to the manufacturer. Five striped bass ranging from 7 to 11 cm in length were placed in each of the 7500 ml aquaria through which air continuously bubbled. Temperature was maintained at 65°F. Concentrations of the product of 0.001 percent (10 mg/l) killed all fish in 10 hours or less, with the fish showing their first signs of distress in 1.5 hours. Concentrations of 0.0005 percent (5 mg/l) did not affect any death nor distress in the fish in a 48-hour exposure period.

Atlas 2082A is an emulsifier that has been used in aerial spray formulations. It is a preparation of alkyl aryl sulfonate and polyoxyethylene sorbitan esters of mixed fatty and resin acids, and has an estimated 48-hour TL_m to cohe salmon underyearlings of 20.7 mg/l. A limiting concentration is estimated to be approximately 2.1 mg/l (2990).

A possible synergistic effect between synthetic detergents and ammonia has been reported by Herbert (2096), who states that a solution containing both ammonia (ammonium chloride, 10 mg/l as N) and synthetic detergents (mixture of seven proprietary powders at 10 mg/l as Manoxol O.T.) was more toxic than either solution alone. In 7.5 hours, no trout died in tests on either of the individual substances. But when combined, 50 percent of the fish died in 36 and 199 minutes (2097). This work also demonstrated that at low oxygen levels (2.16 mg/l), 1.8 mg/l of mixed detergents (as Manoxol O.T.) allowed only 44-percent survival of rainbow trout at 20° ±0.3°C in 12 hours, whereas the control without detergent (at a dissolved-oxygen level of 2.11 mg/l) had no fatalities.

Although Burgess (2962) reports that the toxicity of syndets to fish varies from 7 mg/l for sodium lauryl sulfate to 2 mg/l for the polyglycol ethers, a preliminary study on a quaternary ammonium compound indicates even lower possible toxicity values. Using dodecylacetamido dimethyl benzyl ammonium chloride and the fathead minnow, 24-, 48-, and 96-hour TL_m values were found to be, respectively, 0.72, 0.65, and 0.65 mg/l (2987). These values were obtained at a pH of 7.6, dissolved oxygen 7.8 mg/l, total alkalinity 34 mg/l, and

hardness 30 mg/l. Diquat, also a quaternary ammonium compound and which is used as a herbicide, had a 48-hour  $TL_m$  for rainbow trout at 18°C of 70 mg/l, and for chinook salmon at 20°C of 28.5 mg/l. The proprietary quaternary Hyamine 1622 had a 48-hour  $TL_m$  for coho salmon at 20°C of 53 mg/l (2988).

The gradual decrease in bottom fauna of a carp pond is described to the inflow of synthetic detergents (2098). This paper also reports that decomposition of cellulose by "actively fermenting river mud" is hindered by detergents, but no figures are available in the abstract.

Jacob and Nisbet (2099) claim that quaternary ammonium compounds in concentrations of 1.2 to 2.0 mg/l can be used to control algae without "permanent" injury to fish. The compounds tested were described as "rather toxic" to minnows, varying from a minimum lethal concentration of 1 mg/l to 3-4 mg/l at 20°C depending on the length of the alkyl chain.

Several authors have investigated the effect of surface-active agents on fish-food organisms. Freeman (1712) tested the toxicity of certain sodium sulfonates toward Daphnia magna (temperature 23° ±1°C, pH of compound solutions in the range tested not related to effect), determining the average 100-hour toxicity threshold and the toxicity ranges. His results are summarized in the following tabulation:

Toxicity of Sodium Sulfonates to Daphnia magna (After Freeman) (1712)

·	Concentration in mg/l for:			
Compound tested	0% kill	50% kill	100% kil	
Sodium n-butylsulfonate. Sodium benzenesulfonate. Sodium p-chlorobenzenesulfonate. Sodium n-nitrobenzenesulfonate. Sodium n-nitrobenzenesulfonate. Sodium n-phenolsulfonate. Sodium 2-phenolsulfonate. Sodium 2-bidhorobenzene-2-sulfonate. Sodium 2-bidhorobenzenes-sulfonate. Sodium p-bromobenzenesulfonate.	1637 1895 1687 1000 556 318 389 200	3380 2840 2394 2335 1876 1474 1468 523	7827 8000 3007 5618 5623 3187 3890 843	
Sodium naphthalene-β-sulfate	55	135	308	
odium anthraquinone-x-sulfonate	10	12	30	

The results demonstrated that the more complex the ring structure of the aromatic compound, the more toxic the sulfonate; thus, in order of increasing toxicity: benzene, naphthalene, anthraquinone. The substitution of various groups on the benzene ring increased the toxicity (1712). Daphnia was also used as a test organism by Sierp and Thiele (2089). The results of their study with alkyl sulfate and alkyl aryl sulfate are tabulated as follows:

Influence of Surface-Active Agents on Daphnia (After Sierp and Thiele) (2089)

		4	Percent	Surviving		
Concentra- tion m/l	Sulf 24	ate (time 48	in hrs.) 100	Aryl Su 24	Alkyl Ifate (tim 48	e in hrs.) 100
0 5 10 15 25 35 50	>80 80 80 20-80 20-80 20-80 >20	>80 >80 >80 20-80 20-80 <20 0	>80 >80 >80 20-80 20-80 <20 0	>80 >80 >80 >80 20-80 0 0	>80 >80 20-80 0 0	>80 20-80 >20 0 0 0

To determine the molluscacidal effect of surface-active agents, Jakowski (2043) tested several anionics and

nonionics against the snail Stagnicola reflexa. Some of his results are given in Table 10-5.

Vallejo-Friere et al. (2042) compared the molluscacidal activity of various cationic quaternary ammonium compounds on *Australorbis* snails. Some of their findings are summarized in Table 10-6.

Other diversified effects of surface-active agents on aquatic animals have been reported. Nardone et al. (2100) found that surface-active materials disrupt permeability and pseudopod formation in the rhizopod Pelomyxa carolinensis. In tests with radioactive Na-22 and P. carolinensis, it was observed that the anionic alkyl aryl sulfonate (G-3300) did not promote or inhibit sodium uptake; the cationic N-soya-N-ethyl morpholiniumethosulfate (G-271) inhibited sodium uptake; and the nonionics polyoxyethylene sorbitan monolaurate (Tween 20), polyoxyethylene sorbitan monopalmitate (Tween 40), polyoxyethylene sorbitan monostearate (Tween 60), polyoxyethylene sorbitan monooleate (Tween 80), sorbitan monolaurate (Span 20), and sorbitan monooleate (Span 80), all caused an increased sodium uptake. According to Butzel et al. (2101) treatment of Paramecium aurelia with anionics caused the organism to lose its ability to respond to a difference in electrical potential. Cationics and nonionics were without effect on the normal movement of the animals toward the cathode.

Soaps in concentrations of 1000 to 2500 mg/l were lethal to mosquito pupae by reducing the surface tension of the water so that the pupae were unable to maintain their position and suffocated. Solutions containing 5000 to 10,000 mg/l were directly toxic to the pupae (805). In another paper, Ginsbury (756) claims that soap in a concentration of 2000 mg/l completely destroys mosquito larvae and pupae.

#### TABLE 10-5

## TIME IN MINUTES FOR MOLLUSCACIDAL EFFECT OF SURFACE-ACTIVE AGENTS ON STAGNICOLA REFLEXA

(After Jakowski) (2043)

	(Alter agreement)	(2010)					
			gent C	oncer mg/	itrati  l	on,	
Trade Name	Surface-Active Agent	0.5	•	10	20	50	
	NIONICS		MINU	TES			
Areskap 100	Sodium monobutyl phenylphenol mono-	21	10.5	8	7	5	
Aresket 300	sulfonate* Sodium monobutyl- biphenyl sulfonate*	19.5	15	12			
Aresklene 400	Disodium salt of dibutyl phenyphenol	34.5	18.5	9	6.5	5.5	
Duponol 80	disulfonate* n-octyl-sodium	60	30	25.5	5 4	3	
Santomerse D	sulfate Sodium decylbenzene sulfonate*	23.25	10.5	8	6	6	
Santomerse 3	Sodium dodecylbenzene sulfonate*	9	7	7	6	1	
Tergitol 08	Sodium 2-ethylhexyl sulfate*	>300 >	>300 >	-300	6	4	
•	NONIONIC	cs					
Sterox SE	Polyoxyethylene thioether	45	22	7	5	3.5	
Tergitol NPG	Alkyl-aryl- polyglycolether	13	8.5	7	6	3	
* Chemical form 2	ecording to Rosen and Goldsmith	(1900).					

Water plants, too, may be affected by the presence of surface-active agents. Experiments have shown that the rooted plants Ranunculus aquatilis, Potamogeton pectinatus, and Potamogeton densus are unable to grow in 2.5 mg/l of the alkyl aryl sulfonate detergent, Santomerse. The alga Cladophora and the moss Eurhynchium, however, grow normally in 5 mg/l of the detergent (1756). Degens et al. (821) found that concentrations of 40 mg/l of synthetic detergents were not harmful to several species of water plants.

Roberts (2102) immersed strands of the plants Callitriche, Ranunculus aquatilus, and Apium in dishes filled with a treated sewage effluent, 2.5 mg/l alkyl benzene sulfonate diluted in spring water, and a spring water control. Within two weeks, the effluent (with 2-6 mg/l ABS) and the 2.5 mg/l ABS samples showed browning, loss of leaves, and turgidity, whereas the control was unaffected. Teepol, an alkyl sulfate, gave similar results. Lissapol, a nonionic, showed no adverse effect even at doses of 20 mg/l against the same three plants.

According to Wurtz-Arlet (2103) concentrations of 1.0, 5.0 and 10.0 mg/l of a nonionic surface-active agent stimulated green algal growth during the first few days, but later caused a retardation. Growth was retarded from the start by 50 mg/l. Five mg/l of a cationic surface-active agent hindered growth of green algae and 10.0 mg/l of an anionic proved slightly toxic for 25 days, after which growth commenced. Concentrations of the cationic quaternary Diquat of as low as one mg/l dem-

### TABLE 10-6

## 48-HOUR PERCENTAGE KILL OF AUSTRALORBIS SNAILS IN AQUEOUS SOLUTIONS OF QUATERNARY AMMONIUM COMPOUNDS

(After Vallejo-Friere) (2042)

	(After Vallejo-Friere)	1/4	044)			
Trade Name	Compound		Conce	ntrati	on mg	
Trace Nume	Compound	1	2.5	5	10	20
Ammonix Dme	Cetyldimethylethyl- ammonium Br	80	100	100	100	100
Ammonix G	Cetyldimethylbenzyl-	0	54	96	100	100
Ammonix Trm	Ammonium Cl Cetyltrimethylethyl- ammonium Br	80	100	100	100	100
Bromat	ammonium Br Cetyltrimethyl- ammonium Br	26	92	100	100	100
BTC	Alkyldimethylbenzyl- ammonium Cl	0	0	0	32	100
BTC 471	Alkylethylbenzyldi- methylammonium Cl	0	18	100	100	100
BTC 927	Alkyldimethylbenzyldi- methylammonium Cl	0	62	84	100	100
	Cetyldimethylammon- ium Br	4	64	100	100	100
	Cetylpyridinium Cl	1	92	100	100	100
Hyamine 10X	Diisobutylcresoxy-	0	24	100	100	100
Hyamine 1622	ethoxyethyldimethyl- benzylammonium Cl Diisobutylphenoxy- ethoxyethyldimethyl-	2	20	64	100	100
Onyxide	benzylammonium Cl Octadecenyldimethyl- ethylammonium Br	4	90	100	100	100
Roccal	Dimethylbenzyl- ammonium Cl	0	10	80	100	100
Tetrosan 3, 4D		0	16	70	94	100
Triton K60	ammonium Cl Lauryldimethylbenzyl- ammonium Cl	- 0	8	46	64	100

onstrated some toxicity to Ceratophyllum demersum and Elodea densa in laboratory screening tests. Hyamine 1622, another proprietary quaternary, killed E. densa at a concentration of 2 mg/l (2988).

Williams et al. (2104) observed that species of the blue-green alga Oscillatoria were inhibited in growth by 5 mg/l of either one of the ammonium chloride cationic complexes known as Arquad C and Arquad D. Pearson et al. (2105) reported that 10 mg/l of sodium dodecyl sulfate or 1.0 mg/l of zephiran chloride showed

#### **TABLE 10-7**

#### TOXICITY OF QUATERNARY AMMONIUM COMPOUNDS TO ALGAE (22°C) (After Palmer and Maloney) (2041)

Period of Incubation in Days

2 mg/l Concentration 3 7 14 21 3 7 14 21 3 7 14 21 of the Compound or Cylindro-Mixture Indicated spermumMicrocystis Scenedesmus Methyldodecylbenzyl TPNNPNNNTTTN trimethyl ammonium chloride (50%), 50% water Cetyldimethyl ammonium NNNNNNNNNNN bromide (2%), alkylate ether alcohol (10%), 85% inert Dodecylacetamido PPPNTPPNTT dimethyl benzyl ammonium chloride (100%) High molecular alkyl-PPNNNINNNNPNN dimethyl-ammonium chloride (10%) Mixed trimethyl and  $N \ N \ N \ N \ N^{\scriptscriptstyle 1} N \ N \ N \ N \ P \ N \ N$ trimethyl-octadecadrenyl ammonium chlorides (25%), 75% water Methyl dodecyl benzyl NNNNNNNPPPN trimethyl ammonium chloride plus tridecyl methyl hydroxy ethyl imidazolinium chloride (10%), 90% water Chlorella Gomphonema Nitzschia Methyldodecylbenzyl PPNNTTTNTTN trimethyl ammonium chloride (50%), 50% water Cetyldimethyl ammonium NNNNNNNNNN bromide (2%), alkylate ether alcohol (10%), 85% inert Dodecylacetamido TTTTTTTTTTT dimethyl benzyl ammonium

Methyl dodecyl benzyl PPNNNNNNNNN trimethyl ammonium chloride plus tridecyl methyl hydroxy ethyl imidazolinium chloride

PNNNNNNNPNNN

NSNNNNNNNNN

T = Toxic. No growth occurred in presence of test chemicals, but did T=Toxic. No growth occurred in presence of test chemicals, but the in controls.

P=Partially toxic, Growth occurred in presence of test chemical, but not as profuse as in control.

N=Non-toxic, Growth in test chemical and control the same.

N1, P1, T2 = Glococapsa substituted for Microcystis.

chloride (100%)

High molecular alkyl-

dimethyl-ammonium chloride (10%)

Mixed trimethyl and

(10%), 90% water

75% water

trimethyl-octadecadrenyl

ammonium chlorides (25%),

marked inhibitory effects on kelp. In the same study using giant kelp Macrocystis pyrifera, Clendenning and North (2106) reported that the concentration of zephiran chloride causing a 50 percent inactivation of photosynthesis in bottom kelp fronds during a 4-day exposure was less than 1 mg/l, while 5-10 mg/l of sodium dodecyl sulfate were required for a similar effect (also see 2107). ABS at 5 mg/l and 2 mg/l gave complete inactivation in 48 and 96 hours, but at 0.5 mg/l it was only slightly detrimental in 96 hours, not at all in 48 hours. It is expected that the 96-hour TLm to photosynthesis is in the range of 0.5-1.5 mg/l of ABS (2108).

In a series of preliminary screenings, Palmer and Maloney (2041) tested the toxicity of several quaternary ammonium compounds to various algae. Their results are summarized in Table 10-7. The culture medium approximated Gerloff's modification of Chu No. 10 with the amount of nitrate doubled. Tests were carried out in 25 ml Erlenmeyer flasks in an illuminated room at 22°C with algae inoculations of approximately 125,000

per ml.

The Orsanco Aquatic Life Advisory Committee, in a recommendation to the Commission (see Ohio River Valley Water Sanitation Commission, Chapter III), summed up the available data on surface-active agents as follows. The average TLm values for the alkyl benzene sulfonates range from 3.5 to 6 mg/l. Laboratory tests for the sodium dodecyl benzene sulfonates indicate a 96-hour TLm of 3.5 mg/l. However, amounts of surfactants that are safe for aquatic life under continuous exposure remain unknown (2109).

### CONCLUSION

In conclusion, it is interesting to cite some European developments. One of the recommendations of the British Committee on Synthetic Detergents of 1956 was that "manufacturers of household synthetic detergents should investigate the feasibility of producing efficient washing products based on materials which can be readily oxidized or eliminated, and will not cause persistent foaming, during sewage treatment by present available (2120). Consequently, whereas the ordinary synthetic detergent of today is only capable of about 67 percent decomposition, attempts have been made to manufacture new types that will be capable of 94 percent decomposition. Some of these compounds have already given encouraging experimental results in effluents at Luton and the River Lee in England (82). Finding effective substitutes for ABS has been the main area of research in the development of these new detergents (2110). Surface-active agents based on sucrose esters, for instance, have proven very satisfactory in preliminary tests (2111).

McGauhey and Klein (2114) state that presently in both England and Germany serious consideration is being given to requiring the householder to use a detergent readily decomposed by the normal biochemical processes currently used in sewage treatment. Where these possible restrictions or new products will lead is a matter of conjecture. Chances are, however, that surfaceactive agents will continue to be a major water-quality problem for several more years.

#### APPENDIX A-1

# WATER QUALITY OBJECTIVES FOR THE EXPORTED AND SUBSURFACE OUTFLOW OF GROUND WATER FROM BUNKER HILL BASIN

Santa Ana Regional Water Pollution Control Board

## RESOLUTION 54-4 (Amended)

WHEREAS on October 17, 1952 this Board adopted a policy statement which reads in part as follows: "Water quality objectives for all surface streams, underground water basins, the ocean, its bays and tidewater area, will be formulated from time to time," and

WHEREAS the State Engineer on December 29, 1953 submitted a report to this Board concerning a discharge of industrial waste within Bunker Hill Basin in which were set forth certain tentative "standards to be considered the reasonable upper limit for the principal constituents in the ground waters of Bunker Hill Basin," and

WHEREAS the aforesaid standards were considered by this Board at its June 11, 1954 meeting in connection with the establishment of water quality objectives for Bunker Hill Basin and this Board at the said meeting ordered a further hearing on this matter, and

WHEREAS on August 12, 1954 a hearing was held at which all agencies and persons who had expressed an interest in the subject of water quality objectives for Bunker Hill Basin were invited to attend and at which certain valuable suggestions were presented to this Board by those attending, and

WHEREAS this Board finds and declares as a result of the aforesaid report, meeting and hearing and from its own knowledge and belief, the exported and subsurface outflow of ground water from Bunker Hill Basin is beneficially used and reused in the lower basins for domestic, agricultural and industrial purposes, and

WHEREAS this Board finds and declares likewise that ground water extracted and used within the Bunker Hill Basin is beneficially used and reused for domestic, agricultural and industrial purposes, and

WHEREAS this Board finds that in order to protect the aforesaid beneficial uses of water, it is necessary to establish water quality objectives for the exported and subsurface outflow of ground water from Bunker Hill Basin and likewise it is necessary to establish water quality objectives for ground water extracted and used within Bunker Hill Basin;

NOW THEREFORE BE IT RESOLVED that this Board hereby declares that it intends to protect the aforesaid beneficial uses of water from unreasonable impairment in quality.

BE IT FURTHER RESOLVED that, until further notice and hearing, the following water quality objectives are hereby adopted for the exported and subsurface outflow of ground water from Bunker Hill Basin,

such objectives representing the maximum tolerable concentration of each of the constituents named:

tration of each of the constitution	
Total dissolved solids Total hardness (as CaCO ₃ ) Chloride	500 parts per million 300 parts per million 60 parts per million 300 parts per million 0.20 parts per million 0.8 parts per million
Sodium percent	40

BE IT FURTHER RESOLVED that, in order to maintain the foregoing water quality objectives for the exported and subsurface outflow of ground water from Bunker Hill Basin, and until further notice and hearing, the following water quality objectives are hereby adopted for the ground water extracted and used within said basin, said objectives to be used as the basis for prescribing requirements for the discharge of sewage and/or industrial waste within said Basin and to represent the maximum tolerable increment in concentration of each of the substances named over that normally found in adjacent ground water unaffected by sewage and/or industrial waste disposal:

Total dissolved solids Total hardness (as CaCO ₃ ) Chloride Bicarbonate Boron Fluoride Dissolved sulfide Sodium percent	250 parts per million 50 parts per million 40 parts per million 100 parts per million 0.1 parts per million 0.4 parts per million None
------------------------------------------------------------------------------------------------------------------------------------	----------------------------------------------------------------------------------------------------------------------------------------

BE IT FURTHER RESOLVED that, as future changes in conditions indicate or as the quality of ground water within Bunker Hill Basin is or may be affected by factors other than sewage and/or industrial waste disposal, the foregoing water quality objectives for the ground water extracted and used within said Basin are subject to modification in any or all respects necessary to carry out the purpose of this resolution as hereinbefore stated.

BE IT FURTHER RESOLVED that, when requirements are prescribed for a particular discharge of sewage and/or industrial waste, nothing in the foregoing shall preclude: (1) The prescribing, when necessary, of requirements in addition to compliance with the foregoing water quality objectives for ground water extracted and used within Bunker Hill Basin (2) The modification of said objectives, when such modification is found to be reasonable and in conformity with the purpose of this resolution as hereinbefore stated.

BE IT FURTHER RESOLVED that, when requirements are prescribed for each major discharge of sewage and/or industrial waste within Bunker Hill Basin, where such discharge may affect ground water, and after study of available pertinent hydrological data, at least

three indicator water wells which are in active production or capable of active production of water shall be selected to measure compliance with requirements prescribed, said wells and the method of determining such compliance to be described in the resolution prescribing such requirements.

BE IT FURTHER RESOLVED that, whenever it is found that the increase in concentration in one or more of the constituents of the water sampled from any such

aforesaid indicator well has reached 50 percent of any prescribed increment in concentration, the discharger or discharger deemed responsible shall be notified in writing that a pollution is considered to be threatened.

BE IT FURTHER RESOLVED that this resolution is hereby made a supplement to the preliminary statement of long-range plans and policies with respect to water pollution control as adopted by this Board on October 17, 1952.

(Adopted January 28, 1955)

#### APPENDIX A-2

#### STATE OF CALIFORNIA

## REGIONAL WATER POLLUTION CONTROL BOARD NO. 4

LOS ANGELES REGION

#### RESOLUTION NO. 60-76

Prescribing Requirements for the Disposal of Sewage Treatment Plant Effluent-Whittier Narrows Water Reclamation Plant Sanitation Districts of the County of Los Angeles (File 60-129)

- WHEREAS, in compliance with Section 13054 of the Water Code of the State of California, the Sanitation Districts of the County of Los Angeles have filed with this Regional Water Pollution Control Board a Report on Waste Discharge in their letter of August 24, 1960, proposing:
  - a) Through the joint efforts of the County of Los Angeles, the Los Angeles County Flood Control District, the Central and West Basin Replenishment District, and the Los Angeles County Sanitation Districts, a program has developed which will result in the construction of a 10 m.g.d. demonstration water reclamation plant located just above the Whittier Narrows Dam;

The sewage that will be treated from the water reclamation plant will be diverted from the Districts' trunk sewer which passes through the plant site, a line that serves the western portion of San Gabriel Valley.

c) This plant will be designed, constructed, and operated by the Los Angeles County Sanitation Districts, and the effluent from the plant will be spread by the Los Angeles County Flood Control District in percolating areas to the south along the Rio Hondo River;

d) Los Angeles County will furnish the money to build the plant, and the Water Replenishment Dis-

trict will buy the water developed; and

WHEREAS, this Board has caused the following investigation to be made with respect to this proposed waste discharge:

- Field investigations were conducted by the staff of this Board.
- Copies of the proposal were sent to interested governmental agencies. Replies were received from:
- Los Angeles County Health Department—letters dated September 22 and October 24, 1960.
- Los Angeles County Flood Control District—letter dated October 26, 1960.
- State Department of Water Resources-communication dated October 27, 1960;
- State Department of Public Health-letter dated November 10, 1960; and

WHEREAS, based upon the foregoing investigations this Board finds that:

- 1. This proposal is a direct result of an engineering report submitted to the Los Angeles County Board of Supervisors in November, 1958, on the potential reclamation of sewage in Los Angeles County, which in turn was based on a study of potential reclamation of water from sewage in Los Angeles County, reported by a Board of Engineers in 1949. One of the chief recommendations of the 1958 report was "That said waste water reclamation envision the construction and operation of a demonstration plant at the Whittier Narrows Reservoir area to provide 10 million gallons daily of reclaimed water for recharge of ground water.'
- 2. The proposed sewage reclamation plant will be located north of San Gabriel Boulevard and west of Rosemead Boulevard between the cities of South El Monte and Montebello, Los Angeles County.
- 3. The proposed plant will employ the standard-rate activated sludge process followed by chlorination with provision for step aeration. All solids removed in the course of treatment, including sludge, grease, and screenings, will be pumped back into the Los Angeles County Sanitation Districts' Joint Outfall "B" for ultimate disposal through the Districts' sewerage system. The design will permit partial or complete bypassing of the plant.
- 4. The sewage which it is proposed to reclaim will be essentially domestic in character. Sewage samples taken in 1955 and 1960 from Joint Outfall "B" in the vicinity of the proposed plant, and analyzed by the Department of Water Resources, averaged 1435 mmho electrical conductivity, 164 ppm hardness, 121 ppm chloride, 129 ppm sulfate, 0.6 ppm boron, and 52% equivalent sodium ratio. The mineral quality of such waters is acceptable for domestic uses and Class 2 for irrigation.

5. Effluent from the proposed reclamation plant will be spread in the following areas at various times by the Los Angeles County Flood Control District:

a) San Gabriel River, near Siphon Boulevard, by conveyance by means of an unlined canal and pipeline. Waste water flows will then be spread within the unlined river bed downstream as far as Florence Avenue, and/or within the San Gabriel Spreading Grounds.

Rio Hondo, by direct discharge upstream of San Gabriel Boulevard. Waste water flows will percolate in the stream bed above the Rio Hondo outlet works of Whittier Narrows Dam and thence either be introduced into the unlined rising water channel for spreading in the Rio Hondo Spreading Grounds West Side or be con-

- veyed downstream in the lined Rio Hondo and diverted into the spreading grounds on the east side of the channel.
- c) A spreading grounds area within Whittier Narrows Reservoir, generally enclosed by Rosemead Boulevard, the Southern California Edison Company right-of-way for transmission lines near Legg Lake, and the Flood Control District's Zone I Bypass Ditch.
- There is one surface diversion in the Whittier Narrows area, a diversion from the San Gabriel River about 0.5 miles downstream of the dam for citrus irrigation.
- 7. The principal aquifers underlying the reclamation plant site and downstream area are in hydraulic continuity with the ground surface and with one another. Liquids discharged on the surface may percolate to all of these aquifers.
- 8. Ground waters of the Whittier Narrows and Montebello Forebay are beneficially used for domestic, agricultural, and industrial purposes, and constitute the principal source of recharge to the producing aquifers of the Central Basin and West Coast Basin. These waters are of excellent quality, generally containing less than 60 ppm chloride, less than 150 ppm sulfate, and 200-500 ppm total dissolved solids. However, the effects of spreading imported Colorado River water have already been indicated by increasing concentrations of mineral constituents; and
- WHEREAS, on November 18, 1960, a letter transmitting a proposed copy of this resolution was submitted to the Los Angeles County Sanitation Districts and copies thereof sent to interested governmental agencies and individuals with advice that objections thereto would be considered by this Board, if submitted in writing on or before December 7, 1960; and
- WHEREAS, objections and recommendations received by the Board have been reviewed and considered;
- NOW, THEREFORE, BE IT RESOLVED, that in order to prevent a condition of pollution of the receiving waters and to prevent creation of a nuisance, this Regional Water Pollution Control Board in accordance with authority granted by Division 7 of the Water Code of the State of California, prescribes the following requirements for the disposal of reclaimed sewage wastes into the proposed spreading areas of the Los Angeles County Flood Control District, as described hereinbefore, subject to the provisions of Section 13054 of said Water Code, which reads in part that requirements may be revised from time to time:
  - The discharge of raw sewage or any wastes containing visible solids of sewage origin shall be prohibited.
  - 2. The effluent shall be well oxidized and stable.
  - 3. The discharge of wastes shall not cause odors of sewage origin.
- The wastes discharged shall at no time contain substances in concentrations toxic to human, animal, plant or fish life.

- 5. The wastes discharged shall not contain phenols, cresols, or any other substances in concentrations sufficient to impart objectional tastes, odors or foaming to useable waters.
- 6. The quality of the effluent discharged from the sewage treatment plant shall at no time exceed the following maximum limits of the constituents listed:

CONSTITUENTS	MAXIMUM LIMI
Total dissolved solids, ppm	1000
Sulfate plus chloride, ppm	500
Chloride, ppm	250
Boron, ppm	2.0
Sodium equivalent ratio	60%
Lead, ppm	0.1
Fluoride, ppm	1.5
Alkyl benzene sulfonate detergents	(ABS), ppm 2.0
Arsenic, ppm	0.05
Selenium, ppm	0.05
Hexavalent chromium, ppm	0.05
Copper, ppm	3.0
Iron and manganese together	0.3
Zine	15

- BE IT FURTHER RESOLVED, that this Board does hereby inform the County Sanitation Districts of Los Angeles County that the State Department of Public Health has advised the Board that they believe, in order to protect the public health the following conditions should be observed.
  - "1. The public should be prevented from having contact with the sewage and sewage effluent.
  - 2. The chemical and bacterial content of the sewage percolated into the ground water should be regulated so that waters taken therefrom for domestic use are not contaminated.
  - 3. Use of the sewage effluent for irrigation should comply with the provisions of the regulations of the State Department of Public Health.
  - The breeding of nuisance and/or disease vectors in the sewage effluent should be prevented.
  - 5. A monitoring program of the effluent quality and the quality of the receiving waters should be maintained."
- BE IT FURTHER RESOLVED, that no condition or conditions shall exist or be permitted to exist which may constitute a public nuisance under the laws of the State of California as the result of the operation of the sewage reclamation plant and disposal of effluent as proposed; and
- BE IT FURTHER RESOLVED, that for the purpose of checking compliance with the conditions hereinbefore specified, and pursuant to the authority granted by Section 13055 of the Water Code of the State of California, the Los Angeles County Sanitation Districts shall commence on the first of the month following the start of operation of the sewage reclamation plant, and shall continue thereafter a monitoring program for observing, sampling, analyzing, and reporting as follows:

#### A. Location of Sampling Stations.

1. A sampling station shall be located just before the reclaimed sewage effluent leaves the water reclamation plant.

- B. Type, Frequency and Techniques of Sampling and Analyzing.
  - 1. All samples shall be taken and all analyses shall be performed in accordance with the latest edition of "Standard Methods for Examination of Water, Sewage, and Industrial Wastes" published by the American Public Health Association except that for specific analyses newer techniques and newer analytical instruments, such as the spectrophotometer, may be used if, in the judgment of the Executive Officer, results are obtained consistent with the objectives of these waste discharge requirements.

2. Once per month the sewage reclamation plant effluent shall be sampled hourly during the period operators are on duty and composited in proportion to flow. On this composite sample the following analyses shall be made:

BOD (5 day at 20°C) Suspended solids Total dissolved solids Sulfate

Chloride

Boron

Sodium equivalent ratio

ABS detergents

 ${f Phenols}$ 

This series of analyses shall be known as the "partial analysis".

3. Once each quarter the analyses on the composite sample for that day from the sewage reclamation plant shall be expanded to include the following determinations:

Lead Fluoride Arsenic Selenium

Hexavalent chromium

Copper

Iron and manganese together

Zine

This series of analyses, plus the "partial analyses" shall be known as the "extended analysis".

#### C. Records and Reports.

- 1. Complete records shall be maintained of all aspects of the monitoring program and results therefrom.
- Two copies of all such reports shall be furnished upon completion to the Los Angeles Regional

Water Pollution Control Board for each calendar month within fifteen (15) days after the end of such calendar month.

3. Said records and reports are public documents and shall be available for inspection during business hours at the office of the Los Angeles Re-

gional Board; and

BE IT FURTHER RESOLVED, that the staff of this Board be, and hereby is, directed to coordinate with the Los Angeles County Sanitation Districts, the Los Angeles County Flood Control District, and the Department of Water Resources in a program to establish several appropriate wells as sampling stations for obtaining data to determine the effect, if any, which the proposed waste water disposal will have on underground receiving waters. Such data would consist of, but would not be limited to, analyses of samples pumped once every quarter at each station for the following constitutents:

Total dissolved solids Sulfate Chloride

ABS detergents;

and

BE IT FURTHER RESOLVED, that in prescribing these requirements it is the intent of this Board to:

1. Preserve the quality of the receiving waters, insofar as they may be affected by this waste discharge, suitable for domestic, agricultural, and industrial uses.

2. Prevent creation of a nuisance as a result of this

discharge; and

BE IT FURTHER RESOLVED, that the requirements listed above do not authorize commission of any act resulting in injury to the person or property of

another; and

- BE IT FURTHER RESOLVED, that the County Sanitation Districts of Los Angeles County are hereby advised that these requirements do not exempt the operator of this waste disposal facility from any other law which may be applicable. The requirements listed above are not a permit; they do not legalize this proposed waste disposal facility, and they leave unaffected any further restraints on the disposal of wastes at this site which may be contained in other statutes; and
- BE IT FURTHER RESOLVED, that the Executive Officer be authorized and he is hereby directed to certify and submit copies of this resolution to the County Sanitation Districts of Los Angeles County and to such other agencies and individuals as may have need therefor or as may request same.

#### APPENDIX B

## KANSAS STATE BOARD OF HEALTH, RADIATION PROTECTION REGULATIONS

28-35-11. Maximum Permissible Dose and Concentrations. The maximum permissible doses specified in this regulation shall not be considered to apply to intentional radiation exposures applied for diagnostic or therapeutic purposes by persons licensed to practice one or more of the healing arts within the authority granted to them by the Kansas healing arts statute or by persons licensed to practice dentistry or podiatry within the authority granted to them by Kansas licensing laws applying to dentists and podiatrists.

