SELENIUM IN CALIFORNIA VOLUME 1

History, Chemistry, Biology, Uses, Management

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Selenium in California
Volume 1

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FOREWORD

This report was prepared under contract for the California State Water Resources Control Board (SWRCB). It is intended to provide a compendium of the present knowledge on selenium and its effects on the environment. However, there are two aspects of the report that need clarification.

First, the report begins with a discussion of selenium from the perspective of the available literature. The literature is replete with the nutrient deficiency concerns of selenium. Selenium toxicity, expecially in the aquatic environment, is a relatively recent discovery. The SWRCB is concerned that the aquatic toxicity aspects of selenium be understood and controlled in order to protect the beneficial uses of the waters of the State. The SWRCB must also emphasize that aquatic toxicity does not necessarily translate to human toxicity, nor is there any evidence of human teratogenicity with selenium. Also, to date there is no evidence of human toxicity from environmental exposure to selenium in California. However, investigations are continuing.

Second, the report indicates uncertainty regarding the effectiveness of subsurface agricultural drainage flow reduction on reducing the total selenium load discharged to surface waters. This conclusion was based on the author's conservative review of the limited published information available in 1988. Since that time, numerous studies have been completed which show that drainage flow reduction is an effective management tool to reduce selenium discharge loads. Generally, the selenium picked up by subsurface drainage systems has been leached from soils and is now in solution in the ground water that growers need to drain in order to maintain crop

productivity. Reducing deep percolation losses by more efficient agricultural practices tends to lower the ground water table and reduces the hydraulic pressures which drive the selenium upward into the subsurface drainage systems. Therefore, reducing deep percolation results in a direct reduction in selenium loads discharged from agricultural subsurface drainage systems.

Based on this new information, the San Joaquin Valley Drainage Program is recommending that the reduction of agricultural subsurface drainage flows through more efficient agricultural practices is the first essential step in controlling selenium discharges from seleniforous areas. Drainage flow reduction is also an effective tool to be used in concert with other management strategies, e.g., treatment or pond disposal, if the reduction in selenium load achievable through flow reductions are not sufficient to meet water quality objectives.

With these clarifications, we hope you will find this document as a useful reference document on selenium.

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Executive summary

Selenium in California: Volume 1

Selenium plays an important role in biology, especially in animal nutrition. It is also used in many commercial applications. Selenium occurs naturally in the environment in amounts which occasionally cause nutritional deficiency or toxicity problems in livestock and wildlife and even more rarely in humans. It is distinguished from most other biologically active elements by the narrow range in concentration between adequate and excess (Chapter 1, 2, 3).

Selenium is an essential nutrient

The benefits of selenium for nutrition and health were not discovered until the late 1950's. Selenium's essential role in animal and human nutrition was established in more detail in the 1960's. Subsequent research has revealed more about the biochemical roles selenium plays and the importance of selenium for animal and human health, but the complex, interactive role selenium plays in health and disease has frustrated scientists' attempts to completely understand its function (see Chapter 3).

Subclinical selenium malnutrition and attendant health risks are poorly understood and probably more likely to occur than acute effects. Adequate selenium in the diet apparently provides protection against various types of cancer and other diseases.

Selenium deficiency diseases are probably rare in California residents, but they might occur among homesteaders who rely on home-grown food and fish and game in the selenium-deficient areas of California, or among individuals in special at-risk categories, including premature infants and individuals on total parenteral nutrition.

Selenium supplements for humans are now used in several areas of the world. Selenium supplements have been recommended by several authorities in the U.S. but consensus about the selenium requirement for optimal health is still lacking. More details on selenium and human health will be included in Volume 2 of this report.

No evidence of health risk in California

Selenium poisoning in humans is very rare, but has been reported in China and the western U.S. (not California) from selenium in the diet, industrial exposure, contaminated food, and from errors in mixing dietary supplements (Chapter 3). Researchers in California have found elevated selenium levels in some fish and game, food, and water. The State Department of Health Services has issued advisories to limit consumption of fish and waterfowl in several areas where elevated selenium levels have been detected in some samples. Research has also suggested that high levels of selenium in the soil or irrigation water can lead to increased selenium levels in crops. However, extensive surveys have uncovered

few commodities with elevated selenium levels, and even these higher levels are considered safe. The State Department of Health Services has stated that selenium exposure poses little or no risk to the residents of California but recommended further research, continued analysis, and evaluation of public health impacts. People in selenium-deficient areas may benefit from consumption of California foods with slightly higher than average selenium levels.

Uses of selenium

Selenium is used in a number of commercial and industrial products including photocopiers, glass, plastics, rubber and photocells, and feed supplements (Chapter 5).

There is no question of the potential hazard from careless use of selenium in industry or in feed and food production. It is equally clear that judicious use of the selenium in trace quantities is essential for nutritionally complete feeds and food products.

Environmental problems

Environmental problems involving both selenium-deficient livestock and wildlife and the more widely publicized selenium poisoning, e.g., at Kesterson National Wildlife Refuge have occurred in California.

Selenium deficiency is widespread among livestock in California and recent studies suggest that it may be responsible for the decline in deer populations in some areas. Additional research is needed to confirm these findings and identify other areas where selenium deficiency may be a problem.

Human activity has contributed to selenium release and concentration in some areas. As a result selenium poisoning of fish and aquatic birds has occurred. Selenium enters the state's water resources primarily as a result of agricultural irrigation practices and associated cropland drainage systems (Chapter 4). Selenium in drainage water from areas with seleniferous soils and groundwater is concentrated by biological processes. This can lead to high levels of selenium in birds and fish which can cause reproductive failure and death (Chapter 3).

In soil and water, organisms such as bacteria and fungi can increase or decrease the availability and toxicity of selenium and selenium compounds. Microorganisms can also volatilize selenium and remove it from the soil and water (Chapter 3).

Further research is needed to quantify the amounts and forms of selenium in soils, vegetation, and aquatic systems, their relationship to human activity, and their behavior over time.

Mitigating selenium problems

There are three basic options for dealing with areas with elevated and potentially hazardous selenium levels--treatment , disposal, and source reduction (Chapter 6).

A variety of chemical and biological treatments have been proposed to remove

selenium from water and soil but none of the current candidates offers any clear advantage and most are expensive and unproven at the field scale.

Disposal of selenium-enriched waters and soil has also been explored. Original plans for Delta or ocean disposal have not been found acceptable at this time. Deep-well injection is being evaluated but is not risk-free.

Source reduction is most likely to be cost-effective. Selenium release can be controlled by changing irrigation methods and cropping systems. While the volume of drainage water can be effectively reduced, it is uncertain whether the total selenium load entering the state's water can be reduced substantially. If the load remains similar and the concentration increases, some localized problems may worsen.

A combination of management and treatment strategies may be needed to satisfy the many environmental, economic, wildlife, and human health concerns that resource managers currently face.

"Complete technical information to make sound water management decisions is lacking, and extensive research programs have been initiated by Federal agencies, state agencies, and the University of California. Unfortunately, critical decisions must be made before research findings are complete, and research alone is not likely to provide a solution to the problem. Indeed, a solution free of risk, significant and costly trade-offs, and deep seated value judgements is not probable. As such, the future will ultimately be decided in the political arena" Letey et al., 1986.

Introduction

Our purpose in preparing this volume has been to assemble an extensive review of selenium in California. It follows an earlier State Water Resources Control Board volume on Mercury in California (1973) and is intended to provide a ready reference document for decision-makers, managers, and researchers who are working on projects that may involve selenium in California.

We have attempted to summarize the uses, behavior, benefits and problems associated with selenium in California. The enormous scope of this project has forced us to make many decisions to limit coverage and to emphasize what appeared most important.

A second volume will provide more detailed information on specific topics that this work suggested were particularly important, including a more complete discussion of selenium and human health; selenium deficiency and toxicity in livestock and wildlife; the systems approach to environmental problems; the management of agricultural land to minimize selenium releases; and an update on selenium treatment methodology.

Acknowledgements

We would like to thank the many scientists and individuals within industry, state, local, and federal agencies and institutions who so freely shared their time and research with us.

We would also like to thank the information specialists within the U.C. library system who have been very helpful with both computer searches and document retrieval, with special acknowledgement to Myra Russell at U.C. Riverside's BioAgricultural library for her assistance.

We also appreciate the support and reviews provided by Dale Watkins and the members of the State Water Resources Control Board Division of Water Rights .

The organizers of the various conferences and programs on selenium over the last few years also deserve special credit for their work. This type of endeavor is rarely acknowledged and poorly rewarded yet among the most important for improving integration and interdisciplinary consideration on this type of complex environmental problem.

And a final debt is owed to the many scientists, often unsung and unheralded, whose research has provided the basic information that is included in this report.

Chapter 1. Historical Review

"All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy."
Parcelus 1493-1541

A. Introduction

Selenium was perhaps first observed by Arnold de Villanova in the 14th Century. In his writings he described the vaporization of sulfur and a reddish deposit, sulphur rubeum, which appeared on the container walls (Mellor, 1960). Selenium was discovered and described scientifically in 1817 by Swedish chemists Jon J. Berzelius and J. G. Gahn, studying the residues of a pyrite refining operation in Gripsholm, Sweden (Weast, 1970; Lindqvist, 1984). The atomic weight, 79, was determined by Eilhard Mitscherlich, a German chemist. Using his own law of isomorphism, he correctly surmised that sulfate and selenate of potassium have the same atomic ratio and by comparing the weight of the two compounds he arrived at the correct atomic weight for selenium (Ihde, 1964).

Native selenium was described by A. M. del Rio in 1828. Its use in industry and science was heralded by Willoughby Smith's discovery in 1873 that selenium's electrical conductivity varied with light intensity (Lansche, 1967). Since then, selenium has become important in many commercial products, including photocopiers, batteries, and electronic products; and in industrial processes, including glass and plastic production and alloying metals.

Selenium, like many other elements, is both an essential nutrient and a potential poison. It is distinguished from other biologically active elements by the narrow range between these opposites. Very few problems with selenium toxicity or deficiency have been observed in people in California. However, environmental problems involving both selenium deficiency of livestock and wildlife and the more widely publicized selenium poisoning, e.g., at Kesterson National Wildlife Refuge (Ohlendorf et al., 1984) have occurred.

Long before scientific analysis identified selenium as the poison, selenium toxicity had been observed. It affected Marco Polo's horses on China's Silk Road in the 13th Century: "*It is a fact that when they take that road they cannot venture among the mountains with any beast of burden excepting those accustomed to the country, on account of a poisonous plant growing there, which if eaten by them has the effect of causing the hoofs of the animals to drop off*" (Komroff, 1926).

In 1560 a Columbian priest described corn and other vegetables that were poisonous (apparently from elevated selenium content) and caused hair loss and fetal malformation (Benavides and Mojica, 1959). Selenium poisoning of animals near Irapuato, Mexico was observed in the 1650's. The disease, known locally as Soliman disease, was erroneously thought to be caused by mercury (Anderson et al., 1961). The toxicity of the fruit of the Monkey Pod tree (*Lecythis ollaria*) from South America was reported in 1763 by

Jacquin (Jacquin, 1763); this was later found to be caused by selenium accumulation in the pods (Kerdel-Vegas, 1966).

Selenium poisoning has also been locally important in the Western United States. In the 1850's, a disease of horses (now known to be caused by selenium) was described by an army veterinarian (Madison, 1860). The symptoms of selenium poisoning in animals were described at the Kansas Agricultural Experiment Station in 1891 and at the Wyoming Agricultural Experiment Station in 1893, although the causative agent was not known (Moxon and Rhian, 1943). The worst case of apparent selenium livestock poisoning known occurred in 1907-1908 near Medicine Bow, Wyoming when over 15,000 sheep died (Galston, 1964).

The toxicity of selenium was first established in animals by Japha (1842). Additional cases of selenium poisoning in Europe were described late in the century (Czapek and Weil, 1893). Selenium poisoning of humans apparently occurred in England from contaminated beer in 1901 (Tunnicliffe and Rosenheim, 1901).

In the U.S., work on selenium related problems was undertaken at the Nebraska Agricultural Experiment Station in 1904 (Peters, 1904). In 1910 the South Dakota Agricultural Experiment Station suggested the need for cooperative research on alkali (selenium) poisoning (Anderson et al., 1961). This research was begun in 1931, when an interdisciplinary team composed of K.W. Franke, chemist, T.D. Rice, soil scientist, A.G. Johnson, plant pathologist, and H.W. Schoening, veterinarian, began a preliminary field survey (Franke et al., 1934).

A U.S. Department of Agriculture conference in Washington, D.C. on alkali poisoning was also held in 1931. This meeting set an agenda for future research and led to a presidential order in 1933 authorizing $35,000 for research on alkali disease within the Department of Agriculture. Appropriations for this work continued until World War II (Anderson et al., 1961).

Selenium-based pesticides were developed by Gnadinger in the 1930's (Gnadinger, 1933). At the same time, Nelson and associates (1933) warned against the use of selenium in insecticides because of possible problems from bioconcentration and potential toxicity. Selenium based pesticides were primarily used on ornamental plants, although they were used on some food crops (Smith, 1961). The use of selenium-based pesticides on food crops was largely discontinued after Hoskin (1938) found that selenium accumulates in grapes and citrus.

Although C.A. Cameron published a note on selenium absorption by plants in 1880 (Cameron, 1880), more detailed research on the effects of selenium on plants did not begin until the 1920's when Stoklasa (1922) found that selenite was more toxic for barley plants than selenate. The first detection of selenium in plants was reported by the French chemist M. F. Taboury in 1932 (Taboury, 1932). The Wyoming Agricultural Experiment Station published two reports on selenium in

vegetation and soils in the mid-30's (Beath et al., 1934, 1935).

The first greenhouse studies of selenium uptake by plants and differences in accumulation rates were undertaken in 1935 (Hurd-Karrar, 1935). A study of selenium concentrations in wheat from several areas of the world demonstrated the large ranges which could occur (Robinson, 1936). A more detailed review of foods from many countries in the early 1970's revealed even larger differences in selenium levels (Weisner et al., 1974).

In response to public recognition of selenium-related health problems and livestock poisoning, the Federal Resettlement Administration purchased more than 115,000 acres of seleniferous lands in South Dakota, helped resettle the residents, and established a management program to reduce the risk of future selenium problems in that area (Anderson et al., 1961).

In the late 1930's H.G. Byers and his associates undertook extensive studies of selenium levels in the soils of North America (Byers, 1935, 1936, 1937; Byers et al., 1936, 1938; Byers and Lakin, 1939). A U.S. Department of Agriculture study in 1939 warned of potential problems from selenium in the soils of the western San Joaquin Valley (Lakin and Byers, 1941). Ten years later, U.S. Geological Survey scientist David Love proposed a major research program on selenium and other potentially toxic elements. Love predicted that millions of dollars would be lost if the interactions between soil, geology, and irrigation were not better understood and recommended an interdisciplinary research program (Harris, 1987).

The first major summary of selenium occurrence in soils was published by Swaine (1955). Strategies to prevent selenium poisoning by livestock were described two years later by Beeson (1957). Animal poisoning from selenium has continued to occur on an isolated basis since the first reports in the 1860's (Trelease and Beath, 1949; Harris, 1986).

Until the well-publicized poisoning of wildlife at the Kesterson Wildlife Refuge in the San Joaquin Valley occurred in the 1980's (Harris, 1986), there was little research on selenium problems in California. Large numbers of deformed chicks and embryos were found at Kesterson Reservoir in 1983 (Ohlendorf et al., 1984). This led to the first symposium on selenium held at U.C. Berkeley in December, 1983. The University of California's task force on salinity and drainage in the San Joaquin Valley (including selenium problems) held its first meeting in 1984. This was followed by a concerted effort by State and Federal agencies to understand the nature and distribution of selenium problems in California (Deverel et al., 1984; Presser and Barnes, 1984,1985; Letey et al., 1986; Wiggett and Alfors, 1986). By early 1987, more than one hundred and fifty studies were underway with a total of 23 million dollars committed for research (Port, 1987). The interest and investment in selenium research led to special

sections on selenium at both the American Society of Agronomy and the American Geophysical Union meetings in 1986.

The most serious effects of selenium in California appear to be those involving fish, birds, and wildlife. In 1986 the National Research Council's advisory committee on San Joaquin Valley agricultural drainage problems recommended adding University of California experts in ecology, fish and wildlife biology, law, and chemical and civil engineering to the program (National Research Council [NRC], 1986).

Some concern has also been raised over human exposure to selenium in California from drinking water or food. Selenium poisoning in humans is rare, but has been reported in China (Yang et al., 1983) and the western U.S. (Anderson et al., 1961; Harris, 1986) from selenium in the diet, industrial exposure (Glover et al., 1979), contaminated food (Tunnicliffe and Rosenheim, 1901), and from errors in mixing dietary supplements (Helslzour, 1985; Fan, 1986).

The research effort in California has revealed elevated selenium levels in fish and game, food, and water in some locations. Advisories were issued by the State Department of Health Services to limit consumption of fish in western Merced and Stanislaus counties in 1985, and fish from the Salton Sea and certain diving ducks in Suisun and South San Francisco bays (Fan, 1987a).

In 1986, researchers found high selenium levels in celery and cauliflower grown in the Arroyo Grande Valley of San Luis Obispo County (Oster et al., 1987). Other surveys have shown few other commodities or locations with elevated selenium levels (Burau et al, 1987; Fan, 1987b).

The State Department of Health Services reported that it was likely that selenium exposure posed little or no risk to the residents of California, but recommended further research, continued analysis, and evaluation of public health impacts (Fan, 1987b). Research on the health risk of selenium in California was underway in 1987 as part of the San Joaquin Valley Drainage Project research effort.

The benefits of selenium for nutrition and health were not discovered until the late 1950's (Schwarz and Foltz, 1957). Selenium's essential role in animal and human nutrition was established in more detail in the 1960's (Schwarz, 1965). Subsequent research has revealed more about the biochemical roles of selenium (Rotruck et al., 1972, 1973), and the importance of selenium for animal and human health (see Chapter 3 and Volume 2). The complex, interactive role selenium plays in human health and disease has frustrated scientists' attempts to determine its function. Selenium supplements for animals and people are now used in several areas of the world.

Cases of clinical selenium deficiency have been identified in China, Finland, and elsewhere (Levander, 1982; Gissel-Nielson et al., 1984). Deficiency diseases are probably rare in California, although they might occur among homesteaders who rely on homegrown food and fish and game in the selenium-deficient areas of California, or among

individuals in special at-risk categories, including premature infants, children undergoing diet therapy, and people on total parenteral nutrition (Levander, 1982).

Subclinical selenium malnutrition and attendant health risks are poorly understood and probably more likely to occur than acute effects. Adequate selenium in the diet appears to provide some protection against various types of cancer and infection (Robinson et al., 1979; Salonen et al., 1984; Combs and Combs, 1986). Although selenium supplements have been recommended (Passwater, 1980), consensus about the selenium requirement for optimal health is lacking. It will continue to be a matter of debate for many years because of the difficulties involved in human epidemiology (Keen, 1987). More details on the interrelationship between selenium and human health are included in Volume 2 of this report.

Recent research has identified selenium deficiency diseases and problems in both domestic livestock and wildlife in California (Jessup, 1987; Nelson and Miller, 1987; Norman, 1987; Smith, 1987). Long-term studies of deer herds in Northern California suggest that selenium levels in the deer are declining, although the magnitude of this change and the reasons for it have not been identified (Smith, 1987).

Selenium's dual role as an essential nutrient and an environmental toxin will provide a research challenge for years to come. The complexity of the environment, the inter-relatedness of various parts of the environment, the often far-reaching impacts of seemingly simple actions, and the very limited information available on selenium's biogeochemical cycles and effects on people, plants, and other organisms must be better understood.

The words of the National Research Council (1976) remain relevant today:

"Our relative ignorance concerning the ecologic fate of selenium prevents us from making absolute statements regarding its fate in the ecosphere. Although the broad qualitative pathways of the natural cycling of selenium appear to be well outlined, we know much less about the quantitative aspects of such cycling. A similar state of affairs exists in the case of industrial cycling and industrial emissions."

An abbreviated chronology of events involving Kesterson Reservoir

The problems at Kesterson Reservoir have been the catalyst for much of the work on selenium in California. The following chronology presents some of the highlights from the history of this reservoir.

1941

A U.S. Department of Agriculture study warns of possible problems from trace elements (selenium) in the western San Joaquin Valley.

1942

The Westlands Landowners Association is formed to lobby for water supply for the west side of the San Joaquin Valley.

1949

David Love recommends an interdisciplinary research program on selenium and irrigation in the Western U.S.

Valleywide drainage and salinity problems acknowledged in Bureau of Reclamation report to Congress.

1960

The San Luis Unit is authorized by Congress, including provision for a master drain to the San Joaquin Delta.

1966

Congress requires an agreement between the U.S. and California regarding the San Luis Drain discharge point.

1967

The State of California abandons its role in the Valley Master Drain.

1968

The Bureau of Reclamation begins work on the San Luis Drain and begins acquiring land for a Kesterson Reservoir.

1972

Kesterson Reservoir begins collecting irrigation runoff and is made a part of the National Wildlife Refuge System.

1976

The Westlands drainage collector system is constructed to serve the first 42,000 acres.

1979

San Joaquin Interagency Drainage Program recommends discharge of agricultural drainage water at Chipps Island, west of the Delta.

1981

Subsurface drainage from the Westlands Water District begins arriving at Kesterson Reservoir. The State Water Resources Control Board [SWRCB] requests an environmental impact report from the U.S. Bureau of Reclamation on the effects of agricultural waste discharge from the San Luis Drain. The manager of San Luis National Wildlife Refuge reports dead and dying vegetation and other abnormalities.

1982

Fish samples taken at Kesterson show high selenium levels. Central Valley Regional Water Quality Control Board [CVRWQCB] letter to Bureau of Reclamation asks for filing of a report of waste discharge for Kesterson Reservoir.

1983

Large numbers of deformed chicks and embryos attributed to selenium toxicosis are found at Kesterson. The U.S. Geological Survey studies confirm the presence of high levels of selenium in Kesterson Ponds.

1984

Jim and Karen Claus petition the Regional Water Quality Control Board to regulate or close down the Kesterson Reservoir as a menace to public health. The matter is referred to the State Board which holds an initial hearing in October. Two State-Federal teams are set up to deal with Kesterson and San Joaquin Valley drainage problems. The U.S. General Accounting Office includes Kesterson on a list of neglected federal toxic dump sites.

1985

Congressional hearings by the House Subcommittee on Water and Power Resources are held at Los Banos. The SWRCB orders the Bureau of Reclamation to produce a cleanup plan for Kesterson Reservoir. The U.S. Dept of Interior announces plans for immediate closure of Kesterson Reservoir and the San Luis Drain and termination of irrigation deliveries, subsequently changed to an end to drainage in 1986.