- a. The radiation doses to which individuals are exposed shall be kept to the lowest practicable level at all times.
- b. The maximum permissible dose for an individual shall be considered to include all doses, from internal and external sources, from all types and energies of radiation, whether delivered simultaneously or successively, to the region of interest, during the period of measurement.
- c. When the source of radiation is outside the body, the maximum permissible dose rate for individuals occupationally engaged in radiation work shall not exceed those values specified in Appendix B of these regulations.
- d. When the source of radiation is within the body, radiation doses shall be controlled by limiting the average rates at which radioactive materials are taken into the body, either by inhalation or by ingestion. Where such intake results from the occurrence of radionuclides in air or water, the average concentration of the radionuclides in air or water used by individuals occupationally engaged in radiation work shall not exceed the maximum permissible concentration specified in Appendix F, Table I, of these regulations.
- e. No owner or user shall utilize any radiation source so as to cause any individual in his employ under 18 years of age to receive radiation exposure exceeding one-tenth the maximum permissible dose for occupationally exposed individuals, as established in section c, of this regulation, or to be exposed to airborne or water-borne radioactive materials in concentrations in excess of the limits specified in Appendix F, Table II, of these regulations.
- f. The radiation dose to any population group shall be limited to one-tenth the maximum permissible amounts stated in Appendix B and the exposure of population groups to radioactive materials in air or water shall be limited to the concentrations specified in Appendix F, Table II, of these regulations.
- g. No owner or user shall possess or utilize any radiation source so as to cause any individual outside the confines of the controlled area or any population group to receive radiation exposure exceeding

- one-tenth the maximum permissible dose for occupationally exposed individuals, as established in section c of this regulation, or to be exposed to airborne or water-borne radioactive materials in concentrations in excess of the limits specified in Appendix F, Table II, of these regulations.
- h. The determination of the dose received by individuals and degree of radiation hazard present in all places to which these regulations apply shall be guided by nationally recognized standards such as, (1) the recommendations of the National Committee on Radiation Protection and Measurements as published in Handbooks of the National Bureau of Standards, (2) recommendations and reports of the Federal Radiation Council, and (3) standards established in regulations of the United States Atomic Energy Commission.

(Authorized by G.S. 1959 Supp., 48-1103) (Effective September 1, 1961)

28-35-26

Maximum Permissible Concentrations of Radionuclides in Water *

	m m	ICI		
Element Atomic Number	Instanci t		Table I	Table II
Actinium 89	1901076-1-		(uc/ml)	(ue/ml)
Actimum 89	Aces	s I S I	6 × 10-5	$\begin{array}{c} 2 \times 10^{-6} \\ 3 \times 10^{-4} \end{array}$
	Ac ²²⁸	Ť	$9 \times 10^{-3}$	$3 \times 10^{-4}$
	AC220	Ş	$3 \times 10^{-3}$	9 × 10-5
Americium 95			$3 \times 10^{-3}$	9 × 10~5
Americium 95	Am ²⁶¹	s I S I	$1 \times 10^{-4}$	4 × 10-8
	$Am^{248}$	Ĭ	$8 \times 10^{-4}$	$2 \times 10^{-5}$
	Am	ສັ	1 🗙 10-4	$4 \times 10^{-8}$
A A2 #4		1	8 × 10→	$3 \times 10^{-5}$
Antimony 51	Sb123	SI	$8 \times 10^{-4}$	$3 \times 10^{-5}$
	G1 704	Ĩ	$8 \times 10^{-4}$	$3 \times 10^{-5}$ $2 \times 10^{-5}$ $2 \times 10^{-5}$
	Sb ¹²⁴	ន្ទ	$7 \times 10^{-4}$ $7 \times 10^{-4}$	$2 \times 10^{-5}$
	Sbizs	Ä	7 X 10-4	$2 \times 10^{-5}$
	50	S	$3 imes10^{-8}$	$1 \times 10^{-4}$
Argon 18			3 🗙 10~8	$1 \times 10^{-4}$
A15011 10	A87	Sub		
	Att	Sub		
Arsenic 33	$As^{r_2}$	S	$1 \times 10^{-2}$	$5 \times 10^{-4}$
		I	$1 \times 10^{-2}$	5 × 10 4
	As ⁷⁴	Š	$2 \times 10^{-3}$	$5 \times 10^{-5}$
	As ⁷⁶	I S I S I	$2  imes 10^{-8}$	$5 \times 10^{-5}$
	Ago	Ş	$6 \times 10^{-4}$	$2 \times 10^{-6}$
	$As^{rr}$	Ť.	$6 \times 10^{-4}$	$2 \times 10^{-5}$
	As.	န	$2 \times 10^{-8}$	8 × 10-5
Astatine 85	A 1007		$2  imes 10^{-3}$	$8 \times 10^{-5}$
Therefore on	Atzu	s I	$5 \times 10^{-5}$	$2 \times 10^{-6}$
Barium 56		ī	$2 \times 10^{-3}$	$7 \times 10^{-8}$
Darrum bb	$\mathbf{B}\mathbf{a}^{181}$	S I S I	$5 \times 10^{-3}$	2 × 10→
	***	1	$5 \times 10^{-3}$	$2  imes 10^{-4}$
	Ba ¹⁴⁰	ន្ទ	$8 \times 10^{-4}$	$3 \times 10^{-5}$ $2 \times 10^{-5}$
Dowlessian or		1	8 × 10 <del>-4</del>	$2 \times 10^{-5}$
Berkelium 97	$\mathbf{Bk^{249}}$	S	$2  imes 10^{-2}$	$6 \times 10^{-4}$
T		1	$2  imes 10^{-2}$	6 × 10→
Beryllium 4	.Be ⁷	s I	$5 \times 10^{-2}$	$2 \times 10^{-8}$
		Ĩ	$5 \times 10^{-2}$	2 € 10-8
Bismuth 83	Bi208		1 × 10-8	4 × 10-5
		ř	1 × 10-3	$4 \times 10^{-5}$
	Bi ²⁰⁷	ŝ	2 × 10-*	6 × 10-5
		SISISISI	$2 \times 10^{-8}$	6 × 10-8
	Bi210	S	$1 \times 10^{-3}$	4 × 10-⁵
		1	$1 \times 10^{-3}$	4 × 10-5
	Blas	S	$1 \times 10^{-3}$	4 × 10-4
		1	$1 \times 10^{-2}$	4 × 10⁻⁴

^{*} The values are taken from Appendix B of 10 CFR 20.
(Authorized by G. S. 1959 Supp., 48-1103)
(Effective September 1, 1961)

WATER QUALITY CRITERIA									
	28-35-26—Co			1:	Element Atomic Number	Isotope 1, 2 Au ¹⁹⁶	s	Table I (uc/ml) $5 \times 10^{-3}$	Table II $(uc/ml)$ $2 \times 10^{-4}$
Maximum Permissi	ble Conce	ntration	is of Radionuc	liaes	Gold 79	Au ¹⁹⁸	Ĩ S	$\begin{array}{c} 4 \times 10^{-3} \\ 2 \times 10^{-3} \end{array}$	$1 \times 10^{-4}$ $5 \times 10^{-5}$ $5 \times 10^{-5}$
	in Wat	er ~		Table II		-	Ĭ	$\begin{array}{c} 1 \times 10^{-8} \\ 5 \times 10^{-8} \end{array}$	5 × 10-5 2 × 10-4
Element _	Isotope 1, 2		$Table\ I \ (uc/ml)$	(uc/ml)		Au ¹⁹⁹	I	$4 \times 10^{-8}$	$2 \times 10^{-4}$ $2 \times 10^{-4}$
Atomic Number Bromine 35	Br ²⁰	S I	8 × 10 ⁻⁸ 1 × 10 ⁻⁸	$3 \times 10^{-4} \\ 4 \times 10^{-5}$	Hafnium 72	Hf ¹⁸¹	s I	$^{2}_{2}  imes ^{10^{-3}}_{10^{-3}}$	$\begin{array}{c} 7 \times 10^{-8} \\ 7 \times 10^{-5} \end{array}$
Cadmium 48	Cq300	S	5 V 10-8	2 × 10-4	Holmium 67	Ho166	S I	$\begin{array}{c} 9 \times 10^{-4} \\ 9 \times 10^{-4} \end{array}$	$3 \times 10^{-8}$ $3 \times 10^{-5}$ $3 \times 10^{-8}$
	$Cd_{^{315m}}$	ş	5 × 10 ⁻³ 7 × 10 ⁻⁴ 7 × 10 ⁻⁴	$2 \times 10^{-4} \\ 3 \times 10^{-5} \\ 3 \times 10^{-6}$	Hydrogen 1	$\mathbf{H}_{8}$	S Sub	1 × 10 ⁻¹	
	$Cd^{135}$	I S I S I	i × 10-3 1 × 10-3	$3 \times 10^{-6} \\ 4 \times 10^{-8}$	Indium 49	In118m	S I	$4 \times 10^{-2} \\ 4 \times 10^{-2}$	$1 \times 10^{-3}$ $1 \times 10^{-8}$
Calcium 20	Ca45	s	$3 \times 10^{-4}$ $5 \times 10^{-3}$	$9 \times 10^{-6}$ 2 × 10 ⁻⁴		In ^{114m}	S I	5 × 10 ⁻⁴ 5 × 10 ⁻⁴	$2 \times 10^{-6}$ $2 \times 10^{-5}$ $4 \times 10^{-4}$
	Ca47	S I	$\begin{array}{c} 1 \stackrel{>}{\times} 10^{-8} \\ 1 \stackrel{>}{\times} 10^{-8} \end{array}$	$\begin{array}{c} 5 \times 10^{-5} \\ 3 \times 10^{-5} \end{array}$		Iniism	ŝ	$1 \times 10^{-2}$ $1 \times 10^{-3}$	4 × 10→ 9 × 10→
Californium 98	Cf249	S	1 × 10→	$^{4}_{2}  imes ^{10^{-6}}_{2}$		Inus	S I	$3 \times 10^{-8} \\ 3 \times 10^{-8}$	$9 \times 10^{-5}$
	Cf ²⁵⁰	I S I	7 × 10 ⁻⁴ 4 × 10 ⁻⁴ 7 × 10 ⁻⁴	1 × 10−5	Iodine 53	I128	SI	$5 \times 10^{-8}$ $3 \times 10^{-8}$	$2 \times 10^{-6}$ $9 \times 10^{-6}$
	Cf ²⁵³	s I	7 × 10 ⁻⁴ 7 × 10 ⁻⁴	$\begin{array}{c} 3 \times 10^{-5} \\ 2 \times 10^{-6} \\ 2 \times 10^{-6} \end{array}$		I139	s I	$1 \times 10^{-5}$ $6 \times 10^{-8}$	$4 \times 10^{-7}$ $2 \times 10^{-4}$
Carbon 6	C14	s	$2 \times 10^{-2}$	8 × 10→		List	1	$6 \times 10^{-5}$ $2 \times 10^{-3}$	2 × 10 ⁻⁶ 6 × 10 ⁻⁵ 6 × 10 ⁻⁸
Cerium 58	(CO ₂ )	Sub S	3 × 10-3	9 × 10 ⁻⁵		I.138	S I	$2 \times 10^{-8}$ $5 \times 10^{-8}$ $2 \times 10^{-4}$	$2 \times 10^{-4}$ $7 \times 10^{-3}$
Corrain to	Ce ¹⁴⁸	I S	$3 \times 10^{-8} \\ 1 \times 10^{-8}$	$9 \times 10^{-5}$ $4 \times 10^{-5}$		I188	S I S	1 🗴 10-8	$\begin{array}{c} 4 \stackrel{\frown}{\times} \stackrel{10-5}{10-4} \\ 1 \stackrel{\frown}{\times} 10^{-4} \end{array}$
,	Ce ¹⁴⁴	S S I	$\begin{array}{c} 1 \times 10^{-3} \\ 3 \times 10^{-4} \end{array}$	$\begin{array}{c} 4 \times 10^{-5} \\ 1 \times 10^{-5} \end{array}$		Ţ186	Ι	$\begin{array}{c} 4 \times 10^{-8} \\ 2 \times 10^{-2} \\ 7 \times 10^{-4} \end{array}$	$ \begin{array}{c} 1 \\ 6 \\ \times \\ 10^{-4} \\ 2 \\ \times \\ 10^{-5} \end{array} $
Cesium 55	Cs181		$\begin{array}{c} 3 \times 10^{-4} \\ 7 \times 10^{-2} \end{array}$	$1  imes 10^{-5}$ $2  imes 10^{-8}$		Lrsz	s I	$2 \times 10^{-8}$	$7 \times 10^{-6}$
Cesium 55	Cs ^{184m}	S I S	$3 \times 10^{-2}$ $2 \times 10^{-1}$ $3 \times 10^{-2}$ $3 \times 10^{-2}$ $3 \times 10^{-4}$	$^{9}_{6} \times ^{10^{-4}}_{10^{-3}}$	Iridium 77		S I	$\begin{array}{c} 6 \times 10^{-3} \\ 5 \times 10^{-3} \end{array}$	$\begin{array}{c} 2 \times 10^{-4} \\ 2 \times 10^{-4} \end{array}$
	Cs ¹⁸⁴	S I S	$3 \times 10^{-2}$ $3 \times 10^{-4}$	1 × 10−3		Ir192	S I	$1 \times 10^{-8}$ $1 \times 10^{-8}$	$4 \times 10^{-8}$ $4 \times 10^{-5}$
	Cs185	Ĩ	$\overset{1}{\cancel{\times}}\overset{\widehat{\cancel{1}}\overset{0}{\cancel{-3}}}{\overset{3}{\cancel{\times}}}\overset{1}{\cancel{0}}\overset{-3}{\overset{3}{\cancel{\times}}}$	9 × 10 ⁻⁶ 4 × 10 ⁻⁵ 1 × 10 ⁻⁴ 2 × 10 ⁻⁴		Ir ¹⁹⁴	Š I	1 × 10 ⁻⁸ 9 × 10 ⁻⁴	$3 \times 10^{-5}$ $3 \times 10^{-5}$
	Cs ¹⁸⁶	Ĩ	$7 \times 10^{-3} \\ 2 \times 10^{-8}$	2 × 10 ⁻⁴ 9 × 10 ⁻⁵ 6 × 10 ⁻⁵	Iron 26	Fe ⁵⁵	S	$^{2}_{7}{}^{\times}^{10^{-2}}_{10^{-2}}$	$\begin{array}{c} 8 \times 10^{-4} \\ 2 \times 10^{-8} \end{array}$
	Cs187	81818181 81	2 × 10 ⁻³ 4 × 10 ⁻⁴	$2 \times 10^{-5}$		$\mathbf{F}e^{50}$	I S I	$2 \times 10^{-8}$ $2 \times 10^{-8}$	6 × 10~8 5 × 10~8
Chlorine 17	Clss		$1 \times 10^{-8}$ $2 \times 10^{-8}$	4 × 10 ⁻⁵ 8 × 10 ⁻⁵	Krypton ⁹ 36	Kr ^{85m} Kr ⁸⁵	Sub Sub		
Chorne 11	Clas	s I s	$\begin{array}{c} 2 \times 10^{-3} \\ 1 \times 10^{-2} \end{array}$	$\begin{array}{c} 6 \times 10^{-6} \\ 4 \times 10^{-4} \end{array}$		Kr ⁸⁷	Sub S	7 × 10 ⁻⁴	$2 \times 10^{-5}$
Chromium 24		s I S	1 × 10 ⁻² 5 × 10 ⁻²	4 X 10→	Lanthanum 57		I	$7 \times 10^{-4}$	$2 \times 10^{-8}$
_		I	$\begin{array}{c} 5 \times 10^{-2} \\ 5 \times 10^{-2} \\ 2 \times 10^{-2} \end{array}$	$2 \times 10^{-3}  2 \times 10^{-3}  5 \times 10^{-4}$	Lead 82		SI	$1 \times 10^{-2}$ $1 \times 10^{-2}$	4 × 10→ 4 × 10→ 1 × 10→
Cobalt 27		S I	1 × 10 ⁻² 8 × 10 ⁻² 6 × 10 ⁻²	$\begin{array}{c} 3 & \stackrel{?}{\sim} 10^{-4} \\ 4 & \stackrel{?}{\times} 10^{-4} \\ 3 & \stackrel{?}{\times} 10^{-8} \end{array}$		Pbzro	S I S I	$4 \times 10^{-6}$ $5 \times 10^{-3}$	$\begin{array}{c} 1 \times 10^{-4} \\ 2 \times 10^{-5} \\ 2 \times 10^{-5} \end{array}$
	Cossa Cossa	I I	6 × 10-2 4 × 10-3	2 × 10-3 1 × 10-4		Pb ²¹⁸		6 × 10→ 5 × 10→	$z \times 10^{-3}$
	Co.	I S I S I S I	$3 \times 10^{-3}$ $1 \times 10^{-3}$	2 × 10 ⁻⁵ 1 × 10 ⁻⁴ 9 × 10 ⁻⁵ 5 × 10 ⁻⁵	Lutetium 71	Lu ¹⁷⁷	S	$3 \times 10^{-8} \\ 3 \times 10^{-8}$	$\begin{array}{c} 1 \times 10^{-4} \\ 1 \times 10^{-4} \end{array}$
			$\stackrel{\overset{\bullet}{1}}{\times}\stackrel{\overset{\bullet}{10}}{\stackrel{-8}{\sim}}$ $1\times10^{-2}$	3 × 10_2	Manganese 25	Mn ⁸²	S I	$1 \times 10^{-8} \\ 9 \times 10^{-4}$	$\begin{array}{c} 3 \times 10^{-5} \\ 3 \times 10^{-5} \end{array}$
Copper 29		S	$6 \times 10^{-8}$	3 × 10 ⁻⁴ 2 × 10 ⁻⁴		Mn54	S I S I S I	$\frac{4 \times 10^{-8}}{3 \times 10^{-8}}$	$\begin{array}{c} 1 \times 10^{-4} \\ 1 \times 10^{-4} \end{array}$
Curium 96		s I	$\begin{array}{c} 7 \times 10^{-4} \\ 7 \times 10^{-4} \end{array}$	$2 \times 10^{-6}$ $3 \times 10^{-6}$		Mn ⁵⁸		$\frac{4 \times 10^{-3}}{3 \times 10^{-8}}$	$\begin{array}{c} 1 \times 10^{-4} \\ 1 \times 10^{-4} \end{array}$
•	Cm ²⁴⁸	s I	$\begin{array}{c} 1 \times 10^{-4} \\ 7 \times 10^{-4} \end{array}$	5 × 10-8 2 × 10-5 7 × 10-8	Mercury 80	Hg ^{197m}	SI	${}^{6 imes10^{-8}}_{5 imes10^{-8}}$	$2 \times 10^{-4}$ $2 \times 10^{-4}$ $3 \times 10^{-4}$
	. Cm ²⁴⁴	S I S	$2 \times 10^{-4}$ $8 \times 10^{-4}$	$7 \times 10^{-6}$ $3 \times 10^{-6}$		Hg ¹⁹⁷	I S I	$9 \times 10^{-3} \\ 1 \times 10^{-2}$	$3 \times 10^{-4}$ $5 \times 10^{-4}$ $2 \times 10^{-8}$
	Cm ²⁴⁵	S I S	$1 \times 10^{-4}$ $8 \times 10^{-4}$ $1 \times 10^{-4}$	4 × 10-6 3 × 10-5 4 × 10-6		Hg ²⁰⁸	SI	$\begin{array}{c} 5 \times 10^{-4} \\ 3 \times 10^{-8} \end{array}$	2 × 10-3 1 × 10-4
	Cm ²⁴⁸	I	8 × 10-4	$\begin{array}{c} 4 \times 10^{-6} \\ 3 \times 10^{-5} \\ 4 \times 10^{-4} \end{array}$	Molybdenum 42	_ Mo99	8 1	$\begin{array}{c} 5 \times 10^{-8} \\ 1 \times 10^{-8} \end{array}$	$\begin{array}{c} 2 \times 10^{-4} \\ 4 \times 10^{-5} \end{array}$
Dysprosium 66		8 1 8	$1 \times 10^{-2}$ $1 \times 10^{-2}$	4 × 10 ⁻⁴ 4 × 10 ⁻⁵	Neodymium 60	. Nd144		2 × 10 ⁻⁸	7 × 10 ⁻⁵ 8 × 10 ⁻⁵
•	Dy ¹⁶⁶	1	$1 \times 10^{-3} \\ 1 \times 10^{-3}$	$4 \times 10^{-6}$		$Nd^{147}$	ŝ	$\begin{array}{c} 2 \times 10^{-3} \\ 2 \times 10^{-8} \\ 2 \times 10^{-8} \end{array}$	8 × 10 ⁻⁵ 6 × 10 ⁻⁵ 6 × 10 ⁻⁵
Erbium 68	•	8 I	$3 \times 10^{-8} \\ 3 \times 10^{-8}$	$\begin{array}{c} 9 \times 10^{-5} \\ 9 \times 10^{-5} \end{array}$		Nd149	S I S I S I	$8 \times 10^{-3}$ $8 \times 10^{-8}$	$3 \times 10^{-4} \\ 3 \times 10^{-4}$
	Erm	8 I	$3 \times 10^{-8} \\ 3 \times 10^{-8}$	$\begin{array}{c} 1 \times 10^{-4} \\ 1 \times 10^{-4} \end{array}$	Neptunium 93	_ Np ²⁸⁷		$9 \times 10^{-5}$ $9 \times 10^{-4}$	$3 \times 10^{-6}$ $3 \times 10^{-5}$
Europium 63	_ Eu ¹⁸³ (Т/2 <u>—</u> 9,2 l	rs) I	$2 \times 10^{-3} \\ 2 \times 10^{-3}$	$6 \times 10^{-5} \\ 6 \times 10^{-5}$		$Np^{289}$	ន្ទ័	$\begin{array}{c} 4 \times 10^{-8} \\ 4 \times 10^{-8} \end{array}$	$3 \times 10^{-5}$ $1 \times 10^{-4}$ $1 \times 10^{-4}$
	(T/2=13 x		$2 \times 10^{-8}$ $2 \times 10^{-8}$ $6 \times 10^{-4}$	$     \begin{array}{r}       8 \times 10^{-5} \\       8 \times 10^{-5} \\       2 \times 10^{-5}    \end{array} $	Nickel 28	Ni ⁵⁰	Ŝ	$\begin{array}{c} 6 \times 10^{-8} \\ 6 \times 10^{-3} \end{array}$	$2 \times 10^{-4}$
	Eu ¹⁵⁴	I	6 × 10→	$2 \times 10^{-8}$		Ni ⁶⁸	ŝ	$\begin{array}{c} 8 \times 10^{-4} \\ 2 \times 10^{-2} \end{array}$	$\begin{array}{c} 2 \times 10^{-8} \\ 3 \times 10^{-6} \\ 7 \times 10^{-4} \end{array}$
	Eu156	S	$6 \times 10^{-3}$ $6 \times 10^{-8}$	$2 \times 10^{-4}$ $2 \times 10^{-4}$	s.	Nies	ŝ	$4 \times 10^{-3}$ $3 \times 10^{-3}$	$7 \times 10^{-4}$ $1 \times 10^{-4}$ $1 \times 10^{-4}$
Fluorine 9	_ Frs	SI	$2 \times 10^{-3}$ $1 \times 10^{-2}$	8 × 10 ⁻⁴ 5 × 10 ⁻⁴	Niobium (Colum-	$Nb^{93m}$	SISISISISISISI	1 × 10-2 1 × 10-3	$\begin{array}{c} 4 \times 10^{-4} \\ 4 \times 10^{-4} \end{array}$
Gadolinium 64	- Gq122		6 × 10 ⁻⁸	$2 \times 10^{-4}$	bium) 41	Nb95		$3 \times 10^{-8}$ $3 \times 10^{-8}$	1 × 10 ⁻⁴ 1 × 10 ⁻⁴
	$G_{q_{120}}$	S I S I	$6 \times 10^{-3}$ $2 \times 10^{-3}$ $2 \times 10^{-3}$	2 × 10-4 8 × 10-5 8 × 10-5		Nbor	s I	$3 \times 10^{-2}$ $3 \times 10^{-2}$	$9 \times 10^{-4}$ $9 \times 10^{-4}$
Gallium 31	_ Ga ⁷⁹	Š	1 × 10-8 1 × 10-8	$4 \times 10^{-6} \\ 4 \times 10^{-6}$	• The values are take	n from Appe	endix B	of 10 CFR 20.	
Germanium 32	_ Ge ⁿ	S	$5 \times 10^{-3}$	2 × 10 ⁻⁸ 2 × 10 ⁻⁸	( Author	ized by G. S effective Sep	P TASA 6	upp., so-rroot	
		Ĭ	5 × 10-9	2 X 10 0		_			

M	28-35-2				Element		σr.	able I are a
Maximum Pern	nissible Co	oncentro	ations of Radi	onuclides	Atomic Number Samarium 62	Isotope 1, 1 Sm ¹⁴⁷	(uo	able I Table II (ml) (uc/ml)
Element	ın '	Water ³	*				I 2 ×	10-s* 6 × 10-s 10-s 7 × 10-s
Atomic Number	Isotope	., .	Table	- 4010 11		Sm ¹⁵¹	§ 1 X	10 ⁻² 4 × 10 ⁻⁴ 10 ⁻² 4 × 10 ⁻⁴
Osmium 76	Os ¹⁸⁵		$(uc/ml)$ $2 \times 10^{-6}$			Sm153		10-8 8 × 10-5
	Osimi	Ŧ	2 🛈 10−8	7 🗘 10-5	Scandium 21	- Scis	S 1X	108- 4 × 10-5
	Os ¹⁹¹	Ĭ	7 × 10-2	3 × 10-8		Scar		108~ 4 × 10-6
		S	5 × 10⊸ 5 × 10⊸	2 ∨ 10-4		Sc48	i š×	10-8 9ั⊋ ีกั-ธ
	Os ¹⁹⁸	S I	2 × 10 ⁻³ 2 × 10 ⁻³	6 € 10-5	Selenium 34	C	I ŠX	3 × 10-5 10-4 3 × 10-5
Palladium 46	- Pđ ¹⁰⁸	s	1 × 10-2				S 9 × 8 × 1	$10^{-3}$ $3 \times 10^{-4}$
	Pd109	S	$8 \times 10^{-3}$	$3 \times 10^{-4}$ $3 \times 10^{-4}$	Silicon 14		S 3×	10-2 9 > 10-4
Phosphorus 15	_ 1289	I	$3 \times 10^{-8} \\ 2 \times 10^{-3}$		Silver 47	. Ag195		10 ⁻³ 2 × 10 ⁻⁴
		S	$\begin{array}{c} 5 \times 10^{-4} \\ 7 \times 10^{-4} \end{array}$	$\stackrel{2}{ imes}\stackrel{10^{-5}}{ imes}$		Ag110m	S 3 × 1 S 9 × 1 I 9 × 1 S 1 × 1	10-3 1 × 10-4
Platinum 78	- Pt ^{un}	. 8	4 × 10-8	1 × 10-4		Agui	Ĩ 🦠 Ŝi	10-4 3 😯 10-8
	Pt198m		$3 \times 10^{-3} \\ 3 \times 10^{-2}$	1 × 10-4	Sodium 11	•		LU~* 4 ∨ 1ñ-6
	Pt197m	I S	$3 \times 10^{-2}$ $3 \times 10^{-2}$	1 × 10-3			S 1×1	(0−8 4 ∨ 10−8
	Pt197	S I S	$3  imes 10^{-2}$	9 × 10-4		Na ²⁴	I 9×1 S 6×1 I 8×1	
Plutonium 94	_	I	$\frac{4 \times 10^{-3}}{3 \times 10^{-3}}$	1 × 10 ⁻³ 1 × 10 ⁻³ 1 × 10 ⁻⁴ 1 × 10 ⁻⁴ 1 × 10 ⁻⁴	Strontium 38	Sr85m	S 2×1	4 / 40
- tatomam 94	. Pu288	ន្	$1 \times 10^{-4}$	5 × 10-●		Sres	§ 2×1 S 3×1	0-1 7 × 10-8
	Pu ²³⁹	្ទំ	8 × 10-4 1 × 10-4 8 × 10-4	3 × 10-5 5 × 10-6	* · · · · · · · · · · · · · · · · · · ·	Sree	$I = \tilde{5} \hat{\times} \hat{1}$	0−s 2 2 10−s
	Pu ²⁴⁰	ģ	8 × 10-4 1 × 10-4	3 × 10−5 5 × 10−9		Sr00	S 3 × 1 8 × 1	0-4 0-4 1 × 10-5 0-8 1 × 10-7
	$Pu^{2d}$	I S	8 × 10→ 7 × 10⊸	3 🗸 10-5		Srm	I 8 X 10 S 4 X 10 S 2 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1 X 10 S 1	
	Pu242	I S I S I S I S I S I S I	$\begin{array}{c} 4 \times 10^{-2} \\ 1 \times 10^{-4} \end{array}$	$\begin{array}{c} 2 \stackrel{>}{\times} 10 \stackrel{\checkmark}{-} \\ 1 \times 10 \stackrel{-}{-} \end{array}$				^{0—8} 7 × 10−5
Polonium 84	<b>-</b>		$9 \times 10^{-4}$	$^{5} \times ^{10^{-6}}$ $^{3} \times ^{10^{-5}}$	S-10	Sr ⁹²	$ \begin{array}{ccc} \tilde{S} & \tilde{2} \times 10 \\ \tilde{I} & \tilde{2} \times 10 \end{array} $	?~8 7 <del>1</del> 10−5
		s	2 × 10-5 8 × 10-4	$7  imes 10^{-7}$	Sulfur 16	Sas	S 2×10	)~8 6 × 10-5
Potassium 19	$\mathbf{K}_{\mathbf{e}\mathbf{s}}$	ន	9 × 10-8	3 × 10-5	Tantalum 73	Ta ¹⁸²	- 77.20	- / ( = 0
Praseodymium 59	Pr142	I ~	6 × 10~	$\stackrel{3}{ imes} \stackrel{10-4}{ imes} \atop \stackrel{2}{ imes} \stackrel{10-6}{ imes}$	Technetium 43	_ :	I ÎXÎ	3 ⁻⁸ 4 × 10 ⁻⁸ 3 ⁻⁸ 4 × 10 ⁻⁵
		s I S	9 × 10→ 9 × 10→	$3 \times 10^{-5}$ $3 \times 10^{-5}$	Toometium 45	Tc96m	S 4×10 3×10	1 × 10-4 1 × 10-4
•	Pr ¹⁴⁸	8 1	$1 \times 10^{-6}$ $1 \times 10^{-8}$	5 × 10-5		Tcos	\$ 3 \$ 10	1 × 10-4
Promethium 61	$P_{m^{M7}}$	ន	6 × 10-8	$5 \times 10^{-6}$ $2 \times 10^{-4}$		LC _{84m}	S 3 × 10 I 1 × 10 I 5 × 10 I 5 × 10 I 2 × 10 S 2 × 10	~* 4 \/ 10~4
	$Pm^{149}$	S I	$^{6   imes  10^{-3}}_{1   imes  10^{-3}}$	$2 \times 10^{-4}$ $4 \times 10^{-5}$		Tc ⁹⁷	5 × 10 5 × 10	-2 4 × 10-4 -8 2 × 10-4 -2 2 × 10-3
Protoactinium 91	Pa280		ī × 10−8	4 × 10~5		Tc99m	I 2 × 10- S 2 × 10- I 8 × 10-	-4 8 <del>2 10-4</del>
		s I S	$7 \times 10^{-8}$ $7 \times 10^{-8}$	$2 \times 10^{-4}$ $2 \times 10^{-4}$	· ·	Tc**	D 1 X 10-	
	Pass	I	3 × 10-5	9 × 10~7	Tellurium 52	_	5 × 10-	-s Ž X 10-4
	Pa ²⁸³	S I	$\begin{array}{c} 8 \times 10^{-4} \\ 4 \times 10^{-8} \\ 3 \times 10^{-8} \end{array}$	$2 \times 10^{-5}$ $1 \times 10^{-4}$			S 5 × 10- I 3 × 10- S 2 × 10- I 2 × 10- S 8 × 10- S 8 × 10-	* 2 × 10-4 * 1 × 10-4
Radium 88	Ra223	s	2 × 10-5	1 × 10-4	•	Te ^{127 m}	S 2×10- I 2×10- S 8×10-	6 × 10-8 5 × 10-5
	Ra224	I	$1 \times 10^{-4}$	7 × 10-7 4 × 10-6			S 8 × 10- I 5 × 10-	3 × 10-1
	Ra ²²⁶	S I	$7 \times 10^{-5}$ $2 \times 10^{-4}$	2 × 10→ 5 × 10→	•	Te ^{129m} (	S ixin⊣	8 3 × 10-5
**************************************	Razzs	Î S I	4 × 10-7 9 × 10-4	$1 \times 10^{-8}$ $3 \times 10^{-8}$			S 2 × 10~	2 8 ♦ 10-4
	Lam	S I	$\begin{array}{c} 8 \times 10^{-7} \\ 7 \times 10^{-4} \end{array}$	3 × 10−8 3 × 10−5		Te ^{181m} S	2 × 10-4 2 × 10-4	* 6 × 10−8
Radon 86	$Rn^{220}$	s	====			Те ¹⁸²	2 × 10→ 1 1 × 10→ 9 × 10→	$4 \times 10^{-5}$ $3 \times 10^{-5}$
	$R_{n^{222}}$	s I S			Terbium 65	Tb ¹⁸⁰ S	V / 10	$2 \times 10^{-5}$
Rhenium 75	Relas	ន	2 × 10-2			ĩ	1 × 10-8 1 × 10-8	$^4 imes10^{-5}\ ^4 imes10^{-5}$
•	Re ¹⁹⁸	Ĩ S	$8 \times 10$ -8	6 × 10-4 3 × 10-4 9 × 10-5	Thallium 81	TI ²⁰⁰ S	$1 \times 10^{-2}$ $7 \times 10^{-3}$	4 × 10-4
•	Re ¹⁸⁷	Ĩ	$3 \times 10^{-8}$ $1 \times 10^{-8}$	9 × 10-5 5 × 10-5		Tl ²⁰¹ §	9 × 10-8	3 ♀ 10-4
•		I S I S	$7 \times 10^{-2} \ 4 \times 10^{-2}$	$\begin{array}{c} 5 \times 10^{-5} \\ 3 \times 10^{-8} \\ 2 \times 10^{-8} \end{array}$		Tl208 §	5 × 10-8 4 × 10-8	2 × 10→ 1 × 10→
	Reiss	S I	$4 \times 10^{-2}$ $2 \times 10^{-8}$ $9 \times 10^{-4}$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		T1200 S T1201 S T1202 S T1204 S T1204 S	$\begin{array}{c} 4 \times 10^{-8} \\ 2 \times 10^{-8} \\ 3 \times 10^{-8} \\ 2 \times 10^{-8} \end{array}$	1 × 10-4 7 × 10-5 1 × 10-4
Rhodium 45	Rh108m	S	4 × 10-1		Thorium 90	Th228 C		1 × 10-4 6 × 10-5
4	Rh ¹⁰⁵	S I S I	$3 \times 10^{-1}$	$1 \times 10^{-2} \\ 1 \times 10^{-2}$		Trieso I	2 × 10 ⁻⁴ 4 × 10 ⁻⁴	$\begin{array}{c} 7\times10^{-6}\\1\times10^{-6} \end{array}$
		Ĭ	4 × 10 ⁻⁸ 3 × 10 ⁻⁸	$\begin{array}{c} 1 \times 10^{-4} \\ 1 \times 10^{-4} \end{array}$	•	III S	5 × 10 ⁻⁶ 9 × 10 ⁻⁴	$\begin{array}{c} 2 \times \overline{10^{-6}} \\ 3 \times \overline{10^{-6}} \end{array}$
Rubidium 37	Rb80	ន្ទ	$2 \times 10^{-8}$		•	In S	$\begin{array}{c} 5 \times 10^{-5} \\ 1 \times 10^{-3} \end{array}$	2 × 10-4 4 × 10-5
	Rb87	S I S I	$7 \times 10^{-4}$ $3 \times 10^{-3}$	$7 \times 10^{-6}$ $2 \times 10^{-5}$ $1 \times 10^{-4}$		These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These S I These	$3 \times 10^{-5} \\ 3 \times 10^{-4}$	1 × 10-4 1 × 10-5
The state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the s			5 × 10-8	$\begin{array}{c} 1 \times 10^{-4} \\ 2 \times 10^{-4} \end{array}$		Th ²⁸⁴ S	2 × 10 ⁻⁴ 4 × 10 ⁻⁴ 5 × 10 ⁻⁵ 9 × 10 ⁻⁵ 5 × 10 ⁻⁵ 1 × 10 ⁻⁵ 3 × 10 ⁻⁶ 3 × 10 ⁻⁴ 5 × 10 ⁻⁴	$\hat{1} \times \hat{10}^{-6}$ 2 × 10 ⁻⁵ 2 × 10 ⁻⁵
Ruthenium 44	Rus	S I	1 × 10-2 1 × 10-2	$\begin{array}{c} 4 \times 10^{-4} \\ 3 \times 10^{-4} \end{array}$	Thulium 69	Tm ¹⁷⁰ S	1 × 10-8	5 × 10-₹
	Ru ¹⁰³	I S I S	$1 \times 10^{-2}$ $2 \times 10^{-3}$ $2 \times 10^{-3}$	8 × 10-5		Tm ^m S	1 × 10 ⁻⁸ 1 × 10 ⁻³	$5 \times 10^{-5}$
•	Ru ¹⁰⁵	ន្ទឹ	3 × 10 ⁻⁸ 3 × 10 ⁻⁸	8 × 10-5 1 × 10-≠		. 1	1 × 10~2	5 × 10-4 5 × 10-4
	Ru ¹⁰⁸	Į S	4 × 10-4	$1 \times 10^{-4}$ $1 \times 10^{-6}$ $1 \times 10^{-6}$	* The values are taken from (Authorized b	Y G. S. 1959 S	Supp. 48-1103)	٠
		Ι	3 × 10 ⁻⁴	1 × 10-5	(Effective	e September	1, 1961)	

#### 28-35-26-Continued

## Maximum Permissible Concentrations of Radionuclides in Water *

Tin 50	Isotope 1, 8 Sn ¹²⁸ Sn ¹²⁶	s I S I	Table I $(uc/ml)$ 2 × 10 ⁻⁸ 2 × 10 ⁻⁸ 5 × 10 ⁻⁴ 5 × 10 ⁻⁴	
Tungsten (Wolfram) 74	M184 M182 M181	SI SI SI	$\begin{array}{c} 1 \times 10^{-2} \\ 1 \times 10^{-2} \\ 4 \times 10^{-3} \\ 3 \times 10^{-3} \\ 2 \times 10^{-3} \\ 2 \times 10^{-3} \end{array}$	$\begin{array}{c} 4 \times 10^{-4} \\ 3 \times 10^{-4} \\ 1 \times 10^{-4} \\ 1 \times 10^{-4} \\ 7 \times 10^{-5} \\ 6 \times 10^{-5} \end{array}$
Uranium 92	U280 U282 U284 U284 U286 U298 U208	SISISISISISISISI	1 × 10 -4 1 × 10 -4 8 × 10 -4 8 × 10 -4 9 × 10 -4 9 × 10 -4 9 × 10 -4 9 × 10 -4 8 × 10 -8 1 × 10 -8 1 × 10 -8 1 × 10 -8 1 × 10 -8 5 × 10 -4 5 × 10 -4	5 × 10-6 5 × 10-6 3 × 10-5 3 × 10-6 3 × 10-6 3 × 10-5 3 × 10-5 3 × 10-5 3 × 10-5 3 × 10-5 2 × 10-5 4 × 10-5 4 × 10-5 2 × 10-5 2 × 10-5
Vanadium 23	Ang	s I	9 × 10 ⁻⁴ 8 × 10 ⁻⁴	$3 \times 10^{-5}$ $3 \times 10^{-5}$
Xenon 54	Xe ₁₈₃ Xe ₁₈₃	Sub Sub Sub		
Ytterbium 70	Yb175	s I	$3 \times 10^{-3}$ $3 \times 10^{-8}$	1 × 10 ⁻⁴ 1 × 10 ⁻⁴
Yttrium 39	Дэл <u>т</u>	SISISISI	6 × 10 ⁻⁴ 6 × 10 ⁻¹ 1 × 10 ⁻¹ 1 × 10 ⁻¹ 8 × 10 ⁻⁴ 8 × 10 ⁻⁴ 2 × 10 ⁻³ 2 × 10 ⁻³ 8 × 10 ⁻⁴ 8 × 10 ⁻⁴	2 × 10 ⁻⁵ 2 × 10 ⁻⁶ 3 × 10 ⁻⁶ 3 × 10 ⁻⁸ 3 × 10 ⁻⁵ 3 × 10 ⁻⁵ 6 × 10 ⁻⁵ 6 × 10 ⁻⁵ 3 × 10 ⁻⁵ 3 × 10 ⁻⁵
Zinc 30	Zn ^{es} Zn ^{es}	S I S I S I	$3 \times 10^{-3}$ $5 \times 10^{-3}$ $2 \times 10^{-8}$ $2 \times 10^{-8}$ $2 \times 10^{-8}$ $5 \times 10^{-2}$ $5 \times 10^{-2}$	$\begin{array}{c} 1 \times 10^{-4} \\ 2 \times 10^{-4} \\ 7 \times 10^{-5} \\ 6 \times 10^{-5} \\ 2 \times 10^{-8} \\ 2 \times 10^{-8} \end{array}$
Zirconium 40	_ Zr ⁹³ Zr ⁹⁵	S I S I	$2 \times 10^{-2}$ $2 \times 10^{-2}$ $2 \times 10^{-3}$ $2 \times 10^{-3}$	$ 8 \times 10^{-4} $ $ 8 \times 10^{-4} $ $ 6 \times 10^{-5} $ $ 6 \times 10^{-5} $

Element Atomic Number	Isotope
Atomic ivanion	17-07

Table II (uc/ml) Table I (uc/ml)  $2 \times 10^{-6}$  $2 \times 10^{-6}$ 

Footnetes.
1Soluble (S); Insoluble (I).
2"Sub" means that values given are for submersion in an infinite cloud of gaseous material.

Note 1. In any case where there is a mixture of more than one radionuclide, the limiting values for (these) purposes should be determined as follows:

a. If the identity and concentration of each radionuclide in the mixture are known, the limiting values should be derived as follows: Determine, for each radionuclide in the mixture, the ratio between the quantity present in the mixture and the limit otherwise established in this Appendix for the specific radionuclide when not in a mixture. The sum of such ratios for all the radionuclides in the mixture may not exceed "1" (i.e., "unity").

Example: If radionuclides A, B, and C are present in concentrations CA, CB, and Cc, and if the applicable MPC's are MPCA, MPCB, and MPCc respectively, then the concentrations shall be limited so that the following relationship exists:

$$\frac{C_A}{MPC_A} + \frac{C_B}{MPC_B} + \frac{C_C}{MPC_C} \ge 1$$

- b. If either the identity or the concentration of any radionuclide in the mixture is not known, the limiting values for purposes of this Appendix shall be:
  - (1) For purposes of Table I, Col. 2—3  $\times$  10⁻⁷ (2) For purposes of Table II, Col. 2—1  $\times$  10⁻⁸
- c. If the conditions specified below are met, the corresponding values specified below may be used in lieu of those specified in paragraph 2 above.

Element (atomic number) and Isotope	$Table\ I$ $(uc/ml)$	Table II (uc/ml)
If it is known that Sreo, Pies, Poese, Poese, Atsi, Razes, Razes, Razes, Razes, These, Passi, These, and Th-nat are not present.	9 × 10 ⁻⁵	3 × 10-4
If it is known that Sr ⁸⁰ , I ¹²⁰ , Ph ²¹⁰ , Po ²¹⁰ , Ra ²²³ , Ra ²²³ , Ra ²²³ , Pa ²³¹ , and Th-nat are not present	. 6 × 10 ⁻⁵	2 × 10-6
If it is known that Sr ⁹⁰ , Pb ²¹⁰ , Ra ²²⁰ , and	$2  imes 10^{-5}$	6 × 10-7
If it is known that Razza and Razza are not	$3 \times 10^{-6}$	1 × 10-7
If it is known that alpha-emitters and Sr ⁹⁰ , Il ²⁹ , Pb ²⁰⁰ , Ac ²²⁷ , Ra ²²³ , Pa ²³⁰ , Pu ²⁴¹ , and Bk ²⁴⁰ are not present		,
If it is known that alpha-emitters and Pozze,	· 	
If it is known that alpha-emitters and Acza		
If it is known that Acces, These, Pass, Puess, Puess, Puess, Puess, Puess, Puess, and Ciess are not present		
If Passi, Puss, Puss, Puss, and Cfss are not present		

Note 2. For the purposes of 28-35-19, section a, paragraph (1), sub-paragraph (b), the values in Table II of this Appendix shall be multiplied by 5,000.

Note 3. For the purposes of 28-35-19, section a, paragraph (2), subparagraph (b), the values in Table II of this Appendix shall be multiplied by 500.

[•] The values are taken from Appendix B of 10 CFR 20. (Authorized by G. S. 1959 Supp., 48-1103) (Effective September 1, 1961)

#### APPENDIX C

## STATE OF MISSOURI

## WATER QUALITY OBJECTIVES—MISSISSIPPI RIVER GENERAL OBJECTIVES

All wastes, including sanitary sewage, storm water, and industrial effluents, shall be in such condition when discharged to the Mississippi River that they will not create conditions in that stream which will adversely affect the use of those waters for the following purposes: source of domestic water supply or industrial water supply, navigation, fish and wildlife, recreation, agriculture and other riparian activities.

In general, adverse conditions are caused by:

A. Excessive bacterial, physical or chemical contamination.

B. Unnatural deposits in the stream, interfering with fish and wildlife, recreation, or destruction of aesthetic values.

C. Materials imparting objectionable colors, tastes or odors to waters used for domestic or industrial purposes.

D. Floating materials, including oils, grease, garbage, sewage solids, or other refuse.

## SPECIFIC OBJECTIVES

In more specific terms, adequate controls of pollution will necessitate the following objectives for:

A. Sanitary Sewage and Storm Water

Sufficient treatment for adequate removal or reduction of solids, bacteria and chemical constituents which may interfere unreasonably with the use of these waters for the purposes afore-mentioned. Adequate protection for these waters would be provided by:

(a) Substantially complete romoval of floating and settleable solids; and

(b) Removal of not less than forty-five percent of the total suspended solids.

#### B. Industrial Wastes

(1) Chemical Wastes—Phenolic Type

Industrial waste effluents from phenolic hydrocarbon and other chemical plants will cause objectionable tastes or odors in drinking or industrial water supplies and may taint the flesh of fish. Adequate protection should be provided for these waters if the concentration of phenol or phenol equivalents does not exceed a monthly average of 2 parts per billion and a maximum of 5 parts per billion at any point in these waters following initial dilution.

(2) Chemical Wastes—Other Than Phenolic Adequate protection should be provided if:

(a) The pH of these waters following initial dilution is not less than 6.7 or more than 8.5.

- (b) The odor-producing substances in the effluent are reduced to a point that following initial dilution with these waters the mixture does not have a monthly average threshold odor number in excess of 30.
- (e) Oils and floating solids are reduced to a point such that they will not create fire hazards, coat hulls of water craft, injure fish or wildlife or their habitat, or will adversely affect public or private recreational development or other legitimate shoreline developments or uses. In order to accomplish this it will be necessary to reduce concentrations of such materials discharged to the point where after initial dilution the stream shall be free of noticeable floating solids, oil, grease and sleek.

(3) Highly Toxic Wastes

Adequate protection should be provided for these waters if substances highly toxic to human, fish, aquatic or wildlife are eliminated or reduced to safe limits.

(4) Deoxygenating Wastes

Adequate protection of these waters should result if sufficient waste reduction process changes or if sufficient treatment is provided to accomplish substantially the same objectives as are herein set up for sanitary sewage.

## WATER QUALITY OBJECTIVES—BLUE RIVER JACKSON COUNTY, MISSOURI

The Missouri Water Pollution Board, in cooperation with the Missouri Conservation Commission, has established Water Quality Objectives for the Blue River in Jackson County, Missouri. The Blue River has been divided into three zones which we believe will allow the maximum use of the stream for the various users. Zone 1-Above the entrance of Brush Creek. This zone is established for recreational usage. The allowable concentrations of pollutants are to be based upon a stream flow of 1.88 cfs., which is exceeded 90% of the time according to the U.S.G.S. gauge at Bannister Road. Zone 2-From Brush Creek to Guinotte Dam. This zone allows for industrial use of the stream, and will also allow fish to survive for short periods of time. This zone is not utilized for fishing. The allowable concentrations of pollutants are to be based upon a stream flow of 1.88 cfs., plus additional flow not pumped from Blue River as provided by industry on a sustained basis. Zone 3-Below Guinotte Dam—Essentially the same Water Quality Objectives as for the Missouri River in the Metropolitan Kansas City area.

Each industry will be required to maintain effective waste reduction and prevention programs irrespective of any objectives established for pollutants in the Blue River.

## WATER QUALITY OBJECTIVES—BLUE RIVER ZONE 1 (UPSTREAM FROM BRUSH CREEK)

No taste and odor producing substances to be discharged. Dissolved Oxygen-greater than 5.0 mg/l. Biochemical oxygen demand-3-4 mg/l. pH-6.5-8.5Odor—none Color-not objectionable Seum and floating debris-none Sludge deposits-none Iron-1.0 mg/l. Copper—0.2 mg/l. Total Chromium—1.0 mg/l. Cyanide—0.02 mg/l. Zinc—0.01 mg/l.

Cadmium—0.2 mg/l. Emulsified Crude Oil—0.3 mg/l. Chloride—less than 250 mg/l. Sulfate—less than 250 mg/l. Nickel—0.8 mg/l.

Aluminum-0.07 mg/l.

Ammonia—0.3 mg/l.

Lead-0.1 mg/l.

Fluoride—1.5 mg/l.

Floating Oil-none

Complete treatment of sanitary sewage. Unpolluted cooling water may be discharged to stream provided the temperature elevation does not kill fish.

## WATER QUALITY OBJECTIVES—BLUE RIVER ZONE 2 (BRUSH CREEK TO GUINOTTE DAM)

Floating Oil-none Sludge Deposits--none

No taste and odor producing substances to be discharged. Treatment of organic waste to maintain Dissolved Oxygen of 3 mg/l. in stream. Complete treatment of sanitary sewage.

pH-6.0-9.5

 $I_{ron}$ —5 mg/l.

Copper—1.0 mg/l.

Total Chromium—5.0 mg/l.

Cyanide—0.02 mg/l.

 $Z_{inc}$ —0.3 mg/l.

Cadmium—0.4 mg/l.

Emulsified Crude Oil-0.3 mg/l.

Chloride—less than 250 mg/l. Sulfate—less than 250 mg/l.

Nickel-0.8 mg/l.

Aluminum—0.07 mg/l.

Ammonia-0.3 mg/l.

Lead-0.1 mg/l.

Fluoride—1.5 mg/l.

Unpolluted cooling water may be discharged to stream provided temperature elevation does not kill fish.

Odor-none

Color-not objectionable

No seum or floating debris.

#### WATER QUALITY OBJECTIVES-BLUE RIVER ZONE 3 (BELOW GUINOTTE DAM)

- 1. Primary treatment of sanitary waste until such time as Kansas City pipes waste to Missouri River.
- 2. No taste and odor producing substances to be discharged.
- 3. No floating oil.
- 4. Primary treatment of wastes containing floating and settleable organic solids to prevent formation of sludge banks and floating materials.
- 5. Eliminate batch discharges of toxic wastes.
- 6. Additional treatment of organic wastes as necessary to prevent a nuisance in the stream.

## WATER QUALITY OBJECTIVES-MISSOURI RIVER

"Subject to (a) such higher objectives as may be desired by any State and (b) such other modification as may be deemed necessary, after appropriate investigation, by the State Water Pollution Control Agency concerned, the Engineering Section, Missouri Basin Health Council recommends the following for consideration by the member States as a tentative guide for water pollution control activities in the Missouri Drainage Basin:

- 1. Toxic substances including metallic ions, phenolic compounds, oils, alkalies, and acids should be virtually eliminated from sewage effluents.
- 2. Removal of settleable and floating solids to prevent sludge banks, floating materials, and nuisance conditions should be required as the minimum acceptable treatment.
- 3. For industrial wastes similar in nature to municipal wastes, treatment should be based on the same premise as recommended for municipalities. For industrial wastes not comparable to municipal wastes, treatment should be provided as necessary to prevent deterioration of water quality for beneficial uses in the receiving stream.
- 4. Additional treatment over that specified in item 2 above should be provided as necessary to protect downstream water uses. Quality objectives for certain water uses are:
  - (a) For water serving as a source of domestic supply, raw water bacteriological quality should conform to that recommended in "Manual of Recommended Water Sanitation Practices,' 1946, Public Health Bulletin 296, pages 11-13.
  - (b) 'For bathing or swimming waters, monthly arithmetical average 'most probable number' of coliform organisms should not exceed 1,000 per 100 ml. during any month of the recreation season; nor exceed this number in more than 20 percent of the samples examined during any such month; nor exceed 2,400 per 100 ml. on any day. For nonbathing or nonswimming waters, the monthly arithmetical average 'most probable number' of coliform organisms should not exceed 5,000 per 100 ml. in any month of the recreational season, nor should exceed this number in more than 20 percent of the samples examined during any such month.'

- (c) For fish and aquatic life a minimum oxygen concentration of 5.0 ppm. is desirable in waters otherwise offering suitable fishery habitat, with 6.0 ppm. for trout streams.
- (d) For bacteriological quality of irrigation water:
  - (1) Sewage used for irrigation of forage crops should be given treatment insuring a consistent reduction in coliform bacteria of not less than 90 percent.
  - (2) Sewage used for irrigation of human food crops should be given treatment insuring a consistent reduction (a) in suspended solids of not less than 75%, (b) in 5 day 20°C. B.O.D. of not less than 75% and

(c) in coliform bacteria of not less than 98 percent, unless discharged into a stream where the volume of dilution water, available during the low flow periods during which irrigation diversions may occur, is at least 10 times greater than the anticipated maximum daily volume of sewage, in which case a bacterial reduction of 90 percent may be acceptable.

Provided, however, that where the time of passage from plant discharge to irrigation diversion is such as to permit the normal death rate of bacteria as evidenced by the die-away curve to provide equivalent bacterial reduction, the requirements of (1) and (2) above may be appropriately modified."

#### APPENDIX D

## CLASSIFICATIONS AND STANDARDS OF QUALITY AND PURITY

Adopted by New York Water Pollution Control Board Pursuant to Article 12, Public Health Law

#### ADOPTING ORDER

Pursuant to the authority contained in Article 12 of the Public Health Law, the Board having held public hearings as therein provided, hereby adopts the following classifications and standards of quality and purity for the waters of New York State:

#### I. GENERAL CLASSIFICATION-STANDARDS SYSTEM

#### 1. DEFINITIONS

The several terms, words or phrases hereinafter mentioned shall be construed as follows:

- a. Best usage of waters as specified for each class shall be those uses as determined by the Board in accordance with the considerations prescribed by Section 1209 of the Public Health Law.
- b. Approved treatment as applying to water supplies means treatment accepted as satisfactory by the authorities responsible for exercising supervision over the sanitary quality of water supplies.
- c. Source of water supply for drinking, culinary or food processing purposes shall mean any source, either public or private, the waters from which are used for domestic consumption or used in connection with the processing of milk, beverages, foods or for other purposes which require finished water meeting U. S. Public Health Service Drinking Water Standards.
- d. Fishing shall include the propagation of fish and other aquatic life.
- e. Agricultural shall include use of waters for stock watering, irrigation and other farm purposes but not as source of water supply for drinking, culinary or food processing purposes.
- f. Tidal salt waters shall mean all tidal waters which are so designated by the Board and which generally shall have a chloride ion content in excess of 250 parts per million.

## 2. CONDITIONS APPLYING TO ALL CLASSIFICATIONS AND STANDARDS

- a. In any case where the waters into which sewage, industrial wastes or other wastes effluents discharge are assigned a different classification than the waters into which such receiving waters flow, the standards applicable to the waters which receive such sewage or wastes effluents shall be supplemented by the following:
  - "The quality of any waters receiving sewage, industrial wastes or other wastes discharges shall be such that no impairment of the best usage of waters in any other class shall occur by reason of such sewage, industrial wastes or other wastes discharges."

b. Natural waters may on occasion have characteristics outside of the limits established by the standards. The standards adopted herein relate to the condition of waters as affected by the discharge of sewage, industrial wastes or other wastes.

## 3. CLASSES AND STANDARDS FOR FRESH SURFACE WATERS

#### CLASS AA

Best usage of waters: Source of water supply for drinking, culinary or food processing purposes and any other usages.

Conditions related to best usage: The waters, if subjected to approved disinfection treatment, with additional treatment if necessary to remove naturally present impurities, meet or will meet U. S. Public Health Service Drinking Water Standards and are or will be considered safe and satisfactory for drinking water purposes.

## Quality Standards for Class AA Waters

Items

Specifications

- Floating solids; settleable solids; oil; sludge deposits; tastes or odor producing substances.
- 2. Sewage or wastes effluents.

5. Toxic wastes, deleterious

other wastes or heated

colored

- 3. pH.
- 4. Dissolved oxygen.

substances.

liquids.

- None attributable to sewage, industrial wastes or other wastes.
- None which are not effectively disinfected.
- Range between 6.5 and 8.5
- For trout waters, not less than 5.0 parts per million; for non-trout waters, not less than 4.0 parts per million.
- None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish life, make the waters unsafe or unsuitable as a source of water supply for drinking, culinary or food processing purposes or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

NOTE No. 1: In determining the safety or suitability of waters in this class for use as a source of water supply for drinking, culinary or food processing purposes after approved treatment, the Water Pollution Control Board will be guided by the standards specified in the latest edition of "Public Health Service Drinking Water Standards" published by the United States Public Health Service.

ards" published by the United States Public Health Service.

NOTE No. 2: With reference to certain toxic substances as affecting fish life, the establishment of any single numerical standard for waters of New York State would be too restrictive. There are many waters, which because of poor buffering capacity and composition, will require special study to determine safe concentrations of toxic substances. However, based on non-trout waters of approximately median alkalinity (80 p.p.m.) or above for the state, in which groups most of the waters near industrial areas in this state will fall, and without considering increased or decreased toxicity from possible combinations, the following may be considered as safe stream concentrations for certain substances to comply with the above standard for this type of water. Waters of lower alkalinity must be specially considered since the toxic effect of most pollutants will be greatly increased.

Ammonia or Ammonium

compounds

Not greater than 2.0 parts per million (NH₈) at pH of 8.0 or above

Not greater than 0.1 part per million (CN)

Ferro- or Ferricyanide

Not greater than 0.4 parts per million (Fe(CN)₆)

Copper

Cyanide

Not greater than 0.2 parts per million

Zinc

Not greater than 0.3 parts per million (Zn)

Cadmium

Not greater than 0.3 parts per million

#### CLASS A

Best usage of waters: Source of water supply for drinking, culinary or food processing purposes and any other usages.

Conditions related to best usage: The waters, if subjected to approved treatment equal to coagulation, sedimentation, filtration and disinfection, with additional treatment if necessary to reduce naturally present impurities, meet or will meet U.S. Public Health Service Drinking Water Standards and are or will be considered safe and satisfactory for drinking water purposes.

#### Quality Standards for Class A Waters

Items

Specifications

1. Floating solids; settleable solids; sludge deposits.

None which are readily visible and attributable to sewage, industrial wastes or other wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. Sewage or waste efflu-

None which are not effectively disinfected.

3. Odor producing substances contained in sewage. industrial wastes or other wastes.

The waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto shall not have an increased threshold odor number greater than 8, due to such added wastes.

4. Phenolic compounds.

Not greater than 5 parts per billion (Phenol).

5. pH.

Range between 6.5 and 8.5.

6. Dissolved oxygen.

For trout waters, not less than 5.0 parts per million; for non-trout waters, not less than 4.0 parts per million.

7. Toxic wastes, oil, deleterious substances, colored or other wastes or heated liquids.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish life, make the waters unsafe or unsuitable as a source of water supply for drinking, culinary or food processing purposes or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

NOTE: Refer to Notes 1 and 2 under Class AA, which are also applicable to Class A standards.

#### CLASS B

Best usage of waters: Bathing and any other usages except as source of water supply for drinking, culinary or food processing purposes.

#### Quality Standards for Class B Waters

Specifications

1. Floating solids; settleable solids; sludge deposits.

None which are readily visible and attributable to sewage, wastes or other wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. Sewage or waste effluents.

None which are not effectively disinfected.

3. pH.

4. Dissolved oxygen.

Range between 6.5 and 8.5. For trout waters, not less than 5.0 parts per million; for non-trout waters, not less than 4.0 parts per million.

5. Toxic wastes, oil, deleterious substances, colored or other wastes or heated liquids.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish life, make the waters unsafe or unsuitable for bathing or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

NOTE: Refer to Note No. 2 under Class AA, which is also applicable to Class B

#### CLASS C

Best usage of waters: Fishing and any other usages except for bathing or as source of water supply for drinking, culinary or food processing purposes.

#### Quality Standards for Class C Waters

Items

Specifications

1. Floating solids; settleable solids; sludge deposits.

None which are readily visible and attributable to sewage, industrial wastes or other amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. pH.

3. Dissolved oxygen.

Range between 6.5 and 8.5. For trout waters, not less than 5.0 parts per million; for non-trout waters, not less than 4.0 parts per million.

4. Toxic wastes, oil, deleterious substances, colored or other wastes or heated liquids.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish life or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

NOTE: Refer to Note No. 2 under Class AA, which is also applicable to Class C standards.

#### CLASS D

Best usage of waters: Agricultural or source of industrial cooling or process water supply and any other usage except for fishing, bathing or as source of water supply for drinking, culinary or food processing purposes.

Conditions related to best usage: The waters will be suitable for fish survival; the waters without treatment and except for natural impurities which may be present will be satisfactory for agricultural usages or for industrial process cooling water; and with special treatment as may be needed under each particular circumstance, will be satisfactory for other industrial processes.

## Quality Standards for Class D Waters

Items

Specifications

1. Floating solids; settleable solids; sludge deposits.

None which are readily visible and sewage, industrial attributable to wastes or other wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. pH.

Range between 6.0 and 9.5. Not less than 3.0 parts per million.

Dissolved oxygen. 4. Toxic wastes, oil, deleterious substances, colored or other wastes, or heated liquids.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to prevent fish survival or impair the waters for agricultural purposes or any other best usage as determined for the specific waters which are assigned to this class.

NOTE: Refer to Note No. 2 under Class AA, which is also applicable to Class A standards.

#### CLASS E

Best usage of waters: Sewage or industrial wastes or other wastes disposal and transportation or any other usages except agricultural, source of industrial cooling or process water supply, fishing, bathing, or source of water supply for drinking, culinary or food processing purposes.

## Quality Standards for Class E Waters

Items

Specifications

1. Floating solids; settleable solids; oil; sludge deposits.

None attributable to sewage, industrial wastes or other wastes in sufficient amounts to interfere with navigation or cause a public nuisance as defined by the Penal Law.

2. pH.

stances.

3. Dissolved oxygen.

Not lower than 5.0. Sufficient dissolved oxygen to prevent odor nuisances due to anaerobic decomposition unless other effective

means are used to control odors. None in sufficient amounts to cause a 4. Odor producing subpublic nuisance as defined by the Penal Law.

#### CLASS F

Best usage of waters: Sewage or industrial wastes or other wastes disposal.

## Quality Standards for Class F Waters

Items

Specifications

1. Floating solids; settleable solids; oil; sludge deposits.

None attributable to sewage, industrial wastes or other wastes in sufficient amounts to cause a public nuisance as defined by the Penal Law. Sufficient dissolved oxygen to prevent

2. Dissolved oxygen.

odor nuisances due to anaerobic decomposition unless other effective means are used to control odors.

3. Odor producing substances.

None in sufficient amounts to cause a public nuisance as defined by the Penal Law.

## 4. CLASSES AND STANDARDS FOR TIDAL SALT WATERS

#### CLASS SA

Best usage of waters: Shellfishing for market purposes and any other usages.

## Quality Standards for Class SA Waters

Items

Specifications None attributable to sewage, indus-

1. Floating solids; settleable solids; oil; sludge deposits.

2. Garbage, cinders, ashes, oils, sludge or other

refuse. 3. Sewage or waste effluents.

4. Dissolved oxygen.

5. Toxic wastes, deleterious substances, colored or other wastes or heated liquids.

trial wastes or other wastes. None in any waters of the Marine District as defined by State Conserva-

tion Law. None which are not effectively disinfected.

Not less than 5.0 parts per million.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to edible fish or shellfish or the culture or propagation thereof, or which in any manner shall adversely affect the flavor, color, odor or sanitary condition thereof or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

of Coli-6. Organisms form group.

The median MPN value in any series of samples representative of waters in the shellfish growing area shall not be in excess of 70 per 100 milliliters.

#### CLASS SB

Best usage of waters: Bathing and any other usages except shellfishing for market purposes.

## Quality Standards for Class SB Waters

Items

1. Floating solids; settleable solids; oil; sludge deposits.

2. Garbage, cinders, ashes, oils, sludge or other refuse.

3. Sewage or waste effluents.

4. Dissolved oxygen.

5. Toxic wastes, deleterious substances, colored or other wastes or heated liquids.

Specifications

None attributable to sewage, industrial wastes or other wastes.

None in any waters of the Marine District as defined by State Conservation Law.

None which are not effectively disinfected.

Not less than 5.0 parts per million.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to edible fish or shellfish or the culture or propagation thereof, or which in any manner shall adversely affect the flavor, color, odor or sanitary condition thereof; and otherwise none in sufficient amounts to make the waters unsafe or unsuitable for bathing or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

#### CLASS SC

Best usage of waters: Fishing and any other usages except bathing or shellfishing for market purposes.

#### Quality Standards for Class SC Waters Specifications

Items

1. Floating solids; settleable solids; sludge deposits.

None which are readily visible and attributable to sewage, industrial wastes or other wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

Items

- Garbage, cinders, ashes, oils, sludge or other refuse.
- 3. Dissolved oxygen.
- Toxic wastes, oil, deleterious substances, colored or other wastes or heated liquids.

#### Specifications

None in any waters of the Marine District as defined by State Conservation Law.

Not less than 5.0 parts per million.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to edible fish or shellfish or the culture or propagation thereof, or which in any manner shall adversely affect the flavor, color, odor or sanitary condition thereof or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

#### CLASS SD

Best usage of waters: Any usages except fishing, bathing, or shellfishing for market purposes.

## Quality Standards for Class SD Waters

Items

Specifications

 Floating solids; settleable solids; sludge deposits.

None which are readily visible and attributable to sewage, industrial wastes or other wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

None in any waters of the Marine District as defined by State Conserva-

Garbage, cinders, ashes, oils, sludge or other refuse.

tion Law.

Not less than 3.0 parts per million.

- 3. Dissolved oxygen.
- Toxic wastes, oil, deleterious substances, colored or other wastes.

None alone or in combination with other substances or wastes in sufficient amounts to prevent survival of fish life or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

## 5. CLASSES AND STANDARDS FOR UNDERGROUND WATERS

#### CLASS GA

Best usage of waters: Source of water supply for drinking, culinary or food processing purposes and any other usages.

Conditions related to best usage: The waters, if subjected to approved disinfection treatment if necessary, with additional treatment if necessary to reduce naturally present impurities, meet or will meet U. S. Public Health Service drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.

#### Quality Standards for Class GA Waters

Items

Specifications

 Sewage or industrial wastes or ineffectively treated effluents; fecal matter, garbage, manure, or other refuse. None within limiting distances of well, spring or infiltration gallery as specified in rules and regulations enacted under provisions of the Public Health Law for protection of a public water supply; none within limiting distances of well, spring, or infiltration gallery as specified in decisions of Water Power and Control Commission; otherwise, if no limiting distances have been specified as indicated above none within 200 feet of a well, spring, or

Items

2. Tastes or odor produc-

3. Toxic wastes, delete-

uids.

rious substances, other

wastes or heated liq-

ing substances.

Specifications

infiltration gallery used as source of a public water supply and none within 100 feet of well, spring, or infiltration gallery used as a source for any other kind of drinking water supply unless a lesser or greater distance is approved, permitted or required by the local health authorities or the State Department of Health; otherwise none in such a way or in sufficient amounts to impair the waters for use as a source of water supply for drinking, culinary or food processing purposes. Nothing in these specifications shall be construed as preventing the location of new wells under the jurisdiction of the Water Power and Control Commission.