April, 1986

The Bureau of Reclamation releases a draft environmental impact statement on the options for cleaning up Kesterson Reservoir. Their preferred option is to immobilize the selenium by flooding the ponds with fresh, selenium-free water.

May, 1986

Westlands Water District finishes plugging drains to end drainage to Kesterson Reservoir.

December, 1986

The Bureau of Reclamation submits their "wet-flex" treatment plan for Kesterson Reservoir to the State Water Resources Control Board.

March, 1987

The SWRCB staff recommends on-site disposal in a sealed waste dump.

August, 1987

The CVRWQCB approves the details of the cleanup and on-site burial option.

March, 1988

Reps. Bevill and Rogers letters to Interior Secretary Hodel asking for change in burial plan due to encouraging results of biological treatments.

(U.S. Bureau of Reclamation, 1949; Office of the Inspector General, 1985; Letey et al., 1986; Bay Inst., 1986; Tanji et al., 1986; Harris, 1986, 1987; Associated Press, 1987; SWRCBTC, 1987; Jacobs, 1987, Benson, 1988.)

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Chapter 2. Basic Physical and Chemical Properties of Selenium

A. Introduction

Selenium [Se], atomic number 34, is a member of the oxygen family, Group VI A, Period 4, of the periodic table. It displays many of the properties of its neighbors in Group VI, sulfur [S] Period 3, atomic #16, and tellurium [Te] Period 5, atomic #52. The average atomic weight of selenium is 78.96.

The electronic structure of the selenium atom is [Ar] $3d^{10}4s^24p^4$ (NRC, 1976). The atomic radius is 1.40Å and the covalent radius is 1.16Å (NRC, 1976). The positive oxidation states of selenium are +4 and +6, with a few chemically unstable at +2. Selenium is found in the -2 state in selenides (Louderback, 1975).

Six stable isotopes of selenium occur naturally, including: ^{74}Se 0.87%, ^{76}Se 9.02%, ^{77}Se 7.5%, ^{78}Se 23.52%, ^{80}Se 49.82%, and ^{82}Se 9.19% (Elkins and Margrave, 1954; Day, 1963). More than two dozen radioactive isotopes have been produced (Combs and Combs, 1986). The more common isotopes decay by positron emission (mass numbers 70, 71, 73, 73m); orbital electron capture (mass numbers 72, 75); isomeric transition (mass numbers 77m, 79m, 81m); and negative beta emission (mass numbers 79, 83m, 83-87) (Weast and Selby, 1967). More information on the physics of selenium can be found in Cooper (1969).

^{75}Se, with a relatively long half-life of about 120 days, has been most useful in biological studies (Rosenfeld and Beath, 1964; Fujimori and Oae, 1986). The unstable ^{77m}Se, half-life 17.5 seconds, which can be created by neutron activation has also proven of value for studies of selenium in biological materials (McKown and Morris, 1977, 1978).

B. Elemental selenium

Elemental selenium, like elemental sulfur, exhibits extensive allotrophy, with five states recognized at room temperature. These allotropes include metallic selenium, vitreous black selenium, amorphous red selenium, and two forms of crystalline red selenium.

1. Metallic selenium

Metallic selenium is the most stable form of this element. The structure is hexagonal with an essentially cubic lattice in which the selenium atoms are displaced alternately in opposite directions. Each selenium atom has two near neighbors in the same chain at 2.32 Å and four more distant neighbors at 3.46 Å. The resulting pattern is a parallel array of infinite spiral chains (Bagnall, 1966).

Metallic selenium is the only form that conducts electricity and the conductivity is related to light intensity. Conductivity may increase 8-25 times in light (Stone, 1966). This property is responsible for two of the common uses of selenium--photocopying machines and photocells. Electrical conductivity is very sensitive to impurities and manufacturers require initial purity exceeding 99.99 percent (Crystal, 1973). Selenium's electrical

conductivity also varies with pressure. Selenium exhibits photovoltaic properties and is used in some photovoltaic cells (Weast, 1979). Selenium may prove useful in amorphous photovoltaic cells (Ovshinksy, 1980) and in photoelectrochemical solar cells (Clark, 1980).

Selenium metal melts at 217°C with the molten element appearing black in bulk and reddish brown in thin films. Unlike sulfur, increasing the temperature of selenium reduces the viscosity as the mean chain length decreases. The boiling point is 685°C (Weast and Selby, 1967).

At room temperature, selenium is thought to be in the Se_8 form, while at 200°C both Se_6 and Se_8 molecules are present (Lansche, 1967). Between 550°C and 900°C Se_2 and Se_6 coexist, with Se_2 the dominant form above 2,000°C (Stone, 1966; Lansche, 1967).

2. Black selenium

Black selenium is made by rapidly cooling molten selenium. It is probably a cyclic polymer with rings of as many as 1,000 atoms (Bagnall, 1966). Black selenium softens at 50°C and is rapidly transformed to elemental selenium at 180-190°C.

3. Red amorphous selenium

Red amorphous selenium can be obtained by reducing selenous acid in aqueous solution with a reducing agent, such as sulfur dioxide, condensing selenium vapor on a cold surface, or treating potassium selenocyanate with hydrochloric acid. The atomic structure is similar to metallic selenium, with a slight increase in interatomic distance and some deformation of structure.

4. Red Crystalline Selenium

Two forms of red crystalline selenium are known. Alpha-monoclinic selenium is most easily obtained by slow evaporation of selenium dissolved in carbon disulfide. Beta-monoclinic selenium is obtained by rapid evaporation of selenium in carbon disulfide. The energy states of the two forms are nearly identical; they apparently differ only in the orientation of the rings. The unit cells of each contain four Se_8 molecules in puckered non-planar rings (Bagnall, 1966).

C. Inorganic chemistry

In the interests of uniformity and retrievability the nomenclature of International Union of Pure and Applied Chemists should be used for naming and indexing organic selenium compounds International Union of Pure and Allied Chemists (IUPAC, 1979). Questions about the naming of inorganic selenium compounds can be resolved by reference to the Commission on Nomenclature of the International Union of Pure and Applied Chemistry report, Section C (IUPAC, 1971).

Elemental selenium is very reactive. Selenium combines with fluorine, chlorine, and bromine to make well-defined halides. Elemental selenium burns with a blue flame forming selenium monoxide, dioxide and trioxide (Elkins and Margrave, 1954).

Selenium dioxide, the combustion product, is converted to selenious acid, H_2SeO_3, by the absorption of water from the air or dissolution in water (Rosenfeld and Beath, 1964). Selenious acid is weakly dibasic and very soluble in water. The acid forms both selenite salts and hydrogen selenite salts.

Selenic acid, H_2Se0_4, is fairly strong and very soluble in water. It is formed by oxidizing elemental selenium, selenium dioxide, selenious acid, or selenites. Selenium trioxide combines readily with water to become selenic acid, a strong oxidizing agent (Bagnall, 1966). The bases of this acid form selenate salts or hydrogen selenates (Elkins and Margrave, 1954).

Both metal and hydrogen selenides are known. Hydrogen selenide, H_2Se, is released when metal selenides are hydrolyzed by passing hydrogen and selenium vapor over pumice at 350°C or when metallic selenium is heated to 400°C (Bagnall, 1966). This colorless gas has a strong unpleasant odor, not unlike hydrogen sulfide. It is quite poisonous, with an LD_{50} in guinea pigs of 0.001 ppm for 8 hours (Dudley and Miller, 1941). It is more water-soluble than its sulfur relative and creates a stronger acid. Heating metallic selenium with other metals produces metallic selenides, most of which are not water soluble.

Selenium sulfides with a composition between Se_2S and Se_3S have been produced by reducing selenious acid with hydrogen sulfide. It is not a true compound, but a mixture with selenium replacing sulfur at several positions in the S_8 rings (Bagnall, 1966).

D. Organic chemistry

The nomenclature and reactions of the organic selenium compounds are similar to those of the organic sulfur compounds (Rosenfeld and Beath, 1964; Klayman and Gunther, 1973). There are, however, two distinctive differences between selenium and sulfur that lead to dissimilar behavior in biological systems: 1) differences in the ease of reduction of oxyanions, with tetra-selenium likely to be reduced while tetra-sulfite is more likely to be oxidized, and 2) the differing hydride acid strength (Combs and Combs, 1986). This results in a considerable difference in behavior of the seleno-hydryl group of selenocysteine compared with the sulfhydryl group on cysteine (Huber and Criddle, 1967).

Although many organic selenium compounds have been prepared synthetically or detected in the environment, relatively few organic molecules containing selenium have been investigated in detail (Jensen and Kjaer, 1986). Much of the information on the organic chemistry of selenium reported in the literature involves basic laboratory chemistry of synthetically derived compounds. Although some organic compounds which contain selenium in natural systems have been studied, this knowledge is largely confined to artificial systems. Further research is necessary to determine more clearly which organic selenium compounds exist in the environment and their chemical pathways and behavior. Many of

these organic forms exist in nature as partially decayed seleniferous vegetation from both recent periods and past geologic ages.

The largest class of organic compounds containing selenium is the organo-selenides. Several other diselenide compounds are also found in plants. Dialkyl-diselenides are a second class of organo-selenides. These can be reduced to selenols or oxidized to selenic acids, selenonic acids, or selenenic acids. Dimethyl-diselenide emissions from *Astragalus* species were observed in nature by Evans et al. (1968). Several other diselenide compounds are also found in plants.

Selenols are simple organoselenium compounds and are selenium analogs of thiols and alcohols. Aliphatic selenols are water-soluble and readily oxidized by atmospheric oxygen to diselenides.

Selenic amino acids, such as selenocysteine have been observed in plants (Petersen and Butler, 1962). These tend to be amphoteric and can form salts in acid or basic solutions. They are water-soluble and moderately strong oxidizing agents which are reduced to diselenides.

Organic selenoxides have been observed in nature in plants (Petersen and Butler, 1962; Spare and Virtanen, 1964). These easily form monohydrates in water. Selenium ions such as trimethylselenonium ion are reported as the major form of selenium excreted by animals (Byard, 1969). Hydrolysis of these compounds results in the formation of a diorganoselenide and a corresponding alcohol.

Many amino acids, containing selenium have been described including selenocysteine, selenocystine, selenomethonine, seleno-cystathionine, Se-methylselenocysteine and Se-methylseleno-methionine (Bowen, 1966). Shrift and associates have described selenium-containing amino acids in a series of papers (Shrift and Virupaksha, 1963, 1965; Virupaksha and Shrift, 1963, 1965).

While the primary pathway of selenium into both higher plants and the environment involves inorganic selenium forms, organic selenium compounds, especially those formed by plants, animals, and bacteria, are inter-mediary compounds involved in the cycling of selenium in natural systems. While their formation in living systems is fairly well understood, their breakdown in the environment is poorly understood. Volatile forms of selenium may be formed by animals and microbes (Jiang et al., 1983; Reamer and Zoller, 1980).

Synthetic organoselenium chemistry could be used to explore organic selenium decomposition pathways in nature but no reports of this approach are published. Most of the organoselenium compounds synthesized contain selenium in the -2 oxidation state. Many of these compounds eventually degrade to form elemental selenium, which is inert and generally non-toxic. The biochemical pathway or pathways for this process and the factors that influence rates of oxidation are not well understood.

References on the organic chemistry of selenium compounds which outline chemical

nomenclature, structure of compounds, and some chemical reactions can be found in Klayman and Gunther (1973), Ihnat (nd), Paulmier (1986), Liotta (1987), and Patai and Rappaport (1986). The recent volume on organoselenium chemistry may also be of value (Liotta, 1987). For more detail on biochemistry see Muth et al. (1967), Combs and Combs (1986), Chapter 3 of this report and Volume 2.

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Chapter 3. The Basic Biological Properties of Selenium

"Selenium has a considerable role in biochemical systems. It is essential to the health of animals and human beings, but at the same time it is poisonous. The concentration range from trace metal requirement to lethality is very narrow..."

Charles Wilber 1980

A. Introduction

Selenium has been identified as an essential nutrient for humans, animals, fish, birds, and some microorganisms. It is also a potential poison for them and for plants. Selenium problems are rare in natural ecosystems and uncommon in managed ecosystems. Selenium deficiency is most likely to occur on young soils in areas with high rainfall. Selenium toxicity is commonly encountered in arid and semi-arid regions with alkaline, seleniferous soils derived from marine sediments.

Biological processes are very important in determining the form and manner in which selenium is found. Biological processes can convert inorganic selenium to organic forms, solid forms to gasses, insoluble forms to highly soluble forms, chemically reactive to less reactive forms, and high toxicity to low toxicity forms. Under certain conditions, bioavailable forms can be converted to immobile forms, such as metallic selenium.

Biological processes can also concentrate selenium. Selenium accumulating plants, for example, may reach selenium concentrations of 4,000 µg/g growing next to other plants with only 2 µg/g (Beeson, 1961).

B. Selenium in microorganisms

Unraveling selenium's role in the life of microorganisms will be essential to understand the fate of selenium compounds in the environment. When soil organic matter is broken down by microorganisms, organic selenium compounds in soils can be released into the environment. Microorganisms also play critical roles in selenium cycles in aquatic systems by influencing the solubility and bioavailablity of selenium compounds in soils and sediments, and as entry points into the aquatic food chain. Understanding the basic biological relationships of selenium and microorganisms may also provide needed insights into the behavior of selenium in other biological systems.

Selenium appears to be a required micronutrient for some microorganisms. Formic dehydrogenase enzyme activity in *Escherichia coli* was detected only when there were adequate amounts of both selenium and molybdenum (Fukuyama and Ordal, 1965). Not only was formate metabolism shown to require selenium but selenium was also part of the electron donor pathway for nitrate metabolism (Pinsent, 1954). It is uncertain whether selenium is an integral part of the enzymes or simply acts as a catalyst (Enoch and Lester, 1972).

Selenium has been shown to move across the cell membranes of a variety of microorganisms (Shrift, 1961). Competition for transport across cell membranes between chemically similar sulfur and selenium

compounds has been shown for *Penicillium chrysogenum* (Yamamoto and Segel, 1966) and *Chlorella vulgaris* (Shrift, 1954; Shamberger and Willis, 1971).

Selenium compounds can be oxidized and reduced by microorganisms. For example, *Salmonella heidelberg* can reduce selenite to elemental selenium (McCready et al., 1966). *Micrococcus lactilyticus* can reduce selenite to elemental selenium and, more slowly, reduce colloidal selenium to selenide (Woolfolk and Whitely, 1962). The ability of these organisms to detoxify selenite compounds may explain their tolerance of high selenium levels. The ability of specific strains of microorganisms adapted to high selenium conditions to reduce selenite to selenium has practical significance in areas where selenium exists in concentrations toxic to other life forms.

An *E. coli* substrain developed resistance to selenate toxicity after a 24-48 hour lag time, and maintained this resistance in future generations (Shrift and Kelly, 1962). An algae, *Chlorella vulgaris*, developed a stable resistance to seleno-methionine (a selenium-containing amino acid) which appeared to be due to a decreased permeability to the selenium compounds in the growth medium (Shrift et al., 1961a,b). Decreased uptake adaptation was also noted in *E. coli* (Stanford and Olson, 1959). Strains of *Bacillus megaterium* from soils high in selenium had higher levels of selenoreductase than did strains from soils with little selenium (Letunova, 1970).

The availability and toxicity of selenium for microorganisms is strongly affected by the nature and concentrations of other compounds present in the environment. For example, while selenite can severely inhibit yeast respiration in pure culture, the presence of arsenite, arsenate, or phosphate, as in a natural environment, can reduce this effect (Bonhorst, 1955). Sulfate can even reverse the toxic effects of selenate on yeast growth (Fels and Cheldelin, 1949). In contrast, the presence of methionine can enhance the toxicity of selenite to *E. coli* (Scala and Williams, 1962). These interactions become extremely complex with changing environmental conditions and the large and diverse microbial communities found in the environment.

Microorganisms such as *E. coli* and yeast have been shown to convert inorganic selenium forms into selenoamino acids, particularly selenomethionine (Tuve and Williams, 1961). Selenocystine, another amino acid, was found to be produced by *E. coli*, *Proteus vulgaris*, and *Salmonella thompson* (Weiss et al., 1965). Hidiroglou et al. (1968) reported microbial proteins containing selenium were produced by rumen bacteria in the presence of selenite. Selenomethionine can effectively substitute for normal methionine in several *in vitro* enzymatic reactions and in certain protein syntheses in *E. coli* (Jenkins, 1968; Hoffman et al., 1970). Six selenium-containing amino acids, selenocysteine, selenocystine, selenomethonine, selenocystathionine, Se-methyl-selenocysteine and Se-methylseleno-methionine were identified almost 20 years ago (Bowen, 1966). Shrift and associates reported on selenium-containing amino acids in a series of papers

(Shrift and Virupaksha, 1963, 1965; Virupaksha and Shrift, 1963, 1965).

Comparisons of results from these studies on selenium incorporation in amino acids and enzyme reactions is difficult because of varying methodologies, analytical techniques, and the microorganisms or strains used. These factors make it difficult to clarify the basic principles.

Dimethylselenide is one of the simplest yet most environmentally important organic selenide compounds. It is produced by bacteria, plants, and, animals, as a volatile liquid or gas (McConnell, and Portman, 1952a; McConnell and Roth, 1966; Reamer and Zoller, 1980; Jiang et al., 1983a).

The methylation of mercury compounds by microorganisms poses a serious ecological threat. In contrast, methylation of selenium compounds from inorganic salts to dimethylselenide may reduce the toxicity of selenium (McConnell and Portman, 1952b; Frankenberger et al., 1987). Fleming and Alexander (1977) reported that inorganic selenium compounds were converted to dimethylselenide by microorganisms isolated from raw sewage. Microorganisms in soil and sewage sludge have also been shown to produce dimethyldiselenide and methylmethylselenite (Reamer and Zoller, 1980). Little is known about the toxicity of these compounds. A synergistic toxicity between inorganic mercury salts and dimethylselenide has been observed (Parizek et al., 1971).

The interactions between rhizobia and selenium may also warrant investigation because many of the accumulating plants are legumes. Several soil microbes, including fungi, yeast, bacteria, and actinomycetes can reduce selenite and selenate to elemental selenium (Bautista and Alexander, 1972; Alexander, 1977). Two distinct cultural groups of *Rhizobium* spp. associated with *Astragalus* spp. differed widely in their ability to reduce selenite (Allen and Allen, 1981). Isolates from the group that resembles clover and pea rhizobia strongly reduced 0.05 percent selenite, while the other group of rhizobia did not. The association between *Rhizobium* spp. and *Astragalus* spp. is complex, and there is considerable specificity in host/symbiont relationships (Allen and Allen, 1981). Other bacterial genera that may reduce selenite to selenium include *Clostridium*, *Corynebacterium*, and *Micrococcus* (Alexander, 1977).

Some of the fungi are also selenium accumulators. For example, Quinche (1979) showed that *Agaricus bitorquis* accumulated high concentrations of selenium. A review of 95 species of mushrooms showed that differences were substantial between species, with some containing concentrations as high as 43 µg/g dry weight (Quinche, 1983). A review of mushrooms in Finland, a country with many selenium-deficient soils, showed that some species could be significant sources of dietary selenium, most notably *Boletus edulis*, with an average of 17 µg/g dry weight (Piepponen et al., 1983). Other significant selenium accumulating genera included *Macrolepiota*,

Agaricus, Gasteromycetes, Lactarius, and Marasmius (Piepponen et al., 1983).

The relationship between mycorrhizal fungi and selenium uptake and availability is possibly of considerable importance but little studied. *Boletus* spp., whose high selenium content was discovered in Finland, are capable of forming ectotrophic mycorrhizae (Alexander, 1977). Mycorrhizae are known to increase uptake of sulfur (Alexander, 1977) and may also improve selenium uptake, a beneficial feature in selenium deficient soils and a potential problem in seleniferous soils.

The volatilization of soil selenium reported by Abu-Erreish et al. (1968) was attributed to molds in the soil. More recently Frankenberger et al. (1987) reported selenium volatilization from three soil fungal isolates from the Panoche loam. Alexander (1977) mentions volatilization of selenium by genera including *Aspergillus, Candida, Cephalosporium, Corynebacterium, Fusarium,* and *Penicillium.*

The behavior of selenium in soil is strongly influenced by microorganisms. Organic matter apparently plays a large role in this process. Added soil organic matter can, for example, enhance the microbial conversion of selenium forms in soils to volatile products (Doran and Alexander, 1977). Decreasing organic matter by continuous cultivation and use of chemical fertilizers can change soil microbial populations and soil pH, which may affect selenium mobility.

C. Selenium in plants

1. Essentiality and phytotoxicity

Selenium is taken up by plants but is rarely essential for plant growth. However, selenium is essential for animal nutrition and this dietary requirement is usually met by the selenium contained in plant materials consumed by animals. Selenium levels of plants growing on seleniferous soils may be high enough to cause poisoning in animals which consume large quantities of selenium enriched material. If the selenium content of plants consumed is low then selenium deficiencies become apparent. Much of our knowledge about selenium in plants is based on efforts to better understand the critical role of selenium in animal health.

Selenium toxicity to crop plants cultivated in the field has not been reported (Hemphill, 1972; NRC, 1976). However, selenium has been shown to be toxic to alfalfa, bush beans, wheat and other crop plants when added to nutrient cultures at low concentrations under controlled conditions (Broyer et al., 1966). Crop plants are also sensitive to the addition of small amounts of selenium to soil. Studies from the 1930's indicate that selenium toxicities can develop when inorganic selenium compounds are applied to cotton, cereals, and forage grasses (Hurd-Karrer, 1935, 1937; Beath et al., 1937a,b; Mason and Phillips, 1937; Walsh and Fleming, 1952). Plant tissue selenium concentrations, even in highly seleniferous soils, rarely exceed 100 µg/g; but where selenium compounds have been added to soils, concentrations in plants have ranged

from 300 µg/g (Rosenfeld and Beath, 1964), where visible symptoms may appear, to 1,000 µg/g in alfalfa (Soltanpour and Workman, 1980). A plant selenium concentration of 1,842 µg/g in bush bean roots grown in solution culture has been recorded (Wallace et al., 1980).

2. Selenium accumulation in plants

Selenite and selenate ions can both be taken up by plant roots (NRC, 1976) but selenate is preferred (Ganje and Whitehead, 1958). These ions are then metabolically incorporated into soluble amino acids and/or protein-bound amino acids. Plants also take up selenium directly in organic forms (Johnson et al., 1967). Stadtman (1974) and Brown and Shrift (1982) have published extensive reviews on the biochemical role of selenium in plants. Most plants that take up selenium cannot distinguish it from sulfur and incorporate selenium into cellular components in place of sulfur through enzymatic processes normally used for sulfur. Elemental selenium is largely regarded as unavailable for plant uptake (Peterson and Butler, 1966).

Selenite is taken up passively by plant roots, whereas selenate is taken up metabolically (Peterson et al., 1981). Leggett and Epstein (1956) reported that selenate associates with the same binding sites for uptake by plant roots as sulfate. Thus, sulfate and selenate behave as competing ions for plant uptake (Hurd-Karrer, 1933). This has been supported by recent research (Mikkelsen, 1987; Mikkelsen et al., 1988).

Plants differ tremendously in their ability to concentrate soil selenium in their tissues. Kingsbury (1964) divided plants into three categories with regards to selenium: a) obligate accumulators; b) facultative accumulators; and c) non-accumulators. Obligate selenium-accumulating plants grow only where soils have enough selenium to support the metabolic needs of the plant; their presence in nature indicates seleniferous soils. Facultative selenium accumulating plants are able to accumulate selenium in their tissues when it is present in soils but can also grow in soils containing little or no selenium (Izbicki and Harms, 1986). Kingsbury (1964) reported that in general non-accumulating plants concentrate soil selenium by a factor of 1 to 10, facultative accumulating plants by a factor of 100, and obligate accumulating plants by a factor of 100 to 1000.

Obligate selenium-accumulating plants serve as qualitative "indicator" plants. They are usually associated with semi-arid seleniferous soils and are active in cycling selenium from inorganic soil forms to organic forms which are then deposited on the soil when the plant parts decay (Davis, 1972). Because these plants have the unique ability to absorb selenium from the soil in a form not ordinarily available to other plants they are known as selenium "converters", i.e. they convert relatively unavailable selenium to selenium available to other plants (Moxon and Olson, 1974). Many selenium- accumulating plants are deep-rooted and may absorb selenium from

lower levels of the soil profile (Adriano, 1986).

Moxon and Olson (1974) and Rosenfeld and Beath (1964) divided selenium-accumulating plants into three categories roughly equivalent to the above categories of Kingsbury (1964). These categories are: a) primary indicators; b) secondary indicators; and c) non-accumulators. Table 3.1 is adapted from Adriano (1986), Ganje (1965), and Rosenfeld and Beath (1964).

Table 3.1. Selenium accumulator/indicator plants.

Primary Indicators	Secondary Indicators
Astragalus	*Atriplex*
Haplopappus	*Castilleja*
Stanleya	*Machaeranthera*
Xylorhiza	*Sideranthus*
	Aster
	Mentzelia

Note: variation between different species of the same genera is often very large.

Cooper et al. (1974) reported selenium concentrations for selenium-accumulating plants in the *Astragalus* and *Stanleya* genera from Wyoming ranging from 199 µg/g dry weight to a high of 3,939 µg/g. In the same study *Atriplex*, a facultative accumulator, had a selenium concentration of 300 µg/g while an unspecified non-accumulating grass had a selenium concentration of only 23 µg/g dry weight.

In California, a facultative accumulator, Diablo locoweed (*Astragalus oxyphysus*), is commonly found in upper alluvial fans, terraces, and foothills of the interior Coast Ranges and can be used as an indicator plant in those areas (Armstrong, 1984). In the areas of lower alluvial fans and the floor of the San Joaquin Valley other species can serve as indicator plants. For example, *Atriplex lentiformis*, Quail Bush, is widely distributed in the San Joaquin Valley floor and is an important forage and wildlife cover plant as well as a facultative selenium accumulator (Kingsbury, 1964). These two species were the subject of a U.S. Geological Survey Report by Izbicki and Harms (1986).

Substantial genetic differences in selenium accumulation may occur among non-accumulator varieties. For example, selenium concentration among six varieties of soybeans, *Glycine max*, varied by 600% when grown in the same field in Iowa (Wauchope, 1978). Similar differences were observed among twelve varieties of soybeans grown on clay soils in Mississipi (Wauchope, 1978).

The National Research Council [NRC] (1976) suggested a maximum safe tolerance level of 2 µg/g of selenium in animal feeds. Although the U.S.G.S. investigators found a few plant samples above this level (e.g., *Astragalus oxyphysus* and *Atriplex lentiformis*), most samples fell well below it (Izbicki and Harms, 1986). They recommended that the use of selenium indicator plants be accompanied by tissue analysis, that different plant species be tested at each location, that concentrations in individual plants of the same species be determined, and that obligate accumulating plants be identified,

since they are the most effective indicators of potential selenium problems.

The stage of growth and the age of the plant can also affect selenium concentrations. Selenium concentrations in plants generally decline with age (Rosenfeld and Beath, 1964) or with successive harvests of forage crops on the same site (Gissel-Nielsen, 1971a).

3. Increasing selenium concentration in plants

Selenium as an essential element in animal nutrition can be provided as part of the animals' feed. Animal feeds with potentially toxic levels of selenium should be disposed of or mixed with low selenium feeds, but this is much less common than feeds with inadequate selenium.

There are four general methods to correct selenium deficiencies in plants: a) soil-applied fertilizers with selenium contaminates (Robbins and Carter, 1970; Gissel-Nielsen, 1971b) or additions; b) soil-applied selenium (Watkinson and Davies, 1967); c) foliar-applied selenium, and d) seed-applied selenium (Gissel-Nielsen, 1984). These are discussed in more detail in Chapter 5.

It is important to understand the effects of selenium applications to plants especially under soil conditions where selenium bioavailability is low. Most experience with selenium application has been with pastureland and agricultural crops. Experimental work is needed to determine the best strategies for improving the selenium content of range browse.

Potential recycling of selenium-enriched plant material or sediments will require research to explore the impacts of transferring and applying the selenium removed through treatment processes from areas at sites with selenium toxicity to areas of natural selenium deficiency. Potential impacts on plants, animals, birds, fish, and the environment must also be considered.

4. Metabolic pathways of selenium in plants

Selenium accumulating plants store most of the selenium taken up from soils in free amino acids (Peterson and Butler, 1966). By preventing the incorporation of seleniferous amino acids into proteins, accumulating plants avoid selenium-induced phytotoxicities. In agricultural crops such as cereals (non-accumulators) some of the seleniferous amino acids are incorporated into amino acids and can interfere with normal plant metabolism, in particular those aspects involving sulfur. While selenium and sulfur are relatively similar chemically, they differ enough to cause substantial changes in plant biological functions (Anderson and Scarf, 1983).

Selenium can also be emitted by plants as a gas. Dimethyldiselenide emissions from *Astragalus* species were observed in nature by Evans et al. (1968) and in other plants (Lewis et al., 1966; Zieve and Peterson, 1984). Asher et al. (1967) characterized some of the volatile emissions from alfalfa, *Medicago sativa*. They also found that cuttings emitted volatile selenium.

D. Selenium in terrestrial ecosystems

The impact of selenium on terrestrial ecosystems is complex and depends on many physical, chemical, and biological factors. The outline of the selenium cycle has been suggested (Shrift, 1964), but many questions remain to be answered. In natural terrestrial ecosystems, deficiencies of selenium are more common than toxicities, although the effects of deficiency are less dramatic. In managed terrestrial ecosystems human activities have altered natural cycles and created selenium problems involving both deficiency and excess. (See also volume 2.)

Water management related to agriculture is the principal vehicle for the development of selenium toxicity problems in managed terrestrial ecosystems. Selenium deficiency may result from changes in vegetation management, fertilizer application, changes in organic matter and soil properties, or continued removal of micronutrients in crops without replacement.

Selenium toxicity problems associated with natural or managed aquatic systems are more common and severe than those in terrestrial systems in California. However, the two systems interact and terrestrial selenium problems can occur.

The most serious aspect of selenium problems in terrestrial ecosystems, as in aquatic systems, is the biomagnification of selenium as it is cycled in food chains. Consumer organisms at higher trophic levels are the most seriously affected as higher and higher levels of selenium are concentrated in fewer and fewer organisms. Selenium will enter the food chain as soluble ionic forms taken up by microorganisms and plants which are then consumed by higher organisms. This is described in greater detail later in this chapter. Little information is available about the environmental exposure to selenium or the effects of selenium on species other than domestic livestock and a few fish and wildlife species. Studies of gopher snakes and bull frogs in the San Joaquin Valley revealed selenium concentration of up to 45 µg/g (Ohlendorf, 1987). These levels may cause reproductive problems or even reproductive failure.

With intensively managed systems, such as irrigated agriculture, short periods (years) of selenium toxicity might be expected to be followed by slow but steady declines in toxicity as selenium is washed from the soil system, volatilized, biologically fixed, or harvested and removed. However, if the selenium is simply transferred by water from a seleniferous area into another seleniferous area or a non-seleniferous area, where it is subject to concentration in water bodies by evaporation and biomagnification in the food chains, the net effects may be worse.

Terrestrial plants grown on soils with naturally high selenium concentrations, soils receiving selenium rich wastes (i.e. ash from coal fired power plants and spent ore from sulfide or copper mining and refining), or soils receiving applications of selenium enriched irrigation drainage water will accumulate selenium (U.S. Department of Interior [USDI],

1985). As described earlier in this chapter the accumulation of selenium by plants is highly variable among plant species. Some native deep-rooted plants are recognized specifically for high concentrations of accumulated selenium, while cultivated crops typically include relatively low levels of selenium, especially in the plant parts consumed such as grains, fruits, and edible vegetative parts.

Unless other food sources become unavailable, animal consumption of plants containing high selenium concentrations is usually limited. Domestic livestock have been poisoned by consuming plants with toxic levels of selenium, but the incidence of such events is rare. Human food chain selenium contamination is rare even on seleniferous soils and where selenium contaminated drainage water is applied to food crops.

Preliminary indications from current research suggest that although selenium is taken up by human food crop plants the concentrations are not hazardous in the plant parts normally harvested and consumed. However, long-term studies on the effects of using recycled drainage water containing selenium for irrigation still need to be conducted (U.S. Department of Interior, 1985; Burau et al., 1986; Grattan et al., 1986, 1987).

In natural and managed rangelands in the western United States selenium movement from soil to plant to animals in the food chain is well documented. "Alkali disease" and the "blind staggers" are syndromes associated with seleniferous soils and range plants growth on them (Moxon and Rhian, 1943; Izbicki and Harms, 1986). However, selenium deficiencies in grazing livestock are more common and more costly. These deficiency problems are discussed in greater detail in the next section.

Wildlife species are also vulnerable to selenium poisoning and deficiency diseases. Long-term research in northern and eastern California has revealed declining deer fawn survival (Jessup, 1987; Norman, 1987a; Smith, 1987). Treatment with selenium supplements has improved fawn survival significantly. The causes for this change in selenium nutrition are unknown. It has been suggested that current range management practices which encourage a shift from shrubby deep-rooted perennial vegetation to annual grasses, may lower the selenium content of the deer diet (Smith, 1987).

It has also been suggested that acid rain might be involved in the decline of selenium content in plants (Frost, 1984; Gissel-Nielsen, 1984; Maugh, 1984; Smith, 1987). The marked decline in the selenium content of Swedish crops (Norrmann, 1984) may be related to this. While soils are often considered well-buffered and resistant to acid rain more recent research has shown that young soils (such as the volcanic soils in the study area) are at particular risk to acid rain (Bunyard, 1986). Soil pH declines of 0.7 have been observed in Swedish soils; this is sufficient for half of the base cations, calcium, magnesium, and potassium to be lost (Bunyard, 1986).

Other natural populations of wildlife can be affected by selenium, including: amphibians,

rodents, predatory mammals, and birds which feed on aquatic and terrestrial organisms. Very little documentation of selenium problems in terrestrial ecosystems exists but this may largely be due to lack of study. Much more research is needed to confirm or deny the existence of the many possible consequences of selenium excess and deficiency.

The effect of high selenium levels in prey eaten by rare and endangered species, such as the San Joaquin Kit Fox, is a special concern; but until more detailed field studies are completed the actual impact of selenium, if any, will remain unknown. Birds which might feed on selenium-contaminated fish or waterfowl in the San Joaquin Valley as well as mammals may be at risk. Field studies have shown an increase in populations of bald eagles and peregrine falcons in California (Berger, 1985; Jurek, 1987), but the apparent feeding of raptors on coots that have accumulated high selenium concentrations is a cause for concern (U.S. Dept. of Interior, 1986). This apparently led to the death of a Marsh Hawk at Kesterson Reservoir in 1987 (Benson, 1988). While the accumulation rate may in some cases be sufficiently great to cause problems without long term exposure, e.g., migratory waterfowl, selenium supplementation could prove of value in improving survival of rare and endangered species that are adversely affected by selenium deficiency, if any exist.

Selenium toxicity and deficiency in terrestrial ecosystems have been inadequately studied to provide answers to the many questions that can be asked about selenium deficiency and toxicity in the environment.

E. Selenium in mammals

Selenium at elevated levels in the diet has long been known to be toxic to animals. This occurs most commonly when mammals feed on accumulator plants growing in seleniferous soils. The identification of selenium as a toxic element was not fully established until the 1920's and early 1930's in the Dakotas, Wyoming, and elsewhere (Anderson et al., 1961). Range animal poisoning typically results from consumption of plants from genera such as *Astragalus* spp. which can accumulate very high levels of selenium (Izbicki and Harms, 1986). The toxicity of these plants is often compounded by high levels of alkaloids which are also toxic to animals (Ralphs and James, 1985). It may by difficult to determine which poison predominates without detailed analyses and examinations because selenium and alkaloid poisoning produce similar symptoms. If exposure is high enough, death may occur from either selenium or alkaloid toxicities alone, or their combined effects. Detailed studies may be needed to isolate the actual poison (Hartley et al., 1985).

Selenium is also an essential nutrient for animals. Deficiency diseases of selenium were first identified and treated in animals and animal research has provided considerable insight into human requirements for selenium. Studies of selenium metabolism have primarily

focused on selenite and selenate rather than the many organic selenium compounds which are still not well understood. Selenium can be volatilized by animals. Dimethylselenide, dimethyldiselenide, and other gasses may be produced (McConnell and Portman, 1952a; Bryant et al., 1982; Jiang et al., 1983b).

1. Chronic poisoning

Chronic poisoning in chickens, rats, and dogs resulted from dietary selenium of 5 µg/g. Seleniferous wheat, containing 6.4 µg/g as selenite, led to selenosis in rats (Halverson et al., 1966). Selenium levels of 6 µg/g in the diet led to reduced life span in rats. Half of a group of male rats fed 2 mg Se/liter as sodium selenite in drinking water died in 35 days, while female rats were less strongly affected (Schroeder and Mitchener, 1971). Rabbits with long-term exposure to sodium selenite in water (0.005 mg Se/kg of body weight) experienced impairment of liver function and increased glutathionine in the blood (Pletnikova, 1970).

Animals may be affected by airborne selenium. Particle size and selenium chemical form will determine the effect of airborne selenium on animals. Threshold sizes for the retention or rejection of particles containing selenium will vary with the animal species. Selenium particles carried by the mucociliary system to the intestine may be absorbed in the stomach or intestines. Selenium derived from particles that accumulate in the lungs may also be absorbed. The selenium can then either collect in tissue or be excreted. Relatively high tissue concentrations have been found in people with long-term industrial exposure to airborne selenium. The toxicity of selenium gasses is little studied and poorly known. Some indications of health risk from selenium fumes and gasses are presented in the section on human exposure.

Studies of domestic livestock provided the first detailed information on the toxic effects of selenium. These were reported by investigators working in Wyoming and South Dakota (Franke, 1934a; Franke, 1934b; Franke et al., 1934; Moxon, 1937). Two basic types of chronic selenium poisoning were described--the blind staggers and alkali disease. It was once wrongly believed that alkali in the soil was the cause of this domestic livestock toxicity (Rosenfeld and Beath, 1964).

Blind staggers apparently involves both selenium and toxic plant alkaloids because it cannot be reproduced entirely in experiments with selenium alone (Maag and Glenn, 1967). The alkaloids in some of the accumulator plants are described by Hartley et al. (1985). Animals with the blind staggers have impaired vision, stumble about, wander randomly, and eventually die.

Alkali disease, on the other hand, can be induced by feeding animals selenium-enriched foods, typically containing more than 5 µg Se/g, over a period of several weeks or months. While Maag and Glenn (1967) were unable to induce the typical effects of alkali disease using inorganic selenium, other studies using organic selenium compounds in seleniferous grains and selenium salts have been able to produce the disease (NRC, 1976).

No cases of selenium toxicity in livestock have been documented in California by U.C. Extension Veterinary Specialist Dr. Ben Norman (1987b). After extensive searches and questioning of farmers and ranches he did discover one anecdotal account from a ranch near Buttonwillow in 1946. Cattle were apparently affected by eating Prince's Plume, *Stanleya pinnata*, a selenium accumulator. Plant tissue recently collected from the same species in the same area contained 199 µg Se/g dry weight. (Norman, 1987a).

Recovery from both diseases can be good at early stages of the illness but long term exposure causes irreversible damage. Olson (1969) describes options to treat or avoid selenium poisoning in animals. Urinary secretion is the primary means of selenium removal by animals (Glover et al., 1979), except for ruminants which may have higher fecal levels as a result of microbial activity in the rumen which limits gastrointestinal absorption (Wright, 1967).

Respiration may also play an important role in selenium removal when higher levels of selenium are administered. Rats receiving 1.9 mg Se/kg of body weight exhaled almost 30 percent of the dose as volatile selenium (Olson et al., 1963). McConnel and Roth (1966) found that rats administered very high doses of selenite (beyond the amount normally considered lethal--3.5 mg Se/kg body weight) eliminated up to 60% through respiration within 24 hours. An increase in dietary protein increased exhalation of selenium in rats (Ganther et al., 1966). Selenium retention is increased by feeding a diet deficient in selenium (Burk et al., 1972). The rate of selenium excretion is high near-lethal dosages, decreases at moderate levels, and then virtually disappears as desirable levels are approached (Glover et al., 1979).

Removal of selenium in urine, fecal matter and as gasses is related to the body burden, which tends to limit the potential for toxicity (Burk et al., 1972). As body burden increases the portion of total selenium removed from the body through volatilization of selenium from the lungs increases up to thirty percent of total removal. The gasses emitted by animals probably include dimethylselenide (McConnell and Portman, 1952a).

Blood levels of selenium have been determined for cattle and game animals in many areas of California. Although blood selenium levels are slightly elevated in cows in some areas of the Coast Range and San Joaquin Valley, they are well within accepted levels (Bureau of Animal Health, 1986). These are shown in Table 3.2. Selenium poisoning is associated with blood selenium levels over 2-3 µg/g (Dinkel et al., 1957; Maag et al., 1960; Olson, 1969).

Table 3.2: Highest individual blood selenium levels in cattle at selected sites in California

Location	Blood selenium µg/g
Firebaugh	0.610
Merced A	0.495
Kern T305R21ES34-36	0.450
Fresno	0.353
Kern County	0.352
Santa Maria	0.350
Merced.B	0.349
near Kesterson NWR	0.327
Gaviota	0.305

Bureau of Animal Health, 1986.

2. Acute poisoning

Acute selenium poisoning in terrestrial organisms was first described by Czapek and Weil in 1893. Respiration becomes labored, garlic breath is noticed, and initial nervous excitation is followed by drowsiness or sleep, spasms, and finally death. The rapid absorption of selenium is reflected in the very fast response of animals to acute poisoning. The minimum lethal doses for several animals are summarized in Table 3.3.

Table 3.3. Minimum lethal doses of selenium in selected animals.

Organism and Selenium form	Response/dose mg/kg body weight
Rabbits, rats, cats, sodium selenate or sodium selenite intravenously, oral, subcutaneously or intraperitoneally[1]	1.5-3.0 lethal dose
Cattle, sodium selenite[2]	9.0 lethal dose
Horses, sodium selenite[2]	2.2 lethal dose
Pigs, sodium selenite[2]	15.0 lethal dose
Male rats, oral elemental Se[3]	LD_{50}--6700
Male rats, oral sodium selenite[3]	LD_{50}--7
Rabbits oral sodium selenite[4]	LD_{50}--2.3
Guinea pigs, oral sodium selenite[4]	LD_{50}--5.1
Mice, oral sodium selenite[4]	LD_{50}--7-8
Female rats, oral sodium selenite[4]	LD_{50}--10-13
Rabbits, 24 hr oral, sodium selenite[5]	LD_{50}--8.6

[1]Smith et al., 1937; [2]Miller and Williams, 1940; [3]Cummins and Kimura, 1971; [4]Pletnikova, 1970; [5]Berschneider et al., 1976.

Elemental selenium is less toxic than sodium selenate, which in turn is less toxic than sodium selenite. Organic forms of selenium are not well studied in mammals but are apparently much more toxic than inorganic forms to some organisms (Glover et al., 1979). The chemical form may be much more important than the actual concentration (NRC, 1976). The toxicity of various organic selenium compounds is still largely unknown.

There is some concern about possible mutagenic and teratogenic effects from selenium compounds. The organic selenium compounds are suspected of being a possible cause of both teratogenic and mutagenic effects and exposure of pregnant women to these organic compounds should perhaps be limited (Fan, 1986; Glover et al., 1979; NRC, 1976). However, sodium selenate appeared to provide some protective effects against these effects from other materials (Glover et al., 1979).

Selenium dust and selenium gasses have not been well studied either. Studies with rabbits, rats, and guinea pigs suggest selenium dust can be poisonous (Hall et al., 1951). Selenium dioxide at concentrations of 150-600 mg/m^3 was fatal to rats (Filatova, 1951). Half of the rats continuously exposed to hydrogen selenide (0.2 mg/liter of air) for one hour died within twenty-five days (Dudley and Miller, 1937). The LD_{50} for guinea pigs exposed to hydrogen selenide for eight hours was 0.001 µg/g (Combs and Combs, 1986).

3. Selenium deficiency diseases

Selenium deficiency diseases in animals were not identified until the 1950's (Schwarz and Foltz, 1957). This initial discovery of the nutritional requirement for selenium has been followed by many others but the understanding of selenium and its roles in animal and human nutrition is still limited. Research in this area is complicated by the interactions between selenium and vitamin E (Thompson and Scott, 1969), selenium and vitamin C (Mykkanen and Mutanen, 1986; Poovaiah and Omaye, 1986; Robinson et al., 1985), selenium and other trace metals (Olson et al., 1963; Chen et al., 1985; Hussein, 1985; Hussein et al., 1985; Whanger, 1985), selenium and calcium (Lowry et al., 1985), and selenium and organic compounds (Hazell, 1985, Mason, 1985; Solomons et al., 1986).