None attributable to sewage, industrial wastes or other wastes in sufficient amounts to make the waters unsafe or unsuitable as a source of water supply for drinking, culinary or food processing purposes.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to make the waters unsafe or unsuitable as a source of water supply for drinking, culinary or food processing purposes, or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

NOTE: In determining the safety or suitability of waters in this class for use as a source of water supply for drinking, culturary or food processing purposes after approved treatment if necessary, the Water Pollution Control Board will be guided by the standards specified in the latest edition of "Public Health Service Drinking Water Standards" published by the United States Public Health Service.

#### CLASS GB

Best usage of waters: Source of industrial or other water supply and any other usages except as source of water supply for drinking, culinary or food processing purposes.

Conditions related to best usage: The waters without treatment and except for natural impurities which may be present will be satisfactory for agricultural water supply or industrial process cooling water; and with special treatment as may be needed under each particular circumstance, will be satisfactory for other industrial processes.

## Quality Standards for Class GB Waters

Items

Specifications

 Toxic wastes, deleterious substances, other wastes or heated liquids.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to make the waters unsafe or unsuitable for any best usage as determined for the specific waters which are assigned to this class.

The foregoing classifications and standards of quality and purity have state-wide application.

## 6. SPECIAL CLASSES—SURFACE WATERS

## CLASS A—SPECIAL (INTERNATIONAL BOUNDARY WATERS)

This special class with its quality standards, adopted by the Water Pollution Control Board on December 6, 1954, has been assigned to the waters of the Niagara River, which constitute a portion of the boundary waters covered by a treaty between the United States and Canada and under the supervision of an International Joint Commission. The definition, specifications and standards applying to this class have been filed with the Secretary of State for publication in the "Official Compilation of Codes, Rules and Regulations of the State of New York."

## CLASS AA—SPECIAL (LAKE CHAMPLAIN DRAINAGE BASIN)

This special class with its quality standards, adopted by the Water Pollution Control Board on December 11, 1956, has been assigned to the waters of Lake Placid and its tributaries, and Lake George and its tributaries. The definition, specifications and standards applying to this class have been filed with the Secretary of State for publication in the "Official Compilation of Codes, Rules and Regulations of the State of New York."

## SPECIAL CLASS (LOWER GENESEE RIVER)

This special class with its quality standards, adopted by the Water Pollution Control Board on April 20, 1959, has been assigned to the waters of the Genesee River between its outlet into Lake Ontario and the Barge Canal Dam at Court Street, Rochester. The definition, specifications and standards applying to this class have been filed with the Secretary of State for publication in the "Official Compilation of Codes, Rules and Regulations of the State of New York."

#### APPENDIX E

# CLASSIFICATIONS AND WATER QUALITY STANDARDS FOR NORTH CAROLINA

(Adopted by the State Stream Sanitation Committee on 19 November 1953)

## SECTION I. DEFINITIONS

The definition of any word and phrase used in Section II, III, or IV shall be the same as given in Section 143-212, Article 21 of the General Statutes of North Carolina. The following words and phrases, which are not defined in said section, shall be construed to have the following meanings:

- 1. Source of water supply for drinking, culinary or food-processing purposes shall mean any source, either public or private, the waters from which are used for human consumption, or used in connection with the processing of milk, beverages, food or for other purposes which require water meeting the "Public Health Service Drinking Water Standards."
- 2. Approved treatment, as applied to water supplies, means treatment accepted as satisfactory by the health authorities responsible for exercising supervision over the sanitary quality of water supplies.
- 3. Bathing shall include swimming, diving, wading, and similar uses but shall be regarded as a best usage only for waters in which such uses are or may be expected to be subjected to effective sanitary supervision and control.
- 4. Fishing shall include the propagation of fish and such other aquatic life as is necessary to provide a suitable environment for fish.
- 5. Shellfish culture shall include the use of waters for the propagation, storage and gathering of oysters, clams and other shellfish for market purposes.
- 6. Agricultural shall include the use of waters for stock watering, irrigation, and other farm purposes but not as sources of water supply for drinking, culinary or food-processing purposes.
- 7. Waste disposal shall include the use of waters for the disposal of sewage, industrial waste or other waste either before or after treatment.
- 8. Tidal salt waters shall mean all tidal waters which are so designated by the State Stream Sanitation Committee and which generally have a natural chloride ion content in excess of 500 parts per million.
- 9. Swamp waters shall mean those waters which are so designated by the State Stream Sanitation Committee and which are topographically located so as to generally have very low velocities and certain other characteristics which are different from adjacent streams draining steeper topography.
- 10. Offensive condition shall be construed to mean and include any condition or conditions resulting from the

presence of sewage, industrial wastes or other wastes within the waters of the State or along the shorelines thereof which shall either directly or indirectly cause foul or noxious odors, unsightly conditions, the breeding of abnormally large quantities of mosquitoes or other insect pests, or shall damage private or public water supplies or other structures, result in the development of gases which destroy or damage surrounding property, herbage or grasses, or which shall affect the health of any person residing or working in the area.

11. Best usage of waters as specified for each class shall be those uses as determined by the State Stream Sanitation Committee in accordance with the stipulations in Article 21, General Statutes of North Carolina.

## SECTION II. RULES APPLICABLE TO CLASSES AND STANDARDS

- 1. In cases where sewage, industrial wastes or other wastes are discharged directly into waters which are assigned a different classification than the waters into which such receiving waters flow, the standards applicable to the waters which receive such sewage, industrial wastes or other wastes shall be supplemented by the following:
- "The quality of any waters receiving sewage, industrial wastes or other waste discharges shall be such that no impairment of the best usage of waters in any other class shall occur by reason of such sewage, industrial wastes or other waste discharges."
- 2. Tests or analytical procedures to determine conformity or nonconformity with standards will, insofar as practicable and applicable, be made in accordance with the methods given in the latest edition of "Standard Methods for the Examination of Water and Sewage," published by the American Public Health Association, or, where other tests or analytical procedures have been found to be more applicable and satisfactory, same may be used upon acceptance and approval by the Committee.
- 3. In making tests or analytical determinations of classified waters to determine conformity or non-conformity with the established standards, samples shall be collected in such manner and at such locations as approved by the Executive Secretary of the Committee as being representative of the receiving waters after reasonable opportunity for dilution and mixture with the waste discharged thereto. When, in the opinion of the Executive Secretary it becomes necessary or desirable, samples will be collected from sewage and industrial waste outfalls and discharges from such outfalls will be

metered or otherwise measured to determine the volume of flow.

4. Natural waters may on occasion have characteristics outside of the limits established by the standards. The standards adopted herein relate to the condition of waters as affected by the discharge of sewage, industrial wastes or other wastes.

# SECTION III. ESTABLISHED CLASSES FOR FRESH SURFACE WATERS AND THE STANDARDS OF WATER QUALITY AND PURITY WHICH SHALL BE APPLIED THERETO

#### Class A-I

Best Usage of Waters: Source of water supply for drinking, culinary, or food-processing purposes or any other usage requiring waters of lower quality.

Conditions Related to Best Usage: This class is intended primarily for waters having watersheds which are uninhabited and otherwise protected as required by the State Board of Health and which require only approved disinfection, with additional treatment when necessary to remove naturally present impurities, in order to meet the "Public Health Service Drinking Water Standards" and will be considered safe for drinking, culinary, and food-processing purposes.

## Quality Standards for Class A-I Waters

#### Items

#### Specifications

- Floating solids; settleable solids; sludge deposits; tastes or odorproducing substances.
- None attributable to sewage, industrial wastes or other wastes.
- Sewage, industrial wastes or other wastes.
- None
- Toxic wastes; oils; deleterious substances; colored or other wastes.
- None

Note No. 1: In determining the safety or suitability of waters in this class for use as a source of water supply for drinking, culinary or food-processing purposes after approved disinfection, the Committee will be guided by the physical, chemical and bacteriological standards specified in the latest edition of the "Public Health Service Drinking Water Standards" and the requirements of the State Board of Health as set forth in the "Rules Relating to the Protection of Unfiltered Public Water Supplies."

#### Class A-II

Best Usage of Waters: Source of water supply for drinking, culinary or food-processing purposes and any other best usage requiring waters of lower quality.

Conditions Related to Best Usage: The waters, if subjected to approved treatment equal to coagulation, sedimentation, filtration and disinfection, with additional treatment if necessary to remove naturally present impurities, will meet the "Public Health Service Drinking Water Standards" and will be considered safe for drinking, culinary or food-processing purposes.

## Quality Standards for Class A-II Waters

Items

Specifications

 Floating solids; settleable solids; sludge deposits. Only such amounts attributable to sewage, industrial wastes or other wastes as will not, after reasonable opportunity for dilution and mixture of same with the receiving waters, make the waters unsafe or unsuitable as a source of water supply for Items

Specifications

drinking, culinary, or food-processing purposes, injurious to fish and wildlife, or impair the waters for any other best usage established for this

- 2. Sewage, industrial wastes or other wastes.
- Odor producing substances contained in sewage, industrial wastes or other wastes.

None which are not effectively treated to the satisfaction of the Committee and in accordance with the requirements of the State Board of Health.

Only such amounts, whether alone or in combination with other substances or wastes, as will not, after reasonable opportunity for dilution and mixture of same with the receiving waters, cause taste and odor difficulties in water supplies which cannot be corrected by treatment as specified under "Conditions Related to Best Usage," impair the palatability of fish, or have a deleterious effect upon any best usage established for waters of this class.

Phenolic compounds.

Not greater than 3.0 parts per billion (phenols).

5. pH.

Shall be normal for the waters in the area, which generally shall range between 6.0 and 8.5, except that swamp waters may have a low of 4.3.

6. Total hardness.

Not greater than 100 parts per million as CaCO₃.

7. Dissolved oxygen.

Not less than 5.0 parts per million for trout producing waters; not less than 4.0 parts per million for non-trout waters, except that swamp waters may have a minimum of 3.0 parts per million.

8. Toxic wastes; oils; deleterious substances; colored or other wastes; or heated liquids. Only such amounts, whether alone or in combination with other substances or wastes, and only such temperatures as will not render the waters unsafe or unsuitable as a source of water supply for drinking, culinary, or food-processing purposes, injurious to fish and wildlife or adversely affect the palatability of same, or impair the waters for any other best usage established for this class.

Note No. 1: In determining the safety or suitability of waters in this class for use as a source of water supply for drinking, culinary or food-processing purposes after approved treatment, the Committee will be guided by the physical, chemical and bacteriological standards specified in the latest edition of the "Public Health Service Drinking Water Standards."

Note No. 2: It is recognized that certain toxic substances will seriously affect fish life; however, the establishment of a single numerical standard for North Carolina waters would be too restrictive. In view of this and since there are many waters which, because of poor buffering capacity and composition will require special consideration, limiting values for such toxic materials will be established on the basis of the characteristics of the particular waters under consideration.

#### Class B

Best Usage of Waters: Bathing and any other usage except as source of water supply for drinking, culinary or food-processing purposes.

Conditions Related to Best Usage: The waters, under proper sanitary supervision by the controlling health authorities, will meet accepted standards of water quality for outdoor bathing places and will be considered safe and satisfactory for bathing purposes. Also, suitable for other uses requiring waters of lower quality.

## Quality Standards for Class B Waters

#### Items

## Specifications

1. Floating solids; settleable solids; sludge deposits.

Only such amounts attributable to sewage, industrial wastes or other wastes as will not, after reasonable opportunity for dilution and mixture of same with the receiving waters, make the waters unsafe or unsuitable for bathing, injurious to fish and wildlife, or impair the waters for any other best usage established for this class.

2. Sewage, industrial wastes or other wastes.

None which are not effectively treated to the satisfaction of the Committee. In determining the degree of treatment required for such waste when discharged into waters to be used for bathing, the Committee will take into consideration the quantity and quality of the sewage and wastes involved and the proximity of such discharges to the waters in this class.

3. Phenolic compounds.

Not to exceed 3.0 parts per billion (phenols).

4. pH.

Shall be normal for the waters in the area, which generally shall range between 6.0 and 8.5, except that swamp waters may have a low of 4.3.

5. Dissolved oxygen.

Not less than 5.0 parts per million for trout producing waters; not less than 4.0 parts per million for non-trout waters, except that swamp waters may have a minimum of 3.0 parts per million.

6. Toxic wastes; oils; deleterious substances; colored or other wastes; or heated liquids.

Only such amounts, whether alone or in combination with other substances or wastes, and only such temperatures as will not render the waters unsafe or unsuitable for bathing, injurious to fish and wildlife or adversely affect the palatability of same, or impair the waters for any other best usage established for this class.

Note No. 1: Refer to Note 2 under Class A-II which also applies to Class B Standards.

Note No. 2: In assigning this classification to waters intended for bathing, the Committee will take into consideration the relative proximity of sources of pollution and will recognize the potential hazards involved in locating swimming areas close to sources of pollution and will not assign this classification to waters, the bacterial quality of which is dependent solely upon adequate disinfection, and where the interruption of such treatment would render the water unsafe for bathing.

#### Class C

Best Usage of Waters: Fishing and any other usage except for bathing or as a source of water supply for drinking, culinary or food-processing purposes.

Conditions Related to Best Usage: The waters will be suitable for fish and wildlife propagation. Also suitable for other uses requiring waters of lower quality.

## Quality Standards for Class C Waters

#### Items

#### Specifications

1. Floating solids: settleable solids; sludge deposits.

Only such amounts attributable to sewage, industrial wastes or other wastes as will not, after reasonable opportunity for dilution and mixture of same with the receiving waters. make the waters unsafe or unsuitable for fish and wildlife, or impair the waters for any other best usage established for this class.

2. pH.

Shall be normal for the waters in the area, which generally shall range between 6.0 and 8.5, except that swamp waters may have a low of 4.3.

Items

3. Dissolved oxygen.

Specifications.

Not less than 5.0 parts per million for trout producing waters; not less than 4.0 parts per million for non-trout waters, except that swamp waters may have a minimum of 3.0 parts per million.

4. Toxic wastes; oils; deleterious substances; colored or other wastes; or heated liq-

Only such amounts, whether alone or in combination with other substances or wastes, and only such temperatures as will not render the waters injurious to fish and wildlife or adversely affect the palatability of same, or impair the waters for any other best usage established for this class.

Note No. 1: Refer to Note No. 2 under Class A-II which is also applicable to Class C Standards.

#### Class D

Best Usage of Waters: Agriculture, industrial cooling and process water supply, fish survival and any other usage, except fishing, bathing or as a source of water supply for drinking, culinary or food-processing purposes.

Conditions Related to Best Usage: The waters without treatment and except for natural impurities which may be present therein will be suitable for agricultural uses and will permit fish survival. The waters will also be usable after special treatment by the user as may be needed under each particular circumstance for industrial purposes, including cooling and process waters.

## Quality Standards for Class D Waters

#### Items

#### Specifications

1. Floating solids; settleable solids; sludge deposits.

Only such amounts attributable to sewage, industrial wastes or other wastes as will not, after reasonable opportunity for dilution and mixture of same with the receiving waters, render the waters unsuitable for agriculture, industrial cooling purposes and fish survival.

2. pH.

Shall be normal for the waters in the area, which generally shall range between 6.0 and 8.5, except that swamp waters may have a low of 4.3.

3. Dissolved oxygen.

4. Toxic wastes; oils; deleterious substances; colored or other wastes or heated liquids.

Not less than 3.0 parts per million. Only such amounts attributable to

sewage, industrial wastes or other wastes and only such temperatures as will not render the waters unsuitable for agriculture, industrial cooling purposes and fish survival.

Note No. 1: Refer to Note No. 2 under Class A-II which is also applicable to Class D Standards.

#### Class E

Best Usage of Waters: Navigation and disposal of sewage, industrial wastes, or other wastes, and any other uses except agriculture, source of industrial cooling waters, fishing, bathing, or source of water supply for drinking, culinary or food-processing purposes.

Conditions Related to Best Usage: Waters will be suitable for navigation where navigable waters are involved, and may be used for waste disposal to the extent that the stream will accommodate same within the limits of the prescribed specifications for this class. This class will not be assigned to waters which can, in the light of consideration prescribed by the Statutes, be properly assigned to a higher class.

## Quality Standards for Class E Waters

#### Items

#### Specifications

1. Floating solids; settleable solids; oils; sludge deposits.

Only such amounts attributable to sewage, industrial wastes or other wastes as will not interfere with navigation in navigable waters, and will not create an offensive condition in waters, whether or not navigable.

2. pH.

Not lower than 4.3 in waters used for navigation. Otherwise, it shall be maintained at such levels as not to adversely affect the quality of waters in any other class to which these waters may be tributary.

3. Dissolved oxygen.

Sufficient to prevent the development of an offensive condition.

4. Odor-producing substances.

Only such amounts as will not create an offensive condition.

## SECTION IV. ESTABLISHED CLASSES FOR TIDAL SALT WATERS AND THE STANDARDS OF WATER QUALITY AND PURITY WHICH SHALL BE APPLIED THERETO

#### Class SA

Best Usage of Waters: Shellfishing for market purposes and any other usage requiring waters of lower

Conditions Related to Best Usage: Waters will meet the sanitary and bacteriological standards given in the latest edition of "Manual of Recommended Practices for Sanitary Control of the Shellfish Industry," recommended by the Public Health Service and will be considered safe and suitable for shellfish culture.

### Quality Standards for Class SA Waters

#### Specifications

1. Floating solids; settleable solids; sludge deposits.

None attributable to sewage, industrial wastes or other wastes.

Sewage, industrial wastes, or other

None which are not effectively treated to the satisfaction of the Committee and in accordance with the requirements of the State Board of Health.

wastes.

3. pH. 4. Dissolved oxygen.

5. Toxic wastes; oils; deleterious substances; colored or other wastes: or heated liquids.

6. Organisms of coliform group.

Range between 6.8 and 8.5. Not less than 4.0 parts per million, except that swamp waters may have a minimum of 3.0 parts per million. Only such amounts, whether alone or in combination with other substances or wastes, and only such temperatures as will not make the waters unsafe or unsuitable for fish and shellfish or their propagation, impair the palatability of same, or impair the waters for any other best usage established for this class.

The coliform bacterial content of the water shall not exceed the limits the latest edition of specified in "Manual of Recommended Practices for Sanitary Control of the Shellfish Industry," recommended by the Public Health Service.

Note No. 1: Refer to Note No. 2 under Class A-II which will also apply to Class SA Standards.

#### Class SB

Best Usage of Waters: Bathing and any other usage except shellfishing for market purposes.

Conditions Related to Best Usage: The waters, under proper sanitary supervision by the controlling health authorities, will meet accepted sanitary standards of water quality for outdoor bathing places and will be considered safe and satisfactory for bathing purposes.

## Quality Standards for Class SB Waters

Items

1. Floating solids; settleable solids; sludge deposits.

2. Sewage, industrial other wastes, O F wastes.

Specifications

None attributable to sewage, industrial wastes or other wastes.

None which are not effectively treated to the satisfaction of the Committee. In determining the degree of treatment required for such wastes when discharged into waters to be used for bathing, the Committee will take into consideration the quantity and quality of the sewage and wastes involved and the proximity of such discharges to the

waters in this class.

Shall be normal for the waters in the area, which generally shall range between 6.0 and 8.5, except that swamp waters may have a low of 4.3.

Dissolved oxygen.

3. pH.

Not less than 4.0 parts per million, except that swamp waters may have a minimum of 3.0 parts per million.

5. Toxic wastes; oils; deleterious substances; colored or other wastes; or heated liquids.

Only such amounts, whether alone or in combination with other substances or wastes, and only such temperatures as will not make the waters unsafe or unsuitable for bathing, injurious to fish or shellfish, or adversely affect the palatability of same, or impair the waters for any other best usage established for this class.

Note No. 1: In assigning waters to this class, the Committee will take into consideration the proximity of points of sewage, industrial waste and other waste discharges and will recognize the potential hazards involved in locating bathing areas close to sources of pollution. Waters will not be assigned to this class if the bacterial quality of these waters is solely dependent upon adequate disinfection and where the interruption of such treatment would render the waters unsafe for bathing purposes.

Note No. 2: Refer to Note No. 2 under Class A-II which will also apply to Class SB Standards.

#### Class SC

Best Usage of Waters: Fishing, and any other usage except bathing or shellfishing for market purposes.

Conditions Related to Best Usage: The waters will be suitable for fishing and fish propagation. Also suitable for other uses requiring waters of lower quality.

## Quality Standards for Class SC Waters

#### Items

#### Specifications

1. Floating solids; settleable solids; sludge deposits.

Only such amounts attributable to sewage, industrial wastes or other wastes as will not, after reasonable opportunity for dilution and mixture of same with the receiving waters, make the waters unsafe or unsuitable for fish, shellfish and wildlife, or impair the waters for any other best usage established for this class.

2. pH.

Shall be normal for the waters in the area, which generally shall range between 6.0 and 8.5, except that swamp waters may have a minimum of 4.3.

3. Dissolved oxygen.

Not less than 4.0 parts per million, except that swamp waters may have a minimum of 3.0 parts per million.

#### Items

 Toxic wastes; oils; deleterious substances; colored or other wastes; or heated liquids.

#### Specifications

Only such amounts, whether alone or in combination with other substances or wastes, and only such temperatures as will not render the waters injurious to fish and shellfish, adversely affect the palatability of same, or impair the waters for any other best usage established for this class.

Note No. 1: Refer to Note No. 2 under Class A-II which will also apply to Class SC Standards.

#### Class SD

Best Usage of Waters: Navigation and any other best usage, except fishing, bathing, or shellfishing for market purposes.

Conditions Related to Best Usage: Waters will be suitable for navigation, and in certain instances where there is either no practical means of treatment known or where the degree of treatment required to satisfy the standards for a higher class is economically impractical, these waters may be used for the disposal of sewage, industrial

wastes or other wastes until feasible treatment processes become available, but in no instance shall any such usage result in the development of an offensive condition.

## Quality Standards for Class SD Waters

Items

 Floating solids; settleable solids; sludge deposits.

2. pH.

3. Dissolved oxygen.

4. Toxic wastes; oils; deleterious substances; colored or other wastes.

Specifications

Only such amounts attributable to sewage, industrial wastes or other wastes as will not interfere with navigation, or cause an offensive condition. Not lower than 4.3 in waters used for navigation. Otherwise, it shall be maintained at such levels as not to adversely affect the quality of waters in any other class to which these waters may be tributary.

Sufficient to prevent the development of an offensive condition.

Only such amounts, whether alone or in combination with other substances or wastes and only such temperatures as will not render the waters unsuitable for navigation, or create an offensive condition.

#### APPENDIX F

## MIAMI RIVER DRAINAGE BASIN

#### Objectives

The water pollution survey of the streams in the Miami River drainage basin was made to obtain information upon which regulatory pollution measures could be based. The general objective or desired result of the regulatory measures is to restore and preserve the main stream and its tributaries for uses consistent with public health and welfare requirements, giving due consideration to the social and economic progress within the communities.

Recommended reductions of sewage and industrial wastes pollution are presented elsewhere in this report. Compliance with these will result in degrees of modification permitting uses of the streams for (1), domestic water supply; (2) industrial water supply; (3), fish and wildlife and; (4), at least limited recreation.

The policy which has been adopted is to fix water quality objectives consistent with water uses. For instance, where municipal water supplies are involved, this department has exercised its authority to revise upward these objectives. Streams and sections thereof consequently fall into zones of water quality.

Polluting materials are usually divided into three broad classifications: deoxygenating, highly toxic, and chemical. More specific objectives for these materials follow:

Deoxygenating Wastes: These wastes are usually organic compounds, either in suspension or solution, which use the oxygen in the water in the process of decomposition. Where the organic pollution is proportionately great, the oxygen content in the water is depleted, and fish and other wildlife are killed, oxidation ceases, and anaerobic decomposition or septic action increases with the attendant disagreeable odors and toxic effects. Adequate protection of the waters against unreasonable oxygen depletion should result if sufficient treatment is provided sewage and industrial wastes for substantially complete removal of settleable solids together with sufficient removal of other organic matter so as to hold the dissolved oxygen content above a critical point. The minimum dissolved oxygen content for the Miami River and its tributaries has been established at 4 ppm. A few exceptions are made where water use requires higher quality.

Highly Toxic Wastes: The highly toxic wastes are those which are poisonous in nature due to specific compounds or mixtures used in some types of industry. Cyanides, chrome and copper from metal plating operations, cyanides from gas plants, and lead from special manufacturing operations are typical.

Adequate protection will probably be provided the waters of the Miami River if substances highly toxic to human, fish, aquatic or wildlife are eliminated or reduced

to the following concentrations after initial dilution at times of critical flow:

Commide (on CN)	not over 0.15 ppm
T 3 / am Dh)	not over 0.55 ppm
Lead (as Pb)	not over 0.40 ppm
Copper (as Cu)	mot over 2 00 mm.
Chromium (hexavalent) (as	Cr)not over 2.00 ppm.

Chemical Wastes: Industrial wastes other than those in the deoxygenating and highly toxic classification are presented herein under the general classification of chemical wastes. Deleterious effects of these wastes include objectionable tastes and odors, tainting of fish flesh, excessive sludge deposits and oil concentrations, and excessive acidity or alkalinity. Probably the most offensive wastes from the standpoint of tastes and odors are the phenolic wastes from coke, synthetic resin, oil refining, petroleum eracking, tar, road oil, creosoting, wood distillation, and dye manufacturing industries. Industries producing chemical wastes other than phenolic are oil well and oil refining, gasoline filling and bulk stations, synthetic pharmaceutics, synthetic fibers, iron and steel, alkali chemicals, rubber fabrication, dye manufacturing, and acid manufacturing.

Adequate protection will probably be provided the waters of the Miami River and its tributaries if, after initial dilution at times of critical flow, the following values are maintained.

ames are maintained.	
pH	Between 6.3 and 9.0
Chlorides	_ Not over 250 ppm
Phenols	Substantially complete removal (Tentatively not over 25 ppb. to 30 ppb. especially during critical flow periods in cold weather.)
Iron	_Not over 5 ppm
Manganese	Not over 5 ppm
Oils	Substantially complete _removal
Zinc (as Zn)	_Not over 15 ppm
Nitrates	_ Not over 10 ppm
Free Acid	None
Color and Odor	$_{}{f To}$ be non-offensive
Other toxic wastes, deleterious substand high temperature liquids	ances

#### LAKE ERIE POLLUTION SURVEY INTERIM REPORT OF 1951

Objectives for Maximum Allowable Concentrations of Coliform Bacteria:

Water Supply (Raw waters subject to filtration treatment): The monthly average "most probable numbers" of coliform organisms in water from lake intakes should not exceed 5,000 per 100 ml in any month, nor exceed

this number in more than 25 per cent of the samples of such waters examined during any month.

Recreational: For waters used for recreational purposes involving any bathing or swimming activities, the monthly arithmetical average "most probable numbers" of coliform organisms should not exceed 1,000 per 100 ml during any month of the recreational season, nor should exceed this number in more than 25 per cent of the samples examined during any such month. For waters used for recreational purposes not involving bathing or swimming, the monthly average "most probable numbers" of coliform organisms should not exceed 5,000 per 100 ml in any month of the recreation season, nor should exceed 5,000 per 100 ml in more than 25 per cent of the samples examined during any such month.

## MAUMEE RIVER BASIN Objectives

Bacteria: At water works intakes on streams of the Maumee River Basin the monthly arithmetical average of "most probable numbers" or, as an alternate, of "indicated numbers" of coliform organisms should not exceed 5,000 per 100 milliliters (5,000 per 100 ml) in any month; nor exceed this density in more than 20% of the samples of such waters examined during any month; nor exceed 20,000 per 100 ml in more than 5% of such samples.

For non-bathing or non-swimming recreation the monthly arithmetical average of "most probable numbers" or of "indicated numbers" should not exceed 5,000 per 100 ml in any month of the recreational season, nor should exceed this number in more than 20% of the samples examined during such a month. For bathing and swimming waters the monthly arithmetical average of "most probable numbers" or of "indicated numbers" of coliform organisms should not exceed 1,000 per 100 ml; nor should exceed this number in more than 20% of the samples examined in such month; nor should exceed 2,400 per 100 ml on any one day.

Dissolved Oxygen: The minimum dissolved oxygen objective for the Maumee River and its tributaries has been established at 4 ppm which, during critical summer conditions, is comparable to 50% dissolved oxygen saturation.

Toxic Wastes: Pending the results of studies and research now in progress by qualified technical groups, the following should serve as a guide to the reasonable protection of the waters of the basin:

- Jan Vanili,	
Lead (as Pb)	not one 0 ar
Chromium (hexavalent as Cr) Cadmium (as Cd)	not over 0.4 not over 2.0
Zinc (as Zn)  Nickel (as Ni)  Nitrate (as N)	not over 1

It is emphasized that exceptions to the above must be made where water uses require higher quality; and, further, that some of the above substances may cause damages in lower concentrations than noted under certain conditions and in certain combinations. Taste and Odor: In general, wastes producing tastes and odors shall be limited to the extent required to prevent undue damage to reasonable and necessary water uses. Treatment shall be given to wastes containing phenols, oils, and allied derivatives to obtain substantially complete removal of these substances at their source.

Color: Discharge of color producing substances which impair reasonable and necessary water uses will not be permitted. At least partially pertinent to this category are iron and manganese. The concentrations of each of these substances shall not exceed 5 ppm (as Fe and Mn, respectively). This objective will provide reasonable protection for all water uses.

pH: No substance will be permitted which will cause the pH of the receiving water to fall outside a pH range between 6.3 and 9.0.

Suspended Solids and Floating Materials: Substantially complete removal of settleable solids and floating materials will be required to prevent nuisance conditions and sludge deposits. Additional removal of suspended solids may be required to prevent turbidity causing excessive damages to water uses.

Dissolved Solids: Objectives concerning damages from dissolved solids related to toxicity, oxygen depletion, taste and odors, pH, and color are discussed under these effects. Additional limitations on dissolved solids will be applied to prevent excessive hardness or other damaging effects. Chlorides (as Cl) should not exceed 100 ppm at any location within the basin.

Temperature: Operations resulting in excessive stream temperatures which impair other water uses, reasonable and necessary in the public interest, will not be permitted

Fluorides: In case control of these wastes becomes necessary the maximum tolerable at water works intakes is fixed at 1.5 ppm.

Special Conditions: Insofar as practicable the effect of sewage or waste discharges on the receiving waters shall be considered after they are mixed with the waters and beyond a zone of immediate effect. The extent to which this is practicable depends on local conditions and the proximity and nature of other water uses.

## MUSKINGUM RIVER BASIN Objectives

The major objective of a proposed water pollution control program in Muskingum River Basin is to secure and maintain the quality of the water in the various streams and sections thereof suitable for those uses which in the public interest are reasonable and necessary.

The establishment of waste treatment requirements or other corrective measures to obtain effluents consistent with the basic objective involves the proper correlation of several basic factors. These include the quantity of the waste discharged, the concentration of the pollutants, dilution and natural purification capacity of the receiving stream, population and industrial growth trends, and the water quality required for downstream uses. Data pertinent to evaluating the magnitude of these factors are presented in this report.

It is recognized that water uses may vary for different streams and even for different sections of the same stream. Also, the maximum allowable concentration of polluting substances will vary for each particular water use. Due allowance must also be made for the variation of the effects of a particular substance alone and in the presence of other substances.

In the application of water quality objectives, consideration must be given for proper sharing of water resources, future developments, and other special needs in

the public interest.

The use of surface water as a source of public water supply is in general, always a major consideration. Although at present only a small part of the waters of this basin are so used, the future growth in the population of the basin may require greater use of these waters for such purposes. At present, recreational, wildlife preservation, and industrial uses are given the major consideration, except where public water supplies are involved. Eleven communities in the basin, having a total population of 159,273 persons (1950), obtain their water supplies from surface sources. In addition, two other communities having a combined population of 30,249 persons, obtain part of their water from surface sources. Waterways furnishing these supplies must be maintained at the highest possible quality.

For recreational and wildlife preservation purposes, a stream should be free of settleable solids, toxic concentration of heavy metals, and acids or alkalies; and should have a dissolved oxygen concentration equal to that required for maintaining aquatic life. For the latter, a concentration of at least 4.0 ppm is considered

essential.

In general, the water quality required for industrial use is similar to that given above for sustaining wildlife and for permitting recreation. Heavy metals, and acids or alkalies such as mentioned above, may be injurious to industrial processes and to equipment. In addition, water supplies for industrial use should be free from high concentrations of such salts as the chlorides and sulfates of sodium, calcium, and magnesium. These are also injurious to industrial piping and process equipment.

Due to the multipurpose use of most waters in this basin, water quality objectives to maintain these waters in a condition suitable for reasonable and necessary uses must be sufficiently flexible to meet the varying conditions which exist. Where limits for polluting characteristics are given in the following paragraphs, they are to be considered as the maximum permissible. They will serve as guides in determining pollution abatement and control measures. If, in the public interest, a higher quality of water is needed, more restrictive limits may be required. Conversely, future conditions may warrant lesser requirements.

In considering water quality objectives, pollution may be classified on the basis of effects on water quality as follows: Bacterial contamination, deoxygenation, toxicity, taste and odor, color, hydrogen-ion concentration, suspended and floating matter, excessive dissolved solids, and high temperatures.

Bacterial: Bacterial quality is particularly pertinent with respect to uses of water for public water supply and for recreational purposes. Bacterial pollution usually is associated with domestic sewage. This is understandable by reason of the disease organisms that may

be contained in human excretions. However, bacterial increases are coincident with organic decomposition, and bacterial concentrations will vary with organic content and with stages of deoxygenation and decomposition. The densities of coliform organisms (intestinal bacteria) furnish accepted criteria for the evaluation of public water supplies and recreational waters.

The accepted standard method for estimating coliform organisms is the fermentation dilution tube method. From this method a most probable number (MPN) index can be obtained. It should be realized, however, that this is merely an index of the number of coliform bacteria which, more probably than any other number, would give the results shown by the laboratory exam-

ination.

Recently, a membrane filter technique has been developed for determining directly the actual number of coliform organisms in a sample of water. Studies have indicated that this procedure and the standard dilution tube method do not measure precisely the same group of micro-organisms. When the limitations of the test are fully recognized and the difficulties of interpretation are known, this technique may be used. It is likely, that, when the sanitary significance of results, as well as the interpretation that may be given to coliform densities determined by this method, are established, it will be adopted as a standard method.