White muscle disease of lambs was the first selenium deficiency disease of animals clearly identified and treated (Muth et al., 1958; Muth and Allaway, 1963). Many other selenium-related deficiency effects in animals have been identified or suggested since then, including: ill-thrift, edema, retained placenta, sudden death, hepatic necrosis, muscular dystrophy, hemorrhagic ileitis, and ecchymotic hemorrhages (Combs and Combs, 1986; NRC, 1976; Williams et al., 1982). Animals have been shown to respond positively to selenium supplements for prevention or treatment of selenium deficiency (Hartley, 1967; NRC, 1976). Adequate selenium in the diet improves birth survival, reduces retained placentas, and improves growth (Robinson,

1986). Selenium supplementation has also been shown to improve immune system response in animals. Adding 0.9 µg/g selenium to a basal diet with 0.068 µg/g for weaned pigs provided the highest antibody response but humoral and cell mediated immunity were not significantly improved (Blodgett et al., 1986). Levels of 0.1-0.2 µg/g selenium in the diet are considered adequate (Kubota et al., 1967; NAS, 1984a).

Deficiency diseases typically become apparent when dietary levels fall below 0.1 µg/g selenium (Kubota and Allaway, 1972). There is some uncertainty over adequate selenium blood levels in sheep and cattle, with values from 0.01 µg/ml to 0.20 µg/ml proposed as adequate (Williams et al., 1982). In California blood levels of selenium above 0.08 µg/ml are considered adequate and levels of 0.04 µg/ml or below are regarded as deficient (Nelson and Miller, 1987; Norman, 1987a). Bovine blood levels have been taken in many areas of California (Williams, 1980; Williams et al., 1982; U.C. Vet Med, 1984; Norman, 1987), with particular attention to the Kesterson area, Table 3.4 (Bureau of Animal Health, 1986)

Table 3.4. Bovine blood selenium levels of selected herds in California (deficiency <0.04 µg/ml).

Location	Average blood selenium conc. µg/ml
Fresno County	
Clovis	0.026
Orange Cove	0.016
Reedley	0.028
Riverdale	0.010
Sangar	0.020
Sangar	0.030
Tollhouse	0.016
Inyo-Mono Counties	
Olancha	0.035
Kern County	
Bakersfield 1	0.030
Bakersfield 2	0.016
Caliente	0.027
Woody	0.026
Madera County	
Friant	0.018
North Fork	0.013
T 115 R19E	
S 14,22,23,24,26	0.038
Mariposa County	
Catheys Valley	0.016
Coulterville	0.030
Hornitos	0.022
Raymond	0.022
Merced County	
Atwater	0.010
Atwater & El Nido	<0.010
Denair	0.016
El Nido	0.010
Gustine	0.031
Merced 1	0.019
Merced 2	0.025
Merced	<0.010
Riverdale	<0.010
Monterey County	
Watsonville	0.020
San Joaquin County	
Acampo 1	0.012
Acampo 2	0.010
Clements	0.022
Linden	0.013
Lodi 1	0.010

(continued) Location	Average blood selenium conc. µg/ml
Lodi 2	0.011
Lodi 3	0.01
Lodi	<0.010
San Luis Obispo County	
Paso Robles	0.037
Stanislaus County	
Farmington	0.020
Knights Ferry	0.010
Knights Ferry	<0.010
Modesto	0.033
Oakdale 1	0.012
Oakdale 2	0.016
Oakdale 3	0.011
Turlock 1	0.013
Turlock 2	0.015
Tulare County	
Porterville	0.018
Visalia 1	0.023
Visalia 2	0.038
Visalia 3	0.015

Bureau of Animal Health, 1986; U.C.Vet. Med., 1984.

Herds with white muscle disease in Northern California had a group mean selenium blood level of less than 0.031 µg/ml (Williams et al., 1982). Selenium deficiency disease can be treated by administering selenium as selenite with vitamin E; using selenium-enriched feeds; adding selenium-enriched fertilizers to pasture and range to increase selenium content of forage; administering selenium drenches; supplying selenium salts in water; providing selenized salt; and by administering selenium-enriched pellets or boluses inserted in the stomach (NRC, 1976; Kuchel and Buckley, 1969).See also Chapter 5.

The benefits of selenium supplementation were demonstrated in a study at the Johnson Ranch located in the Sierra foothills near the Tulare-Fresno County Line. Two one-ounce boluses (ten percent elemental selenium and ninety percent iron) per animal were administered to selected selenium-deficient cows (Nelson and Miller, 1987). This treatment increased the weight of calves produced by these cows by more than eight percent. This was accompanied by earlier calf delivery which is also advantageous.

This rather dramatic improvement led to a study of the effects of a combined treatment of selenium and vitamin E for calves born to the same herd in 1986. Male calves born to untreated cows with low blood selenium were injected with a solution of selenium and vitamin E. At the conclusion of the experiment, treated calves were 111 pounds heavier than the controls. Male calves born to cows previously treated with selenium additions and subsequently treated with an injection of a selenium and vitamin E solution gained 47 pounds more than controls (Nelson and Miller, 1987). The response of female calves of untreated cows to injections was significant but smaller.

Recent experiments with selenium supplementation of deer in northeastern California have produced even more impressive results. Preliminary analysis suggests that selenium supplementation may have almost doubled fawn survival (Jessup, 1987; Norman, 1987; Smith, 1987). More detailed studies will be needed to confirm this.

Blood level studies of game animals and preliminary maps of probable areas of selenium deficiency suggest that selenium deficiency may be a key factor in reproduction and survival in several important hunting areas of California. Long-term research on these herds shows that deer fawn survival was historically higher.

It has been suggested that a decline in plant selenium levels, which might be related to changes in range management, may have led to low blood selenium levels. Burning to remove perennial brush and shrubs which may contain higher levels of selenium than the resulting annual grasses and the general deterioration in range quality as a result of many years of overgrazing may be implicated. Deficiency may also be related to the removal of forbs, shrubs, and trees with deeper roots and mycorrhizal associations which may improve selenium uptake.

Changes in pasture management have been correlated with the emergence of selenium deficiency in animals (Muth, 1955; Ewan et al., 1968). Selenium decreases have been attributed to the change to more intensive production methods and increased fertilizer use, which can lead to larger plants with lower selenium concentrations, i.e., the dilution effect (Brown and Carter, 1969; NRC, 1976; Jarrell and Beverly, 1981; Williams et al., 1982).

The possible effects of acid rain and air pollutants on selenium cycling have also been suggested as contributing factors in selenium deficiency in people in China and the decline in selenium in Scandinavian crops (Frost, 1984; Gissel-Nielsen, 1984). Other possible contributing factors include leaching, the decreased plant availability of selenium with declining soil pH from cultivation, competition between different ions in the soil as a result of changes in soil chemistry related to fertilization and cultural practices, and the effect of fertilizers, chemical controls, and pollutants on soil microorganisms.

F. Selenium in human nutrition and disease

1. Introduction

It is now well established that selenium is an essential nutrient for humans and has anti-cancer, cardiovascular, and immune system strengthening properties (NRC, 1976; Van Fleet and Watson, 1984; Watson, 1985). An early study of rats fed a low protein, high selenium diet, largely from seleniferous feedstuffs, suggested selenium was a carcinogen (Nelson et al., 1943), but in view of the "questionable histological findings... and the absence of clear confirmation of their conclusions...evidence for carcinogenic activities of selenium must be considered weak" (Combs and Combs, 1986). This early report contributed to a delay in further studies of selenium in humans (Frost, 1980).

Although selenium can cause health problems when large quantities are administered or obtained in food and water, cases of selenium poisoning in China occurred in individuals consuming low protein diets and almost 5,000 μg selenium per day (Yang et al.,

1983). A lack of sufficient selenium is more likely than too much (Levander, 1982; Keen, 1987).

2. Selenium as an essential nutrient for humans

It must be admitted that we just don't know the optimum intake of selenium or, for that matter, of other essential trace elements.
Frost 1980

Although studies in the late 1950's showed that selenium was an essential nutrient, these were not readily accepted because of the earlier suggestion that it was a carcinogen. This led the Food and Drug Administration to prohibit the use of selenium supplements for humans. This erroneous belief was gradually erased by a series of studies in the late 1960's and 1970's. For example, Muth and associates (1967) reported no carcinogenic effects for selenium in a comprehensive study on rats. About the same time Shamberger and Rudolph demonstrated that a sodium selenide solution blocked development of skin carcinogenesis in rats (Frost 1980). In 1969, Shamberger and Frost reported in the Canadian Medical Association Journal that a study designed to correlate high levels of selenium with high cancer rates had instead suggested that there are "*possibly protective effects of selenium against human cancer*" (Shamberger and Frost, 1969).

Schrauzer et al., (1980) showed that selenium reduces mammary adenocarcinoma in mice. And more recently a detailed survey of areas with very low cancer rates (Blondell, 1983) found that higher levels of dietary selenium were associated with a lower incidence of cancer.

Selenium may provide protection from cancer as a result of increased "trapping" of chemical forms of carcinogens (Ip and Daniel, 1985; Van Fleet and Watson, 1984; Watson, 1985). The anti-oxidant role of selenium may also be important, as glutathione peroxidase with selenium in the active site reduced hyperperoxide levels, which reduces oxidation reactions (Watson and Leonard, 1986).

Recent studies have highlighted relationships between selenium deficiency and other diseases. Chinese investigators have shown that humans develop a selenium deficiency disease much like other mammals (Yang, 1979). Keshan disease is a cardiomyopathic disease found in a selenium-deficient region of China. Peak incidence of the disease occurs in the winter months. Adding 15 μg/g of sodium selenite to table salt proved effective in preventing the disease. Hair and blood samples showed that the affected people had selenium levels of 0.12 μg/g in hair and 0.01 μg/ml in the blood. This contrasts with 0.2 μg/g in hair and 0.068 μg/ml in blood for residents of selenium-deficient areas in New Zealand and a typical blood level of 0.15 μg/ml in the United States (Frost, 1980).

Much of the important work on selenium as a nutrient has been done in New Zealand where selenium deficiency diseases of animals are common and where sub-clinical selenium deficiencies may occur in humans. Ranchers reported relief from the symptoms of selenium deficiency when they treated themselves with

sheep drench providing 1 mg of selenium (Robinson, 1975).

Investigations of areas with selenium-deficient soils in Finland and Sweden have also led to improved understanding of selenium needs and availability. The primary group with low selenium intake in this region were vegetarians (Abdulla et al., 1982). Selenium deficiency is also possible in formula-fed infants who may receive only 25-35% as much selenium as breast fed infants (Gissel-Nielsen et al., 1984). This may have an impact on health and development of infants. The protein base of infant formula may also affect the uptake of selenium (Lonnerdal, 1985; Solomons et al., 1986). Casey and Hambridge (1985) suggested that infant formula should perhaps be supplemented with selenium.

Selenium also may be of great value in the treatment of a number of other diseases. Research has unfortunately been limited and much evidence is anecdotal or must be inferred from studies with other mammals. Sufficient information is available to suggest the role that selenium may play in treatment or prevention of rheumatoid arthritis, some types of arthropathy and joint pain, chronic pancreatitis, weakness and easy tiring, depression, atherosclerosis, infections, periodontal disease, retinal vascular damage and retinopathy associated with diabetes, cystic fibrosis, and some types of heart disease (NRC, 1976, 1983; Wallach and Garmaise, 1979; Frost, 1980; Oldfield, 1980; Spallholz, 1981; Aalbers and Houtman, 1985; Kondo, 1985; Meisel and Wouters, 1985; Tolonen et al., 1985; Boyne and Arthur, 1986; Brown et al., 1986; Combs and Combs, 1986; Rose et al., 1986; Watson and Leonard, 1986). See Volume 2 of this report for a more detailed discussion.

After the suggestion was made that amyotrophic lateral sclerosis might be related to high levels of dietary selenium, a survey was done which, as with cancer, showed exactly the opposite. Not enough data are available to make this more than an interesting observation (Gissel-Nielsen et al., 1984).

There is also increasing evidence that selenium may offer some protection against the effects of aflatoxins (Brucato et al., 1986), heavy metals (Frost, 1980; Harris, 1985), and other toxins, including organophosphates (Wilber, 1983; Brown et al., 1986). However, selenium, like many other materials, is toxic in overdoses and may increase susceptibilty to aflatoxins and carcinogens if present in excess (Newberne, 1984; Watson and Leonard, 1986).

3. Selenium as a poison in humans

The direct effects of selenium poisoning may often be misdiagnosed because many of the symptoms are associated with other diseases and even with selenium deficiency. It is currently impossible to make definitive statements about the extent and occurrence of selenium poisoning in humans.

Selenium toxicosis has been reported in humans in many areas of the world, including China (Frost, 1980), Venezuela (Kerdel-Vegas 1966), and the western United States (Anderson et al., 1961; Kilness and Simmons,

1985). The symptoms of selenium toxicosis in humans include extreme lethargy, weakness, nervousness, numbing and tingling of the extremities, headaches, dizziness, paralysis, motor disturbance, loss of hair and nails, lesions of the skin and nervous system, nausea, diarrhea, vomiting, liver function disturbance, ridged or poor nails, and garlic breath (Gissel-Nielsen et al., 1984; Kilness and Simmons, 1985; Fan, 1986).

One of the best documented cases of selenium toxicity in humans in the United States, with known dosage, was reported after several individuals took selenium supplements with over 180 times the labeled selenium content (Anon, 1984). This resulted in individuals taking 27,000 µg of selenium per day. One woman took selenium supplements for 33 days despite bloody diarrhea and other signs of selenium poisoning. She temporarily lost one fingernail and her hair, but few permanent signs were observed (Jacobs, 1987). A fifteen-year-old girl survived after eating 22.3 mg of selenium as sodium selenate with no apparent lasting adverse effects (Civil and McDonald, 1978). An accidental and fatal poisoning involved consumption of gun-blueing solution (3% selenious acid) by a three-year-old (Fan, 1986). A reduction in selenium intake will usually result in remission of symptoms from selenium poisoning. However, chronic exposure to overdoses may lead to permanent damage.

There is also some concern about the effect of selenium exposure on reproduction (NRC, 1976). No embryotoxic or teratogenic effects were seen in hamsters given intravenous sodium selenite, but reproductive system disturbance from selenium compounds have been noted in many species (NRC, 1976; Combs and Combs, 1986; Fan, 1986). A thorough evaluation of the hazards from the many common selenium compounds is needed.

4. Dietary recommendation for selenium

The current diet recommendation for selenium is 50-200 µg/day (NRC, 1980). This recommendation is based on the results of animal studies. A selenium balance trial determined that healthy young North American males required 70 µg/day to maintain their selenium balance (Levander et al., 1981). This is considerably higher than the estimate of 20 µg/day required for young women in balance trials in New Zealand (Stewart et al., 1978). It may be attributed to a lower body selenium level, smaller size, and/or differences in the diet.

Selenium status may be affected by diet, diseases, drugs, smoking (decreases blood selenium levels), alcohol (decreases blood selenium), and activity (Combs and Combs, 1986) and dietary recommendation should be considered as general goals rather than specific prescriptions (See also expanded treatment of this subject in Volume 2).

Dietary standards for maximum dietary levels are as difficult to develop as those for minimum requirements. They depend on the same complex set of factors and insufficient information is available about many aspects of the interactions and behavior of selenium in

humans. Combs and Combs (1986) suggest an upper safe limit of 775 µg per person per day for chronic oral consumption. Levels of up to 1,000 µg/day probably offer little risk if limited to days or weeks (Combs and Combs, 1986) and much higher short term exposure may be acceptable. The fact that healthy individuals in the areas where selenosis occurs in China had a daily intake of 5,000 µg of selenium (Yang et al., 1983) suggests that these recommendations are quite conservative.

Westermarck (1977) found no signs of selenium poisoning in patients receiving the equivalent of 1,600 µg/day for a 70 kg male. Dietary protein appears to offer some protection against selenium poisoning (Gortner, 1940). Torula yeast, methionine (if dietary vitamin E is adequate), inorganic sulfur compounds, and other food supplements have also shown varying degrees of protection (Combs and Combs, 1986).

Some standards for selenium content of foods have been developed. These include: 0.3 µg/g fresh weight for shellfish (Hayes and Phillips, 1986) and 2.0 µg/g for fish (Nauen, 1983). The finding of moderately elevated levels of selenium in fish and game in some areas of California led to warnings in the 1987 Sport Fishing Regulations and Public Health Advisories. These suggest, for example, that no one should eat more than four ounces of corvina, croaker, sargo, and tilapia from the Salton Sea in a two week period and that pregnant or nursing women should avoid eating any fish (Dept. of Fish and Game, 1987). They also cover fish and game from the Kesterson area and some species of birds from Suisun Bay.

The recommended levels of selenium to prevent deficiency and avoid toxicity problems are presented in Table 3.5. The wide ranges suggest the lack of knowledge and many unknowns.

Table 3.5 Selenium in the Human Diet

(µg per day)

--27,000 selenium poisoning from mismixed food supplements

10,000

Adverse affects from too much selenium
--5,000 healthy individuals in areas in China where selenosis occurs

--1,600 no observed problems in patients treated with selenium for disease

1,000

-- 775 maximum long-term for seleniferous foods (Combs and Combs, 1986)
-- 500 long term (Sakurai and Tsuchiya, 1975)

-- 250-300 rec. max. (Schrauzer and White, 1978)
-- 210 EPA acceptable daily intake
200 National Academy of Science recommended range
176 Range of U.S Daily diet, general population

100

-- 66-70 Selenium balance studies, U.S.
60 Range of U.S Daily diet, general population
50 National Academy of Science recommended range

--28-32 Apparently adequate in New Zealand and China
--20 Selenium balance study, N.Z.
--16-20 Apparent protection from Keshan disease in China

10 **Adverse affects from too little selenium develop**

Keshan disease and other deficiency problems

1

Sources: Combs and Combs, 1986; Coppock, 1987; Sakurai and Tsuchiya, 1975; Schrauzer and White, 1978; NRC, 1980; Levander, 1983. As noted, requirements vary as a result of many factors. Most recomendations do not include the consideration of the beneficial effects of selenium in cancer and infection protection.

5. Selenium exposure in diet, food and water in California

It is unlikely that either selenium deficiency or toxicity will occur in California except in very unusual cases, i.e. accidents, such as mismixed food supplements, or from interactions between selenium and other materials and drugs for individuals on very restricted diets. There is some (small) risk of exposure for people who are malnourished and eat large amounts of waterfowl and fish (including the internal organs) from areas with high selenium levels.

The advisories on limiting consumption of fish and game from areas with elevated selenium levels would limit added dietary selenium to less than 35 µg/day with the higher levels of selenium detected in fish, 4 µg/g, assuming 100% bioavailability and absorption. As the wide range of suggested intake included in table 3.5 shows, even with these assumptions these limits are conservative. Using Combs and Combs (1986) suggested limit of 775 µg day, a bioavailability of 47%, based on tuna meal; and 90% absorption, would allow the daily consumption of more than a pound of fish (460 gm).

The University of California has completed a number of studies of selenium content of California food crops in the last three years in response to public concern over possible selenium exposure. These included both studies of actual field conditions and laboratory and field studies of selenium enriched soils. Several crops were found to have more selenium than the average. These are shown in Table 3.6. Insufficient information is available to determine if high levels were related to uptake mechanism or simply reflect soil selenium concentration and availability.

Table 3.6. California foods from areas where selenium level would be expected to be high either from selenium in the soil or in irrigation water, or both.

Food	µg/g wet weight
Broccoli, mean	0.490
Celery hearts, highest	0.480
Cauliflower, mean	0.430
Carrot, mean	0.340
Almond, highest	0.163
Walnut, highest	0.116

Burau et al., 1987; Coppock, 1987; Fan, 1987.

The average daily intake from eating these foods would be low. The vegetables collected from farm fields where high selenium levels would be expected would add only 1-20 µg per day to a typical diet (Fan, 1987). This isn't a significant amount in relation to the EPA recommended maximum, let alone the higher allowable level suggested by Combs and Combs (1986). Even someone eating a very unusual diet with 8 ounces (226 gm) of broccoli per day would still be below what several studies have suggested is safe.

There is also a small risk for people using private wells or surface water with high selenium levels. Public water supplies are monitored and have been since the 1970's, but not all private wells have been tested. Exposure to the higher selenium concentration detected in

water could add potentially hazardous levels of selenium with typical water consumption. Intake of 2 liters of water per day with a concentration of 380 µg/l (found in one well in Fresno county) would add as much as 760 µg per day and would, when combined with regular dietary intake, put the individual above even the more generous recommend-ations for daily exposure. Selenium levels of 225 µg/l in the water should pose little hazard for individuals receiving only 100 µg per day in their diet (Combs and Combs, 1986).

Little is known about the extent and seriousness of selenium deficiency in California. It is common in cattle and would be most likely to occur in people who drink selenium deficient water and cultivate and eat their own food in soils with low selenium levels. This is most likely on the western slope of the Sierra Nevada mountains and in northwestern California.

6. Human exposure to airborne selenium

Possible sources of airborne selenium are described in Chapter 4. Among these are industrial processes and the volatilization of selenium from plants, animals, and microbial sources. Burning seleniferous vegetation could release airborne selenium. Both gasses and particulates would be involved.

Smaller (<0.1 µm) and larger particles (>5 µm) are more likely to be deposited in the upper-respiratory tract (International Commission on Radiologic Protection, 1966). From here they would be removed by mucociliary clearance to the gastro-intestinal tract where a large portion of the selenium would be absorbed (Medinsky et al., 1985). Intermediate sized particles would be more likely to be deposited in the lungs, where selenium is also absorbed.

The selenium absorbed in the lungs would then be deposited in tissue or excreted. The major form of excreted selenium is the hepatic metabolite trimethylselenonium, but inorganic compounds have also been detected in urine after injection with radiolabeled selenite (Kiker and Burk, 1974). Deposition in tissues can also occur, and relatively high tissue concentration, have been found in people with long-term industrial exposure.

The risks of selenium fumes and gasses are not well known. Existing data suggest the following concerns and effects from airborne exposure: elemental selenium fumes have been found to cause cough, bronchitis, coryxa, amnestic difficulties, headaches, sleeplessness, irritability, tachycardia, anorexia, substernal burning, inflammation of nasal mucosa, irregular menses, menostasis, nasal bleeding, and pain in extremities (Hamilton, 1925; Izraelson, 1973; Kinnigkeit, 1962; Nagai, 1959).

Selenium dioxide exposure has been linked to indigestion, epigastric pain, lassitude, irritability, garlic breath, pulmonary edema, irritation of the eyes, acute burns to eyes in high concentrations, rhinitis, bleeding of nose, headaches, anorexia, irritability and nervous disorders (Glover et al., 1979).

Excessive hydrogen selenide exposure causes vomiting, nausea, metallic taste,

dizziness, lassitude, fatigue, acute irritation of eyes, lungs, and throat, and pulmonary edema (Buchan, 1947; Glover, 1970; Glover et al., 1979). It is a colorless and extremely toxic gas, with recommended exposure <0.01 mg/kg/8hr (Gerhardsson, 1984). Acute cases may occur at concentrations of less than 0.07 mg/m^3 (Glover et al., 1979). No fatal cases have been reported. The 30 day LD_{50} for pigs was 0.001-0.004 mg H_2Se/liter of air (Dudley and Miller, 1937).

Not a great deal is known about selenious acid (H_2SeO_3) but it is a toxic species (Combs and Combs, 1986). People working with animals that were exhaling dimethylselenide in response to selenate injections experienced severe pharyngitis and bronchitis. Symptoms recurred after minimal reexposure to selenate dust, possibly due to allergic sensitization (Motley et al., 1937). Pulmonary edema was perhaps caused by dimethylselenide formation in lungs from SeO_2 (Hamilton, 1925). The 24 hr LD_{50} for dimethylselenide in rats by intraperitoneal injection [ipi] was 1300 mg Se/kg body weight and the 24 hr LD_{50} mouse, ipi, was 1600 mg Se/kg body weight (McConnell and Portman, 1952b).

Removal of selenium in urine, fecal matter and as gasses is related to the concentration in the body. This tends to limit the potential for toxicity if selenium is ingested in modest doses (Burk, 1976).

G. Selenium in birds

1.Toxicity

Chronic poisoning in chickens resulted from levels of 7-8 µg/g dietary selenium (Ohlendorf, 1985). Poley and Moxon (1938) showed that chicken egg hatch and survival were depressed at 5 µg/g and halted at 10 µg/g. Low hatch rates for eggs have been used to locate potentially seleniferous areas (Rosenfeld and Beath, 1964). The eggs may be fertile but include gross deformities such as missing eyes and beaks and distorted wings and embryos (Franke and Tully, 1935; Franke et al., 1936; Carlson et al., 1951; Gruenwald, 1958). Selenium may reduce survival as a result of induced anemia even when chicks appear normal (Kury et al., 1967).

Suspected selenium poisoning of waterfowl led to the subsequent Kesterson Reservoir studies. Reproductive problems were noted in 1982 with few signs of difficulty in adult birds (Ohlendorf, 1985). Surveys of selenium levels in birds have shown the importance of bioaccumulation, with levels of selenium in eared grebe eggs at Kesterson Reservoir reaching 130 µg/g (Ohlendorf et al., 1986a; Saiki, 1985b). Coots in the contaminated areas lost nine times more eggs to embryonic mortality than would be expected (Ohlendorf et al., 1986b). Subsequent studies revealed similar concentrations in the Grasslands waterfowl area with duck and avocet eggs containing almost 7 µg/g selenium and liver concentrations up to 85 µg/g (Ohlendorf et al., in press).

Some field research on the effects of selenium on avian reproduction has been done (Ohlendorf et al., 1986a,b,c; Ohlendorf et al., in press; Ohlendorf, 1986, 1987; Heinz, 1986). Very little is known about the effects of selenium toxicity and deficiency on wild birds, game species, and perhaps most critically, on rare and endangered species.

Eleven of twelve mallards fed 100 µg/g Se for a study on reproduction, approximately the food source concentration at Kesterson Reservoir, died before the study was completed (Ohlendorf, 1987). Ten µg/g of selenomethionine affected mallard reproduction more than 10 µg/g of sodium selenite. Embryo defects from these studies were similar to those observed at Kesterson reservoir (Ohlendorf, 1986). Mallards fed 16 µg/g selenomethionine produced many embryo deformities similar to those found at Kesterson Reservoir (Heinz, 1986). Adult mallards fed 8 µg/g produced fewer deformities, but many of the ducklings that hatched died within three days (Ohlendorf, 1985). Studies with other birds, including chickens, quail, and mallards, suggest that problems become apparent at dietary levels of 7 µg/g (Ohlendorf, 1986). Analysis of field data on reproductive success of coots, stilts, and grebes suggested some species differences in selenium tolerance (Ohlendorf et al., 1986b).

Birds higher in the food chain are more likely to be affected. Eared grebe eggs, for example, had more than double the selenium content of coot and stilt eggs at Kesterson Reservoir in 1983 (Ohlendorf et al., 1986b). Resident populations are most affected but transients and migratory species in the Pacific Flyway may also be affected by the high levels of selenium in some areas of California, notably the Salton Sea, Central Valley, and perhaps, parts of the San Francisco Bay area (Smith, 1986; Ohlendorf, 1985, 1986, 1987; Ohlendorf et al., 1986a,b,c; Herrgesell, 1987; Koranda et al., 1979; White et al., 1987). Some selenium concentrations measured in birds are presented in Table 3.7.

Table 3.7. Selenium levels in Calif. birds

Tissue selenium type and location	Tissue conc., µg/g
Bird livers, Kesterson[3]	17-160¥
Bird livers, Volta[3]	1.8-14¥
Bird livers, South Grasslands[3]	9.7-85¥
Cinnamon Teal liver, Tulare Lake DD[1]	5.7¥
Double crested cormorant liver, Salton Sea[1]	9.7§
Duck livers, Imperial Valley[4]	11.2-15.6¥
Duck livers, Sacramento Valley[4]	3.6-5.1¥
Surf scoter liver, Suisun Bay[1]	10-35§
Scaup liver,Suisun Bay[1]	3.6-19§
Eggs, Kesterson[2]	6-70¥
Eggs, Volta[2]	0.59-3.4¥

§ Fresh weight basis, ¥Dry weight basis
[1]White et al., 1987; [2]Ohlendorf et al., 1986a,b,c; [3]Ohlendorf, 1985; [4]Koranda et al., 1979.

The effects of selenium on rare and endangered species are of special concern.

Some of the species that may be affected include residents in the San Joaquin Valley and Salton Sea. Species high on the food chain would be most susceptible.

2. Deficiency

Birds are also susceptible to selenium deficiency diseases. Reduced growth, muscle myopathy, pancreatic degeneration, exudative diathesis, lesions, and myocardial failure have all been related to selenium deficiency (Creech et al., 1957; Patterson et al., 1957; Schwarz and Foltz, 1957; Rahman et al., 1960; Scott et al., 1967; Thompson and Scott, 1970; Pond et al., 1971; Gries and Scott, 1972; Combs and Combs, 1986). Dietary selenium of at least 0.50-0.06 μg/g of feed is needed to prevent exudative diathesis in chicks (Thapar et al., 1969; Mathias and Hogue, 1971; Scott and Thompson, 1971; Noguchi et al., 1973). Conservative recommendations for the dietary selenium requirements of chickens, ducks, and turkeys are between 0.1 and 0.2 μg selenium/g (NAS, 1984b).

The dietary requirement for selenium is affected by the bioavailability of the selenium in the food. Bioavailability is not well understood, but differences are recognized and have been compared in a few studies (Hazell, 1985; Lonnerdal, 1985; Mason, 1985; Combs and Combs, 1986). It is known that the food treatment affects bioavailability. For example, Laws et al. (1986) found that selenium in freeze-dried meal was more bioavailable than meal dried at 82°C. Humaloja and Mykkanen (1986) explored the mechanism of absorption in chickens and found selenomethionine more rapidly crossed the epithelial tissue lining the intestine than did selenite salts.

Selenium deficiency has been reported in birds in the U.S. (NRC, 1976). Selenium deficiency in California birds might occur in areas where cattle and deer exhibit deficiency diseases but this co-occurrence has not been reported in the literature. This may reflect the limited research that has been done or differences in food sources.

H. Selenium in fish

" Complete reproductive failure can occur with little or no mortality or tissue pathology present in the adult population."
A. Dennis Lemly 1987

1. Introduction

Effects of selenium on fish have been summarized by Lemly (1987). Selenium is an essential nutrient for fish but can also be toxic. The transition between safe levels and toxic levels is unusually rapid. Kumar and Prakesh (1971) and Niimmi and LaHam (1975) found that the selenoamino acids were ten times more toxic to algae and fish than inorganic forms of selenium. Elevated selenium levels in water or diet can lead to a variety of pathological symptoms, reproductive failure, and death. The symptoms of selenium exposure include edema (Sorensen and Bauer, 1984; Sorensen et al., 1984; Finley, 1985); cellular distortion, including changes in the blood (Sorensen and Bauer, 1983; Finley, 1985); necrosis and rupture of the egg follicles in the ovary (Sorensen et al., 1984). Spinal and skeletal

deformities are seen in progeny of fish that do reproduce with high selenium exposure (Lemly, 1987). Most deformities are lethal before growout.

Selenium exposure has also been shown to reduce the temperature tolerance of fathead minnows (Watenpaugh and Beitinger, 1985). This may be important in the warm water areas of California where the removal of riparian trees results in higher water temperatures in the summer. Most of the waterways affected by selenium in the San Joaquin Valley have few riparian trees as a result of agricultural practices.

Selenium is differentially accumulated in fish. The highest concentrations are in the liver, followed by female reproductive tissue, axial muscles, and male reproductive tissue (Sager and Cofield, 1984).

Whole body fish sampled nationwide averaged about 0.5 µg/g wet weight, or about 2.0 µg/g dry weight (Ohlendorf, 1986). The range within California fish varies from <1 µg/g to more than 430 µg/g dry weight (Table 3.8).

Table 3.8. Selenium concentrations in fish tissues collected in California.

Fish tissue and source	Average tissue conc. µg/g
Black crappie liver,	
Stony Gorge Reservoir	2.1[4]
Brown trout liver	
Hot Creek	5.1[6]
East Walker River	3.8[4]
Brown bullhead,	
San Antonio Reservoir	2.6-3.0[4]
Channel catfish liver	
Alamo River (Calpatria)	2.3[6]
New River (Westmorland)	2.1[6]
Salt Creek Slough	3.4[6]
San Joaquin River (Vernalis)	2.0[4]
Whitewater River	3.8[1]
Colorado River	3.1[4]
Croaker, Salton Sea	3.9[1]
Croaker liver, Salton Sea (South)	6.2[6]
Croaker flesh, Salton Sea (South)	3.8[6]
Gambusia, Tulare Lake DD	4.2[1]
Green sunfish liver,	
Grasslands	5.5[4]
Chino Creek	2.8[4]
Green sunfish flesh, Grasslands	2.3[4]
Largemouth bass liver,	
Lake San Antonio	3.1[4]
Lake Nacimiento	29.0[6]
Mud Slough	3.3[6]
Alamo River	4.4[6]
San Diego River	3.2[6]
San Antonio Reservoir	2.8-5.5[4]
Lake Nacimiento	2.1[4]
Largemouth bass flesh,	
Lake San Antonio	1.1[4]
Lake Nacimiento	0.7[4]

continued

Fish tissue and source	Average tissue conc. µg/g
Mosquitofish	
Kesterson	16-320[2]
Kesterson	90-430[3]
San Luis Drain at KNWR	90-110[3]
South Grasslands	5.2-18[3]
North Grasslands	5.4-8.6[3]
Volta Wildlife Area	1.2-3.0[3]
Kesterson pond 6	35.0[4]
Kesterson pond 5	27.0[4]
Orange mouth corvina liver, Salton Sea (South)	2.3[6]
Orange mouth corvina flesh, Salton Sea (South)	3.6[6]
Salton Sea	3.1[4]
Rainbow trout liver	
Sacramento River (Keswick)	4.0[4]
Sacramento River (Shasta Dm)	3.1[6]
McCloud River (Shasta Lake)	6.5[4]
McCloud River (Shasta Lake)	9.1[6]
Hardscrabble Creek	2.8[4]
Sacramento squawfish liver	
McCloud River (Shasta Lake)	2.6[6]
Sargo liver, Salton Sea (South)	5.6[6]
Sargo flesh, Salton Sea (South)	2.1[6]
Smallmouth bass liver, Lake San Antonio	3.5[4]
Smallmouth bass, flesh Lake San Antonio	1.1[4]
Steelhead liver, Indian Creek	3.9[4]
Striped bass, liver	
O'Neill Forebay	2.4[4]
San Joaquin River	1.67[5]
Striped mullet, Tijuana Slough	3.2-6.1[4]
San Joaquin River	1.67[5]
Sturgeon muscle, Suisun bay	1.9[1]
Tilapia liver	
Salton Sea	4.5[1]
Salton Sea (South)	3.9[6]
Salton Sea	8.30[1]
San Gabriel River	3.8[6]

continued

Fish tissue and source	Average tissue conc. µg/g
Tilapia flesh, Salton Sea (South)	1.7[6]
White bass liver, Lake Nacimiento	2.9[4]
White bass flesh, Lake Nacimiento	0.9[4]
Yellow bullhead liver, Greason Drain	3.9[6]
Zill's cichlid liver, Salt Creek Slough	17.0[6]

§ Fresh weight basis; ¥ Dry weight basis.
[1§]White et al., 1987. [2¥]Saiki, 1985a; [3¥]Ohlendorf et al., in press; [4§]Agee,1986; [5§]Greenberg and Kopec, 1985;[6§]Linn et al., 1986;

2. Toxicity

Selenium poisoning in fish is complicated by many factors including species, life stage, sex, nutritional status, health, form of selenium, concentration, and duration of exposure (Lemly, 1985a). Water conditions such as hardness, temperature, and suspended solids are also important. This makes accurate predictions of selenium toxicity difficult because these contributing factors and, more critically, their interactions are poorly understood.

Selenium pollution from coal fired power plants has provided considerable information on the effects of selenium on fish. Selenium-rich effluent from power plant fly ash had a severe effect on the fish in a cooling reservoir in North Carolina. Selenium levels of 10-20 µg/liter in the reservoir eliminated 16 of the 20

original fish species. Two of the surviving species were sterile (with adults persisting), one species recolonized from elsewhere as sterile adults, and only one was seemingly unaffected (Lemly, 1985b). These results indicate the potential adverse impact of selenium-rich drainage from agriculture and industrial processes. The differences between North Carolina and California environments, fish species, and food chains make only rough comparisons possible.

Other investigators have reported toxicity problems when selenium levels in water reached 40-53 µg/L (Hodson et al., 1980). A diet with mayfly nymphs containing 14 µg/g selenium killed 3 of 4 bluegills tested (Finley, 1985).

The following results have been reported for some key California fish species:

a. Salmon

Studies of chinook salmon have demonstrated their sensitivity to selenium in the water and in the diet (Hamilton et al., 1987; Palmisano, 1987). Selenium levels in food as low as 6.5 µg/g reduced survival of fry and growth of fingerlings. Effects were observed as low as 3.2 µg/g (Hamilton et al., 1987).

Selenium exposure also reduced salmon's ability to meet the challenge of adjusting to salt water, with more than 50 percent reduction in survival with 26 µg/g in the diet (Hamilton et al., 1987). Selenium also inhibited the osmoregulatory ability of fish and reduced migratory behavior (Palmisano, 1987).

b. Trout

Trout are sensitive to selenium in the diet as well. Hilton et al. (1980) reported reduced growth of trout fed 13 µg/g sodium selenite. They suggested that long-term exposure to 3 µg/g sodium selenite in the diet might be toxic.

Trout with liver selenium levels of 9.1 µg/g did not have measurable selenium in the flesh, so perhaps trout concentrate selenium in the liver to an unusual degree (Agee et al., 1985).

c. Striped bass

Striped bass populations have declined rapidly in the Delta and San Francisco Bay. Studies found that until 1977 the survival for juveniles was correlated with Delta water outflow, but after 1977 this relationship broke down. In 1979 the Cooperative Striped Bass Study showed that the bass population was in very poor health with many deformities and weakened immune systems (SWRCB, 1980). Many factors, including selenium poisoning (Greenberg and Kopec, 1985) have been suggested as the cause of this decline in striped bass. Additional research, some of it now underway, is needed to understand the reasons for the problems in striped bass reproduction.

d. Orangemouth corvina

Orangemouth corvina from the Salton Sea had flesh selenium levels exceeding 3 µg/g (Agee, 1986). This level is possibly high enough to affect reproduction and survival of corvina.

e. Mosquitofish

Mosquitofish appear to have a high tolerance for selenium and are the only fish species found in Kesterson Reservoir and the

San Luis Drain. Mosquitofish are collected for use in fish selenium toxicity testing. Their survival in high selenium water may lead to very high selenium levels in fish, birds, and other predators that consume them.

3. Selenium deficiency in fish

Selenium is also an essential nutrient for fish. Bell et al. (1986) found that rainbow trout develop selenium deficiency problems when dietary selenium was 0.025 µg/g. Ataxia occurred in about 10 percent of the deficient trout and both liver and nerve abnormalities were observed. A level of about 1 µg/g appeared sufficient for nutritional requirements. Gatlin and Wilson (1984, 1986) have explored the selenium requirements of catfish. They found the selenium requirement of catfish was 0.25 µg/g (dry diet).

I. Selenium in shellfish

Shellfish serve as effective filters and test organisms for trace elements and chemicals in water. As a result state agencies rely on data from shellfish, mussels and clams for one of their marine toxics monitoring program. Analysis for selenium was added to this program in 1984. The State Mussel Watch Program detected selenium levels in excess of the International Standard (0.3 µg/g fresh weight) at several sample stations in 1985-86. These data, and data for clams are reported in Tables 3.9 and 3.10.

Table 3.9. Selenium concentrations in mussels at selected sites in California

Location	Concentration µg/g fresh weight
Bodega Head	3.06
Mare Island	3.71
Point Pinole	2.26
Treasure Island	4.43
San Mateo Bridge	3.78
Dumbarton Bridge	4.40

Stephenson et al., 1986.

Table 3.10. Selenium concentrations, µg/g.in two species of clams at selected sites in California

Site	Eastern softshell *Mya arenaria*	Japanese littleneck *Tapes japonica*
Bayview[1]	2.7¥	4.5¥
Coyote Point[1]	2.7¥	5.8¥
Foster Creek[1]	5.6¥	9.9¥
Redwood Creek[1]	8.4¥	9.7¥
Albany Hills[1]	4.1¥	5.2¥
Tara Hills, near Pinole1	7.4¥	
San Pablo Bay[2]	0.36§	

§ fresh weight basis; ¥ dry weight basis
[1]Girvin et al., 1975; [2]White et al., 1987.

J. Selenium in aquatic insects

Little is known about the physiological role selenium plays in insects. Selenium content of insects ranged up to 295 µg/g dry weight at Kesterson Reservoir and 326 µg/g at the San Luis Drain (Saiki, 1985b). Waterboatmen at Westfarmers evaporation pond near Tulare Lake contained 30-100 µg/g selenium (Schroeder and Palawski, 1987). Bottom-dwelling invertebrates at Grassland Water

District averaged 6.9 µg/g but ranged as high as 22 µg/g while free-swimming invertebrates averaged 6.2 µg/g and ranged as high as 60 µg/g (San Joaquin Valley Drainage Program, 1987).

K. Selenium in aquatic ecosystems

Selenium behavior in aquatic ecosystems will depend on many environmental factors. Over time selenium in an undisturbed system appears to be concentrated in the upper layer of the sediment (Lemly, 1987). However, roots, bottom feeders (particularly invertebrates), and microbes can mobilize selenium and move it to the surrounding environment. Selenium may also be mobilized as the roots die back in winter or as a result of drought stress in the summer.

The two major concerns about selenium in aquatic ecosystems are bioconcentration (by living organisms) and biomagnification in the food chain. For example, algae have been found to bioconcentrate selenium several thousand times (Foe and Knight, 1986). Schuler (1987) found selenium levels increased 155 times from water to sediment, 1308 from water to submerged vegetation, and 921 times from water to emergent vegetation. Saiki (1985b) found that bioconcentration and biomagnification increased selenium levels more than 1,000 fold in animals and fish. Selenium contamination of aquatic ecosystems is the primary concern in the San Joaquin Valley (SWRCBTC, 1987).

Biomagnification in the food chain may be on the order of 2-6 times per step in the food chain (Ohlendorf, 1986). Thus, levels of selenium in the water must be kept very low to avoid toxic effects as a result of bioconcentration and biomagnification in the food chain.

L. Selenium in the ocean

Thermodynamic calculations predict that when sea water is in thermodynamic equilibrium, selenium will occur as selenate near the surface or in well mixed water where oxygen is present, (oxic conditions), and as selenite in deep water or poorly mixed water where oxygen is very limited (anoxic conditions) (Sillen, 1961; Turner et al., 1981). In intermediate cases, with a pE of 6.1, selenate and selenite should be in equilibrium. Yet field measurements have shown that while selenate is indeed the predominant species in oxic seawater, up to 35 percent of the total selenium is present as selenite (Sugimura et al., 1976; Cutter, 1978; Measures and Burton, 1980; Measures et al., 1980).

More recent research by Cutter (1982) suggests that selenium is preferentially taken up by surface water biota. Bioaccumulation and bioconcentration are important factors in the ocean. Selenium levels of fish meal, for example, are as high as 2 µg/g, an increase of several thousand times higher than the seawater concentration of 0.05 to 0.09 µg/L (NRC, 1976; Wilber, 1983).

Organisms in sea water preferentially take up selenite over selenate. Selenate is usually taken up only in selenite-deficient areas. The uptake of organic selenium is less clearly

understood. This form of selenium is converted to selenide metabolically in organisms, perhaps by reductive incorporation. It is then transferred to the deep sediments as detritus, primarily as selenide. Regeneration in oxic waters occurs as this organic selenide is dissolved, oxidized to selenite, which in turn is slowly oxidized to selenate, the thermodynamically stable form of selenium in the ocean. In anoxic water this process appears to progress only to the first step, the production of dissolved organic selenide.

Under very anoxic conditions selenate and selenite are gradually reduced, presumably to elemental selenium, metal selenides, dimethylselenide, and hydrogen selenide. Methylation was not observed in clean waters but may be more prevalent in ocean waters affected by pollution (Cutter, 1982).

Cutter (1982) found that selenium behavior was very different from sulfur in sea water. The small differences in the chemical behavior of selenium and sulfur mentioned in Chapter 2 are very important in sea water because of the important role biological processes play in selenium cycling.

M. Summary

Selenium is both an essential nutrient and potential poison. The dietary requirements for birds, animals, fish, and man are not widely different. A selenium level of from 0.1-0.2 µg/g dry weight in the diet appears to be sufficient for many mammals, including humans, as well as birds and fish.

Selenium toxicity may be observed when total diets provide more than 2 µg/g dry weight of diet. The toxicity of different forms of selenium varies widely and is not yet well understood. The organic selenium compounds appear to be more toxic than the inorganic salts, which are more toxic than elemental selenium. Toxicity is intimately linked to other factors in the diet, notably low protein, and has been observed in normal populations (in China) only where the diet was very poor.

Problems of selenium poisoning occur as a result of bioconcentration and biomagnification, which can increase selenium levels thousands of times over the background level. This has led to observed and well documented problems among fish and wildlife, especially aquatic birds.

No well documented cases of livestock poisoning from selenium have occurred in California. Human poisoning has occurred only from errors in food supplement production, not from dietary exposure.

Selenium deficiency is observed in cattle and wild animals in much of California, even near Kesterson Reservoir. Selenium deficiency may also occur in humans.