A rough estimate of the density of coliform organisms may be obtained by the use of the indicated number. This number is obtained by taking the reciprocal of the smallest positive dilution in a decimal series of plantings in fermentation tubes. This procedure was recommended in the 1917 Standard Methods and remained the only official method for the expression of coliform results until the publication of the 1936 edition of Standard Methods. Many water works operators still use this method, due to their familiarity with the procedures of calculation. For all practical purposes, the estimation of the coliform concentration by any one of the three methods described, allowing for the limitations of each, will furnish a satisfactory basis for establishing waste treatment requirements.

At water works intakes in the area covered by this report, the monthly arithmetical average estimate of coliform organisms should not exceed 5,000 per 100 milliliters (5,000 per 100 ml) in any month; nor exceed this density in more than 20 per cent of the samples of such waters examined during any month; nor exceed 20,000 per 100 ml in more than five per cent of such samples. Ît is felt that, if coliform reductions are accomplished to attain such quality, accepted practices of water treatment will assure safe public supplies.

Meeting the objective for public water supplies at existing intakes may assure satisfactory bacterial water quality for certain recreational uses in protected stream zones and may assure water quality suitable for bathing or swimming in a few stream areas. For non-bathing or non-swimming recreation, the monthly arithmetical average estimate of coliform organisms should not exceed 5,000 per 100 ml in any month of the recreational season, nor should exceed this number in more than twenty per cent of the samples examined during such month. For bathing and swimming waters, the monthly arithmetical average estimate of coliform organisms should not exceed 1,000 per 100 ml; nor should exceed this number in more than twenty per cent of the samples examined in such month; nor should exceed 2,400 per 100 ml on any one day. It must be emphasized, however, that even though all bacteria from sewage pollution were to be removed, other factors beyond the control of water pollution control agencies may still make waters of the inland streams of the basin unsuitable for bathing. Careful consideration must be given to natural, public health, and economic factors in justifying the application of bathing water quality objectives to waters of the basin.

Deoxygenation: Deoxygenating wastes may utilize the dissolved-oxygen content of a stream by biochemical oxidation processes or purely chemical processes. Organic wastes such as sanitary sewage and those from food processing are examples of the first; spent pickle liquor is an example of the latter. In either case, the material causing the oxygen demand may be in suspension or solution. Where such wastes are discharged to a stream in excessive amounts, they may deplete the dissolved-oxygen content of a stream; cause the destruction of fish and aquatic life, or inhibit their propagation; and contribute to anaerobic decomposition with attendant nuisances, disagreeable odors, toxic effects, and public health menace.

Biochemical demands for oxygen take place over a period of several days to a month whereas chemical demands for oxygen may take place over a period of several hours. The rate of oxidation of a specific substance is an important factor in determining the allowable concentration of that substance in the stream.

Adequate protection of the main stream in this basin from unreasonable oxygen depletion, in general, should result if sewage and industrial wastes are treated to obtain substantially complete removal of settleable solids. On tributaries, especially the smaller ones, treatment facilities removing from 65 per cent to 90 per cent of the oxygen demanding properties of wastes discharged to them should provide adequate water quality. These statements are predicated on the complete elimination of spent pickle liquor in all instances.

Toxic Wastes: There are many substances, alone or in combination, which at critical concentration are toxic to humans, animals, fish and other wildlife. The effects of these concentrations may range from serious conditions affecting the public health or from conditions causing direct fish kills to minor disturbances which may be serious only if continued over a prolonged period of time.

The chemical characteristics of the receiving water have a significant effect on the toxicity of individual pollutants to fish and other aquatic life. Also some substances alone may have only a slightly toxic effect but in combination with certain other substances the effect may be much greater. As an example, zinc is slightly toxic alone, however, in the presence of copper the effect is very toxic.

Although, as mentioned above, there are many substances and combinations of substances which are toxic, it is likely that a great many of these will not be discharged to the streams in sufficient quantity to be a problem, possibly because such wastes are not normally

found in the basin or because their value tends to preclude their discharge as waste products. However, some substances were encountered during this investigation which are troublesome to certain uses in concentrations above certain limits. Occurrence of these substances above such limits will be prima-facie evidence that excessive pollution exists. Pending the results of studies and research now in progress by qualified technical groups, the following should serve as a guide to the reasonable protection of the waters of this basin:

Parts per million (ppm) Cyanide (as CN) not over 0.15 Lead (as Pb) not over 0.1 Copper (as Cu) not over 0.3 Chromium (as Cr) not over 1.0 (trivalent + hexavalent) Cadmium (as Cd) not over 0.4 Zinc (as Zn) Nickel (as Ni) not over 1.0 not over 2 Nitrate (as N) not over 10

It is emphasized that exceptions to the above must be made where water uses require higher quality; and, further, that some of the above substances may cause damages in lower concentrations than noted under certain conditions and in certain combinations.

pH and Alkalinity: The greatest source of acid waste in this basin is spent acid pickle liquors which also contain appreciable amounts of ferrous iron. These wastes originate primarily in the Canton, Massillon, Dover, Zanesville, Shelby and Mansfield areas. The effects of these wastes on a stream include: The conversion of carbonate hardness to sulfate hardness; the reduction of alkalinity; the formation of sludge banks as a result of the coagulation of the iron; and, the lowering of the pH of stream water.

The drainage from coal mines which are principally located in the southeastern section of the basin comprises another source of acid iron wastes. The effects of these wastes on a stream are not unlike acid iron wastes incident to processing steel in steel mills and allied industries. The problem not only involves drainage from active mines but, more difficult of correction, drainage from abandoned mines. Drainage from worked out or abandoned facilities becomes a public problem primarily because of inability to fix responsibility. Studies and research in progress by the Coal Industry Action Committee sponsored by interstate and Federal agencies should give possible guidance toward satisfactory correction of waste disposal from active and abandoned mines.

The program for acid control involves: (1) Effective treatment, salvage or control of concentrated spent pickle liquors to prevent discharges of acids or iron; (2) good operating practices to reduce these constituents of rinse waters; and, (3) the treatment and control of acid rinse waters or other acid wastes for reducing critical constituents to meet requirements of the receiving stream. The main streams generally will be protected if the total acid content of all acid wastes is reduced to insure a residual from each source of 15% of the total acid consumed in process; tributaries generally will be protected if the total acid content of all sources is reduced to insure a residual of 4% of the total acid consumed.

Under present conditions, it is estimated that such a policy will result in water having a satisfactory pH

(meeting an objective of not less than 6.3) and with a desirable residual alkalinity. A residual alkalinity of not less than 30 parts per million is established as an objective.

Encouragement will be given to control of acid wastes by methods other than neutralization and precipitation of the iron salts with lime, because of addition of hardness by the latter method. Where neutralization is practiced, use of high calcium lime, as opposed to material having high magnesium content, is recommended in order to reduce hardness due to highly soluble magnesium sulfate. Sedimentation and proper disposal of iron and undissolved sulfates will be required.

Industrial wastes with caustic alkalinity will require treatment or control to insure that the pH of the receiving stream will not greatly exceed 9.5.

Suspended Solids and Floating Material: Substantially complete removal of settleable solids and floating material will be required to prevent nuisance conditions and sludge deposits. In the Tuscarawas River the problem of suspended solids is aggravated by high concentrations of iron principally as oxides and sulfates. Measurements indicate that the total load of iron as Fe on the streams of this basin averaged approximately 50 tons per day. Concentrations of greater than 100 ppm were observed in the Tuscarawas River during the survey. The formation and settling of iron "floc" in an area where major pollution originates, results in the entrapment and deposition in sludge beds of oils, greases, and other foul smelling materials. These are picked up in concentrated forms during freshets and carried to other points of use, or redeposited on the stream bed as flow decreases, to be picked up again and carried further downstream.

In view of these conditions, the minimum requirements shall be substantially complete removal of settleable iron, particularly in blast furnace gas washer wastes and in rolling mill wastes. Also, in the control of waste pickle liquor . . provision shall be made to prevent the discharge of iron with the waste. If the acid in the waste pickle liquor is controlled by neutralization, the measures must include precipitation of the iron.

Dissolved Solids: Objectives concerning damages from dissolved solids related to toxicity, oxygen depletion, taste and odors, pH, and color, are discussed under these effects. Dissolved solids are of concern also with respect to hardness. Large quantities of pickling acid, principally sulfuric acid used in the steel industry, result in wastes which react with alkalinity in the river or with alkalinity added to neutralize the acid and form sulfate hardness. Unless proper care is exercised in the control and treatment of acid and iron salts, (see preceding section on pH and alkalinity) excessive sulfate hardness will be added to the river. Some carbonate hardness will be changed to sulfate hardness by discharge of dilute pickle rinse waters. Also, some hardness will be added if neutralization of concentrated pickle wastes is practiced. However, in consideration of the economic aspects of a higher degree of control, the general objectives will be met if discharges of residual acid wastes are limited as previously stated and if, in the treatment or control of concentrated pickle liquors,

practical methods are followed to reduce the discharge of hardness to the river.

The elimination of excessive chloride (Cl-) concentrations as contributed by brine wastes from existing sources represents a major objective in the pollution abatement program of Tuscarawas and Muskingum Rivers. Pending the time when process changes, connected with which are problems of most significant economic magnitude, can be instituted, it will be necessary to give diligent attention to control of brine wastes discharges. The effort must be to keep concentrations in stream waters to a minimum based on the relation of existing chloride loads to average daily stream flows (yearly average).

## CUYAHOGA RIVER BASIN

#### Objectives

The basic objective of the pollution survey of streams of the Cuyahoga River Basin was the establishment of criteria upon which regulatory pollution abatement and control measures could be based for the restoration and maintenance of water quality consistent with reasonable and necessary water uses.

The formulation of treatment requirements or other corrective measures for sewage and industrial wastes discharges to obtain effluents which will be consistent with stream water quality objectives involves the proper correlation of several basic factors. These include the quantity and characteristics of wastes discharged; dilution and natural purification capacity of the receiving stream, population and industrial growth trends; and, the water quality required for downstream uses. Information pertaining to these factors is included in this report.

It is recognized that water uses may vary for different streams and for different sections of a particular stream. Also, the maximum allowable concentrations of polluting substances will vary with the different water uses. Furthermore, the effects of a particular substance may also vary, depending on the presence or absence of other substances in the receiving waters.

The cost of pollution prevention or abatement is not necessarily the same for reclamation of polluted waters as for the preservation of relatively unpolluted water; consequently, water quality objectives formulated for the purpose of restoring a polluted stream or section of a stream to a minimum quality consistent with downstream water uses cannot be considered as inviting the lowering of the water quality of cleaner streams throughout the basin.

In the application of water quality objectives, consideration must be given to provision for proper sharing of water resources, to provision for further development, and to other special needs in the public interest.

Use of the surface waters of the upper portion of this basin for public water supplies is a high priority need. Water quality objectives, designed to meet the requirements of this use, will be applied to protect existing and future supplies.

For the reasons discussed above, water quality objectives established to maintain the basin's waters in a condition suitable for reasonable and necessary uses

must be sufficiently flexible to meet the varying conditions which exist. Where limits for polluting wastes are given in the following paragraphs, they are to be considered as the maximum permissible. They will serve as guides in determining pollution abatement and control measures. More restrictive limits may be required if consideration of all factors at specific locations shows that a higher quality of water is needed in the public interest. Conversely, if changes or future conditions warrant, requirements less restrictive will be given consideration.

In applying the principles stated in the preceding paragraphs to the Cuyahoga River Basin it is particularly pertinent to note that surface water use, in general,

may be classified according to area. In the upper part of the basin, including the area tributary to the Cuyahoga River above Kent, and in the Little Cuyahoga River, a major tributary, there are surface water uses which require water of good quality. Existing uses include public water supplies, industrial water supplies, recreational uses (including fishing), and livestock watering. Also, it is highly important that water from drainage areas not now specifically developed for such uses, may need to be preserved for future developments. Availability of adequate quantities of water within the basin for all of the uses in the area is somewhat limited and may become critical in the foreseeable future. For these reasons emphasis is placed on the desirability of preserving water quality in the upper portion of Cuyahoga River Basin.

Under present conditions, heavy population concentrations and natural drainage conditions, result in a separate subdivision of the basin from Kent downstream to the confluence of Mill Creek with Cuyahoga River insofar as water uses are concerned. The objectives for this section of the stream are to abate nuisance conditions, to improve water quality for industrial uses, and to eliminate or reduce substances which interfere with the

natural purification processes in the stream.

The objectives for Cuyahoga River from the confluence of Mill Creek to its mouth and for tributaries to this section are to abate nuisance conditions and to improve water quality for legitimate water uses.

In considering water quality objectives, pollution may be classified on the basis of effects on water quality as follows: bacterial contamination; deoxygenation; toxicity; taste and odor; undesirable pH conditions; suspended solids and floating materials.

Bacterial: Bacterial quality is particularly pertinent with respect to uses of water for public water supply and for recreational purposes. Bacterial pollution usually is associated with domestic sewage. This is understandable by reason of the disease organisms that may be contained in human excretions. However, bacterial increases are coincident with organic decomposition, and bacterial concentrations will also vary with organic content and with stages of deoxygenation and decomposition. The densities of coliform organisms (intestinal bacteria) furnish accepted criteria for the evaluation of public water supplies and recreational waters.

Two acceptable methods are used for determining the density of coliform organisms in water, namely: (1) The fermentation dilution tube method; and (2) the membrane filter technique. The fermentation dilution tube method was accepted as a standard method in 1936 whereas the membrane filter technique was given limited acceptance as an alternate method in 1956. From the first method a most probable number (MPN) index is obtained. This number is merely an index of the number of coliform bacteria which more probably than any other number, would give the results shown by laboratory examination.

The membrane filter technique determines directly the actual number of coliform organisms in a sample of the water tested. Studies have indicated that this procedure does not measure precisely the same group of microorganisms as the fermentation dilution tube method. In applying the results of tests by this method to standards developed for use with the dilution tube method, consideration should be given to the differences between the two tests.

A rough estimate of the density of coliform organisms may be obtained by the use of the indicated number (Phelps index). This number is obtained by taking the reciprocal of the smallest positive dilution in a decimal series of plantings in fermentation tubes. This procedure was recommended in the third edition of "Standard Methods for Water Analyses" (1917) and remained the only official method for the expression of coliform results until the publication of the eighth edition of "Standard Methods for the Examination of Water and Sewage" (1936). Many water works operators still use this method due to their familiarity with the procedures of calculation. For all practical purposes the estimation of the coliform concentration by any one of the three methods described, allowing for the limitations of each, will furnish a satisfactory basis for establishing waste treatment requirements.

At water works intakes in the area covered by this report, the monthly arithmetical average estimate of coliform organisms should not exceed 5,000 per 100 milliliters (5,000 per 100 ml) in any month; nor exceed this density in more than 20 percent of the samples of such waters examined during any month; nor exceed 20,000 per 100 ml in more than five percent of such samples. It is felt that, if coliform reductions are accomplished to attain such quality, accepted practices of water treatment will assure safe public supplies.

Meeting the objective for public water supplies at existing intakes may assure satisfactory bacterial water quality for certain recreational uses in protected stream zones and may assure water quality suitable for bathing or swimming in a few stream areas. For non-bathing or non-swimming recreation, the monthly arithmetical average estimate of coliform organisms should not exceed 5,000 per 100 ml in any month of the recreational season, nor should exceed this number in more than twenty percent of the samples examined during such month. For bathing and swimming waters, the monthly arithmetical average estimate of coliform organisms should not exceed 1,000 per 100 ml; nor should exceed this number in more than twenty percent of the samples examined in such month; nor should exceed 2,400 per 100 ml on any one day. It must be emphasized, however, that even though all bacteria from sewage pollution were to be removed, other factors beyond the control of water pollution control agencies may still make waters of the inland streams of the basin unsuitable for bathing. Careful consideration must be given to natural, public health, and economic factors in justifying the application of bathing

water quality objectives to waters of the basin.

Deoxygenation: Deoxygenating wastes may utilize the dissolved oxygen content of a stream by biochemical oxidation processes or purely chemical processes. Organic wastes such as sanitary sewage or industrial wastes from food processing industries are examples of the first; spent pickle liquor is an example of the latter. In either case, the material causing the oxygen demand may be in suspension or solution. Where such wastes are discharged to a stream in excessive amounts, they may deplete the dissolved oxygen content of a stream; cause the destruction of fish and aquatic life, or the inhibition of their propagation; and, give rise to anaerobic decomposition which is attendant with nuisances, disagreeable odors, toxic effects, and public health menaces.

Biochemical demands for oxygen usually take place over a period of several days to a month whereas chemical demands for oxygen may take place over a period of several hours. The rate of oxidation of a specific substance is an important factor in determining the allowable concentration of that substance in the stream.

Adequate protection of the main streams in this basin from unreasonable oxygen depletion, in general, should result if sewage and industrial wastes are treated to obtain substantially complete removal of settleable solids, and the removal of at least 85 per cent of the oxygendemanding constituents of these wastes (complete treatment). The required degree of treatment will prevent the depletion of dissolved oxygen in the streams below established objectives. For the Cuyahoga River upstream from its confluence of Little Cuyahoga River, the minimum dissolved-oxygen objective is 4.0 milligrams per liter. This criterion meets requirements for normal water uses, including the protection of fish common to the waters of the basin and other aquatic life. For that portion of the Cuyahoga River downstream from confluence with Little Cuyahoga River, the dissolved oxygen objective is 3.0 mg/l. This criterion is based on the avoidance of nuisance conditions and the maintenance of satisfactory self-purification processes which require aerobic con-

Toxic Wastes: There are many substances, alone or in combination, which, at critical concentrations are toxic to humans, animals, fish and other wildlife. The effects of these concentrations may range from serious conditions affecting the public health or from conditions causing direct fish kills to minor disturbances which may be serious only if continued over a prolonged period of time.

The chemical characteristics of the receiving water has a significant effect on the toxicity of individual pollutants to fish and other aquatic life. Also, some substances alone may have only a slightly toxic effect, but in combination with certain other substances the effect may be much greater. As an example, zinc is slightly toxic alone, however, in the presence of copper the effect is very toxic.

Although, as mentioned above, there are many substances and combinations of substances which are toxic, it is likely that a great many of these will not be discharged to the streams in sufficient quantity to be a problem possibly because such wastes are not normally found in the basin or because their value tends to preclude their discharge as waste products. However, some substances were encountered during this investigation, which are troublesome to a few uses in concentrations above certain limits. Occurrence of these substances above such limits will be prima-facie evidence that excessive pollution exists. Pending the results of studies and research now in progress by qualified technical groups, the following should serve as a guide to the reasonable protection of the waters of this basin:

Milligrams per liter (mg/l) Not over 0.15 Cyanide (as CN) Not over 0.1 Lead (as Pb) Not over 0.3 Copper (as Cu) Not over 1.0 (Total) Chromium (as Cr) Not over 0.4 Cadmium (as Cd) Not over 1.0 Zinc (as Zn) Not over 2 Nickel (as Ni) Not over 10 Nitrate (as N)

It is emphasized that exceptions to the above must be made where water uses require higher quality; and further, that some of the above substances may cause damages in lower concentrations than noted under certain

conditions and in certain combinations.

Tastes and Odors: Prevalent offensive wastes produced in the basin, from the standpoint of tastes and odors, are the phenolic and other types of wastes from the production and use of coke, the processing and use of by-products from the coke plant, and the refining of petroleum products. It is recognized that there are taste and odor substances from other industries, such as chemical, tanning, etc., as well as from natural resources. The objectives, with respect to wastes containing phenols, oils, greases and allied derivatives, and certain organic and inorganic chemicals are based on their reduction by means of known practical methods of operation or treatment. By the use of these methods it is expected that some residuals will remain in the industrial wastes discharged to the lower section of the Cuyahoga River.

pH and Alkalinity: Waste pickle liquor acids and iron salts, originating for the most part in the Cleveland area, are the major cause of serious damaging effects on water quality in the Cuyahoga River resulting from acid discharges. The effects of pickle liquor discharges are: (1) Carbonate hardness is converted to sulfate hardness, (2) alkalinity is reduced, (3) sludge banks are formed by the coagulation and precipitation of suspended matter

by iron salts; and the pH is lowered.

The program for acid control in the Cuyahoga River Basin includes: (1) The effective treatment, salvage, or control of concentrated waste pickle liquors to prevent the discharge of acid and iron; and (2) the practice of good operations to reduce acid and iron in rinse waters. The treatment of dilute acid rinses in the lower section of the Cuyahoga River will not be required, at least for the present, provided acceptable practices are followed with respect to control of the amount of iron and acid in the rinses. Normally, it is considered that this condition will be met if the total acid in all wastes does not exceed 10% of the acid used. On tributary streams of the basin a further reduction of acid and iron will be required.

The above criterion not only takes into consideration the effects of the acid constituent of the pickle liquor, but also takes into consideration the deoxygenating effect of the iron constituent of spent pickle liquor. For the streams of the Cuyahoga River Basin the deoxygenating effect of the iron constituent of spent pickle liquor is much more critical than the effect of the discharged acid on the alkalinity of the stream. The above given limits of acids that may be discharged is based on the effects of the iron constituent of pickle liquor on the oxygen resources of the stream.

Under present conditions, it is estimated that such a policy will result in stream water having a satisfactory hydrogen-ion concentration meeting an objective of 6.3 (pH index) and with desirable residual alkalinity. A residual alkalinity of not less than 75 mg/l is established as an objective. These objectives are established to protect industrial process equipment and ships from corrosive waters.

Suspended Solids: Substantially complete removal of settleable solids and floating material will be required to prevent nuisance conditions and sludge deposits. The problem of suspended solids in the lower reaches of the Cuyahoga River is aggravated by high concentrations of iron. Data collected during our survey indicate that nearly 90 tons of iron as Fe were discharged daily to the Cuyahoga River. Concentrations of nearly 100 mg/l of iron were found in samples of the lower Cuyahoga River. The presence of iron in the river concentrations of 50-100 mg/l as Fe causes the coagulation of suspended solids, oils and greases which in turn settle to the bottom of the river to form sludge deposits. Upon undergoing anaerobic decomposition, these deposits give rise to the production of foul smelling gases which in turn cause the flotation of some of the sludge.

In view of the above, the minimum requirement shall be substantially complete removal of settleable iron (ferric iron) particularly in blast furnace gas washer wastes and in mill scale wastes from rolling mills. Also, in the control of spent pickle liquor . . . provision shall be made to prevent the discharge of iron with the waste. If acid in the pickle liquors is controlled by neutralization, the measures must include the precipitation of the iron.

Dissolved Solids: Objectives concerning damages from dissolved solids related to toxicity, oxygen depletion, taste and odors, pH and color, are discussed under these effects. Dissolved solids are also of concern with respect to hardness. Large quantities of pickling acid, principally sulfuric, used in the steel industry, result in wastes which react with alkalinity in the river or with alkalinity added to neutralize the acid and form sulfate hardness. Unless proper care is exercised in the control and treatment of acid and iron salts (see preceding section on pH and alkalinity), excessive sulfate hardness will be added to the river. In addition, some carbonate hardness will be changed to sulfate hardness by discharge of dilute pickle rinse waters. However, in consideration of the economical aspects of a higher degree of control, the general objectives will be met if discharges of residual acid wastes are limited as previously stated and if, in the treatment or control of concentrated spent pickle liquors, practical methods are followed to reduce the discharge of hardness to the river.

The discharge of wastes containing high concentrations of chlorides such as brine wastes shall be controlled so that the concentration of chlorides in the receiving stream shall not exceed 250 mg/l as Cl⁻.

Color: The objective is control of color-producing substances as required to prevent impairment of reasonable and necessary uses. Iron and manganese are significant with respect to color. Iron is particularly significant because of the large quantities in wastes in the low level section of the Cuyahoga River.

The objectives for color due to iron will be met if the concentration of iron is kept within the objectives listed under suspended solids and deoxygenating wastes.

Temperature: High temperatures occur in the Cuyahoga River in the Akron and Cleveland area. This is due to the use of large volumes of river water for cooling purposes. High stream water temperatures are objectionable because it increases the rate of deoxygenation of pollution loads, decreases the solubility of oxygen in the stream, and thus lowers the critical point on the oxygen "sag" curve. An increase in water temperature also intensifies the effects of toxic substances on aquatic life.

At present the effects of temperature on necessary and desirable water uses is not now significant and, therefore, state regulatory action with respect to temperature is not considered necessary at this time.

Special Conditions: Insofar as practicable, the effect of sewage or waste discharges on the receiving waters shall be considered after they are mixed with the waters and beyond a zone of immediate effect. The extent to which this is practicable depends on local conditions and the proximity and nature of other water uses.

Where limitations on waste discharges are determined by public water supplies and where these limits are more restrictive than for other water uses, the objectives shall be applied to conditions at the water supply intakes.

Every effort will be made by the regulatory agency (1) to preserve the present cleanliness of basin waters and (2) to improve the water quality insofar as such action is consistent with the public interest. Objectives as offered, therefore, do not invite the loading of waters to the maximum allowable, but do serve as a guide to a sound pollution abatement and control program.

### MAHONING RIVER BASIN Objectives

The basic objective of the proposed program for abatement and prevention of pollution in the Mahoning River Basin is to secure and maintain a water quality in the various streams and sections of streams suitable for those uses which, in the public interest, are reasonable and necessary.

Establishment of treatment requirements, or other corrective measures, for wastes discharged to the streams involves the proper correlation of several factors so that the final waste effluents will be consistent with the basic objective. The factors involved include quality and quantity of wastes discharged, dilution and natural purification capacities of the receiving streams, water uses, population and industrial growth trends, technical knowledge with respect to corrective measures, costs of such measures, and quality of water required for the various uses.

The water pollution survey by the Ohio Health Department and information from other sources provide data on wastes discharged, stream flows, population trends, and water uses which are presented elsewhere in this report. This section is concerned primarily with water quality objectives to be applied in correlation with other factors.

It is recognized that the water uses may vary for different streams and for different sections of a particular stream. Also, the maximum allowable concentrations of polluting substances will vary with the different water uses. Furthermore, the effects of a particular substance may also vary, depending on the presence or absence of other substances in the receiving waters.

The cost of pollution prevention or abatement is not necessarily the same for reclamation of polluted waters as for the preservation of relatively unpolluted water; consequently, water quality objectives formulated for the purpose of restoring a polluted stream or section of a stream to a minimum quality consistent with downstream water uses cannot be considered as inviting the lowering of the water quality of cleaner streams throughout the basin.

In the application of water quality objectives, consideration must be given to provision for proper sharing of water resources, provision for further development, and other special needs in the public interest.

Use of the surface waters of the basin for public water supplies is a high priority need. Water quality objectives, designed to meet the requirements of this use, will be applied to protect existing and future supplies.

For the reasons discussed above, water quality objectives established to maintain the basin's waters in a condition suitable for reasonable and necessary uses must be sufficiently flexible to meet the varying conditions which exist. Where limits for polluting wastes are given in the following paragraphs, they are to be considered as the maximum permissible. They will serve as guides in determining pollution abatement and control measures. More restrictive limits may be required if consideration of all factors at specific locations shows that a higher quality of water is needed in the public interest. Conversely, if changes or future conditions warrant, requirements less restrictive will be given consideration.

In applying the principles stated in the preceding paragraphs to the Mahoning River Basin, it is particularly pertinent to note that a rather definite classification of stream areas based on water uses results from existing conditions.

In the upper part of the basin, including the area tributary to the Mahoning River above Newton Falls, Mosquito Creek a short distance above Niles, the Meander Creek drainage area, and areas drained by several smaller tributaries, there are water uses which require water of good quality. Existing uses include public water supplies, industrial water supplies, recreational uses (including fishing), and live stock water supplies. Also, it is highly important that water from drainage areas not now specifically developed for such uses be preserved for future developments. Availability of an adequate quantity of water for all uses in the area has been a serious problem for many years and is becoming more critical. For these reasons, discussed in more detail

in the section on water uses, emphasis is placed on the desirability of preserving water quality in the upper part of the Mahoning Basin.

Under present conditions, heavy industrial concentration along the Mahoning River in Ohio, defined as the Newton Falls to Ohio-Pennsylvania State line section of the river, results in separate subdivision of the basin insofar as uses are concerned. The objectives for this section of the stream are to abate nuisance conditions, to improve quality for existing industrial uses, to eliminate or reduce substances which interfere with the natural purification processes in the stream, and to apply all practical control measures necessary to prevent undue damaging effects on necessary and desirable high priority water uses downstream in Pennsylvania.

The third stream area, considered from the standpoint of present water use, concerns water quality in the lower Mahoning River as it affects public water supplies taken from the Beaver River in Pennsylvania. Public water supplies affected by Mahoning River water quality include the West Pittsburgh water supply and the supplies in the Beaver Falls and New Brighton areas. Other public water supplies farther downstream in the Ohio River may be adversely affected. However, the supplies mentioned are the closest to the sources of pollution and govern the present objectives for improvement in quality.

In considering water quality objectives, pollution may be classified on the basis of effects on water quality as follows: bacterial contamination; deoxygenation; toxicity; taste and odor; color; undesirable pH conditions; suspended solids and floating material; excessive dissolved solids; and high temperature.

Bacterial: Bacterial quality is particularly pertinent with respect to uses of water for public water supply and for recreational purposes. Bacterial pollution usually is associated with domestic sewage. This is understandable by reason of the disease organisms that may be contained in human excretions. However, bacterial increases are coincident with organic decomposition, and bacterial concentrations will vary with organic content and with stages of deoxygenation and decomposition. The densities of coliform organisms (intestinal bacteria) furnish accepted criteria for the evaluation of public water supplies and recreational waters. Two methods are in general use for enumeration of coliform organisms; namely: the most probable number method (MPN); and the indicated number (IN) based on Phelps Index values. The Ohio Department of Health is prone to use the indicated number method as a time saving procedure. In its relations with other States in the Ohio River Basin, objectives are enumerated on the basis of most probable numbers. For all practical purposes, the use of either method as an index of pollution furnishes a satisfactory basis for establishing waste treatment requirements to protect public water supplies.

At waterworks intakes in the area covered by this report, the monthly arithmetical average of "most probable numbers" or, as an alternate, of "indicated numbers" of coliform organisms should not exceed 5000 per 100 milliliters (5000 per 100 Ml.) in any month; nor exceed this density in more than 20 percent of the samples of such waters examined during any month; nor exceed 20,000 per 100 Ml. in more than five percent of

such samples. It is felt that, if coliform reductions are accomplished to attain such quality, accepted practices of water treatment will assure safe public supplies.

Meeting the objective for public water supplies at existing intakes may assure satisfactory bacterial water quality for certain recreational uses in protected stream zones and may assure water quality suitable for bathing or swimming in a few stream areas. For non-bathing or non-swimming recreation, the monthly arithmetical average of "most probable numbers" or of "indicated numbers" should not exceed 5000 per 100 Ml. in any month of the recreational season, nor should exceed this number in more than twenty percent of the samples examined during such month. For bathing and swimming waters, the monthly arithmetical average of "most probable numbers" or of "indicated numbers" of coliform organisms should not exceed 1000 per 100 Ml.; nor should exceed this number in more than twenty percent of the samples examined in such month; nor should exceed 2400 per 100 Ml. on any one day. It must be emphasized, however, that even though all bacteria from sewage pollution were to be removed, other factors beyond the control of water pollution control agencies may still make waters of the inland streams of the basin unsuitable for bathing. Careful consideration must be given to natural, public health, and economic factors in justifying the application of bathing water quality objectives to waters of the basin.

Deoxygenation: Deoxygenating wastes may utilize the dissolved oxygen content of the stream by biochemical oxidation processes or by purely chemical processes. The former are generally organic in nature and may consist of sewage or be contained in effluents from industrial plants. The latter are of industrial origin. In either case, the material causing the oxygen demand may be either in suspension or solution. Where such wastes are discharged to streams in excessive amounts, the oxygen content of the water is depleted; fish and other aquatic life are killed, or their propagation inhibited; oxidation ceases, and anaerobic decomposition or septic action takes place with attendant nuisances, disagreeable odors, toxic effects, and public health menaces. Corrective action should consist of the removal of settleable solids from sewage and industrial wastes and the removal of a sufficient amount of the remaining deoxygenating waste, so that the dissolved oxygen in the stream will be maintained above a critical point required by those water uses considered desirable. For the upper Mahoning River Basin and tributaries, as defined previously, the minimum dissolved oxygen objective has been established at four parts per million. This criterion meets requirements for normal water uses, including the protection of fish common to the waters of the basin and other aquatic life. For the industrial section of the Mahoning River, the dissolved oxygen objective is a minimum of three parts per million. This criterion is based on avoidance of nuisance conditions and maintenance of satisfactory self-purification processes. If this condition is met at the critical points in the industrial section of the river, adequate levels for normal uses will be maintained below the Ohio-Pennsylvania line.

Toxic Wastes: There are literally hundreds of substances, alone or in combination, which, at critical con-

centrations, are toxic to humans, animals, fish, and other wildlife. The toxic effects may range from serious conditions affecting public health or causing direct fish kills to minor disturbances which may be serious only over a long period.

The chemical characteristics, or mineral content, of the receiving water has a great influence on the toxicity of individual pollutants to fish and other aquatic life. Also concentrations of certain substances, considered individually, may not be serious, whereas they may be quite injurious in combination with other substances.

In some instances concentrations of toxic materials, not sufficient to cause direct kills of fish but inimical to fish propagation, possibly may be tolerated in short, most critical, stream sections. Objectives with respect to fish and aquatic life do not apply to the industrial section of the Mahoning River except as they affect the condition of the River below the State line.

The above discussion leads to the conclusion that, in light of existing knowledge, it is impractical to fix final limits on concentrations of toxic substances. The general objective will be to eliminate or prevent concentrations which will be unduly injurious to the reasonable and necessary uses. Insofar as fish and other aquatic life are concerned, determination of whether or not the objective is being met will be based on biological indices of pollution. Application of toxicity limits to protect fish and other aquatic life will generally provide satisfactory protection for other water uses. Should there be exceptions, limits will be based on the specific uses affected.