While the conventional analogies between sulfur and selenium behavior appear to work in many plants and abiotic systems, they often do not in those with strong biological components. Much more work is needed to understand selenium behavior in the environment, particularly the occurrence and forms of selenium and their hazard to wildlife.

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Chapter 4. Sources of selenium

"Soils associated with selenium trouble are derived, for the most part, from rocks of the Cretaceous age. Considerable quantities of selenium are transported in the drainage waters of certain western streams."

Anderson et al. 1961

A. Introduction

The original source of selenium in the environment is the molten magma beneath the earth's crust. Selenium reaches the surface primarily by vulcanism as metallic selenides in sulfoselenides associated with igneous mineral deposits (Rosenfeld and Beath, 1964). Selenium is widely distributed in the environment and in most cases highly dispersed. Selenium averages from 0.05-0.09 µg/g in the Earth's crust, ranking it 68th in elemental abundance (Adriano, 1986). Its pattern of distribution is similar to sulfur, in the approximate ratio of 800-6,000 parts of sulfur to 1 part selenium (Vinogradov, 1964; Adriano 1986).

Selenium is redistributed and concentrated by geological, climatic, biological, and human activity. The most important sources of selenium are sedimentary rocks, seleniferous soils, and selenium-rich mineral deposits. Combustion of fossil fuels and solid waste, microbial activity, and industrial processes release selenium into the atmosphere; and solid waste, coal storage piles, and power plant ash can be sources of selenium-rich leachates. Phosphate fertilizer is a minor source of selenium for agricultural soils. Superphosphate may contain up to 25 µg/g (Swaine, 1978).

This chapter contains two sections, natural sources of selenium and selenium from human activity. Of course these are inter-related and these interactions will be described in more detail in Volume 2 of this report.

B. Natural sources of selenium

1. Distribution in geologic deposits

In most cases selenium is highly dispersed and in low concentrations in geologic deposits. The exceptions are rocks of igneous or volcanic origin which may have between 0.1-5.2 percent selenium in some igneous outflows with primary enrichment (Nazarenko and Ermakov, 1972); and sedimentary rocks, where geological and biological forces have increased selenium concentration (Table 4.1). Elemental selenium is rare but does occur in some sediments and sulfur deposits. Selenium is more commonly found in chemical combination with other cations, primarily metals and metallics. In these it behaves as a non-metal, with three common oxidation-states; selenide Se^{-2}, selenite Se^{+4} and selenate Se^{+6}.

Organisms can concentrate selenium. If several trophic steps are involved concentrations can be increased many thousands of times over the ambient level (Swaine, 1978; Wilber, 1983). Marine fish meal, for example, with 2 µg/g selenium, has a selenium level thousands of times higher than sea water. This phenomenon, described more fully in Chapter 3, also enriches selenium in swamps, peat, freshwater, and marine sediments. Peat, the

first step in coal formation, from the Okeefenokee Swamp in the Southeastern U.S., has been found to have selenium levels similar to coal (Wilber, 1983).

Table 4.1. Selenium abundance in geologic deposits.

Source	Concentration µg/g Average	Range	Range percent
Igneous	0.05	----	
Galena	----	----	0-20
Pyrite	----	----	0-5
Cinnabar	----	0-4,000	
Limestone	0.08	0.16	
Sandstone	0.05	----	
Shale	0.60	<1-675	
Coal	3	0.04-10	
Arizona coal	1.2	----	
Colorado coal	2.3	----	
Wyoming coal	2.3	----	
Phosphate	<20	1-300	
Petroleum	----	0.01-1.4	
Sedimentary uranium and phosphatic vanadium	----	200-300	
Baby King Creek, mudstone/shale	2.4	----	
Moreno formation	----	to 2.4	
Vaqueros formation	----	to 3.9	
Tulare formation	----	to 5.3	
Tejon formation	----	to 4.3	
Kreyenhagen shale	----	to 18.6	
Along I- 5, San Joaquin Valley	<0.005	to 6.0	

Coleman and Delevaux, 1957; Sindeeva, 1964; Gluskoter, et al., 1977; Loebenstein, 1980; Ebens and Shacklette, 1982; Wilber, 1983; Shacklette and Boergen, 1984; Adriano, 1986; Bakhtar et al., 1986; Wiggett and Alfors, 1986; Southard et al., 1987; Lund et al., 1987.

Sediments of the Cretaceous period are particularly rich in selenium, not only in the western U.S. but also in Queensland, Australia (Anderson et al., 1961; McCray and Harwood, 1963; U.S. Department of Interior Task Group (DITG), 1985). High levels of selenium in shales, carbonaceous material in sandstones, and phosphate rock may be largely the result of bioconcentration (Adriano, 1986). The problems with selenium in the San Joaquin Valley and perhaps the Sacramento Valley are associated with marine sediments in the Coast Ranges (Barnes, 1986).

2. Selenium in soils

a. Sources of selenium in soils

Research on soil selenium relationships was prompted by the discovery of selenium deficiency and toxicity syndromes in livestock. Although most plants do not generally require selenium for their growth, animals do. Plants take up and concentrate soil selenium which then becomes available to the animals that eat the plants. Selenium deficiencies in animals are much more common than toxicities. Generally, the higher the selenium concentration is in the soil the higher the plant uptake and resulting plant concentration will be. However, even where soil selenium is present, plant availability may be low. Selenium concentrations in soils are highly variable and depend on climatic conditions, the origin of geologic material, and the forms of selenium in the soil, water systems, and vegetation.

Generally, livestock toxicity problems occur on arid soils under alkaline conditions and deficiency problems develop in areas of higher rainfall on neutral to acid soils, especially where organic matter and/or high iron content leads to selenium fixation in forms that are largely unavailable to plants (Geering, et al., 1968; Johnson, 1975).

b. Forms of selenium in soils

Both organic and inorganic forms of selenium are found in soils (Cary and Allaway, 1969). Organic forms are primarily derived from decaying vegetation which has previously accumulated selenium. Inorganic forms that are found in soils include selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), elemental selenium (Se), and metal selenides. Selenites generally predominate in acid (pH 4.5 to 6.5) and waterlogged soils as oxides and oxyhydroxides of ferric ions (Fe^{3+}) which are extremely insoluble and therefore not readily available for plant uptake (Gissel-Nielsen, 1977). Selenates generally predominate in well-aerated alkaline soils (pH 7.5 to 8.5), where they are soluble, mobile, and readily taken up by plants (Soltanpour and Workman, 1980). The conversion of selenate to selenite is very slow, and the rate of transformation to elemental selenium is even slower (Peterson et al., 1981). The chemical form of inorganic selenium in soils affects the mobility and bioavailability of selenium to plants and consequently animals.

c. Amounts of selenium in soils

Most soils contain measurable amounts of selenium, while a few contain enough to result in plant accumulations toxic to animals. The total selenium content of soils ranges from 1,200 μg/g in an organic matter rich soil noted for toxicity problems in Ireland (Fleming, 1962) to a low of <0.1 μg/g in selenium deficient soils of New Zealand (Wells, 1967). Most seleniferous soils contain less than 6 μg/g total selenium. Elevated selenium levels may be expected to occur in areas with arid or semi-arid climates where soils are derived from marine sediments, particularly shales (Rosenfeld and Beath, 1964; Johnson, 1975).

While it is convenient to analyze soils for total selenium, the resulting data do not necessarily predict selenium availability for plant uptake reliably (Johnson, 1975; Nye and Peterson, 1975). Typically, soils are sampled and extracted with solutions designed to remove a selected part of the total elemental content which is then used to predict potential uptake and accumulation by plants. For example, the water soluble soil selenium fraction has been suggested as a useful predictor of selenium uptake by plants (Lakin, 1972; Workman and Soltanpour, 1980). While this is a useful tool for studying the fate of selenium applied to soils, others have questioned its use as an indicator of plant available selenium (Levesque, 1974a). Hot water extracts and salt extracts have been proposed and studied as predictors of selenium availability to plants with conflicting results when used over a wide range of soils and climatic conditions (Geering et al., 1968; Cary and Allaway, 1973; Soltanpour and Workman, 1980). Although analytical methods have been developed to study the amounts of selenium and its various forms in soils, no soil extraction procedure has been widely used nor refined enough to be easy to use and have reliable predictive value. Numbers are relatively easy to gather, but interpretation has proven to be more difficult. Unfortunately, much of the information and subsequent discussion about selenium in soils lacks either explicit descriptions of the procedures used to measure forms of selenium in soils or clearly stated assumptions used when interpretations of that information are made. This leaves much uncertainty about the methods used to diagnose problem situations, and more critically, makes comparisons between different studies difficult.

Total soil selenium values and plant-available soil selenium values need to be put in the context of the distribution of selenium in the soil profile. Soils develop distinguishable layers with varying properties and characteristics with depth. Selenium is usually not uniformly distributed throughout the soil profile. Topsoil selenium content and availability can be quite different from subsoil selenium contents. As soil properties change with depth, as water moves down soil profiles through rainfall or irrigation, or as soils become waterlogged, selenium distribution in soils will change. Organic matter is generally higher in topsoils and may contain selenium as a constituent, whereas iron compounds are

more commonly associated with selenium at deeper soil depths (Levesque, 1974a,b). Factors which need to be considered in soil profile distribution of selenium can include parent material, rainfall, pH, organic matter, and iron-containing minerals (Adriano, 1986).

The rooting depths of plants growing in these soils also need to be considered, especially in natural systems. Selenium-deficient shallow-rooted annual plants might grow side by side with deep-rooted perennial plants which have active roots in selenium-rich soils at depth. This may result in toxic levels of selenium in the deeply rooted plants and barely detectable levels in the shallow-rooted annuals.

d. Chemical and biological reactions in soils

Selenium exists in soils in a multitude of forms, complexes, and associations. These are dynamic and change with time and as the environment changes. These affect the mobility of selenium in the environment and the availability of selenium for plant uptake into the food chain. Certain soluble forms of selenium enter into reactions with other chemical forms in soils and precipitate as secondary compounds which effectively removes them from plant availability and transport in the environment. They may redissolve when conditions favor such a reaction and become mobile again. Additionally, soluble forms of selenium will adsorb to the surfaces of soil particles under some conditions and subsequently desorb or detach from these surfaces as conditions change. Precipitation and adsorption reactions primarily depend on soil pH, soil oxidation-reduction potential (Eh), water content, soil mineralogical properties, organic carbon content, clay content, $CaCO_3$ content, and cation exchange capacity (Cary et al., 1967; John et al., 1976; and Singh et al., 1981).

Plants and microorganisms will transform selenium to different compounds as well (Chau et al., 1976; Doran and Alexander, 1977; Reamer and Zoller, 1980). See also Chapter 3.

e. Soil properties affecting selenium forms, amounts, and behavior

i. Soil type and particle size distribution

Clay soils retain much more selenium than sandy soils and plants tend to have higher selenium levels on clay soils (Cary et al., 1967; Gissel-Nielsen, 1975).

ii. Soil pH

Soil pH is a strong determinant of selenium form in soils. Selenate is the dominant selenium form in well-aerated alkaline soils and is soluble while selenite is the dominant selenium form in acid or neutral soils and is fairly insoluble. Adsorption of selenium species to the surfaces of clay particles generally decreases with increasing pH (Gissel-Nielsen, 1977). The highest selenium accumulations by plants are found on higher pH soils (Cary and Allaway, 1969). Soil liming, which raises soil pH, tends to increase selenium solubility and hence plant uptake (Geering et al., 1968).

iii. Organic matter

Like clay minerals, organic matter can remove selenium from solution, but the

process is one of assimilation rather than fixation (Cary et al., 1967). The addition of organic matter has been shown to reduce selenium mobility (Mikkelsen, 1987). Microorganisms remove selenium from solution and incorporate it into their biomass. They can also transform adsorbed selenite to soluble organic selenium compounds and selenate (Shrift, 1967). Microorganisms can also produce volatile organic selenium compounds which can escape from the soil as a gas, i.e., hydrogen selenide, dimethylselenide, etc. (Francis et al., 1974; Frankenberger et al., 1986).

iv. Other ions

Sulfate ions in the soil can compete with selenium ions for plant uptake. Adding elemental sulfur or gypsum ($CaSO_4$) to soil can reduce plant selenium uptake (Hurd-Karrer, 1938). However, most soils in the United States with selenium toxicity problems are naturally high in sulfate as well, and many soils with seleniferous vegetation obtain much of the selenium from the deeper soil layers (Olson et al., 1942).

These factors suggest that the practical value of adding sulfate to surface soils to reduce plant uptake of selenium is limited. Adding sulfur to sulfur-deficient soils can decrease selenium concentrations in vegetation, although the reduction may be due to dilution because plants grow larger in response to sulfur additions (Westerman and Robbins, 1974). Neglect of this dilution effect and imprecise measurement of net accumulation rather than tissue concentration has obscured the effects of many soil amendments and practices (Jarrell and Beverly, 1981). Total selenium taken up by plants may actually increase while tissue concentration declines.

Phosphate additions to soils can increase plant selenium accumulation in alfalfa (Carter et al., 1972) and berseem clover (Singh and Malhotra, 1976). This could be because phosphate ions displace selenium already on soil particle surfaces into the soil solution where it can be taken up by plants, or because greater root growth in response to phosphorus additions increases selenium uptake. Conflicting results have been reported where phosphate additions decreased plant selenium concentration (Gissel-Nielsen et al., 1984). The phosphate-selenium interaction doesn't appear to be very important in either case (Mikkelsen and Bingham, 1986). As shown earlier in this chapter, some phosphate fertilizers have relatively high selenium concentrations. Selenium can also be added to phosphate fertilizer and this can be advantageous where selenium deficiencies are encountered (Robbins and Carter, 1970).

Soil fertility may also influence microbial populations, which in turn may affect selenium uptake. Phosphorus and nitrogen fertilizers, for example, may depress microbial populations which may reduce plant trace element uptake. See also Chapter 3.

f. Key questions

Selenium behavior in soils is very complex and depends on a variety of environmental factors and the effects of human activities.

Some of the essential questions that must be considered when assessing or predicting the environmental consequences of soil management and subsequent effects on selenium include the following: How can selenium-contaminated waters be safely applied to agricultural soils, for how long and at what rates? How can soils rich in selenium be farmed and irrigated intensively over time with selenium releases into drainage water, groundwater and the food chain kept at safe levels (both concentration and loading)? How can selenium releases from selenium-rich soils be corrected, treated, controlled, predicted, or avoided by management techniques? Which methods are economically feasible? Many of these questions have not yet been answered.

3. Selenium in California's water

Although some patterns of selenium occurrence have now become evident, the lack of comprehensive data makes it impossible to describe the selenium content of the water in California in detail. The testing that has been done has shown that levels vary widely, both locally and regionally. They also vary over time as a result of the complex interactions between cropping patterns, irrigation, rainfall, groundwater pumping, and drainage.

Long-term monitoring and careful modelling are essential to more accurately predict the effects various climatic and management changes may have on selenium levels in water. Enough is known to suggest the need for considerable caution when interpreting single season or single sample data. The complex relationship between selenium problems and the type of water year has been explored for the San Joaquin River. This work has also shed some light on the nature of problems which might be expected with selenium management in other drainage basins. The results of the San Joaquin River investigations, which remain preliminary due to the short history of reliable selenium data, make it clear that very dry years, with very low precipitation and runoff, are much more important than average conditions (State Water Resources Control Board Technical Committee[SWRCBTC], 1987). These critical years have occurred 21% of the time from 1906-1985. Little is known about the selenium loading in other river basins in relation to water year.

Although the San Joaquin Valley is the best studied area, the processes by which selenium has become concentrated in the irrigation drainage water and other water of the Kesterson area are still not well understood (Deverel et al., 1984). One hypothesis suggests that the selenium originally derived by weathering and oxidation of sedimentary selenosulfides ($SeSo_3^{-2}$) in marine shales of the Coast Range, is released as selenite (Se^{+4}) and selenate (Se^{+6}) salts, while the sulfides go into solution as sulfates (SO_4^{-2}). These materials are then deposited in the alluvial fans on the Valley floor, where they are concentrated by evaporation (Presser and Barnes, 1984). Dissolved selenium may be carried by deeper groundwater flows from the

Coast Range to low-lying discharge areas near the San Joaquin River (Deverel et al., 1984). This may have occurred over geologic time and may still be occurring in the western side of the valley. The shallow groundwater in the western San Joaquin Valley, which is collected in subsurface drains for discharge, was analyzed for selenium and other trace elements. Selenium was found in higher average concentrations in the central (10 µg/L) and western (11 µg/L) portions of the area than in the eastern lands adjacent to the San Joaquin River, where the average selenium concentrations was <1 µg/L. The highest selenium concentrations found in the west side of the San Joaquin Valley, up to 3,800 µg/L (Deverel et al., 1984).

Selenate is the most common form of dissolved selenium in alkaline aquatic systems, such as those of the San Joaquin Valley (Deverel et al., 1984), but selenite and organic selenium compounds may also be found (see also Chapter 2 and 3).

Some of the water studies that have been done are of questionable value as a result of difficulties with the selenium analyses (Burau, 1986; Letey et al., 1986, Harte et al., 1986; Page et al., 1986). Reported concentrations for reference solutions sent to laboratories which regularly provide selenium analytical services differed substantially, and more than half of the laboratories using the graphite furnace method without a background correction reported detectable selenium concentrations in samples which contained concentrations below the instruments' detection limits. These problems have been resolved but historic data need to be carefully assessed before they can be of value.

a. Groundwater

Long-term data are available for some metropolitan water and irrigation systems (California Department of Health Service, vd) and a considerable effort is now being made to evaluate selenium levels in both drinking water and irrigation wells and groundwater in the San Joaquin Valley (Letey et al., 1986; Tanji et al., 1986; Neil, 1986; Everson and Neil, 1986) and other areas of California. Few problem wells with high selenium levels have been detected statewide; however, there are indications that some problem areas may exist. More than 40 percent of shallow groundwater samples in the San Joaquin Valley exceeded the Public Health Service Drinking water standard of 10 µg/L, and a maximum concentration of 3,000 µg/L was found (Deverel et al., 1984). Oster et al. (1987) found that 26 of 151 wells tested in the Coast Range exceeded the drinking water standard, 10 µg/L. These selenium-enriched waters would require considerable dilution to meet the 2 µg/L (or lower) level desirable in surface waters to protect aquatic ecosystems (SWRCBTC, 1987). Everson and Neil (1986) reported that six of 230 wells tested by the U.S.Geological Survey contained more than 10 µg/L and three exceeded 20 µg/L.

The relatively high levels of selenium in some of the City of Davis water wells (30-90 µg/L for Well #13) confirms the desirability of well-by-well analysis (Milich, 1987). The variation among concentrations in the City of

Davis wells was high, with four of seventeen wells above the 10 µg/L standard (Bachman and Milich, 1987). The concentrations in these wells also vary considerably over time (Fitch, 1987). More detailed monitoring of private wells in areas with potentially selenium-rich marine sediments may be desirable. However, studies of the drinking water well at the Freitas ranch (near Kesterson Reservoir) showed selenium concentrations from 1 to 10 µg/L (U.S. Dept. of Interior [USDI], 1984).

Groundwater movement is complex and poorly understood in most areas of California. It is complicated by differential movement through various sediment layers and deposits of old stream channels. This makes developing accurate knowledge of groundwater movement more difficult. This information is important for management and control of groundwater pollution with selenium. It has become clear, however, that selenium-enriched water is not all trapped in perched water tables (Deverel, 1986; Belitz, 1986). Selenium levels of 380 µg/L have been found in groundwater more than 150 meters deep near the California Cotton Gin in Fresno County, and other deep wells also have shown levels from 9-380 µg/L (Deverel, 1986; Belitz, 1986). Presser and Barnes (1985) found selenium concentrations of 65 µg/L for a 600 foot deep well south of Mendota.

Movement of groundwater can be estimated if differences in water table level and hydraulic conductivity are known. An evaluation of 40 townships in the western San Joaquin Valley suggested that water should move an average of about 6 feet per day, but could range from 0.001 to more than 300 feet per day (Grismer and Woodring, 1987). They concluded that lateral flow rates are probably relatively small in general, but being highly variable, could be significant in some areas.

Vertical flow is also difficult to predict as it depends on the distribution of impermeable layers and the effects of drilling, pumping, rainfall and irrigation. These factors must be understood more clearly for selenium management plan development.

b. Surface water

Understanding selenium mobility and movement in surface water systems is equally challenging, and largely unknown (Letey et al., 1986; Tanji et al., 1986). The problems of selenium in surface water are primarily related to enrichment from drainage of agricultural land (see next section). Alternative strategies for drainage water management may increase selenium problems in the creek and river systems and groundwater. Bypassing the Grasslands marshes to protect wildlife within the Grasslands has apparently more than doubled the selenium loading of the San Joaquin River (Bontadelli, 1985; SWRCBTC, 1987). Models suggest that mud slough and salt slough may contribute 81% of input selenium into the San Joaquin River (SWRCTC, 1987).

The mobilization of selenium from the soils of the western San Joaquin Valley has led to increasing selenium loading of the San Joaquin River system, the Delta, and Suisun and San

Francisco bays (Davoren, 1986; Greenberg and Kopec, 1986; Smith, 1986). However, there the effects of this loading are still in doubt. Johns and Louma (1987) concluded that selenium does not appear to be entering the northernmost reach of the San Francisco Bay Delta in levels sufficient to measurably affect bioaccumulation by *Corbicula*. Historically, the high levels of selenium in the soils would probably have led to minor releases except under unusually high rainfall (Barnes, 1986) which helped flush the pulse of selenium through the system.

The highest level of selenium measured by Deverel et al. (1984) in the San Joaquin River was 2 µg/L. More recent samples from the San Joaquin River have ranged from 11 µg/L at Fremont Ford to 2 µg/L near Vernalis (SWRCBTC, 1987). This may be high enough to cause problems through bioconcentration and biomagnification which may increase selenium levels several thousand times over the background level (see Chapter 3).

The increasing use of the Delta as a water source has led to the export of large quantitities of water from the Delta. Harte et al. (1986) found that there was some cause for concern about future contamination of water exports to Southern California from this source. They found that "the consistently high fraction (30-60%) of water flowing south of the Dos Amigos Pumping plant having a San Joaquin River source suggests that further deterioration in the quality of the San Joaquin River water will have a negative impact on drinking water supplies in Southern California." They recommended an expanded monitoring program and more detailed study of the delta and water system hydrology and trace element behavior.

Elevated selenium levels are not restricted to the San Joaquin Valley. Dissolved selenium in the Alamo River, which feeds into the Salton Sea, reached 20 µg/L and was commonly more than 10 µg/L (U.S. Dept. of Interior Task Group, 1985). This survey also reported maximum observed concentrations above 10 µg/L in the Merced River, the Los Angeles River at Long Beach, and the Sacramento River at Keswick. The median values were lower, respectively, 1 µg/L, 1 µg/L, and 4 µg/L. Selenium problems in surface waters result from increased loading, increased concentration as a result of water removal and, perhaps, a lack of annual flushing as a result of flood control projects.

Water samples taken from the Salton Sea in February 1986 averaged 6 µg/L (White et al., 1987). Water samples from San Francisco Bay, where moderate levels of selenium have been reported in biota, were relatively low, ranging from 0.01-0.72 µg/L (Cutter, 1987).

Little data are available on selenium concentrations in lakes. It appears possible that there are some lakes with elevated selenium levels. Fish tissue selenium levels (see Chapter 3) suggest that both San Antonio Reservoir and Lake Nacimiento might be areas for further study. Lakes in Cretaceous marine sediments or with large areas of these sediments in their drainage basins would also be candidates for monitoring.

c. Agricultural drainage

The primary source of selenium contamination of California's surface and groundwaters is agricultural drainage, primarily as subsurface drainage. This water may add selenium to surface waters or to groundwater. Agricultural drainage affects the selenium content of water, soil, and aquatic ecosystems in the San Joaquin and Tulare Lake drainage basins, the Coachella and Imperial Valleys, and other parts of the state.

The pattern of variation in selenium concentration in drainage water and runoff over time is not well known. Recent studies in subsurface drainage of the Broadview Water District have identified a spring pulse, a relatively constant and significant summer concentration, and much lower winter concentrations (Day and Nelson, 1986). Loading estimates for the Grasslands suggested there was a with a high spring input, relatively low summer input, and intermediate winter load (Summers Eng. Co., 1986).

Dissolved selenium concentrations were quite high in some of the drainage water entering the San Luis Drain before it was closed. Izbicki (1984) and Presser and Barnes (1984) reported values of 140-1,400 µg/L. The U. S. Environmental Protection Agency (USEPA) minimum of dissolved selenium for a hazardous waste rating is 1,000 µg/L (USEPA, 1980). The San Luis Drain itself ranged from 260-350 µg/L (Deverel et al., 1984). Studies of other drainage canals have shown both lower values, for example, 45-60 µg/L in drains bordering the Grasslands and higher values, including one discharging water containing 4,200 µg/L (Presser and Barnes, 1985). Other selenium values from surface waterways that are in essence agricultural drains include: 32 µg/L in Salt Slough near Stevenson, 28 µg/L in Mud Slough at Highway 140, 53 µg/L in Agatha Canal near CCID Main Canal, 75 µg/L in Camp 13 ditch at CCID Main Canal (SWRCBTC, 1987; Gilliom, 1986), 2.3-6.9 µg/L in the lower Whitewater River and up to 3.2 µg/L in the Palo Verde Outfall Drain (White et al., 1987).

Evaporation ponds are the most likely areas for problems with selenium. When agricultural drain water is collected in an evaporation pond then evaporation and continued loading of the pond can lead to very high selenium concentrations. Kesterson Reservoir is the most notable example, with water concentrations of 228 µg/L (USDI, 1984); but, many other evaporation ponds in the San Joaquin Valley are potential problem areas as well. Selenium levels measured in evaporation ponds include: 2.6-10 µg/L at the Lost Hills Ranch, Kern County, 25-36 µg/L in the Tulare Lake Drainage District South Evaporation Basin, and 109-581 µg/L at the Westfarmer Evaporation Pond (White et al., 1987); 1,700-2,000 µg/L at the Sumner-Peck Ranch (Westcot, 1987); 200-800 µg/L at the Murietta Farms, 76 µg/L at the Thomsen Ranch, and 16 µg/L at the Carrollo farm (Cervinka et al., 1987).

4. Selenium in the atmosphere

A number of sources move selenium into the atmosphere. It has been found in volcanic gasses (Byers et al., 1936; Suzoki, 1964), and

it appears likely that vulcanism is a major contributor of selenium to the air. The release of volatile selenium from plants, particularly from some of the accumulator species, has also been documented. Dimethyl-selenide (Lewis et al., 1972) and, to a lesser extent, dimethyl-diselenide (Evans et al., 1968), have been identified in volatiles from accumulator plants.

Soils may also contribute selenium to the air as the result of microbial action (Frankenberger et al., 1987) or as dust derived from seleniferous areas. Major pulses of selenium may enter the atmosphere when areas with selenium-rich vegetation are burned. Animals also volatilize selenium, although amounts are limited unless the selenium doses are high (see Chapter 3). Accurate estimates of the quantities contributed to the air by each of these sources have not been made and are perhaps impossible to make.

Selenium continuously enters and is removed from the atmosphere. Its average concentration in air is very low, probably well below 0.01 $\mu g/m^3$ (NRC, 1976). Seven air samples collected in the spring at Cambridge, Massachusetts, contained an average of only 0.001 $\mu g/m^3$ as measured by neutron-activation analysis with chemical separation (Hashimoto and Winchester, 1967). Rainwater or snow water collected in the same area during a period of 2 years (22 sampling times) contained an average of 0.2 µg/L, presumably derived from atmospheric sources (Hashimoto and Winchester, 1967).

C. Selenium from human activities

1. Soil

Human activities are the primary factor in selenium release from soil. These activities include cultivation, irrigation, drainage, and addition of soil amendments. It is likely the selenium concentration in the air in areas with selenium-rich soil are elevated at times from blowing dust from cultivated land.

2. Plants

Management of vegetation will also affect selenium release. Selenium would be released from harvested selenium-enriched plants. Killing plants with elevated selenium levels in ponds and along ditches with herbicides would also lead to selenium mobilization. Burning seleniferous vegetation would lead to gaseous or particulate losses of selenium. Selenium is also released as a gas as plants dry and from microbial decomposition of organic matter.

3. Wetlands

The selenium loading of the San Joaquin River increased substantially as a result of changes in management of the Grasslands area. This wetlands apparently served as a biological filter and groundwater recharge area for selenium in agricultural drainage water; when drainage water was shunted past the area to protect the wildlife and waterfowl, the load to the San Joaquin river increased from 2,614 pounds per year to more than 7,808 pounds (Bontadelli, 1985). More recent estimates suggest the Grasslands removed even more of

the selenium load, perhaps as much as 6,608 lbs per year (SWRCBTC, 1987). In addition to the biological uptake and storage in the Grasslands biota, sediments, and soils, it is likely that some of the selenium percolated into the groundwater as a result of the winter storage in ponds.

4. Water

Selenium also enters water from industrial and commercial sources as well as from natural and agricultural sources. These may be locally important. Major point source contributors to San Francisco Bay are listed in Table 4.2.

Table 4.2. Selenium point source discharges to San Francisco Bay

Source	lbs/yr
Chevron refinery, Richmond	1,179
Tosco refinery, Martinez	565
Exxon refinery, Benicia	431
Palo Alto sewage treatment plants	347
Shell refinery, Martinez	282

Citizens for Better Environment, 1981.

Davoren (1986) speculates that other treatment facilities in San Jose/Santa Clara which also have extensive electronic industry effluent may have similar discharges. Discharges from other municipalities may also have selenium sources. The rapid increase in electronic manufacturing in Tijuana, Mexico (Yoshihara, 1988) may lead to increased selenium discharge to the Tijuana River and Tijuana Slough.

5. Atmosphere

Human activities appear to be a major source of selenium released to the atmosphere. However, data on the actual presence of selenium in the atmosphere are limited (Wands, 1969), and it has not been easy to identify sources. Galloway et al. (1982) estimated total world emissions from natural sources at 3,000 tons and human-caused emissions at 14,000 tons.

Selenium concentrations in urban air in the United States have received little study. Pillay et al. (1971) analyzed 18 samples collected around Buffalo, New York, during 1968-1969. These samples consisted of particulates collected on filter paper and gaseous materials absorbed by a liquid trap. They used neutron activation with chemical separation for analysis and reported values ranging from 0.0037 $\mu g/m^3$ and 0.0097 $\mu g/m^3$ and averaging 0.0061 $\mu g/m^3$. Half of the selenium was in the gaseous fraction and half was in the particulate matter. Using neutron activation analysis, Dams et al. (1970) found selenium concentrations of 0.0025 $\mu g/m^3$ at Niles, Michigan, and 0.0038 $\mu g/m^3$ at East Chicago, Indiana in suspended particulates. In a similar study, selenium levels of 0.0008 to 0.0044 $\mu g/m^3$ were reported for particulate matter of the air (Harrison et al., 1971). Lakin and Davidson (1967) found selenium content of city dusts ranged between 0.05 and 100 $\mu g/g$ for various cities, but had no basis for

estimating the concentration of the element in the air from their data.

Selenium from other industrial sources should also be of little concern, except in the immediate vicinity of an industrial facility. Seliankina and Alekseeva (1970), for example, found that concentrations dropped off from 0.5 $\mu g/m^3$ near a copper refinery to 0.07 $\mu g/m^3$ at 2 km. In a plant producing selenium rectifiers, air analysis revealed between 7 and 50 $\mu g/m^3$ (NRC, 1976).

The emissions for mining and milling have been estimated from reports on the selenium content of ores and concentrates at over 40 large mines and mills. Atmospheric emissions from mining and concentrating result mainly from windblown, finely ground tailings. Yearly emissions are estimated to be one percent of the selenium placed on tailing dumps annually (Davis and Associates, 1972).

Smelting and refining emissions were estimated from reports from two smelters, from the amount of metal produced, and from the estimated selenium content in slags. The estimate of 277 lb/Se emitted per ton of selenium produced in primary selenium refining as done at precious metal refineries is based on reports of experience obtained from two sources (Davis and Associates, 1972). Emissions from secondary production of selenium were estimated at 100 lb/ton of selenium produced, on the basis of an office study of processing methods (Davis and Associates, 1972).

No reliable reports of volatilization losses of selenium in glass manufacturing are available. Emissions are high because the temperature of molten glass is considerably above the boiling point of selenium. The emission factor is estimated at 700 lb/ton of selenium consumed, based on an estimate made for selenium emissions from molten steel of 1,000 lb/ton of selenium added.

Emissions from electrical manufacturing were estimated at 2 lb/ton of selenium consumed, on the basis of information furnished by manufacturers (Davis and Associates, 1972). The emission occurs primarily during the vacuum plating process used in manufacturing selenium-coated plates and drums.

The major compounders of selenium-containing pigments estimated that 15 lb of selenium were emitted per ton of selenium processed (Davis and Associates, 1972). All reported that bag filters were used for emission control. Selenium emissions in other manufacturing processes were assumed to average 10 lb/ton of selenium processed.

Selenium emissions from fuel combustion are also significant. The selenium emission estimate in the Davis and Associates study was based on analyses of metal concentrations studies in fuel oil done for the EPA in 1971 (NRC, 1976). The average selenium content of 10 samples of foreign and domestic crude oil was 0.4 $\mu g/g$. The average for 27 samples of imported residual oil was 0.6 $\mu g/g$.

The estimates of emissions for incinerators developed by Davis and Associates (1972) were based on limited data from a single facility. The data were obtained from a 3-day

study of an incinerator processing about 245 tons of municipal solid waste daily. Analysis of stack emissions indicated a wide range of emissions from day to day, ranging from zero to 63 pounds per million tons (Johnson, 1970). Selenium emissions from incineration of municipal waste may occur and waste burning facilities should probably review their waste stream and emissions for selenium. Large amounts of pigment or electronic waste might be cause for concern.

Selenium in the air has been monitored intermittently in the vicinity of Kesterson Reservoir since 1985. Both particulate and gaseous compounds have been studied in limited tests. Particulate selenium levels reached 0.0148 $\mu g/m^3$ and one relatively high, ≤ 1 $\mu g/m^3$ gaseous concentration was observed in 1985 (USDI, 1986). Acceptable ambient air quality standards for other states include 4 $\mu g/m^3$ for 8 hours, Connecticut); 20 $\mu g/m^3$ for 8 hours, Nevada; and 0.66 $\mu g/m^3$ annual, New York (Radian, 1985). The composition of the gasses will influence the potential impact. Evaluation of options that lead to significant volatilization should include possible health risks of gas exposure.

D. Summary

The primary sources of selenium in California are seleniferous soils and selenium enriched groundwater. These are mobilized primarily by agricultural activities. It appears likely that atmospheric selenium releases are unlikely to pose any problems at this time.

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Chapter 5. The Uses of Selenium

"Of all the semi-metals, selenium is probably the most useful from the purely engineering and mechanical point of view."
R.R. Ross 1980

A. Introduction

Selenium is used in a wide range of products for agriculture, commerce, industry, home, and health products. The leading uses in 1984 were for electronics and photocopiers--35%, glass--30%, pigments and chemicals--25%, and other uses, including metallurgy and agriculture, under 10% (Bureau of Mines [BM], 1986a). The use of selenium for health products is very small in volume but high in value, worth as much as 10 million dollars annually (Oldfield, 1980).

The amount of selenium used in California is unknown but California manufacturers are involved in: glass making, both flat glass and containers; electronics and computers; paints and inks; smelting and metal manufacturing; batteries; agricultural products, and food supplements (California Manufacturers Association, 1987). California is the leading state for health foods and the home of one of the major selenium supplement makers (Price and Brown, 1984; Kallman, 1987).

B. Selenium production and marketing

1. Refining and production

Although selenium is widely distributed in nature, the known deposits are not sufficiently concentrated to justify mining. Nearly all the primary selenium is produced from copper refinery slimes. The processes for gathering selenium are designed for effective recovery of precious metals with selenium recovery of secondary importance. This is reflected in low recovery rates.

Selenium may be recovered by leaching after roasting with appropriate fluxes or by volatilization during roasting or furnacing (NRC, 1976; BM, 1986a). The first step in most slime processing for selenium recovery is decopperization. The copper content of refinery slimes typically varies from 10 to 70 percent. The copper in the slimes is insoluble in cold sulfuric acid. Although some slimes can be decopperized with sulfuric acid and steam, roasting is usually needed to oxidize the contained copper to compounds that are sufficiently soluble for leaching.

Slimes containing moderate quantities of selenium and small amounts of copper may be roasted with sodium carbonate flux following decopperization to form a calcine-containing sodium selenite, which is leached with water. Slimes containing moderate quantities of selenium and copper may be roasted with a flux of sulfuric acid and sodium sulfate. Selenium is volatilized as an oxide and scrubbed from the roaster exhaust gas.

Slimes having relatively low selenium and copper content may be treated by decopperization and dore furnace smelting. Two methods are used. In one, sodium carbonate flux is added to the slime. The slag that forms contains sodium selenite, which is recovered by leaching. In the other method, the slimes are first smelted with appropriate fluxes. Most of the selenium remains in the metal portion of the

melt, which is then refluxed with sodium carbonate to form a rich sodium selenite slag. The selenium is then recovered by leaching. In both methods much of the selenium is volatilized during furnacing and is recovered from the flue gases. All processes use sulfur dioxide to precipitate selenium metal from solutions of selenite and selenious acid.

High-purity selenium is made by several methods, including fractional condensation of volatilized selenium, zone refining, reduction and precipitation from purified selenious acid, and gaseous or wet reduction of purified selenium dioxide.

Table 5.1 World selenium production

Year	Metric Tons
1964	908
1965	777
1966	856
1967	922
1968	870
1969	1273
1970	1295
1971	1134
1972	1186
1973	1116
1974	1211
1975	1118
1976	1135
1977	1370
1978	1422
1979	1601
1980	1276
1981	1285
1982	1132
1983	1325
1984	1350
1985	1122

Bureau of Mines, vd.

World production of selenium has generally increased over the last twenty years (Table 5.1). The United States has been an important producer for most of these years, along with Canada and Japan, but the U.S. share of the market has declined as domestic copper mining and refining have decreased.

In the U.S., most primary selenium has been recovered from anode slimes generated in the electrolytic refining of copper; although some has been recovered from lead slimes and nonferrous flue dusts (BM, 1986a). Primary selenium was recovered from both domestic and imported materials at three U.S. copper refineries in 1985: Asarco at Amarillo, TX; Kennecott at Magna, UT, and Phelps Dodge Refining Corp. at El Paso, TX. Production at the Kennecott refinery was discontinued during the year owing to the cessation of copper mining in Utah. As a result, domestic production decreased significantly (BM, 1986a). High purity selenium metal and various selenium compounds were produced from commercial-grade metal by the three copper refineries and other processors.

Selenium-bearing copper slimes from other domestic copper refiners were either shipped to the above refineries or exported for processing. Consumption declined, net imports fell slightly, and producers' stocks increased substantially in 1985.

Domestic data for selenium are developed by the Bureau of Mines from a voluntary survey of U.S. operations (Table 5.2). The domestic refiners of selenium describe their stocks, primary refined production, and shipments of selenium to consumers. Discrete

data are withheld to avoid disclosing proprietary information.

Table 5.2: U.S. production, trade, and consumption of selenium, metric tons.

Year	Primary production	Imports	Exports	Apparent consumption
1964	408	133	45	373
1965	232	114	45	434
1966	268	130	45	468
1967	256	137	89	469
1968	274	265	184	486
1969	553	248	227	672
1970	443	206	171	515
1971	285	179	68	413
1972	335	195	100	460
1973	285	251	120	558
1974	292	379	75	710
1975	162	403	53	482
1976	182	368	88	449
1977	226	266	31	403
1978	231	363	103	413
1979	266	310	151	376
1980	141	283	82	387
1981	252	312	60	540
1982	243	347	117	526
1983	354	299	93	658
1984	254	377	123	478
1985	na	401	154	na

Bureau of Mines, vd.

2. Prices

Standard commercial-grade selenium averaging 99.5 percent selenium is sold as powder, available in several mesh sizes, or as small lumps or shot. High-purity selenium containing 99.99 percent selenium or better is marketed as pellets or sticks. Specifications for pigment-grade selenium powder generally require a selenium content of 99.8 percent. Other forms of selenium available include selenium dioxide, ferroselenium, sodium selenite, and sodium selenate.

The price of selenium varies considerably. As with other minor metals the relatively small number of producers, the insensitivity of production to prices, low relative prices, and the secrecy of exchanges combine to make the selenium market a volatile one. The price per pound went from a high of $35 in 1974 to $9 in 1976. Prices rebounded in 1977 to a high of $17 and then dropped to $4 in 1983. They have moved up again and ranged from $6.00 to $10.25 per pound in 1985 (Manser, 1984; BM, 1986a,b) and $5 to $6 per pound in 1986 (Crisafulli, 1986). See Baltrusaitis (1986) for the current and future outlook for selenium.

3. Foreign trade

U.S. exports increased to a record-high level of 154 metric tons in 1985, with almost one-third going to the United Kingdom, primarily as scrap. Exports to Mexico and the Philippines accounted for most of the increase in exports over 1984 (BM, 1986b).

Imports of selenium to the U.S. in 1985 were the highest since the previous peak in 1975, when 403 metric tons of selenium were imported. Canada continued to be the largest supplier of imported selenium material. Belgium, Luxemburg, Japan, and the United Kingdom were the other major sources of imports. Approximately 75 metric tons of imported refined selenium, primarily from the United Kingdom, were recovered from scrap that had been exported from the United States for processing.

C. Agricultural uses

Selenium has several current uses in agriculture and has been used for other purposes in the past. The most important use is as a feed supplement to prevent selenium deficiency diseases. Some fertilizer is also selenium enriched to increase the selenium content of plants to meet the selenium nutritional requirements of animals. And finally, selenium is used in some veterinary medicines, (Jones et al., 1977), e.g. Seleen®, a one percent selenium disulphide ointment.

1. Feed supplements

Selenium supplements have been used in the U.S. for swine, turkeys, non-food animals, and chickens (except layers) since January 1974. Use for ewes and young lambs was approved in 1978. Sheep, dairy cattle, and beef cattle were added to the approved list in 1979 (American Feed Manufacturers Association, 1981). Egg laying chickens and ducks were added in the early 1980's. The American Feed Industry Association recently petitioned the Food and Drug Administration to liberalize regulations governing selenium supplements (Code of Federal Regulations: section 573.920--Selenium). These changes were implemented April 6, 1987 (Food and Drug Administration, [FDA] 1987). They allow higher selenium concentrations to be used and remove current premix testing requirements. Table 5.3 illustrates the changes in allowable complete feed levels.

Table 5.3 Feed supplement allowances in ppm.

Species	Before April 6, 1987	After April 6, 1987
Chickens	0.1	0.3
Turkeys	0.2	0.3
Swine	0.1	0.3
Sheep	0.1	0.3
Cattle	0.1	0.3

Food and Drug Administration, 1987.

More concentrated salt-mineral mixes are also allowed under the new regulations. The previous levels of 20 ppm for cattle and 30 ppm for sheep were revised upward to 90 ppm for sheep and 120 ppm for cattle (American Feed Industry Association, 1986; FDA, 1987). About 23 metric tons of selenium have been used each year for feed supplements, this may double or triple with the liberalized regulations (American Feed Industry Association, 1986; Eisenberg, 1987)

Improper supplement mixing has occurred with animal feeds just as it has for human food supplements. In 1982 a swine feed supplement with 280 times as much selenium as the label amount led to swine deaths in the Southeast (U.S. Dept. of Health and Human Services, 1982). The actual level of selenium in the base mineral mix was 2500 ppm and the swine feed as used contained 50 ppm. Other cases have been reported in Iowa and Pennsylvania (Casteel et al., 1985). In Iowa, 88 of 300 pigs affected by selenium poisoning died or were euthanized because of paralysis. Those that recovered took one month longer than normal

to reach marketable size. Concentration in the feed reached 27 ppm (Casteel et al., 1985). In another incident a review of premix preparation in a mill in Washington found that because of labeling errors and over-rich supplements dairy cattle using this mix would be receiving 50 times the approved amount, or 5 ppm (U.S. Dept. of Health and Human Services, 1983).

In France, the use of selenium supplements is limited to feeds, at a level of 0.1 mg Se/kg of feed. The use of selenium in salts is prohibited to prevent possible overuse by animals (Gissel-Nielsen et al., 1984).

2. Injectable selenium

Selenium-deficient animals can also be treated with injections of selenium compounds, typically as sodium selenite and Vitamin E in an oil base (NRC, 1976). Stockmen in some selenium-deficient areas routinely inject all lambs and calves born in the winter, when feed nutritional value is typically much lower. Figures on the use of selenium for this purpose are not available, but it is common in both the Northeastern and Northwestern United States where selenium deficiency is often encountered. Estimated savings from the use of selenium supplements are in the millions of dollars per year.

3. Pellets and boluses

To avoid the cost and labor involved with annual injections or large scale land treatment to improve forage, investigators have developed a variety of selenium pellets and boluses for cattle and other grazing animals (Kuchel and Buckley, 1969; Nelson and Miller, 1987; Norman, 1987; Smith, 1987). These are made up of selenium, usually elemental, in a pellet made of iron, soft glass, plastic, or other material. The California pellet is compressed from ninety percent iron and ten percent selenium and weighs about one ounce (Norman, 1987). These are placed in the animals stomach where the selenium is slowly released.