Although, as mentioned above, there are many substances and combinations of substances which are toxic, it is likely that a great many of these will not be discharged to the streams in sufficient quantity to be a problem, possibly because such wastes are not normally found in the basin or because their value tends to preclude their discharge as waste products. However, some substances were encountered during this investigation which are troublesome to certain uses in concentrations above certain limits. Occurrence of these substances above such limits will be prima facie evidence that excessive pollution exists. Pending the results of studies and research now in progress by qualified technical groups, the following should serve as a guide to the reasonable protection of the waters of this basin:

• *	Parts per million (ppm)
Cyanide (as CN)	substantially none
Lead (as Pb)	
Copper (as Cu)	not over 0.3
Chromium (as Cr)	not over 1.0—trivalent
	not over 0.05—hexavalent
Cadmium (as Cd)	not over 0.4 .
Zinc (as Zn)	not over 0.3
Nickel (as Ni)	
Nitrate (as N)	not over 10

It is emphasized that exceptions to the above must be made where water uses require higher quality; and, further, that some of the above substances may cause damages in lower concentrations than noted under certain conditions and in certain combinations.

Fluorides: During the course of the survey it was found that there were industrial establishments in the basin which had significant fluoride contents. It is the intent that proper control measures will be provided to

assure that excessive concentrations are not discharged. In conformance with this intent an objective of not more than 1.2 ppm of fluoride (as F) in the river at waterworks intakes is established.

Taste and Odor: In general, wastes producing tastes and odors shall be limited to the extent required to prevent undue damage to reasonable and necessary wa-

The most prevalent offensive wastes produced in the basin, from the standpoint of tastes and odors, are the phenolic and other types of wastes from production and use of coke and from processing of by-products from the coke plants. It is recognized that there are taste and odor substances from other industries and natural sources. The objective with respect to wastes containing phenols, oils, greases and allied derivatives, is based on their reduction by means of known practical methods of operation or treatment. Using presently known methods of controlling phenolic wastes, it is to be expected that some residuals will remain in the water in the industrial section of the Mahoning River. Every effort will be made initially to reduce these to such a minimum that undue damage will not persist at downstream water plants. It is believed that known practical methods will reduce phenolic loads to the extent that not over 75 parts per billion (p.p.b.) will be present in the water at the lower end of the industrial section of the river, (i.e., at the State line). As used herein, phenolic loads are intended to include cresols and other phenolic type substances normally measured by current analytical methods. It is contemplated that dissipation in the Mahoning and Beaver Rivers, together with dilution from the Shenango River, will be such that acceptable taste and odor conditions in the finished water at downstream water plants may be obtained with present water treatment practice.

Color: The objective is control of color producing substances as required to prevent impairment of reason-

able and necessary water uses.

Iron and manganese are significant with respect to color. Iron is particularly significant because of the large quantities in wastes in the industrial section of the river.

In establishing a program to meet the above objectives with respect to iron, it is pertinent to consider the conditions prevailing at the time of the survey. The majority of iron wastes were discharged in the Warren to Lowellville section of the Mahoning River. The iron wastes, as discharged, were in both the dissolved and suspended state, principally as sulphates and oxides. The quantities were great, measurements indicating a total load averaging 170 tons per day, and largely uncontrolled. Upon mixing with the oxygen and alkalinity in the water, the dissolved iron was converted to the undissolved state, and during normal stream flow conditions practically all of the iron settled to the bottom, forming sludge banks. During such flow periods, records at downstream water plants indicate a relatively low iron content. However, during fluctuating flow conditions due to rains or other conditions, iron content at downstream plants increased greatly, reaching values in excess of 100 parts per million. Most of the iron is in suspension and settles readily with normal treatment processes. Another unde-

sirable condition, considered more important than the iron concentration itself, accompanies the situation just described. The formation and settling of iron floc in the area where major pollution originates, results in the entrapment and deposition in sludge beds of oils, greases, and other foul smelling materials. These are picked up in concentrated form during freshets and carried to other points of use, redeposited on the stream bed as flow decreases, to be picked up again and carried further down-

In view of these conditions, the minimum requirement shall be substantially complete removal of settleable iron, particularly in blast furnace gas washer wastes and in rolling mill wastes. Also, in the control of waste pickle liquor (discussed later) provision shall be made to prevent the discharge of iron with the waste. If the acid in the waste pickle liquor is controlled by neutralization, the measures must include precipitation of the iron.

pH and Alkalinity: Pickle liquor acid and iron salts, originating for the most part between Warren and Lowellville, are the cause of serious damaging effects on water quality. Carbonate hardness is changed to sulphate hardness, alkalinity is reduced, sludge banks of iron compounds and other materials carried down with the iron floc are formed, and the pH is lowered.

The program for acid control includes effective treatment or control of concentrated waste pickle liquor to prevent discharge of acid or iron, and good operation practices to reduce the substances in rinse water. Treatment of dilute acid rinses probably can be postponed under present conditions of industrial development and stream flow, provided acceptable practices are followed with respect to control of the amount of acid and iron in the rinses. Normally, it is considered that this condition will be met if the total acid in all wastes does not exceed 15 percent of the acid used. In the upper section of the river and on tributaries, further reduction of acid and iron will be required if needed to protect water uses.

Under present conditions, it is estimated that such a policy will result in water having a satisfactory pH (meeting an objective of not less than 6.3) and with a desirable residual alkalinity. A residual alkalinity of not less than 30 parts per million is established as an objective. The objectives for pH and alkalinity are applicable to the water at the State line, below sources of major industrial wastes. A program directed toward equitable industrial use of water and treatment of wastes will improve water quality for industrial uses throughout the industrial section of the river.

Encouragement will be given to control of acid wastes by methods other than neutralization and precipitation of the iron salts with lime, because of addition of hardness by the latter method. Where neutralization is practiced, use of high calcium lime, as opposed to material having high magnesium content, is recommended in order to reduce hardness due to highly soluble magnesium sulphate. Settling out and proper disposal of iron and undissolved sulphates will be required.

Suspended Solids and Floating Materials: Substantially complete removal of settleable solids and floating material will be required to prevent nuisance conditions and sludge deposits.

Dissolved Solids: Objectives concerning damages from dissolved solids related to toxicity, oxygen depletion, taste and odors, pH, and color, are discussed under these effects. Dissolved solids are of concern also with respect to hardness. Large quantities of pickling acid, principally sulphuric, used in the steel industry, result in wastes which react with alkalinity in the river or with alkalinity added to neutralize the acid and form sulphate hardness. Unless proper care is exercised in the control and treatment of acid and iron salts, (see preceding section on pH and alkalinity) excessive sulphate hardness will be added to the river. Some carbonate hardness will be changed to sulphate hardness by discharge of dilute pickle rinse waters. Also, some hardness will be added if neutralization of concentrated pickle wastes is practiced. However, in consideration of the economic aspects of a higher degree of control, the general objectives will be met if discharge of residual acid waste is limited as previously stated and if, in the treatment or control of concentrated pickle liquors, practical methods are followed to reduce the discharge of hardness to the river.

Temperature: High temperatures occur in the heavily industrialized section of the river. Outside of the section of the river principally used for industrial water supply, for which the objective is to prevent nuisance conditions, temperature as related to necessary and desirable water uses is not now a significant factor. State regulatory action with respect to temperature is not considered

necessary at this time.

This statement of policy is not intended to minimize the importance of the problem of excessive temperature in the industrial section of the river. Alleviation of this problem, a limiting factor on industrial production, is probably of more direct economic significance than other pollution problems. However, the problem is of most concern to a group of industries in a contiguous area. In the past, these industries have cooperated to improve the situation by provision of storage and flow regulation. Studies are under way for cooperating in additional similar improvements.

Special Conditions: Insofar as practicable, the effect of sewage or waste discharges on the receiving waters shall be considered after they are mixed with the waters and beyond a zone of immediate effect. The extent to which this is practicable depends on local conditions and the

proximity and nature of other water uses.

Where limitations on waste discharges are determined by public water supplies and where these limits are more restrictive than for other water uses, the objectives shall be applied to conditions at the water supply intakes.

Every effort will be made by the regulatory agency (1) to preserve the present cleanliness of basin waters and (2) to improve the water quality insofar as such action is consistent with the public interest. Objectives as offered, therefore, do not invite the loading of waters to the maximum allowable, but do serve as a guide to a sound pollution abatement and control program.

# SCIOTO RIVER BASIN

### **Objectives**

The basic objective of the proposed program for the abatement and prevention of water pollution in the

streams of the Scioto River Basin is to secure and maintain stream water quality suitable for those uses which, in the public interest, are necessary and reasonable.

The establishment of treatment requirements or other corrective measures for the discharge of municipal or industrial wastes to the streams involve the proper correlation of several factors so that the final effuents will be consistent with the basin objective. The factors involved include the quantity and quality of the discharged wastes, the dilution available in the receiving stream, the capacity of the stream for the assimilation of waste discharges and downstream water uses. Other pertinent data to take into consideration are growth trends of urban population centers as well as the growth trend of industrial development. Most of the information for evaluating many of these items was obtained during the field investigation for this report.

In establishing the treatment requirements presented in this report, it was recognized that water uses may vary for different streams or even for different sections of the same stream. Also, the maximum allowable concentration of a pollutant may vary with different water uses. Furthermore, the effects of a particular substance may also vary, depending on the presence or absence of other substances in the receiving waters.

It is also recognized that consideration must be given to the economic balance between the cost of pollution prevention or abatement and the benefits received. The cost of pollution prevention or abatement is not necessarily the same for reclamation of polluted waters as for the preservation of relatively unpolluted water; consequently, water quality objectives formulated for the purpose of restoring a polluted stream or section thereof to a minimum quality consistent with downstream water uses cannot be considered as inviting the lowering of the water quality of cleaner streams throughout the basin.

In the application of water quality objectives, consideration must be given to provisions for proper sharing of water resources, future development, and other special needs in the public interest.

Use of the surface waters in the upper portion of this basin for public water supply is a high priority need. Water quality objectives, designed to meet the requirements of this use, will be applied to protect existing and future supplies.

For reasons discussed above, water quality objectives established to maintain the surface water of this basin in a condition suitable for reasonable and necessary uses must be sufficiently flexible to meet the varying conditions which exist. Where limits for pollutants are given in the following paragraphs, they are to be considered as the maximum permissible at critical low flows. They will also serve as a guide for determining pollution control measures. More restrictive limits may be required at specific locations if a higher quality of water is needed in the public interest.

In considering water quality objectives, pollution may be classified on the basis of effects on water quality as follows. Bacterial contamination, deoxygenation, toxicity, taste and odor, color, undesirable pH conditions, suspended and floating material, excessive dissolved solids, and high temperature.

Bacterial: Bacterial quality is particularly pertinent with respect to uses of water for public water supply and for recreational purposes. Bacterial pollution of surface waters usually is associated with domestic sewage. This is understandable by reason of the disease organisms that may be contained in human excretions. However, a natural increase in the number of nonpathogenic bacteria in a stream is coincident with organic decomposition, and bacterial concentrations will vary also with organic content and with stages of deoxygenation and decomposition. The densities of coliform organisms (intestinal bacteria) furnish accepted criteria for the evalution of public water supplies and recreational waters.

Two acceptable methods are used for determining the density of coliform organisms in water, namely: (1) The fermentation dilution tube method, and (2) the membrane filter technique. The fermentation dilution tube method was accepted as a standard method in 1936, whereas the membrane filter technique was not established as an alternative standard method until 1956. From the first method a most probable number (MPN) index is obtained. This number is merely an index of the number of coliform bacteria which more probably than any other number, would give the results shown by laboratory examination on a series of decimal plantings.

The membrane filter technique determines directly the actual number of coliform organisms in a sample of the water tested. Studies have indicated that this procedure does not measure precisely the same group of microorganisms as the fermentation dilution tube method. In applying the results of tests by this method to standards developed for use with the dilution tube method, consideration should be given to the differences between the two tests.

A rough estimate of the density of coliform organisms may be obtained by the use of the indicated number. This number is obtained by taking the reciprocal of the smallest positive dilution in a decimal series of plantings in fermentation tubes. This procedure was recommended in 1917 Standard Methods and remained the only official method for the expression of coliform results until the publication of the 1936 edition of Standard Methods. Many water works operators still use this method due to their familiarity with the procedures of calculation. For all practical purposes, the estimation of the coliform concentration by any one of the three methods described, allowing for the limitations of each, will furnish a satisfactory basis for establishing waste treatment requirements.

At water works intakes in the area covered by this report, the monthly arithmetical average estimate of coliform organisms should not exceed 5,000 per 100 milliliters (5,000 per 100 ml.) in any month; nor exceed this density in more than 20 per cent of the samples of such waters examined during any month; nor exceed 20,000 per 100 ml. in more than five per cent of such samples. It is felt that if coliform reductions are accomplished to attain such quality, accepted practices of water treatment will assure safe public supplies.

Meeting the objective for public water supplies at existing intakes may assure satisfactory bacterial water quality for certain recreational uses in protected stream zones and may assure water quality suitable for bathing

or swimming in a few stream areas. For non-bathing or non-swimming recreation, the monthly arithmetical average estimate of coliform organisms should not exceed 5,000 per 100 ml. in any month of the recreational season, nor should exceed this number in more than twenty per cent of the samples examined during such month. For bathing and swimming waters, the monthly arithmetical average estimate of coliform organisms should not exceed 1,000 per 100 ml.; nor should exceed this number in more than twenty per cent of the samples examined in such month; nor should exceed 2,400 per 100 ml. on any one day. It must be emphasized, however, that even though all bacteria from sewage pollution were to be removed, other factors beyond the control of water pollution control agencies may still make waters of the inland streams of the basin unsuitable for bathing.

Careful consideration must be given to natural, public health, and economic factors in justifying the application of bathing water quality objectives to waters of the basin.

Deoxygenation: Deoxygenating wastes utilize the dissolved oxygen content of a stream by either biochemical oxidation processes or purely chemical processes. Organic wastes such as sanitary sewage or the industrial wastes from food processing industries are examples of the first, whereas spent acid pickling liquors are an example of the latter. In either case, the material causing the oxygen demand may be in suspension or solution. Where such wastes are discharged to a stream in excessive amounts they may utilize all of the dissolved oxygen content of the stream, thereby inhibiting propagation or destroying fish and other aquatic life, and give rise to anaerobic decomposition which is attendant with nuisances, disagreeable odors, toxic effects, and public health menaces.

Biochemical demands for oxygen on the dissolved oxygen resources of a stream usually take place at a nearly constant rate over a period of at least several days to a much longer period. In contrast chemical demands for oxygen often take place in a relatively short period of time. From the above it can therefore be seen that the rate at which a particular pollutant exerts its demand for oxygen is an important factor in determining the necessary waste reduction requirements for that load.

The effect of a pollution load on the oxygen resources of a stream is also influenced by the hydraulic characteristics of the receiving stream. The rate of absorption of oxygen from the atmosphere into a stream per unit volume of water increases with surface area. Thus a wide shallow stream would receive more oxygen by this process than a narrow deep stream having the same volume of flow.

The minimum dissolved oxygen objective set forth for the Scioto River and all of its tributary streams is 4.0 milligrams per liter (mg/l). An exception is made for that section of the Scioto River immediately downstream from the outfall sewer of the Columbus sewage treatment plant to the confluence of Big Walnut Creek. For this section of Scioto River, at least currently, a minimum dissolved oxygen objective of 3.0 mg/l has been established. Unless low flow augmentation is provided, a higher objective during periods of critical stream flow would be impractical to obtain with known methods of sewage treatment.

For the present, consideration may be given to a minimum dissolved oxygen concentration of somewhat less than 4.0 mg/l in certain other stretches of streams in this basin which now flow through a relatively inhabited area.

The required degree of treatment of deoxygenating wastes set forth in this report are those which have been determined as necessary to maintain the established minimum dissolved oxygen objectives at critical stream flows under existing wastes loads. In making these determinations, due consideration was given to the self-purification capacity of the receiving stream.

Toxic Wastes: There are many substances, alone or in combination, which at critical concentrations are toxic to humans, animals, fish and other wildlife. The effects of these concentrations may range from serious conditions affecting the public health or conditions causing direct fish kills to minor disturbances which may be serious only if continued over a prolonged period of time.

The toxicity of an individual pollutant to fish or other aquatic life is significantly influenced by the chemical characteristics of the stream water. Also a particular ion which may only have a slight toxic effect under normal stream conditions may become much more toxic in combination with a second ion. As an example, zinc is only slightly toxic alone, however, in the presence of copper the effect is very toxic.

Although, as mentioned above, there are many substances and combinations of substances which are toxic, it is likely that a great many of these will not be discharged to the stream in sufficient quantity to be a problem, because such wastes may not normally be found in the basin or because their value tends to preclude their discharge as wastes products. However a few toxic ions were encountered during this survey in sufficient concentrations to be objectionable to existing water uses. Pending the results of studies and research now in progress by qualified technical groups, the following list of stream water quality objectives should serve as a guide to the reasonable protection of the waters of this basin.

Toxic Ions	Concentrations-mg/l
Cyanides as (CN)	not over 0.15
Lead as (Pb)	not over 0.1
Copper as (Cu)	not over 0.3
Chromium as (Cr)	not over 1.0
Cadmium as (Cd)	not over 0.4
Zinc as (Zn)	not over 1.0
Nickel as (Ni)	not over 2
Nitrate as (N)	not over 10

Occurrence of the above ions in concentrations greater than those given will be prima facie evidence of pollution. It should be noted that exceptions to the above must be made where water uses require a higher quality; and, further, that some of the above ions may cause damages in lower concentrations than noted under certain conditions and in certain combinations.

Taste and Odor: In general, the discharge of industrial wastes that produce tastes and odors shall be modified to the extent required to prevent undue damage to reasonable and necessary water uses.

Probably the most prevalent industrial wastes as far as tastes and odors are concerned are those from the following manufacturing processes: By-product coke, synthetic resins, synthetic fibre, oil refining and associated processes, creosoting, wood distillation, and dye

manufacturing. Treatment shall be given to wastes containing phenols, oils, and allied derivatives to obtain substantially complete removal of these substances at their source.

Color: Discharge of color producing substances shall be limited to those concentrations that will not impair reasonable and necessary water uses.

Iron and manganese are significant with respect to color. Discharges containing significant quantities of either of these ions shall be modified so as to maintain the concentration of each of these ions at less than 5 mg/l in the receiving stream.

pH and Alkalinity: The discharge of strong acid or alkali wastes shall be modified so as to maintain the hydrogen ion concentration within the pH range of 6.3 to 9.0, inclusive. In general, this will provide protection to public and industrial water supplies as well as fish and aquatic life and to other uses.

Suspended Solids and Floating Materials: Substantially complete removal of settleable solids and floating materials will be required to prevent nuisance conditions and sludge deposits.

Dissolved Solids: Objectives concerning damages from dissolved solids related to toxicity, oxygen depletion, taste and odors, pH, and color are discussed under these effects. Dissolved solids are of concern also with respect to hardness. The discharge of sulphuric acid, which is frequently used for the pickling of steel, reacts with the alkalinity of the river water or with alkalinity added to neutralize the acid and form sulphates which increase the hardness of the water.

The quantity of acid wastes discharged to the streams of the Scioto River Basin at the time of this survey was relatively insignificant and thus compliance with pH and alkalinity objectives will be the only requirements imposed on such discharges at this time.

Objectives with respect to the dissolved solids also include the discharge of concentrated brine wastes. The discharge of chloride-bearing wastes shall be controlled in such a manner as to minimize the effect of these wastes on the receiving stream.

Temperature: High temperatures occur in streams of this basin due to discharges of cooling waters from industries and electric generating stations. Water temperature as related to necessary and desirable water uses may be a pollutant but is not now a significant factor in this basin. State regulatory action with respect to temperature, however, may need to be considered at a future time.

Special Conditions: Insofar as practical, the effects of sewage or industrial waste discharges on the receiving stream shall be considered after they are mixed with the stream waters and beyond the zone of immediate effect. The extent to which this is practical depends on local conditions and the proximity and nature of other water uses.

Where limits of concentration of critical constituents of sewage and industrial wastes are determined by the use of a stream for public water supply and where these limits are more restrictive than for other uses, the objectives shall be applied to conditions at the water supply intakes.

Every effort will be made by the regulatory agency to preserve the present cleanliness of basin waters and to improve the water quality insofar as such action is consistent with the public interest. The water quality objectives as set forth in this report do not invite the loading of stream waters of this basin to the maximum allowable, but do serve as a guide to a sound pollution abatement and control program.

### APPENDIX G

# OREGON ADMINISTRATIVE RULES—STATE SANITARY AUTHORITY

Standards of Purity for Waters and Disposal Therein of Sewage and Industrial Wastes

11-010 RESTRICTIONS ON THE DISCHARGE OF SEWAGE AND INDUSTRIAL WASTES. No sewage or industrial waste shall be discharged into any waters of the State of Oregon which in itself or in conjunction with other wastes will cause:

(1) The dissolved oxygen content of the waters to be less than five (5) parts per million.

(2) The hydrogen-ion concentration (pH) of the waters to be outside of the range of 6.5 to 8.5.

(3) The liberation of dissolved gases, such as carbon dioxide, hydrogen sulfide or any other gases, in sufficient quantities to be deleterious to fish or related forms of aquatic life, navigation or other reasonable uses made of such waters.

(4) The development of fungi or other growths having a deleterious effect on stream bottoms, fish or related forms of aquatic life, or which are injurious to health, recreation or industry.

(5) The creation of toxic conditions that are deleterious to fish or related forms of aquatic life or affect the potability of drinking water.

(6) The formation of appreciable bottom or sludge deposits or the formation of any organic or inorganic deposits deleterious to fish or related forms of aquatic life or injurious to public health, recreation or industry.

(7) Objectionable discoloration, turbidity, scum, oily sleek or floating solids, or coat the aquatic life with oil films.

(8) Bacterial pollution or other conditions deleterious to waters used for domestic purposes, livestock watering, irrigation, bathing, or shellfish propagation, or be otherwise injurious to public health.

11-015 MAINTENANCE OF STANDARDS OF PURITY. (1) The degree of sewage or waste treatment required to restore and maintain the above standards of purity shall be determined in each instance by the State Sanitary Authority and shall be based upon the following:

- (a) The uses which are or may likely be made of the receiving stream.
- (b) The size and nature of flow of the receiving stream.
- (c) The quantity and quality of the sewage or wastes to be treated, and
- (d) The presence or absence of other sources of pollution on the same watershed.
- (2) At its discretion, the State Sanitary Authority may require chlorination or equally efficient disinfection of sewage and waste treatment plant effluents wherever and whenever the discharge of unchlorinated effluents shall or may affect the quality of water used for public

or domestic water supplies, irrigation, shellfish growing areas, or swimming and recreational areas.

11-020 CLASSIFICATION OF STATE WATERS.
(1) For the purpose of facilitating the determination of the degree of treatment required for municipal and sanitary sewage the waters of the state of Oregon shall be classified in three divisions as follows:

### Class "A"

Bodies of water which are used or which may be used for public water supplies, swimming and recreation, for irrigation, for the propagation of game and commercial fish, or for the propagation of shellfish and which because of insufficient flow cannot receive, without detriment, wastes other than those that have been given a high degree of treatment.

### Class "B"

Bodies of water which are used or which may be used for public water supplies, swimming and recreation, for irrigation, for the propagation of game and commercial fish, or for the propagation of shellfish, and which, in the opinion of the State Sanitary Authority, provide sufficient dilution to obviate the necessity for the degree of treatment required under Class "A" waters.

### Class "C"

Bodies of water into which the temporary discharge of untreated sewage or wastes may be permitted, if, in the opinion of the State Sanitary Authority, such discharge may not be detrimental to any reasonable use of said waters.

- (2) Unless a higher degree of treatment is found to be necessary by the State Sanitary Authority to meet the requirements of section 11-010 above, municipal or sanitary sewage discharged into the above described classes of waters of the state of Oregon shall, in each instance, receive the following degree of treatment as a minimum:
- (a) Municipal or sanitary sewage discharged into Class "A" waters shall be so treated that the effluent from the treatment plant:
  - (A) Shall be free of noticeable floating solids, oil, grease, sleek, and practically free of suspended solids.
  - (B) Shall indicate an average five-day bio-chemical oxygen demand reduction of not less than 85 per cent and at no time shall the residual effluent B. O. D. be in excess of 50 parts per million.

- (b) Municipal or sanitary sewage discharged into Class "B" waters shall be so treated that the effluent from the treatment plant:
  - (A) Shall be free of noticeable floating solids, oil, grease, and sleek.
  - (B) Shall indicate an average suspended solids reduction of at least 55 per cent.
  - (C) Shall indicate an average five-day bio-chemical oxygen demand reduction of not less than 35 per

- cent, and at no time shall the residual effluent B. O. D. be in excess of 125 parts per million.
- (c) Municipal or sanitary sewage may be discharged without treatment into Class "C" waters; provided, that a temporary permit for such discharge has first been obtained from the State Sanitary Authority, that no such permit shall be valid for a period of time longer than three years, and further that such permits may be revoked for cause at any time after the date of issuance thereof.

### APPENDIX H

# RULES AND REGULATIONS OF THE PENNSYLVANIA SANITARY WATER BOARD WITH RESPECT TO THE DISPOSAL OF WASTES INTO THE UNDERGROUND

(Adopted January 10-11, 1951)

WHEREAS, the underground waters are by law part of the waters of the Commonwealth and their pollution is subject to the provisions of the antipollution law; and

WHEREAS, the course which will be followed by wastes discharged into the underground and the effect of any polluting substance contained in such wastes, cannot, in general, be determined with the same facility as in the case of wastes discharged to surface waters; but

WHEREAS, under certain conditions wastes have been successfully disposed of by discharge into appropriate underground horizons without any known prejudicial

WHEREAS, such disposal may be responsible for the pollution of water supplies when the discharge is made

to inappropriate horizons; and

WHEREAS, it is the responsibility of each producer of polluting wastes to dispose of them without harm to others and the Sanitary Water Board will not relieve him of such responsibility;

NOW THEREFORE, the said Board makes of record its general policy with respect to such disposal as fol-

lows:

- 1. The Board will, except as otherwise provided, consider the disposal of wastes into the underground as potential pollution unless the disposal is within such proximity of the surface that the wastes will be absorbed in the soil mantle and be acted upon by the bacteria naturally present therein before reaching the underground or surface waters.
- 2. Discharge of inadequately treated wastes, except coal fines into the underground workings of active or abandoned mines is prohibited.
- 3. Discharge of wastes into abandoned wells is prohibited.*
- 4. Disposal of wastes into underground horizons will only be accepted as an abatement of pollution when the applicant can show by the log of the strata penetrated and by the stratigraphic structure of the region that it is improbable that such disposal will be prejudicial to the public interest, but any such acceptance will be conditioned and will not relieve the applicant of responsibility for any pollution of the waters of the Commonwealth which may occur, in which case such disposal shall be stopped forthwith.

### RULES AND REGULATIONS OF THE SANITARY WATER BOARD

Article 600-Section 16, Heated Wastes

A. The temperature of the waters of the Commonwealth shall not be increased artificially by amounts that shall be inimical or injurious to the public health or to

animal or aquatic life or prevent the use of water for domestic, industrial or recreational purposes.

B. The heat content of discharges shall be limited to an amount that could not raise the temperature of the entire stream at the point of discharge above 93°F assuming complete mixing. The heat content of discharges may be increased or further limited where local conditions would be benefited thereby.

C. Where downstream circumstances warrant, the area in which the temperature may be artificially raised

above 93°F will be prescribed.

D. A fishway will be required in streams receiving heated discharges where this is essential for the preservation of migratory pathways of game fish, or for the

preservation of important aquatic life.

E. Paragraphs B and C do not apply to streams so impregnated with acid mine drainage that they cannot support a fish population typical of the region except for heated discharges which adversely affect domestic or industrial uses or secondary streams.

F. There shall be no new discharge to waters providing a suitable environment for trout if as a result the temperature of the receiving stream exceeds 58°F or

stream temperature, whichever is higher.
G. Reduction of the heat content of discharges to estuarial waters will be required where necessary to protect the public interest. Estuarial waters are those containing ocean salts. Tidal waters not containing ocean salts are considered as fresh water streams.

### COMMONWEALTH OF PENNSYLVANIA DEPARTMENT OF HEALTH Sanitary Water Board

INDUSTRIAL WASTES PERMIT NO. 1832

This permit is issued subject to the following Special Conditions:

(A—D omitted)

E. The permittee is hereby directed to immediately notify the Pennsylvania Department of Health whenever there is a spill or an accidental discharge of radioactive material and shall advise that Department promptly concerning the pertinent facts and probable danger. The permittee shall maintain rosters of Pennsylvania Department of Health personnel and of downstream users of river water who shall be notified. The necessary information for such rosters shall be furnished to the permittee by the Department of Health. In the event of any such accidental discharge, the Department of Health shall determine whether or not downstream users shall be notified, and by whom.

Moreover, the permittee is required to see to the training and supervision of all operating personnel, in order

Note that the drilling of new wells for waste disposal is subject to Nos. 1 and 4 of this regulation.

to prevent the discharge of such material, fluid or solid, to the waters of the Commonwealth or to the site, with-

out adequate treatment.

F. All industrial wastes discharged to the portion of the Ohio River on which the permittee's plant is located shall meet at least the requirements of the Sanitary Water Board for primary treatment. "Primary treatment" does not apply to the radioactive characteristics of the wastes.

The term "primary treatment," as here used, is such treatment of sewage as, in the opinion of the Board, will remove practically all of the settleable solids; will remove at least 35 percent of the organic pollution load as measured by the biochemical oxygen demand test; will accomplish the removal of oils, greases, acids, alkalis, toxic, putrescible, taste- and odor-producing substances, and other substances inimical to the public interest in the receiving stream; will provide effective disinfection to control disease-producing germs; will provide for satisfactory disposal of sludge; and will produce a final effluent that is suitable for discharge into the receiving stream. "Primary treatment of industrial wastes," as here used, is treatment to a degree equivalent to that set forth herein for sewage.

Moreover, because of the radioisotopes which these wastes may carry, such wastes shall be substantially free of turbidity and suspended solids over and above the amounts of such characteristics in the intake water.

G. The treated radioactive liquid wastes as discharged to the Ohio River shall comply with the Pennsylvania Department of Health Radiation Protection Regulation 433 and any subsequent regulations of the Department of Health.

H. With respect to the amount of radioactivity released in the liquid wastes to the waters of the Commonwealth, this permit is issued subject to the following conditions: (A) that the average radioactivity, exclusive of tritium activity, of these wastes over any consecutive 365-day period, shall not exceed 15,900 microcuries per day, with the maximum discharge not exceeding 62,000 microcuries per day, (B) these wastes shall at no time carry more radioactivity, exclusive of tritium activity, than  $10^{-7}$  microcuries per milliliter ( $U^{226}$  and  $U^{228}$  not present) in excess of that of the plant intake water from the Ohio River, and (C) that the discharge of tritium in these wastes shall be not more than 10 curies per day averaged over any consecutive 365-day period, nor more than 50 curies per day maximum. Moreover, the company shall conduct all its pressurized water reactor operations so as to produce and discharge the least practicable amounts of radioactivity.

I. Although tritium has a short biological half-life (19 days) and a maximum permissible concentration (MPC) of 0.2 microcuries per ml (according to Handbook 52 of the National Bureau of Standards) as compared with an MPC of 10-8 microcuries per milliliter for the general population for unidentified isotopes, its radiological half-life is long enough (4,600 days) to make its

continued presence in the stream undesirable and possibly inimical to aquatic and other life. At the present time, it is reported, there are no practical means for its separation from a liquid. The permittee, however, shall continue to investigate and apply more effective means to remove this potential hazard as rapidly as such means are developed, or attempt to devise some other means or to attempt to find some other substance which will have advantages similar to that of lithium hydroxide without producing the present discharge of tritium. The attention of the permittee is directed to the possibility that tritium may prove objectionable as a constituent of water used for certain industrial processes.

J. The radioactive and other liquid wastes discharged to the effluent channel shall be well admixed with the cooling water so that the waste content of this channel shall be substantially uniform below the effluent weir or

at the sampling rake.

K. The treated effluent shall be discharged to the river in a manner acceptable to the Sanitary Water Board. If any structure is necessary to accomplish this, it shall be well protected against the effects of flood waters, ice, and other hazards and the design of such structure shall

be acceptable to the Sanitary Water Board.

L. Provision shall be made for regulating discharge of the treated effluent so that it shall be equally distributed over the longest practicable period, in order that advantage may be taken of maximum possible dilution by the receiving stream, and means to accomplish uniform 24-hour distribution shall be provided if in the opinion of the Department of Health this shall be found

M. The wastes after treatment and prior to discharge to the effluent channel shall contain no more than 0.05 ppm of hexavalent chromium and 1.0 ppm of trivalent

chromium.

(N—P omitted)

Q. Acknowledgment is made of the company's study now in progress to determine temperatures and percentage of river volume that flows through a narrow river channel between Phillis Island and the mainland to determine the expected rise in river water temperature in this channel when the condenser cooling water is discharged to it. The permittee is hereby advised that the river water temperature rise is tentatively limited to 2° F at points to be determined by the Sanitary Water Board after the results of the thermal studies of the channel and of other data have been reviewed, and that if this limit cannot be maintained with the proposed method of discharge, then complete dispersal of the condenser effluent in the river, or other means for temperature control, may be necessary. The report on the river channel study shall be submitted in duplicate to the Sanitary Water Board within 60 days of completion of the study which is expected to terminate in the last months of 1958, with progress reports on a quarterly

(R-T also omitted)

#### APPENDIX 1

# STATE OF SOUTH CAROLINA WATER POLLUTION CONTROL AUTHORITY

Section III of Classification-Standards System

Established Classes for Fresh Surface Waters and the Standards of Quality and Purity Which Shall be Applied Thereto:

### CLASS AA

Waters meeting State Board of Health regulations as suitable for use for domestic and food-processing purposes with sterilization as only treatment required. Suitable also for uses requiring waters of lesser purity.

## Quality Standards for Class AA Waters

Items

Specifications

 Floating solids; settleable solids; oil; sludge deposits; tastes or odor-producing substances. None attributable to sewage, industrial wastes or other wastes.

2. Sewage or waste efficients.

None.

3. Dissolved oxygen.

Not less than 5 ppm.

 Toxic wastes, deleterious substances, colored or other wastes or heated liquids. None in amounts to exceed limitations set by State Board of Health for waters for this use.

### CLASS A

Waters meeting the State Board of Health regulations as suitable for use as swimming water. Suitable also for other uses requiring waters of lesser purity.

### Quality Standards for Class A Waters

Items

Specifications

 Floating solids; settleable solids; oil; sludge deposits.

None which are readily visible and attributable to sewage, industrial wastes or other wastes and which measurably increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. Sewage or waste efficients.

3. Odor-producing substances contained in sewage, industrial wastes or other wastes.

4. Phenolic compounds.

5. pH.

6. Dissolved oxygen.

 Toxic wastes, deleterious substances, colored or other wastes, or heated liquids. None in such quantity or quality as to raise the coliform bacteria count of these waters above 1,000 per 100 ml.

The waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto shall not have an increased threshold odor number greater than 8, due to such added wastes.

Not greater than 5 parts per billion (Phenol).

Range between 6.0 and 8.0, except that swamp waters may range from pH 5.0 to pH 8.0.

Not less than 4.5 ppm, except that swamp waters may have a low of 2.5 ppm.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish life or make the waters unsafe or unsuitable for bathing.

### CLASS B

Suitable for domestic supply after complete treatment in accordance with regulations of the State Board of Health. Suitable also for uses requiring water of lesser purity.

### Quality Standards for Class B Waters

Items

Specifications

 Floating solids; settleable solids; oil; sludge deposits.

None which are readily visible and attributable to sewage, industrial wastes or other wastes and which measurably increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

Sewage or waste effluents.

3. pH.

4. Dissolved oxygen.

5. Phenolic compounds.

 Toxic wastes, deleterious substances, colored or other wastes, or heated liquids. None in such quantities or qualities as to make the coliform bacteria count of the waters exceed 5,000 per 100 ml.

Range between 6.0 and 8.0, except that swamp waters may range from pH 5.0 to pH 8.0.

Not less than 4.0 ppm, except that swamp waters may have a low of 2.5 ppm.

s. Not greater than 5 parts per billion.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish or make the waters unamendable to standard treatment processes intended to prepare them for domestic use.

CLASS C

Waters suitable for propagation of fish, industrial and agricultural uses and other uses requiring water of lesser quality.

## Quality Standards for Class C Waters

Items

1. Floating solids; settleor other wastes or heated liquids. Specifications

None which are readily visible and attributable to sewage, industrial wastes or other wastes and which measurably increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. pH.

3. Dissolved oxygen.

 Toxic wastes, deleterious substances, colored or other wastes, or heated liquids. non and mixture with the wastes discharged thereto. Range between 6.0 and 8.5, except that swamp waters may range between 5.0 and 8.5.

Not less than 4 ppm, except that swamp waters may have a low of 2.0 ppm.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish life or impair the waters for any other best usage as determined by the Water Pollution Control Authority for the specific waters which are assigned to this class.

### CLASS D

Temporary classification to be assigned waters receiving wastes for which no practicable means of treatment is known. Dischargers of wastes shall make every reasonable effort to avoid creation of nuisance conditions.

As soon as feasible treatment processes are available, Class D waters shall be reclassified to an appropriate class and further waste discharges governed accordingly.

## CLASSIFICATION-STANDARDS SYSTEM FOR THE STATE OF SOUTH CAROLINA APPLYING TO FRESH SURFACE WATERS

(Adopted by the South Carolina Water Pollution Control Authority August 20, 1954)

### Class C .

Waters suitable for fish survival,* industrial and agricultural uses and other uses requiring water of lesser quality.

# Quality Standards for Class C . Waters

Items

Specifications

1. Floating solids; settleable solids; oil; sludge deposits.

None which are readily visible and industrial attributable to sewage, wastes or other wastes and which measurably increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. pH.

Range between 6.0 and 8.5, except that swamp waters may range between 5.0 and 8.5.

3. Dissolved oxygen.

4. Toxic wastes, deleterious substances, colored or other wastes, heated liquids.

Not less than 2.0 parts per million.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to fish survival or impair the waters for any other best usage as determined by the Water Pollution Control Authority for the specific waters which are assigned to this class.

## SOUTH CAROLINA WATER POLLUTION CONTROL AUTHORITY CLASSES AND STANDARDS FOR TIDAL SALT WATERS

(Adopted by the South Carolina Water Pollution Control Authority March 13, 1952)

Best Usage of Waters: Shellfishing for market purposes and any other usages.

# Quality Standards for Class SA Waters

Items

Specifications

1. Floating solids; settleable solids; oil; sludge deposits.

None attributable to sewage or industrial wastes.

2. Garbage, cinders, ashes, oils, sludge or other refuse.

None.

#### Items

- 3. Sewage or waste effluents.
- 4. Dissolved oxygen.
- 5. Toxic wastes, deleterious substances, colored or other wastes heated liquids.

#### Specifications

None which are not effectively disinfected.

Not less than 5.0 parts per million.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to edible fish or shellfish or the culture or propagation thereof, or which in any manner shall adversely affect the flavor, color, odor or sanitary condition thereof or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

6. Organisms of coliform group.

The median MPN value in any series of samples representative of waters in the shellfish growing area shall not be in excess of 70 per 100 milliliters.

#### Class SB

Best Usage of Waters: Bathing and any other usages except shellfishing for market purposes.

## Quality Standards for Class SB Waters

Items

Specifications

1. Floating solids; settleable solids; oil; sludge deposits.

None attributable to sewage or industrial wastes.

2. Garbage, cinders, ashes, oils, sludge or other refuse.

None.

3. Sewage or waste effiuents.

None which are not effectively disinfected.

4. Dissolved oxygen.

Not less than 5.0 parts per million.

5. Toxic wastes, deleterious substances, colored or other wastes or heated liquids.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to edible fish or the culture or propagation thereof, or which in any manner shall adversely affect the flavor, color, odor or sanitary condition thereof; and otherwise none in sufficient amounts to make the waters unsafe or unsuitable for bathing or impair the waters for any other best usage as determined for the specific waters which are assigned to this

6. Organisms of coliform group.

None in excess of the requirements of the South Carolina State Board of Health for bathing water.

#### Class SC

Best Usage of Waters: Crabbing, non-commercial fishing and any other usages except bathing or other shellfishing for market purposes.

## Quality Standards for Class SC Waters

Items

Specifications

1. Floating solids; settleable solids; sludge deposits.

None which are readily visible and attributable to sewage or industrial wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

2. Garbage, cinders, ashes, oils, sludge or other refuse.

None.

[&]quot;Fish survival" as used in this standard means the continued existence of individual fish normally indigenous to waters of this type.

Items

- 3. Dissolved oxygen.
- 4. Toxic wastes, oil, deleterious substances, colored or other wastes or heated liquids.

### Specifications

Not less than 4.0 parts per million.

None alone or in combination with other substances or wastes in sufficient amounts or at such temperatures as to be injurious to edible fish or the culture or propagation thereof, or which in any manner shall adversely affect the flavor, color, odor or sanitary condition of fish or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

#### Class SD

Best Usage of Waters: Any usages except fishing, bathing, or shellfishing for market purposes.

### Quality Standards for Class SD Waters Specifications

1. Floating solids; settleable solids; sludge deposits.

- 2. Garbage, cinders, ashes, oils, sludge or other refuse.
- 3. Dissolved oxygen.
- 4. Toxic wastes, oil, deleterious substances, colored or other wastes.

None which are readily visible and attributable to sewage or industrial wastes or which deleteriously increase the amounts of these constituents in receiving waters after opportunity for reasonable dilution and mixture with the wastes discharged thereto.

Not less than 3.0 parts per million. None alone or in combination with other substances or wastes in sufficient amounts to prevent survival of fish life or impair the waters for any other best usage as determined for the specific waters which are assigned to this class.

### APPENDIX J

# UTAH WATER POLLUTION CONTROL BOARD THE STANDARDS OF QUALITY AND THE REGULATIONS FOR WATER CLASSIFICATION

Adopted by the Utah Water Pollution Control Board, November 19, 1954 and made official by order of the Board, February 24, 1955, pursuant to authority of Section 73-14-6, Utah Code Annotated, 1953 as amended by Session Laws of 1953. Amended by order of the Board, September 7, 1960.

### CLASS "A" WATERS

Class "A" waters shall be so protected against pollution as to be suitable at all times without treatment for domestic water supplies, irrigation, stock watering, fish and wildlife propagation, recreation, as a source for industrial supplies, and for other uses as may be determined by the Board.

Regulations and Standards: No person shall discharge any waste directly into Class "A" waters, or dispose of any wastes in such a way as to result in

- characteristics of said waters exceeding the limits prescribed by U.S. Public Health Service Drinking Water Standards as of February 6, 1946, or
- (2) chemical characteristics of said waters exceeding the recommendations for irrigation water quality as outlined in Chapter 5 of the U.S. Department of Agriculture "Agriculture Handbook No. 60," issued February, 1954.

### CLASS "B" WATERS

Class "B" waters shall be so protected against pollution as to be suitable at all times for domestic supplies which are treated before use by disinfection only. Class "B" waters shall be suitable without treatment for irrigation, stock watering, fish and wildlife propagation, recreation as a source for industrial supplies, and for other uses as may be determined by the Board.

Regulations and Standards: No person shall discharge any wastes directly into Class "B" waters or dispose of any wastes in such a way as to result in

- (1) physical and chemical characteristics of said waters exceeding the limits prescribed by U.S. Public Health Service Drinking Water Standards as of February 6, 1946, or
- (2) chemical characteristics of said waters exceeding the recommendations for irrigation water quality as outlined in Chapter 5 of the U.S. Department of Agriculture "Agriculture Handbook No. 60," issued February, 1954, or
- (3) a monthly arithmetical average "most probable number" (MPN) of coliform organisms in said waters exceeding 50 per 100 milliliters; or in an MPN exceeding this number in more than 20% of the samples collected during any month; or in an MPN exceeding 100 per 100 milliliters in more than 5% of such samples.

### CLASS "C" WATERS

Class "C" waters shall be so protected against pollution as to be suitable at all times for domestic water supplies which are treated before use by coagulation, sedimentation, filtration, and disinfection. Class "C" waters shall be suitable without treatment for irrigation, stock watering, fish and wildlife propagation, recreation (except swimming), as a source for industrial supplies, and for other uses, as may be determined by the Board.

Regulations and Standards: No person shall discharge into Class "C" waters any wastes

- (1) which result in chemical characteristics of said waters exceeding the limits prescribed by U.S. Public Health Service Drinking Water Standards as of February 6, 1946, or
- (2) which result in chemical characteristics of said waters exceeding the recommendations for irrigation water quality as outlined in Chapter 5 of the U.S. Department of Agriculture "Agriculture Handbook No. 60," issued February, 1954, or
- (3) which result in a monthly arithmetical average "most probable number" (MPN) of coliform organisms in said waters exceeding 5,000 per 100 milliliters; or in an MPN exceeding this number in more than 20% of the samples collected during any month; or in an MPN exceeding 20,000 per 100 milliliters in more than 5% of such samples, or
- (4) which result in a monthly arithmetical average biochemical oxygen demand (BOD) in said waters exceeding 5 parts per million (ppm); or in a BOD exceeding this amount in more than 20% of the samples collected in any month; or in a BOD exceeding 10 ppm in more than 5% of such samples, or
- (5) which result in any slicks, floating solids, suspended solids or sludge deposits in said waters which are readily visible, or which result in an appreciable change in color of said waters, or
- (6) which result in a pH of said waters lower than 5.0 or greater than 9.0, or
- (7) which contain any toxic wastes, phenols, or other deleterious substances in such concentrations or at such temperatures as will render said waters injurious to fish life and waterfowl, or unsafe or unsuitable as sources of water supply for domestic use, food processing or industrial use, or unsuit-

able for agricultural purposes, stock watering, or recreation (except swimming).

### CLASS "D" WATERS

Class "D" waters shall be so protected against pollution as to be suitable at all times for general irrigation, but not for irrigation of lawns, recreational areas, pastures used for dairy cattle, root crops or any low growing crops produced for human consumption. Such waters shall be suitable also as a source for industrial supplies and for other uses as may be determined by the Board.

Regulations and Standards: No person shall discharge

into Class "D" waters any wastes

(1) which result in chemical characteristics of said waters exceeding the limits prescribed by U. S. Public Health Service Drinking Water Standards as of February 6, 1946, or

(2) which result in chemical characteristics of said waters exceeding the recommendations for irrigation water quality as outlined in Chapter 5 of U. S. Department of Agriculture "Agriculture Handbook No. 60," issued February, 1954, or

- (3) which result in a monthly arithmetical average "most probable number" (MPN) of coliform organisms in said waters exceeding 5,000 per 100 milliliters; or in an MPN exceeding this number in more than 20% of samples collected during any month; or in an MPN exceeding 20,000 per 100 milliliters in more than 5% of such samples or
- (4) which result in a monthly arithmetical average biochemical oxygen demand (BOD) in said waters exceeding 25 parts per million (ppm); or in a BOD exceeding this amount in more than 20% of the samples collected in any month; or in a BOD exceeding 50 ppm in more than 5% of such samples, or

- (5) which result in any slicks, floating solids, suspended solids, or sludge deposits in said waters which are readily visible, or which result in an appreciable change in color of said waters, or
- (6) which result in a pH of said waters lower than 5.0 or greater than 9.0, or
- (7) which contain any toxic wastes, phenols, or other deleterious substances in such concentrations or at such temperatures as will render said waters unsuitable for the uses designated in the introductory paragraph of this section.

### **CLASS "E" WATERS**

Class "E" waters shall be protected against such pollution as may result in nuisances. They shall have no beneficial uses.

Regulations and Standards: No person shall discharge into Class "E" waters any wastes which will create a condition constituting or resulting in a nuisance. The Board may direct that such waters be suitably isolated by closed conduit, approved fencing, or other means.

The following notes were adopted as modifications to The Standards of Quality and The Regulations for Water Classification on September 7, 1960, and are hereby made a part of said standards and regulations.

NOTE 1: The Board may assign any one of the foregoing classifications to a given water notwithstanding the presence in said water of natural pollutants in excess of limits established by the classification, in which case the subscript "1" shall be added to the usual classification designation (A., B., C., etc.) to denote the modification of water quality. No change in waste discharge restrictions of the basic classification shall be inferred, except that the discharge of any waste in such a way as to increase the concentration of any of the excessive natural pollutants in the classified water is prohibited.

NOTE 2: Wastes discharged to waters of the state under limitations imposed by a given classification shall be further controlled as required to protect water quality designated by all downstream classifications.

### APPENDIX K

# WATER SUPPLY AND POLLUTION ABATEMENT COMMITTEE

Water Quality Objectives for The Potomac River in Washington Metropolitan Area

June 1959

A clean Potomac is the only acceptable water quality objective for the Washington Metropolitan Area. Its early attainment within the greater portion of the river between the Monocacy and Hallowing Point is believed to be feasible. Substantial improvement in the remainder of this zone is an immediate necessity.

These objectives, therefore represent a thoughtful indication of the uses of the Potomac to which the people of the area may aspire within the foreseeable future. Their acceptance by the Washington Metropolitan Regional Conference is in no sense to be considered as an encroachment on the enforcement agencies within the States.

The accomplishment of pollution control to the extent required to meet these objectives will call upon all jurisdictions and agencies in the area concerned with the problem to exert extensive and persistent efforts to this end. This the committee is confident they will do—to and even beyond the limits of their immediate resources.

By the acceptance of these objectives the governmental representatives of the principal jurisdictions will have set for themselves on a voluntary basis the first guidelines as to water quality ever applied to the metropolitan area. These will thus provide the first understandings upon which all can proceed in the development of their respective programs for construction and operation of the necessary control works. The concentration of population and the rapid expansion of the densely occupied land areas dictate the necessity for such coordination in the development of sewage collection and disposal facilities throughout the region.

The following text has been based on the recommendations of the Interstate Commission on the Potomac River Basin. Certain changes have been made therein primarily for purposes of clarification and internal consistency of text. Other changes have been made to reflect the previously stated policy of this committee with respect to effluent discharges above the water intakes.

These objectives have been prepared in the light of present knowledge. With a growth of knowledge and experience as to the behavior of the Potomac, changes in the objectives and the related specific water quality criteria are to be expected. Such changes must always, however, be directed toward ever higher uses as may be in the best regional interest.

The water quality objectives for the Sections indicated below are as follows:

#### SECTION !

# POTOMAC RIVER: MONOCACY RIVER TO GREAT FALLS

General

Objectives: The establishment of conditions:

- 1. suitable for domestic water supplies, fish propagation, and recreational uses;
- 2. conducive to reduction of existing silt loading and prevention of future increases in this loading.

Criteria:

Limiting values of the following water quality characteristics shall be as indicated in 95% of the samples analyzed monthly:

- Coliform Group: Monthly median MPN not to exceed 2,000 per 100 ml.
- 2. pH Range between 6.5 and 8.5.
- 3. D. O.: Monthly median not less than 6.5 ppm; minimum content shall be 4.0 ppm.
- 4. Turbidity: After opportunity for reasonable dilution in the river, the turbidity of the receiving water shall not be measurably increased by any discharges so received.
- 5. Other Conditions: There shall be no floating solids, oil, settleable solids, or sludge deposits attributable to sewage, industrial wastes or other wastes. There shall be no toxic wastes, deleterious substances, colored or other wastes, or heated liquids, taste- or odor-producing substances, either alone or in combinations sufficient to be injurious to fish life or to make the waters unsafe or unsuitable as a source of municipal water supply or other desirable uses. Development should be so designed as to prevent discharge of effluent from sewage treatment plants either into the river or its tributaries.

### SECTION II

# POTOMAC RIVER: GREAT FALLS TO LITTLE FALLS

Objective: The establishment of conditions:

- suitable for domestic water supplies, fish propagation and recreational uses;
- 2. conducive to reduction of existing silt loading and prevention of future increases in this loading.

Criteria:

Limiting values of the following water quality characteristics shall be as indicated in 95% of the samples analyzed monthly:

- 1. Coliform Group: Monthly median MPN not to exceed 2,000 per 100 ml.
- 2. pH Range between 6.5 and 8.5.
- 3. D. O.: Monthly median not less than 6.5 ppm; minimum content shall be 4.0 ppm.
- 4. Turbidity: After opportunity for reasonable dilution in the river, the turbidity of the receving water shall not be measurably increased by any discharges so received.
- 5. Other Conditions: There shall be no floating solids, oil, settleable solids, or sludge deposits attributable to sewage, industrial wastes or other wastes. There shall be no toxic wastes, deleterious substances, colored or other wastes or heated liquids, taste- or odor-producing substances, either alone or in combinations in sufficient amounts to be injurious to fish life or to make the waters unsafe or unsuitable as a source of municipal water supply or other desirable uses. Development should be so designed as to prevent discharge of effluent from sewage treatment plants either into the river or its tributaries.

#### SECTION III

# POTOMAC RIVER: LITTLE FALLS TO KEY BRIDGE

Objective: The establishment of conditions:

- 1. suitable for swimming, fishing, boating, shore recreation, and safe for all species of fish life with favorable conditions prevailing for their propagation;
- 2. conducive to reduction of existing silt loading and prevention of future increases in this loading.

Criteria:

Limiting values of the following water quality characteristics shall be as indicated in 95% of the samples analyzed monthly:

- 1. Coliform Group: Monthly median MPN not to exceed 2,000 per 100 ml.
- 2. pH Range between 6.5 and 8.5.
- 3. D. O.: Monthly median not less than 6.5 ppm; minimum content shall be 4.0 ppm.
- 4. Turbidity: After opportunity for reasonable dilution in the river, the turbidity of the receiving water shall not be measurably increased by any discharges so received.
- 5. Other Conditions: There shall be no floating solids, oil, settleable solids, sewage and waste effluent or sludge deposits attributable to sewage, industrial wastes or other wastes. There shall be no wastes, deleterious substances, colored or other wastes or heated liquids, taste- or odor-

producing substances, either alone or in combinations, in sufficient amounts to be injurious to fish life or to make the waters unsafe for swimming or shore recreation.

### SECTION IV

# POTOMAC RIVER: KEY BRIDGE TO FORT WASHINGTON

Objectives: The establishment of conditions:

- 1. suitable for boating, shore recreation, industrial water supply and safe for the passage of all species of fish, with favorable conditions prevailing for the propagation of the hardier types;
- 2. conducive to reduction of existing silt loading and prevention of future increases in this loading.

Criteria:

Limiting values of the following water quality characteristics shall be as indicated in 95% of the samples analyzed monthly:

- 1. Coliform Group: Monthly median MPN not to exceed 10,000 per 100 ml.
- 2. pH Range between 6.5 and 8.5.
- 3. D. O.: Monthly median not less than 5.0 ppm; with the minimum value greater than 4.0 ppm 97% of the time and greater than 3.0 ppm 99% of the time.
- 4. Turbidity: After opportunity for reasonable dilution in the river, the turbidity of the receiving water shall not be measurably increased by any discharges so received.
- 5. Other Conditions: There shall be no floating solids, oil, settleable solids, or sludge deposits attributable to sewage, industrial wastes or other wastes. There shall be no toxic wastes, deleterious substances, colored or other wastes or heated liquids, taste- or odor-producing substances, either alone or in combinations, in sufficient amounts to make the waters unsafe or unsuitable as a source of industrial process water supply, or for boating, shore recreation, passage of all species of fish or propagation of the hardier species of fish.

### SECTION V

# POTOMAC RIVER: FORT WASHINGTON TO HALLOWING POINT

Objective: The establishment of conditions:

- 1. suitable for boating, fishing, swimming, and shore recreation;
- 2. conductive to reduction of existing silt loading and prevention of future increases in this loading.

Criteria:

Limiting values of the following water quality characteristics shall be as indicated in 95% of the samples analyzed monthly:

- 1. Coliform Group: Monthly median MPN not to exceed 2,000 per 100 ml.
- 2. pH Range between 6.5 and 8.5.

- 3. D. O.: Monthly median not less than 6.0 ppm with the minimum value greater than 4.0 ppm 97% of the time and greater than 3.5 ppm 99% of the time.
- 4. Turbidity: After opportunity for reasonable dilution in the river, the turbidity of the receiving water shall not be measurably increased by any discharges so received.
- 5. Other Conditions: There shall be no floating solids, oil, settleable solids, or sludge deposits attributable to sewage, industrial wastes or other wastes. There shall be no toxic wastes, deleterious substances, colored or other wastes or heated liquids, taste- or odor-producing substances, either alone or in combinations, in sufficient

amounts to be injurious to propagation of fish life or to make the waters unsafe or unsuitable for boating, swimming, fishing, or shore recreation.

As a basic consideration applying to all Sections, any sewage or industrial wastes discharged or permitted to flow into tributaries of the Potomac should be treated to that extent, if any, which may be necessary to maintain such waters in a sanitary and satisfactory condition at least equal to the criteria recommended above for the waters of the Potomac immediately above the confluence of the tributary with the main stream.

The reference "other wastes" under condition No. 5 of the foregoing objectives shall be interpreted to include trash, garbage, dirt, soil or any matter causing or aiding pollution.

### APPENDIX L

# INTERNATIONAL JOINT COMMISSION OBJECTIVES FOR BOUNDARY WATERS QUALITY CONTROL

In order to permit a more accurate evaluation of the nature and extent of pollution, its effects and the remedial measures necessary, the Commission, in the course of the investigation, adopted the following statement of objectives for boundary waters quality control which was developed by the technical advisers:

"The term 'boundary waters' as herein used shall include the waters defined in the references to the International Joint Commission dated April 1, 1946, October 2 and 3, 1946, and April 2, 1948, and are as follows:

St. Clair River, Lake St. Clair, the Detroit River, St. Mary's River from Lake Superior to Lake Huron, and Niagara River from Lake Erie to Lake Ontario.

These objectives are for the boundary waters in general, and it is anticipated that in certain specific instances, influenced by local conditions, more stringent requirements may be found necessary.

General Objectives

"All wastes, including sanitary sewage, storm water, and industrial effluents, shall be in such condition when discharged into any stream that they will not create conditions in the boundary waters which will adversely affect the use of those waters for the following purposes: source of domestic water supply or industrial water supply, navigation, fish and wildlife, bathing, recreation, agriculture and other riparian activities.

"In general, adverse conditions are caused by:

- (A) Excessive bacterial, physical or chemical contamination.
- (B) Unnatural deposits in the stream, interfering with navigation, fish and wildlife, bathing, recreation, or destruction of aesthetic values.
- (C) Toxic substances and materials imparting objectionable tastes and odors to waters used for domestic or industrial purposes.
- (D) Floating materials, including oils, grease, garbage, sewage solids, or other refuse.

# Specific Objectives

"In more specific terms, adequate controls of pollution will necessitate the following objectives for:

(A) Sanitary Sewage, Storm Water, and Wastes from Water Craft

Sufficient treatment for adequate removal or reduction of solids, bacteria and chemical constituents which may interfere unreasonably with the use of these waters for purposes aforementioned. Adequate protection for these waters, except in certain specific instances influenced by local conditions, should be provided if the coli-

form M.P.N. median value does not exceed 2,400 per 100 ml at any point in the waters following initial dilution.

## (B) Industrial Wastes

(1) Chemical Wastes-Phenolic Type

Industrial waster effluents from penolic hydro-carbon and other chemical plants will cause objectionable tastes or odors in drinking or industrial water supplies and may taint the flesh of fish.

Adequate protection should be provided for these waters if the concentration of phenol or phenol equivalents does not exceed an average of 2 ppb and a maximum of 5 ppb at any point in these waters following initial dilution. This quality in the receiving waters will probably be attained if plant effluents are limited to 20 ppb of phenol or phenol equivalents.

Some of the industries producing phenolic wastes are: coke, synthetic resin, oil refining, petroleum cracking, tar, road oil, creosoting, wood distillation, and dye manufacturing plants.

(2) Chemical Wastes-Other Than Phenolic

Adequate protection should be provided if:

(a) The pH of these waters following initial dilution is not less than 6.7 nor more than 8.5 This quality in the receiving waters will probably be attained if plant effluents are adjusted to a pH value within the range of 5.5 and 10.6.

(b) The iron content of these waters following initial dilution does not exceed 0.3 ppm. This quality in the receiving waters will probably be attained if plant effluents are limited to 17 ppm of iron in

terms of Fe.

(c) The odor-producing substances in the effluent are reduced to a point that following initial dilution with these waters the mixture does not have a threshold odor number in excess of 8 due to such added material.

(d) Unnatural color and turbidity of the wastes are reduced to a point that these waters will not be offensive in appearance or otherwise unattractive for the

aforementioned purposes.

(e) Oils and floating solids are reduced to a point such that they will not create fire hazards, coat hulls of water craft, injure fish or wildlife or their habitat, or will

adversely affect public or private recreational development or other legitimate shoreline developments or uses. Protection should be provided for these waters if plant efflents or storm water discharges from premises do not contain oils, as determined by extraction, in excess of 15 ppm, or a sufficient amount to create more than a faint iridescence. Some of the industries producing chemical wastes other than phenolic are: oil wells and petroleum refineries, gasoline filling stations and bulk stations, styrene copolymer, synthetic pharmaceutical, synthetic fiber, iron and steel, alkali chemical, rubber fabricating, dye manufacturing, and acid-manufacturing plants.

(3) Highly Toxic Wastes

Adequate protection should be provided for these waters if substances highly toxic to human, fish, aquatic, or wildlife are eliminated or reduced to safe limits.

Some of the industries producing highly toxic wastes are: metal plating and finishing

plants discharging cyanides, chromium or other toxic wastes; chemical or pharmaceutical plants and coke ovens. Wastes containing toxic concentrations of free halogens are included in this category.

(4) Deoxygenating Wastes

Adequate protection of these waters should result if sufficient treatment is provided for the substantial removal of solids, bacteria, chemical constituents and other substances capable of reducing the dissolved oxygen content of these waters unreasonably. Some of the industries producing these wastes are: tanneries, glue and gelatin plants, alcohol, including breweries and distilleries, wool scouring, pulp and paper, food-processing plants such as meat packing and dairy plants, corn products, beet sugar, fish-processing and dehydration plants."

NOTE: The methods of determination of the chemical constituents referred to in the preceding Objectives are as given in "Analytical Methods for Boundary Waters Quality Control," as prepared by the Board of Technical Advisers. Bacterial determinations are to include the presumptive and confirmed tests for the coliform group of bacteria as given in "Standard Methods for the Examination of Water and Sewage," American Public Health Association, New York.

### APPENDIX M

# OHIO RIVER VALLEY WATER SANITATION COMMISSION REGULATORY ACTIONS

# BACTERIAL-QUALITY OBJECTIVES FOR THE OHIO RIVER Adopted April 4, 1951

As a guide in the establishment of treatment requirements for sewage discharged in the Ohio River, and as a yardstick for evaluating sanitary conditions in waters used for potable supplies and recreational purposes, the Ohio River Valley Water Sanitation Commission on April 4, 1951 adopted these bacterial-quality objectives:

Water Supply Uses—The monthly arithmetical average "most probable number" of coliform organisms in waters of the river at water intakes should not exceed 5,000 per 100 ml in any month; nor exceed this number in more than 20 percent of the samples of such waters examined during any month; nor exceed 20,000 per 100 ml in more than 5 percent of such samples.

Recreational Uses—For bathing or swimming waters, monthly arithmetical average "most probable number" of coliform organisms should not exceed 1,000 per 100 ml during any month of the recreation season; nor exceed this number in more than 20 percent of the samples examined during any such month; nor exceed 2,400 per 100 ml on any day. For non-bathing or non-swimming waters, the monthly arithmetical average "most probable number" of coliform organisms should not exceed 5,000 per 100 ml in any month of the recreational season, nor should exceed this number in more than 20 percent of the samples examined during any such month.

# OHIO RIVER SEWAGE TREATMENT STANDARDS

# Treatment Standard No. 1—CINCINNATI POOL (Adopted April 6, 1949)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River, commonly known as the "Cincinnati Pool", extending from U. S. Corps of Engineers Dam No. 36, located about three miles upstream from Cincinnati, Ohio, and being 461 miles downstream from Pittsburgh, Pennsylvania, to U. S. Corps of Engineers Dam No. 37, located at Fernbank, Cincinnati, Ohio, and being 483 miles downstream from Pittsburgh, shall be so treated as to provide for:

- (a) Substantially complete removal of settleable solids; and
- (b) Removal of not less than forty-five percent of the total suspended solids; and, in addition
- (c) Reduction by not less than 65% of the biochemical oxygen demand of organic wastes, provided, however, that whenever conditions permit, such lesser degree of reduction of biochemical oxygen demand, but not lower than 35%, may be applied to organic wastes if as a result there will

be no impairment in the Cincinnati Pool of a water-quality standard of 4.0 parts per million of dissolved oxygen at the bottom of the oxygen sag in the Ohio River below Cincinnati.

# Treatment Standard No. 2—HUNTINGTON, W. VA., TO CINCINNATI, OHIO (Adopted April 2, 1952)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River extending from U. S. Corps of Engineers Dam No. 27, located about five miles upstream from Huntington, West Virginia, and being 301 miles downstream Pittsburgh, Pennsylvania, to U. S. Corps of Engineers Dam No. 36, located about three miles upstream from Cincinnati, Ohio, and being 461 miles downstream from Pittsburgh, Pennsylvania, shall be so treated as to provide for:

- (a) Substantially complete removal of settleable solids; and
- (b) Removal of not less than forty-five percent of the total suspended solids; and, in addition
- (c) Reduction in coliform organisms in accordance with the following schedule:

Not less than 90% reduction during the months May through November.

Not less than 80% reduction during the months December through April.

# Treatment Standard No. 3—BELOW PITTSBURGH (Mile 15) TO HUNTINGTON (Adopted April 29, 1953)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River extending from the Allegheny County-Beaver County line in Pennsylvania, located approximately 15 miles downstream from the confluence of the Allegheny and Monongahela Rivers at Pittsburgh, to Corps of Engineers Dam No. 27, located about five miles upstream from Huntington, W. Va., and being 301.0 miles downstream from Pittsburgh, Pennsylvania, shall be so treated as to provide for:

- (a) Substantially complete removal of settleable solids; and
- (b) Removal of not less than forty-five percent of the total suspended solids; and, in addition
- (c) Reduction in coliform organisms in accordance with the following schedule:

Not less than 80% reduction during the months May through October. Not less than 85% reduction during the months November through April.

Treatment Standard No. 4-PITTSBURGH AND VI-CINITY (Mile 0.0 to Mile 15) (Adopted April 29, 1953)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River extending from the point of confluence of the Allegheny and Monongahela Rivers at Pittsburgh, designated as Ohio River mile point 0.0, to the Allegheny County-Beaver County line in Pennsylvania, located approximately 15 miles downstream from the confluence of the Allegheny and Monongahela Rivers, shall be so treated as to provide for:

- (a) Substantially complete removal of settleable solids; and
- (b) Removal of not less than forty-five percent of the total suspended solids; and
- (c) Reduction in biochemical oxygen demand of approximately fifty percent; and, in addition
- (d) Reduction in coliform organisms in accordance with the following schedule: Not less than 80% reduction during the months May through October. Not less than 85% reduction during the months November through April.

# Treatment Standard No. 5-CINCINNATI TO OWENS-BORO (Adopted January 13, 1954)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River extending from mile point 483.2 (miles below Pittsburgh, Pensylvania), located about ten miles downstream from Cincinnati, Ohio, and at which point is located Dam No. 37, to mile point 750.0 (miles below Pittsburgh, Pennsylvania), located about six miles upstream from Owensboro, Kentucky, shall be so treated as to provide for:

- (a) Substantially complete removal of settleable solids; and
- (b) Removal of not less than forty-five percent of the total suspended solids.

# Treatment Standard No. 6-OWENSBORO TO HEN-DERSON (Adopted January 13, 1954)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River extending from mile point 750.0 (miles below Pittsburgh, Pennsylvania), located about six miles upstream from Owensboro, Kentucky, to mile point 803.0 (miles below Pittsburgh, Pennsylvania) located near Henderson, Kentucky, shall be so treated as to provide

- (a) Substantially complete removal of settleable solids; and
- (b) Removal of not less than forty-five percent of the total suspended solids; and, in addition

(c) Reduction in coliform organisms in accordance with the following schedule: Not less than 85% reduction during the months May through October. Not less than 65% reduction during the months November through April.

# Treatment Standard No. 7-HENDERSON TO CAIRO (Adopted January 13, 1954)

All sewage from municipalities or other political subdivisions, public or private institutions or corporations discharged or permitted to flow into that portion of the Ohio River extending from mile point 803.0 (miles below Pittsburgh, Pennsylvania), located near Henderson, Kentucky, to Cairo Point, Illinois, located at the con-fluence of the Ohio and Mississippi Rivers and being 981.0 miles downstream from Pittsburgh, Pennsylvania, shall be so treated as to provide for:

- (a) Substantially complete removal of settleable solids: and
- (b) Removal of not less than forty-five percent of the total suspended solids.

## CONCLUSIONS REGARDING TREATMENT NEEDS FOR THE WABASH RIVER BETWEEN TERRE HAUTE, IND. AND VINCENNES, IND.

# Adopted October 4, 1950

On the basis of observed conditions coupled with stream analysis and in accordance with established quality objectives, the following conclusions are reached:

# TERRE HAUTE

Oxygen Conditions-Maintenance of the desired dissolved-oxygen water-quality objectives requires treatment facilities for the Terre Haute pollution load capable of providing substantially complete removal of settleable solids and total reduction of 52 percent in biochemical oxygen demand. Whenever stream flow and temperature conditions permit, an overall reduction in biochemical oxygen demand of less than 52 percent may be applied, if, as a result, there is no impairment to the water-quality objective of 50 percent dissolved-oxygen saturation in the river below Terre Haute. However, under no conditions shall treatment be less than that which will provide for substantially complete removal of settleable solids and the removal of not less than forty-five percent of the total suspended solids, which is the minimum specified under the terms of the Ohio River Compact.

Bacteriological Conditions-Chlorination of Terre Haute sewage is advisable because of the high concentration of coliform organisms discharged, the influence of which is felt as far downstream as Vincennes. Chlorination could be expected to improve the quality of water reaching the Vincennes intake, as well as enhance the recreational potentialities of the stream.

Allocation of Treatment-Allocation of treatment requirements among the various polluters at Terre Haute is a matter that commends itself for attention by the Indiana Stream Pollution Control Board. State, municipal and industrial relationships, as well as technical considerations, are involved in this decision. Among the factors to be weighed are the relative size of domestic and industrial pollution loads and the responsibility to be assigned for their reduction. The equities involved are a matter for decision by the state.

## VINCENNES

At Vincennes treatment of all municipal and industrial wastes providing for substantially complete removal of settleable solids and the removal of not less than forty-five percent of the total suspended solids will be adequate to insure maintenance of desired dissolved-oxygen water-quality objectives in the Wabash River below this city.

# CONCLUSIONS AND RECOMMENDATIONS REGARDING TREATMENT NEEDS FOR THE WEST FORK AND MONONGAHELA RIVERS BETWEEN WESTON, W. VA. AND PITTSBURGH, PA.

# Adopted February 6, 1959

This investigation was made for purposes of evaluating pollution conditions resulting from sewage discharged to the Monongahela and West Fork rivers and for determination of remedial measures in terms of sewage-treatment requirements.

Recommendations resulting from the investigation reflect the following considerations: First, sewage discharges originating within one signatory state shall not injuriously affect water uses in another state; second, waters of the Ohio Valley Compact district shall be placed and maintained in a satisfactory sanitary condition, in accordance with the provisions of Article I of the Compact.

Quality conditions were evaluated in terms of estimated dissolved-oxygen levels and coliform-bacterial concentrations at river flows of varying magnitude. From this analysis the following conclusions are reached:

- 1. Treatment of existing sewage discharges to the Monongahela River (which is formed by the confluence of the West Fork and Tygart rivers) in accordance with the minimum degree of treatment specified in the Compact should insure the maintenance of adequate sanitary quality at points of interstate concern. One point of interstate concern is the West Virginia-Pennsylvania state line at Mile 91.2. Also of interstate concern is the quality of water at the mouth of the Monongahela and its consequent effect on conditions in the Ohio River.
- 2. Sewage discharged in West Virginia to the West Fork River—notably from Weston and Clarks-burg—requires something more than primary treatment to achieve satisfactory conditions in the West Fork River as measured by dissolved-oxygen content and coliform bacteria concentrations.
- 3. To meet local needs with regard to water supplies taken from the Monongahela River at points below certain sewage discharges in Pennsylvania, the sewage-treatment requirements at these places should be somewhat more stringent than those

which are necessary to satisfy interstate necessities alone.

## Recommendations

# It is recommended that:

- 1. The Commission take such action as will express approval from an interstate point of view, of a program in which all sewage discharged into the Monongahela River is treated so as to provide substantially complete removal of settleable solids and the removal of not less than 45 percent of the total suspended solids.
- 2. The State of West Virginia and the Commonwealth of Pennsylvania be invited to utilize such findings in this report as they may find useful in establishing sewage-treatment requirements at certain communities where local conditions claim separate consideration.
- 3. Quality conditions in the Monongahela River be reevaluated at periodic intervals, notably with regard
  to water-quality changes resulting from the operation of sewage-treatment plants and the anticipated
  mitigation of mine-drainage pollution. Data being
  collected at Commission-sponsored monitor stations
  will be most useful toward this end. Equally important, however, will be such additional data as
  can be developed by West Virginia and Pennsylvania with regard to: (a) sewage and industrialwaste loads; and, (b) river-water analyses made
  by them and by water-treatment plants under their
  respective jurisdiction.

# OHIO RIVER VALLEY WATER SANITATION COMMISSION IW-1

# BASIC INDUSTRIAL WASTE REQUIREMENTS

Industrial wastes shall be treated or otherwise modified prior to discharge so as to maintain the following conditions in the receiving waters:

- Freedom from anything that will settle to form putrescent or otherwise objectionable sludge deposits which interfere with reasonable water uses.
- 2. Freedom from floating debris, scum and other floating materials in amounts sufficient to be unsightly or deleterious.
- Freedom from materials producing color or odor in such degree as to create a nuisance.
- 4. Freedom from substances in concentrations or combinations which are toxic or harmful to human, animal or aquatic-life.

These conditions to be maintained in the receiving waters following the discharge of industrial-waste effluents, are basic or minimum requirements. Investigations will be conducted by the Commission as time and circumstances permit to establish the need and validity of altering or adding to the above basic requirements.

Questions concerning compliance with requirements are to be addressed to the signatory state agency in the state in which the industrial plant is operating. Arrangements will be made by the state agency for such contact

and consultation with the Commission as may be necessary or requested.

# OHIO RIVER VALLEY WATER SANITATION COMMISSION

RESOLUTION NO. 17-58 Chloride-control measure Adopted September 12, 1958

(Several introductory paragraphs omitted)

The following measures are hereby adopted by the Commission to be followed by the signatory states for the joint cooperative control of chloride discharges:

- 1. Existing and future discharges of wastes containing significant chloride loads into the waters of the Ohio River Valley Water Sanitation District shall be subject to control by impoundment or by such other methods as may be acceptable to the water pollution-control agency of the state in which the discharge originates, so as to insure that the amount thereof shall conform to a discharge schedule to be formulated, as hereinafter provided, for the purpose of maintaining an acceptable proportion between the amount of such chloride-containing wastes and the volume of flow in the stream into which it is discharged;
- 2. In order to insure appropriate ratios between chloride-waste discharges and volume of stream flows, all impoundment basins and other control methods shall be operated in accordance with schedules to be formulated by the water pollution-control agency of the state in which the discharge originates in consultation with the Ohio River Valley Water Sanitation Commission.

# RESOLUTION NO. 18-58 Implementation of chloride-control program Adopted September 12, 1958

(Introductory paragraph omitted)

(a) Where impoundment basins are employed for control purposes, the discharge from which enters the Ohio River directly or through its tributaries, the preferred minimum storage capacity shall be sufficient to contain three-months production of chloride waste. Deviations from this preferred minimum capacity requirement may be permitted only with the approval of the water pollution-control agency of the state in which the discharge originates after consultation with the Ohio River Valley Water Sanitation Commission.

(b) Each of the signatory states shall compile an inventory of existing industries discharging a significant chloride load, together with the locations and amounts of such discharges. These inventories shall be maintained up-to-date as new industries are granted discharge privileges and shall be made part of the Commission records.

Within one year following the adoption of these chloride-control resolutions each state shall prepare a progress report for presentation at a regular meeting of the Commission on the status of control for each discharger of chloride waste sub-

ject to compliance.

(d) Each state shall conduct, and may request collaboration of the Commission in conducting, such investigations of effluents from political subdivisions that discharge sewage into the Ohio River directly or through its tributaries as may be necessary to determine whether these effluents contain abnormal concentrations of chloride. Where abnormal conditions are revealed, the state shall take appropriate steps to insure correction of such conditions.

(e) The Executive Director is hereby instructed to make periodic reports on chloride concentrations in the waters of the Ohio River Valley Water Sanitation District as revealed from monitor-sta-

tion records.

## RESOLUTION NO. 14-60 Significant chloride load Adopted April 8, 1960

RESOLVED: That for present determination of chloride discharges subject to compliance with the ORSANCO chloride-control measure, a "significant load" is defined as:

1. Any existing discharge to the Ohio River or its tributaries which is equal to or greater than 25 tons per

2. Any discharge from new or expanded operations to the Ohio River or its tributaries which is equal to or greater than 5 tons per day; or

3. Any discharge less than any of the above values which in the opinion of the state agency, causes a local degradation of water quality, although it otherwise satisfies interstate control requirements.

Deviations from the above definitions may be permitted only with the aproval of the water pollution control agency of the state in which the discharge originates after consultation with the Commission.

### APPENDIX N

# INTERSTATE COMMISSION ON THE DELAWARE RIVER BASIN EXCERPTS FROM THE RECIPROCAL AGREEMENT

# Article II—Classification of Zones

It is recognized by the signatory states that due to such variable factors as location, size, character, and flow, and of the many varied uses of the waters of the interstate Delaware River and its aforesaid West Branch, such as water supply, recreation, navigation, industrial developments, maintenance of fish life, shell-fish culture, agriculture, and other purposes, that no single standard of sewage and waste treatment and of quality of receiving waters is practical for all parts of the river. Therefore, in order to apply minimum requirements for the attainment of correction and control of pollution which will be appropriate to the varied factors including the existing and potential quality and uses of the waters, the interstate Delaware River is hereby divided into four zones, to wit:

Zone 1: Zone 1 is that part of the Delaware River and its West Branch extending from the New York-Pennsylvania boundary line to the head of tidewater at Trenton, New Jersey and Morrisville, Pennsylvania.

The drainage basin contributory to this zone, excepting part of the Lehigh River Basin, is relatively sparsely inhabited and contains few sewered communities and relatively few industrial establishments producing waste water. The streams draining this area being, in general, relatively clean and of high elevation, are well adapted as sources of public water supplies, after treatment or purification.

The principal uses of the waters of the Delaware River in Zone 1 are expected to be for water supply after such treatment or purification as may be necessary, and for recreation, bathing, maintenance of fish and aquatic life, agriculture, and for other related purposes.

Zone 2: Zone 2 is that part of the Delaware River extending from the head of tidewater at Trenton, New Jersey and Morrisville, Pennsylvania, to a line drawn perpendicular to the channel of the Delaware River from the mouth of Pennypack Creek in Philadelphia, Pennsylvania, to the corresponding point on the New Jersey shore.

The drainage basin contributory to this zone is somewhat more densely populated than that of Zone 1, and it contains more sewered communities and industrial establishments.

The principal uses of the waters of the Delaware River in Zone 2 are expected to be for water supply, after treatment or purification, and for recreation, navigation, maintenance of fish and aquatic life, agricultural, industrial and other purposes.

Zone 3: Zone 3 is that part of the Delaware River extending from the aforesaid line connecting the mouth of Pennypack Creek in Philadelphia and the correspond-

ing point in New Jersey to the Pennsylvania-Delaware boundary line.

The drainage basin contributory to this zone contains populous metropolitan areas including Philadelphia, Pennsylvania and Camden, New Jersey.

The principal uses of the waters of the Delaware River in Zone 3 are expected to be for navigation, industrial water supply, and other purposes.

The water in this zone, however, should be of such sanitary quality that it will not be unfit for use as sources of water supply, will not be harmful to fish life, and will not adversely affect the quality of the waters of the tidal tributaries.

Zone 4: Zone 4 is that part of the Delaware River extending from the Pennsylvania-Delaware boundary line to the Atlantic Ocean.

The principal uses of the waters of the Delaware River in Zone 4 are expected to be for navigation, industrial water supplies, commercial fishing, shellfish culture, recreation and other purposes.

In order to attain conditions of cleanliness and sanitation of the waters of the Delaware River which will be consistent with the appropriate existing and future quality and uses of such waters, the following minimum requirements shall apply to the several zones herein provided. It is the purpose and intent of such requirements to apply to artificial (not natural) causes of pollution.

# Article III—Minimum Requirements

In order to put and maintain the waters of the interstate Delaware River and its West Branch as aforesaid, in a clean and sanitary condition, no sewage, industrial wastes or other polluting matter shall be discharged into, or be permitted to flow or fall into, or be placed in any respective zone of the interstate Delaware River as herein established, unless such sewage, industrial waste or other artificial polluting matter shall first have been so treated as to produce an effluent which will meet the following minimum requirements:

Zone 1: 1. Such effluent shall be free of noticeable floating solids, color, oil, grease, or sleek, and practically free of suspended solids.

- 2. Such effluent shall be sufficiently free of turbidity that it will not cause noticeable turbidity in the water of the Delaware River.
- 3. Such effluent shall show a reduction of organic substances of at least eighty-five (85) percent as measured by the biochemical oxygen demand, and furthermore, such effluent in no case shall exceed a biochemical oxygen demand of fifty (50) parts per million, and furthermore, the discharge of such effluent, after dispersion in the water of the river, shall not cause a reduction of the dissolved oxygen content of such water of more than five

- (5) per cent. The aforesaid reduction in dissolved oxygen content shall be determined by the average results obtained from dissolved oxygen tests made upon samples collected on not less than six (6) consecutive days from points in the river above and below the point or points of effluent discharge.
- 4. Such effluent shall be of such quality that the most probable number of organisms of the Coli Aerogenes group shall not exceed one (1) per milliliter in more than ten (10) per cent of the samples of sewage effluent tested by the confirmed test, and provided further that no single sample shall contain more than one hundred (100) organisms of the Coli Aerogenes group in one (1) milliliter.
- 5. Such effluent shall be sufficiently free of acids, alkalis, and other toxic or deleterious substances, that it will not create a menace to the public health through the use of the waters of the Delaware River for public water supplies, for recreation, bathing, agriculture and other purposes; nor be inimical to fish, animal or aquatic life.
- 6. Such effluent shall be free of offensive odors and also be free of substances capable of producing offensive tastes or odors in public water supplies derived from the Delaware River at any place below the discharge of such effluent.
- Zone 2: 1. Such effluent shall be free of noticeable floating solids, color, oil, grease, and practically free of both suspended solids and sleek.
- 2. Such effluent shall be sufficiently free of turbidity that it will not cause noticeable turbidity in the water of the Delaware River.
- 3. Such effluent shall show a reduction of organic substances of at least eighty-five (85) per cent as measured by the biochemical oxygen demand, and furthermore, such effluent in no case shall exceed a biochemical oxygen demand of one hundred (100) parts per million, and furthermore, the discharge of such effluent, after dispersion in the water of the river, shall not cause a reduction of the dissolved oxygen content of such water of more than ten (10) per cent. The aforesaid reduction in dissolved oxygen content shall be determined by the average results obtained by dissolved oxygen tests made upon samples collected on not less than six (6) consecutive days from points in the river above and below the point or points of effluent discharge.
- 4. Such effluent shall be of such quality that the most probable number of organisms of the Coli Aerogenes group shall not exceed one (1) per milliliter in more than twenty-five (25) per cent of the samples of sewage effluent tested by the confirmed test, and provided further that no single sample shall contain more than one hundred (100) organisms of the Coli Aerogenes group in one (1) milliliter.
- 5. Such effluent shall be sufficiently free of acids, alkalis, and other toxic or deleterious substances, that it will not create a menace to the public health through the use of the water of the Delaware River for public water supplies, for recreation, industrial and other purposes; nor be inimical to fish, animal or aquatic life.
- 6. Such effluent shall be free of offensive odors and also be free of substances capable of producing offensive tastes and odors in public water supplies derived from

- the Delaware River at any place above or below the discharge of such effluent.
- Zone 3: 1. Such effluent shall be free of noticeable floating solids, oil or grease, and substantially free of both suspended solids and sleek.
- 2. Such effluent shall be sufficiently free of turbidity that it will not cause substantial turbidity in the water of the Delaware River after dispersion in the water of the river.
- 3. Such effluent shall show a reduction of at least fifty-five (55) per cent of the total suspended solids and a reduction of not less than thirty-five (35) per cent of the biochemical oxygen demand. (It is the intent of this requirement to restore the dissolved oxygen content of the river water in this zone to at least fifty (50) per cent saturation. To accomplish this, it may be necessary in the case of certain wastes, to obtain reductions greater than those required under this item.)
- 4. Such effluent, if it be discharged within two miles of a public water works intake or within prejudicial influence thereof, shall at all times be effectively treated with a germicide.
- 5. Such effluent shall be sufficiently free of acids, alkalis, and other toxic or deleterious substances, that it will not create a menace to the public health through the use of the waters of the Delaware River for public water supples, or render such waters unfit for industrial and other purposes; or cause the water of the Delaware River to be harmful to fish life.
- 6. Such effluent shall be practically free of substances capable of producing offensive tastes or odors in public water supplies derived from the Delaware River.
- Zone 4: 1. Such effluent shall be free of noticeable floating solids, oil, or grease, and substantially free of both suspended solids and sleek.
- 2. Such effluent shall be sufficiently free of turbidity that it will not cause substantial turbidity in the waters of the Delaware River after dispersion in the water of the river
- the river.

  3. Such effluent shall show a reduction of at least fiftyfive (55) per cent of the total suspended solids and shall
  be subject to such further treatment as may be needed
  to prevent a nuisance.
- 4. Such effluent, if it be discharged within prejudicial influence of a public water works intake, or of recreational areas, or of shell fish grounds, shall at all times be effectively treated with a germicide, except that in the case of recreational area influence, such treatment need not be provided during the period from October 15th to May 15th of each year.
- 5. Such effluent shall be sufficiently free of acids, alkalis, and other toxic or deleterious substances that it will not create a menace to the public health through the use of the waters of the Delaware River for public water supplies, or render such waters unfit for commercial fishing, shell fish culture, recreational, industrial or other purposes.
- 6. Such effluent shall be practically free of substances capable of producing offensive tastes or odors in public water supplies derived from the Delaware River.

### Intrastate Tributaries

It is further recognized by the signatory states that the quality of the waters of the intrastate tributaries of the Delaware River and its aforesaid West Branch are of interstate concern at their points of confluence with the Delaware River and its West Branch. Therefore, it is also agreed that sewage, industrial waste or other artificial polluting matter discharged into, or permitted to flow or to fall into, or be placed in any intrastate tributary of the aforesaid Delaware River, shall be treated to that degree, if any, necessary to maintain the waters of such intrastate tributary immediately above its confluence with the aforesaid Delaware River in a condition at least equal to the clean and sanitary condition of the waters of the Delaware River immediately above the confluence of such tributary.

## Standard Methods

Analyses and tests regarding the minimum requirements herein prescribed, shall be determined in accordance with the provisions contained in the American Pub-

lic Health Association's latest edition on "Standard Methods for the Examination of Water and Sewage."

## **Future Requirements**

The aforesaid requirements as to treatment of sewage, industrial wastes or other artificial polluting matter and as to the sanitary quality of receiving waters are minima. It is the intent and purpose of these requirements to accomplish reasonable and adequate control of correction of pollution. Due to the many variable factors involved, however, and to the impossibility of forecasting future developments with certainty, it may be necessary in the future to impose additional requirements, particularly in Zones 2 and 3.

The minima herein prescribed, therefore, shall be considered the first steps toward attaining the objectives sought, and if necessary, may be required to be supplemented in the case that the general application of such minimum requirements does not adequately improve and maintain the sanitary quality of the waters of the Delaware River.

### APPENDIX O

# MINIMUM WATER QUALITY CRITERIA FOR STREAMS IN THE POTOMAC RIVER BASIN

(From Water Quality Criteria, Interstate Commission on the Potomac River Basin)

As Approved 8 August 1946, by the Commission and Recommended to the States of the Basin for Their Use

# Principles Involved in the Establishment of Water Quality Criteria

The Water Quality Criteria and Maps showing existing conditions and first step in a progressive program of stream improvement established by the Interstate Commission on the Potomac River Basin shall be used and interpreted upon the basis of the following funda-

- mental principles:
  - (1) The criteria and maps showing existing conditions and first step in a progressive program of stream improvement shall be considered as a cooperative effort on the part of the signatory bodies to establish a uniform yet flexible yardstick for describing and indicating the water quality in the streams of the basin. This quality can be improved from time to time as the necessary work for its betterment is completed. It is a means by which areas of relatively serious pollution can be shown and progress as it is made can be recorded.
  - (2) The criteria and maps are not to be considered as placing in any way an ultimate or final objective on any section of stream.
  - (3) The map indicating existing (present-day) conditions has been prepared upon the basis of information now available to the Commission. Areas will be made more definite and accurate as the state agencies, in pursuing their abatement programs, obtain the necessary information to more completely define the picture.
  - (4) The map showing recommended conditions represents the first step in the improvement of water quality proposed to the signatory bodies. This is to be followed by succeeding steps as time and conditions warrant.

#### Class A Waters

Waters in Class A are suitable for a potable water supply with no treatment necessary except chlorination or disinfection. The waters may also be used for bathing, fish life, recreation and industrial process waters. The waters under this classification shall meet the following minimum requirements:

- Coliform Bacteria
   The most probable number of coliform bacteria present in any 100 ml sample shall not exceed 50.
- (2) Color
  The color of any sample shall not exceed 10 parts
  per million.

- (3) Turbidity
  The turbidity of any sample shall not exceed 10 parts per million.
- (4) pH
  The pH value of the water shall vary between 6.0 and 8.0.
- (5) Dissolved Oxygen
  The average of all monthly tests for DO shall not be less than 7.5 parts per million, with no single observation being less than 6.5 parts per million.
- (6) Other Conditions
  The waters shall contain no toxic substances of any nature such as oils, tars, or free acid at any time. There shall be no floating solids or debris except from natural sources. No taste- or odor-producing substances will be permitted unless they are of natural origin. There shall be no sludge deposits of any nature.

### Class B Waters

Waters in Class B are suitable for bathing, fish life, and for other similar recreational purposes. This water is also satisfactory for domestic water supplies with complete treatment, for industrial process water, and other similar uses. The results of sampling shall meet the following minimum requirements:

- (1) Coliform Bacteria
  The monthly average of all samples shall show
  the most probable number of coliform bacteria
  per 100 ml shall vary between the limits of 50 to
  500. Any one sample shall not contain more than
  1,000 coliform bacteria as the most probable number per 100 ml.
- (2) Color A color of not more than 20 ppm is desirable.
- (3) Turbidity
  A turbidity of not more than 40 ppm is desirable.
- (4) pH
  The acidity or alkalinity of the water shall vary between the limits of 6.0 and 8.5.
- (5) 5-Day Biochemical Oxygen Demand The 5-Day 20°C BOD of all samples during any one month shall not exceed 1.5 ppm. The maximum observed BOD in any sample shall not be more than 3.0 ppm.
- (6) Dissolved Oxygen
  The monthly average of all samples shall show a
  DO content of not less than 6.5 ppm. No one
  sample shall show a DO content of not less than
  5.0 ppm.

(7) Other Conditions Other conditions which shall prevail shall be the same as those enumerated for Class A waters.

### Class C Waters

Waters in Class C are suitable for domestic water supplies, with complete treatment, also for industrial process water, navigation, and similar uses. The minimum conditions which shall prevail for these waters shall be as follows:

(1) Coliform Bacteria

The monthly average of all samples shall show the most probable number of coliform bacteria varying between the limits of 500 to 5,000 per 100 ml.

(2) Color and Turbidity Color and Turbidity may be allowed which can be removed by standard equipment and filtration practices.

(3) pH
The acidity or alkalinity of the waters shall vary between the limits of 6.0 and 8.5.

(4) 5-Day Biochemical Oxygen Demand
The 5-Day 20°C BOD shall show a monthly average of all samples of not more than 2.0 ppm.
The maximum observation on any one sample shall not be more than 4.0 ppm.

(5) Dissolved Oxygen The monthly average of all samples for DO shall not be less than 6.5 ppm, and no single sample shall show a DO content of less than 5.0 ppm.

(6) Other Conditions
Other conditions for this class of water shall be
the same as those for Class A waters.

### Class D Waters

The waters in Class D shall have a satisfactory general sanitary condition and shall not create a nuisance in the surrounding area. The waters can be used for navigation, as cooling water, and for similar purposes. They will in no way affect public health unless used for domestic water supplies or for swimming purposes.

(1) pH
The acidity or alkalinity of the waters shall vary between the limits of 6.0 and 8.5

(2) 5-Day Biochemical Oxygen Demand The monthly average of all samples for 5-Day 20°C BOD shall not be more than 3.0 ppm. The maximum observation of a single sample shall not be more than 5.0 ppm.

(3) Dissolved Oxygen

The monthly average of all samples for DO shall not be less than 4.0 ppm. The minimum daily average of all samples shall not be less than 3.0 ppm nor shall the observation on any one sample be less than 2.0 ppm.

(4) Other Conditions The waters shall contain no toxic substances such as oils, tars, or free acid at any time. There shall be no floating solids or debris except for those from natural sources. If unpreventable, slight localized sludge deposits will be permitted. No offensive odors shall be given off by the waters at any time.

NOTE: These criteria are to be used only in conjunction with a sanitary survey as a guide in determining the minimum water quality for the various classes of water use listed. It is intended that these criteria should apply to conditions which are expected to prevail for the major part of the time.

In the use of the criteria given on the previous pages, consideration should be given to the following:

- 1. They are to be used as a guide to the purity of water in a stream or portion thereof, and only then in connection with a sanitary survey of the area, taking into consideration those factors which may affect materially the interpretation of laboratory results.
- 2. In the enforcement of pollution control it may prove simpler for each state health department, or other pollution control agency, to set up standards for waste discharges which will provide a water quality in the stream equal to that indicated by the Commission maps.
- 3. One map shows existing conditions which the Commission believes to exist on the basis of available information. The other map, showing recommended conditions, represents the first step in the improvement of water quality proposed to the signatory bodies which will be followed by succeeding steps. As better information becomes available to the Commission, and as time and conditions warrant, changes in the classification of areas shown on both maps will be recommended.
- 4. As the criteria and maps showing existing conditions and recommended first step in a progressive stream improvement program are used, and additional information on the condition of the water in the streams becomes available, and as progress in the treatment of wastes advances, the Commission will from time to time review both the criteria and maps and will recommend changes which seem to be desirable. In this respect, it is realized that many points of their practical application, such as sampling in the field, handling, and test procedures, may require standardization. Many of these problems cannot be foreseen now and the solution to many others can be carried out by the state agencies themselves.
- 5. Examination and tests of water necessary to determine quality shall be made in accordance with the procedures contained in the American Public Health Association's latest edition of "Standard Methods for the Examination of Water and Sewage."

In preparing the criteria, the Commission found that they could not prepare rigid standards since the analysis of stream waters involves highly technical sampling procedures. Wide variations result from natural river conditions, solar radiation, tidal variation, and variations in river cross-section. In time the Commission hopes that information will be available for more definite recommendations on sampling procedures.

## APPENDIX P

# GUIDE FOR WATER POLLUTION CONTROL ACTIVITIES MISSOURI DRAINAGE BASIN

Reaffirmed January 7, 1954, Engineering Section, Missouri Basin Health Council

Subject to (a) such higher objectives as may be desired by any State and (b) such other modification as may be deemed necessary, after appropriate investigation by the State Water Pollution Control Agency concerned, the Engineering Section, Missouri Basin Health Council recommends the following for consideration by the member states as a guide for water pollution control activities in the Missouri Drainage Basin:

- 1. Toxic substances including metallic ions, phenolic compounds, oils, alkalies, and acids should be virtually eliminated from sewage effluents.
- 2. Removal of settleable and floating solids to prevent sludge banks, floating materials, and nuisance conditions should be required as the minimum acceptable treatment.
- 3. For industrial wastes similar in nature to municipal wastes, treatment should be based on the same premise as recommended for municipalities. For industrial wastes not comparable to municipal wastes, treatment should be provided as necessary to prevent deterioration of water quality for beneficial uses in the receiving stream.
- 4. Additional treatment over that specified in item 2 above should be provided as necessary to protect downstream water uses. Quality objectives for certain water uses are:
  - (a) For water serving as a source of domestic supply, raw water bacteriological quality should conform to that recommended in "Manual of Recommended Water Sanitation Practices, 1946, Public Health Bulletin No. 296," pages 11-13.
  - (b) For bathing or swimming water, monthly arithmetical average "most probable number" of coliform organisms should not exceed 1,000 per 100 ml during any month of the recreational season; nor exceed this number in more than

20 percent of the samples examined during any such month; nor exceed 2,400 per 100 ml on any day. For non-bathing or non-swimming waters, the monthly arithmetical average "most probable number" of coliform organisms should not exceed 5,000 per 100 ml in any month of the recreational season nor should not exceed this number in more than 20 percent of the samples examined during any such month.

- (c) For fish and aquatic life a minimum oxygen concentration of 5.0 ppm is desirable in waters otherwise offering suitable fishery habitat, with 6.0 ppm for trout streams.
- (d) For bacteriological quality of irrigation water:
  - (1) Sewage used for irrigation of forage crops should be given treatment insuring a consistent reduction in coliform bacteria of not less than 90 percent.
  - (2) Sewage used for irrigation of human food crops should be given treatment insuring a consistent reduction (a) in suspended solids of not less than 75%, (b) in 5-day 20° C BOD of not less than 75% and (c) in coliform bacteria of not less than 98%, unless discharged into a stream where the volume of dilution water, available during the low flow periods during which irrigation diversions may occur, is at least 10 times greater than the anticipated maximum daily volume of sewage, in which case a bacterial reduction of 90 percent may be acceptable.

Provided, however, that where the time of passage from plant discharge to irrigation diversion is such as to permit the normal death rate of bacteria as evidenced by the die-away curve to provide equivalent bacterial reduction, the requirement of (1) and (2) above may be appropriately modified.

## APPENDIX Q

# U. S. PUBLIC HEALTH SERVICE RECOMMENDED SANITARY REQUIREMENTS FOR WATER TREATMENT SYSTEMS

### A. GENERAL REQUIREMENTS

1. Extent of Treatment

For purposes of classification with respect to treatment requirements, waters acceptable for treatment may be divided into four groups. For practical purposes coliform bacterial content of the raw water can be expressed either in terms of "most probable numbers" or "Phelps Index", without changing the limiting coliform averages indicated for the various water groups. (See Public Health Reports Reprint No. 1170 (2), July 15, 1927, pp. 7-11 and 18-19).

Group I. Water Requiring No Treatment. This group is limited to underground waters not subject to any possibility of contamination, and meeting, in all respects, the requirements of the Public Health Service Drinking Water Standards, as shown by satisfactory, regular, and frequent sanitary inspections and labora-

Group II. Waters Requiring Simple Chlorination, or Its Equivalent. This group includes both underground and surface waters subject to a low degree of contamination, and meeting the requirements of the Public Health Service Drinking Water Standards in all respects except as to coliform bacterial content, which should average

not more than 50 per 100 ml in any month.

Group III. Waters Requiring Complete Rapid-Sand Filtration Treatment, or Its Equivalent, Together With Continuous Postchlorination. This group includes all waters requiring filtration treatment for turbidity and color removal; waters of high or variable chlorine demand; and waters polluted by sewage to such an extent as to be inadmissible to groups I and II, but containing numbers of coliform bacteria averaging not more than 5,000 per 100 ml in any one month and exceeding this number in not more than 20 percent of the samples examined in any one month.

Group IV. Waters Requiring Auxiliary Treatment in Addition to Complete Filtration Treatment and Postchlorination. This group includes waters meeting the requirements of group III with respect to the limiting monthly average coliform numbers, but showing numbers of coliform bacteria exceeding 5,000 per 100 ml in more than 20 percent of the samples examined during any one month and not exceeding 20,000 per 100 ml in more than 5 percent of the samples examined during any one month.

Note. "Auxiliary treatment" as used here is presedimentation or prechlorination, or their equivalents, either separately or combined, as may be necessary. Long-time storage, for periods of 30 days or more, represents a permanent and reliable safeguard which in many cases would provide something more than an effective substitute for one or both of the two other methods indicated.

Remarks. (a) Although group I conceivably might include exceptional surface waters free of any possible con-

tamination and further protected by storage, it hardly may be considered as a safe general rule to admit any surface water to a public supply without chlorination as a minimum safeguarding treatment, in view of the present increased hazards of chance contamination resulting from the extension of recreational and migratory travel

to many hitherto inaccessible places.

- (b) The limiting monthly average coliform numbers stated for waters of groups II and III are intended as guides rather than inflexible rules, though they are based on extensive observational data fairly representing present water treatment practice in this country. Consideration should be given to all aspects of the character and quality of the raw water; its range and suddenness of fluctuation in concentration of constituents which would influence the efficiency of the water-treatment process; the size and complexity of the water-treatment plant, and the type of supervision provided, in addition to the bacteriological characteristics of the raw water. Certain recent improvements in water chlorination and its control offer promise of increasing the margin of safety of waterpurification efficiency, with respect to bacterial removal. These improvements have not become fully incorporated into general practice throughout the country, and they should not be regarded as warranting any relaxation in the requirements for raw-water quality which experience and present standards of safety indicate as being necessary for providing adequate protection to sources of water supply in general.
- (c) For waters of group IV, which differ from those of group III only in respect to variability, auxiliary treatment is intended mainly as a factor of safety in controlling variations in coliform numbers within the range of 5,000 to 20,000 bacteria per 100 ml. The larger of these two figures represents the maximum safe limit for prechlorination, or its equivalent, in addition to filtration treatment and postchlorination.
- (d) Waters failing to meet the requirements of groups I, II, or IV are considered as unsuitable for use as a source of water supply, unless they can be brought into conformance with these requirements by means of prolonged preliminary storage, or some other measure of equal permanence and reliability.

# 2. Other Raw Water Requirements

Waters acceptable for treatment, in addition to meeting the aforesaid bacterial requirements, should not contain any toxic, taste-producing, or otherwise harmful substances, or organisms, not readily and completely removable by ordinary water treatment. Raw waters should be free of excessive amounts of acid, microscopic organisms, and organic matters causing any interference with the normal operation and efficiency of water-treatment processes.

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