4. Fertilizer

Selenium deficient soil can be amended with selenium supplements to increase feed quality. This has been done for many years in New Zealand, Finland, Australia, and China (Watkinson and Percival, 1983; Gissel-Nielsen et al., 1984; Korkman, 1984; NRC, 1976). Most of the agricultural land in Finland has been treated since 1985, while about a half million hectares are treated in New Zealand. Soils are also treated in areas where Keshan (selenium deficiency) disease occurs in China.

Application rates and materials vary depending on the crop, soil, and management. Sodium selenate is the preferred form in both New Zealand and Finland. In New Zealand granules with one percent selenium are mixed with granulated fertilizer in bulk blending equipment. In Finland a one percent selenium solution is sprayed into a granulation drum (Korkman, 1984). Misapplication of soil amendments has led to selenosis in grazing animals (NRC, 1976).

Soil amendments are typically applied at rates which provide 14 to 28 grams of

selenium per acre in New Zealand (American Feed Manufacturers Association, 1981). Finnish applications are on the order of 6 to 8 grams/hectare. Sodium selenite and frit selenium have also been used (Gissel-Nielsen et al., 1984) but selenate is taken up more easily. As much as ten percent of applied selenium as selenate shows up in plants versus one percent for selenite (Korkman, 1984). The crop response varies between species. Soil characteristics and cultural practices also affect selenium availability over time. For example, Gupta et al. (1982) found that 2.24 kg selenium/hectare provided a residual affect for 4 to 5 seasons with timothy but only two years for barley. Soil is tilled every year for barley but not for timothy.

Fertilizers with hydrated sodium selenite were tested on barley, spring wheat, and potatoes in selenium-deficient Finnish soils (Korkman, 1980). The potato selenium concentration increased to 100 µg selenium per kilogram of dry matter with 0.05 percent selenium fertilizer while barley and wheat grain selenium concentration increased in relation to the amount of selenium added.

Application of approximately 40 grams of selenium per hectare could produce young clover plants with excessive selenium (Spencer, 1982), so application rates should be watched closely. In a watershed study in New Zealand, Watkinson and van der Elst (1980) found that 99 percent of the selenium applied to the soil as selenate, 17 g/hectare, was retained in the soil profile after 440 days. A brief flush was noted on the second day after application, presumably from material that had fallen directly into the drainageways. More selenium would be mobile in soil with a higher pH.

Soil selenium level can also be increased by soil amendments high in selenium, including rock phosphate; fly ash, 1 to 20 µg/g selenium (Wilber, 1983), depending on coal source and combustion process; and other selenium-enriched materials. Rock phosphate may be relatively high in selenium, 1 to 300 µg/g (NRC, 1976), and phosphate fertilizers may have been an important source of selenium in some areas. Much of the selenium is removed in the industrial production of superphosphate. Selenium enriched materials can also be used to increase soil selenium levels. These can applied directly or as pellets, with selenium solution sprayed on inert materials. For example, van der Elst and Watkinson (1977) made pellets from pumice sprayed with selenate solution.

5. Foliar sprays

Foliar application of selenium has also been used successfully on agricultural crops. Gissel-Nielsen (1981) showed that barley sprayed with selenium at 3 to 5 grams per hectare prevented selenium deficiency in cattle consuming the barley. In a subsequent experiment with potatoes and barley both selenite and selenate sprays raised plant selenium status to adequate levels when sprayed at a rate of five grams of selenium per hectare (Sima and Gissel-Nielsen, 1985). Ylaranta (1983) found that foliar application was more effective than basal application and

that selenate was more effective than selenite for this use.

Very high levels of foliar spray, 1 to 4 kg/ha Se, produced lucerne and timothy with 27 to 142 ppm selenium in the first year. Barley grain contained only 4.3 to 8.4 ppm. A yield reduction of 16 to 37 percent was observed in the first year but no effects were observed in subsequent years (Gupta et al., 1983a).

6. Seed dressing

Seed treatment can also be used to increase the selenium concentration in plants. Gupta et al. (1983b) showed that sodium selenite added to seeds, 50 to 200 g/ha, provided the desired level of plant selenium in both alfalfa and ryegrass. The selenium concentrations in ryegrass were generally higher. Even the highest rates of seed treatment had no effect on yield of alfalfa and ryegrass. Gissel-Nielsen (1975) found that treatment of barley with selenite was not as successful and required rates equivalent to fertilizer amendment.

7. Pesticides

The use of selenium compounds as pesticides was first explored by Gnandinger (1933). This work was undertaken because of the close similarity of selenium to sulphur, a proven miticide. Selenium added to a potassium ammonium sulphide solution proved most effective. A 30 percent solution of this compound, sold as Selocide®, worked well on grapes, citrus, and greenhouse plants. After selenium was found in grapes and citrus fruits (Hoskin, 1938) research was discontinued in California (Boyce and Prendergast, 1938) but some use continued. Onions planted in selenium-treated greenhouse soils were found to contain 3.4 to 5.6 ppm selenium (Fuller, 1946).

Soil applications of selenium to control insects were also evaluated. Leukel (1940) found that sorghum could be protected from aphids by adding sodium selenate, 4 ppm by weight to the soil. Selenium compounds were used primarily in nursery and greenhouse settings until the 1960's, both as a systemic and as spray (Smith, 1961). Sodium selenate was used for systemic applications and Selocide was used for foliar application.

California was the only state that registered selenium insecticides for use on food crops (Smith, 1961). No data are available on the quantities made and where they were used.

D. Commercial uses

The primary uses in the commercial sector involve selenium's light/electrical conductivity response. Foremost among these users is the xerographic industry. Chester Carlan began research on photocopying in 1934, and in 1944 Battelle Research Institute became involved and the pace of research accelerated. Shortly afterward, Xerox joined the research effort (Murphy, 1984; Owen, 1986).

A brief history of xerography:

1950 First commercial model sold to the Army, using a 20 μm thick pure selenium photoreceptor plate.

1953 First xerographic drum model sold to the Navy, using a 80 μm thick pure selenium photoreceptor.

1960 First commercial office photocopier, using 60 μm thick pure selenium on the drum, the Xerox 914.

1966 1/2-1% arsenic added to the photoreceptor, increases hardness and doubles useful life.

1973 First color xerox, with selenium-tellurium alloy used for photoreceptor.

1984 3.9 million selenium alloy photoreceptors manufactured, 2 million by Xerox, 1.9 million by other manufacturers. This used 300,000 kg of pure selenium.

1984 First laser printer sold for moderate cost commercial market.

1986 Laser printers sales were estimated at $453 million in 1986 and expected to rise to $4.9 billion by 1990 (Needle, 1987).

The photoreceptors for photocopiers and laser printers are made of either organic materials or selenium. Selenium photoreceptors are facing increasing competition from a variety of organic photoreceptors, which have been used by IBM and Kodak for some time. However, use of selenium should continue strong for some time (Murphy, 1984; Yafie, 1984).

Selenium is used in a wide range of other commercial products including: photovoltaic cells, electric eyes used to control doors, and light meters for cameras (Davis and Associates, 1972). Selenium cells are also used to convert optical sound tracks to sound on film projectors (Ross, 1980). Selenium is also used in photographic toners (NRC, 1976) and may find increasing use as an X-ray film (Archer, 1985).

E. Industrial uses

Selenium is used in many industrial applications. The primary uses are in pigments for plastics, glass, and ceramics. It is also used in batteries, paints, metallurgy, and in chemical processes as a catalyst.

1. Selenium in plastics

One of the other key uses for selenium is in pigments, used to color both plastics and glass. The use in plastics is slightly higher but the use in coloring glass is also substantial. Selenium is very useful in plastics pigments because the colors made using selenium tolerate high heat, are easy to disperse in the plastic, have good color retention, and excellent color quality (Lynch, 1984). The pigment particles are typically about one micron in size and are dispersed in the molten plastic. Most colors are based on cadmium sulfide, a golden yellow by itself. Replacing some of the sulfide with selenide makes a series of reds and oranges (Kleinschmidt, 1984). Cadmium pigment consumption was 2,000 metric tons in 1982 and use was expected to increase 20 percent by 1984. Twenty-nine percent of this was in cadmium sulfo-selenides. This use may decline if other countries follow the lead of Sweden, which banned cadmium pigments in 1979 for

environmental reasons (Dickenson, 1980; Lynch, 1984).

2. Selenium in glass and ceramic glazes

Selenium is used both as a decolorizer and for some of the more striking colors in glass-making. The decolorizing occurs when the slight pink that selenium imparts to glass combines with the pale green color from Fe^3 to make a very neutral gray which is perceived as clear (Simmingskold, 1984). Selenium is also used to color glass and ceramic glazes. In higher concentrations of 0.1 to 0.3 percent selenium provides a pink-rose color. If both selenium and cobalt are added to glass it becomes a very deep black which has become popular for architectural uses (Simmingskold, 1984).

A yellow color is created when selenium is combined with the oxides of arsenic, antimony, and bismuth. Selenium combined with chromium oxide and silicon produces an emerald green, while additions of selenium to bismuth trioxide and silicon yields a topaz. However, the most important combination in glass coloring and glazes is the pairing of selenium and cadmium. The selenium enters the cadmium sulfide crystal lattice and is, as a result, extremely stable. This combination allows a full series of color from orange through a variety of reds to maroon (Burgyan, 1980).

Selenium also is increasingly used in heat-absorbing glass (LaCourse, 1980). The actual heat absorption is primarily achieved by higher levels of iron in the glass, 0.25-0.75 percent. The addition of 0.002 percent selenium and a small amount of cobalt allows the glass manufacturer to make either grey, bronze, or grey-green tinted heat-absorbing glass. These glasses may reduce solar heat gain by 25 percent and provide substantial energy savings during the cooling season.

Similar colors are created in ceramic glazes. The very high temperatures involved in ceramics production caused problems with selenium glazes until methods were developed to protect the selenium in inclusions of inert crystalline phases (Kleinschmidt, 1984).

Selenite glasses are of value for some scientific work because they will pass the far infared wavelengths (Wright and Dupuy, 1985).

3. Selenium in batteries and electronics

More than 90 patents have been issued for the use of selenium in batteries. Uses vary but most commonly involve selenium's ability to improve the stability and conductivity of the battery plates. Many maintenance-free batteries, for example, use selenium to improve the crystalline structure of the lead plates. Improving the surface characteristics of the plates improves the lifetime of lead acid batteries (Kallup, 1984). This is a growth area for selenium and may ultimately reach 100-139 tons year (Doe, 1984).

Selenium is used in electrolytic cells with cuprous selenide (Cu_2Se) cathodes, a rubidium-copper based electrolyte ($Rb_4Cu_{16}I_7Cl_{13}$), and copper powder as the anode. Selenium has also been used as an

additive for silver oxide in silver oxide--zinc cells (Doe, 1984). Selenium is also used in fuel cells, photoelectric cells, solar cells, and other electronic applications (Clark, 1980; Ross, 1980). High current rectifiers continue to use selenium but silicon-germanium rectifiers have replaced selenium for low current applications (Ross, 1980).

4. Selenium in metallurgy

Selenium can be added to austenitic stainless steel to improve machinability and corrosion resistance (Confente and Bellot, 1984). Selenium is added to copper alloys for the same reason (Ross, 1980). It improves machinability, ductility, and conductivity (Kirk-Othmer, 1982). Selenium also is of value in steel making, because it reduces the surface tension of the molten steel. This retards nitrogen absorption which in turn improves the impact resistance of the steel (Kirk-Othmer, 1982).

5. Selenium in the chemical industry

Selenium has favorable characteristics for use as a catalyst because of its many possible valence states. Its most obvious use is in oxidations but it is also useful in hydrogenation and isomerization (Stiles, 1980).

Selenium catalysts are used in plastics production (Grasselli et al., 1984). The catalysis of acrylonitrile plastic may become one of the more important uses. More than 1.6 billion pounds of acrylonitrile are produced annually in the U.S. (Parker, 1982). Selenium catalysts can significantly reduce the energy required to produce acrylonitriles (Grasselli et al., 1984). Selenium is also involved in some catalytic processes in the petrochemical industry (Stiles, 1980).

Selenium is used to a very small extent in rubber production, because it will cross-link diene rubbers. It is used in place of sulfur to vulcanize natural rubber for applications requiring high heat resistance (Brydson, 1978; Hoffman, 1967) and to achieve higher cross-link density and strength in nitrile rubbers (McWhinnie et al., 1984). Selenium compounds may also prove of value as anti-oxidants and anti-ozonants for natural rubber (McWhinnie et al., 1984).

F. Home uses

Relatively little selenium would be found in a typical home. Most selenium entering the home would probably be in plastic, ceramics, glass, and paints. Some might be brought in as a component of photographic toner or gun blueing. Burning painted wood or colored plastic might eventually lead to a very small buildup of selenium if the ashes are disposed of on-site.

Selenium has also been used in shampoos to control dandruff and is included in veterinary and medical lotions and medicines for some diseases (see also following section). Very small amounts of selenium may enter the home in food, water, and air. Further research is needed to determine the exposure of people living in homes located on seleniferous soils, or with selenium-enriched water.

G. Dietary uses

The use of selenium food supplements has become more common as the cancer prevention and immune system strengthening properties of this element have become clearer (Watson and Leonard, 1986). Selenium food supplements are sold over the counter and by prescription. The value of selenium supplement sales, primarily as a selenium-enriched yeast, may reach $10 million dollars per year (Oldfield, 1980). Retail prices were $0.075 per tablet for supplements with 150 µg of selenium as sodium selenite in early 1987.

As a result of the relatively recent discovery of selenium's importance as an essential nutrient and the comparative lack of research on selenium nutrition in humans, there is as yet no Recommended Daily Allowance (RDA). However, the conservative recommendation is in the range of 50-200 µg per day (Food and Nutrition Board, 1980; Clark, 1985). (See also Volume 2.)

Selenium requirements may be increased by factors such as exposure to air pollution, heavy metals, hazardous chemicals, aging, and high intake of poly-unsaturated fatty acids (Watson and Leonard, 1986). Dietary sources include seafood, particularly herring and tuna, followed by meat, kidney, liver, and vegetables, especially broccoli and garlic. Whole grains from selenium rich areas may also be important sources of selenium. The selenium concentrations in vegetables and whole grains will depend on the soil in which they were grown.

Chapter 5. References

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Chapter 6. Solving Selenium Problems in California

"A systems approach will include all events and objects in that system and identify them as parts of a larger whole. At all levels of analysis, the systems approach seeks to understand phenomenon in terms of the function of each phenomenon in the larger system, in terms of how the phenomenon relate to each other, and in terms of how the system relates to its environment and to other systems in that environment" M.G. Russell, 1982

A. Introduction

This chapter is a preliminary description of the technological and management options for dealing with selenium problems in California. A more complete and thorough treatment of these subjects will be presented in Volume 2. This second volume will contain a more comprehensive review of current research activities in the management and treatment of selenium deficiency and toxicity and related effects on human health, wildlife, and livestock.

Both selenium deficiency and toxicity problems have been identified in California. As mentioned in Chapter 3, selenium deficiency is common among livestock and ongoing studies also suggest it may not be an uncommon problem for wildlife. Much less is known about the extent and possible effects of selenium deficiency in humans in California.

Selenium toxicity, which has received much more publicity, has occurred in a few areas and almost exclusively affected aquatic birds and fish. Selenium enters the state's water resources primarily as a result of agricultural irrigation practices, associated cropland drainage systems, and run-off.

Selenium toxicity problems may also arise from the use of selenium contaminated water resources for irrigation, the discharge of industrial selenium waste into the environment, and the treatment of selenium contaminated areas. The two primary concerns for selenium toxicity are effects on aquatic ecosystems and possible effects on human health.

The most serious problem area for selenium toxicity in California is the western portion of the San Joaquin Valley where soils have naturally high selenium content. Because this is an area with low rainfall, these soils do not release substantial amounts of selenium into the environment until they are irrigated. This agricultural practice releases soluble forms of selenium into the soil water which then enter surface waters and shallow groundwater through cropland drainage systems, irrigation tailwater, and deep percolation into groundwater.

Currently, selenium-contaminated water flows out of and off the San Joaquin Valley soils in two directions. The northern area drains directly or indirectly into the San Joaquin River Delta and includes farms between the Sacramento-San Joaquin River Delta area and the town of Mendota. The southern area with no natural drainage outlet formerly drained into the San Luis Drain ending at the Kesterson Reservoir. Presently, these drainage and runoff waters are confined to the on-site evaporation ponds. It includes farms roughly between the towns of Mendota and Kettleman City. Problem solving efforts

focusing on selenium toxicity in California need to consider the distinct natures of these two problem areas and other areas, such as the Salton Sea, where elevated selenium concentrations have also been found.

B. A systems approach to solving selenium problems in California

Identifying selenium problems in the environment is relatively simple compared to scientifically understanding the very complex nature of both deficiency and toxicity problems. Prior to the discovery of malformed wildlife in Kesterson Reservoir in 1983 and the verification of selenium deficiency diseases in humans in the 1970's, selenium was a relatively unstudied and poorly understood trace element. Subsequent research has contributed greatly to our understanding of scientific processes involved in selenium in the environment and in nutrition, but there are still more questions than answers. While the knowledge base has grown tremendously, the interpretation and translation of this information into practical problem solving remains difficult and often controversial.

Systems approaches to environmental and agricultural problems have emerged in response to the complexity, uncertainty, and the resulting risk-taking involved in effectively managing natural resources to the satisfaction of all affected parties (Wilson, 1984; ESSA, 1982). Selenium problems in California can benefit from this approach, which is discussed in greater detail in volume 2.

In their efforts to understand selenium, scientists have operated objectively and diligently in accumulating basic facts but have cautiously avoided entering into judgments and assessments of this information. The task left for action-oriented public agencies and advocacy groups is to make sense out of this information to effectively correct the problems. Real pressures, such as public accountability, limited time, and limited funds, create an emotional climate where adversarial relationships quickly emerge. Each side then marshals scientific support for their preferred solutions.

While science has provided accurate descriptions of smaller and smaller pieces of a very big puzzle, it has not yet provided an adequate process for assembling these pieces into an interpretable overview of the entire situation. As a result, hastily assembled solutions and policy decisions often emerge without the full benefit of broadbased interdisciplinary scentific input. Social, political and economic realities can force decisions which override scientific considerations.

While science has learned much about selenium in the environment and many substantive questions have been answered, many new data gaps have been identified and much research is still ongoing. In addition, many aspects of selenium behavior have not yet been addressed.

Selenium problems in the California environment are large scale, long-term, and will remain for generations. It is not clear how

the short-term solutions currently proposed will relate to unforseen future problems. Only a short-term data base exists and long-term monitoring and continued evaluation are needed to understand the long-term implications of current decisions. While the beginnings of these elements exist in the form of interagency bodies and on-going monitoring programs, the long-term evaluation processes needed for a successful sustainable program remain unclear. A systems approach to selenium problems in California is one way to effectively approach this task.

While existing information on technical solutions will be summarized in the following sections, it must be qualified as introductory, current only up to this writing (1987), and limited in the holistic perspective desirable for effective policy making. Volume 2 will attempt to remove these qualifications with a more comprehensive treatment of this subject.

C. Selenium deficiency in California

Selenium deficiency is the most widespread selenium problem in California. The livestock and wildlife blood selenium monitoring reported in Chapter 3 suggests that selenium deficiency is a problem in many areas of the state. The extent or seriousness of selenium deficiency in humans is unknown. The difficulty of assessing subclinical selenium deficiency makes this determination very difficult and it is discussed in greater detail in Volume 2.

1. Livestock

Livestock selenium deficiency is common in California. The treatment for this deficiency can involve improving selenium content of fodder, feed or mineral supplements, injections, or boluses. Feed and mineral supplements are probably the most commonly used treatment for livestock. Studies in the early 1980's showed no selenium response for the level of selenium included in mineral blocks. Positive effects were not seen until the selenium concentration reached 300 µg/g (Hathaway et al., 1980).

Injections of selenium and vitamin E are also used in some areas. Selenium enriched stomach pellets called boluses are being studied in extensive long-term field studies by Dr. Ben Norman, the U.C. Veterinary Medicine Specialist. The results have been very encouraging and the use of boluses can be expected to move from experimental to regular use.

Selenium supplements or fertilizer may be needed when use of fertilizer decreases the selenium concentration of forage. The decrease in selenium can be caused by sulfur-selenium competition and the dilution affect (Jones et al., 1987; Pratley and McFarlane, 1974).

Although the use of selenium enriched fertilizers is common in several countries it has has not yet been adopted in California.

2. Wildlife

Blood selenium levels in wildlife have revealed relatively widespread selenium deficiency in a number of game animals,

including deer, elk, and big horn sheep (Jessup, 1986). The options for selenium supplementation of wildlife are limited by economics. Although mineral supplements are perhaps most likely to be used, boluses have also been tested sucessfully in deer. Rare and endangered species might justify even the more costly use of injections. Fertilizer enhancement of forage is also possible, but unlikely to be used on a large scale.

D. Selenium Toxicity

The methods for dealing with selenium fall into two general categories. The first deals with treatments proposed for areas where existing levels of selenium have become unacceptably high. The second more important category deals with the prevention of future problems by control or management of current activities or processes that are contributing to existing and future problems. Solutions are likely to involve combinations of technological options as well as combinations of strategies. The nature and extent of the contamination, economics, and public pressure will largely determine the solutions selected.

1. Treating existing selenium contamination

There are many strategies for dealing with areas with elevated and potentially hazardous selenium levels including concentration, disposal, stabilization, and isolation. No strategy alone may be able to satisfy all the environmental, wildlife, and human health concerns currently pressing on natural resource managers. Combinations of strategies are most likely to emerge as proposed solutions.

Concentration involves the treatment of contaminated soils, sediments, or water resulting in separation of non-contaminated material from the selenium and then eventual use or disposal of the concentrated selenium. Disposal involves the transfer of selenium contaminated material, either concentrated by a prior treatment or as it exists in the environment, to a location where it will pose a reduced risk. Isolation strategies either halt human activity that cause the problem or prevent potential exposures and risks by separating contaminated areas from potential victims. Stabilization strategies manipulate physical, biological, and/or chemical principles to minimize current and future problems.

a. Biological treatments for selenium contamination

Technological developments have been emerging from both the private and public sectors for treating selenium contaminated water, soils, and sediments using biological methods. Most involve the use of specific microbiological techniques recently developed specifically for selenium contamination.

It is also important to remember that selenium contamination often occurs with other potentially toxic contaminants such as boron, arsenic, molybdenum, chromium, copper, nickel, zinc, and high levels of salts. While treatment technologies have been shown to reduce levels of selenium contamination, their

effects on other contaminants have rarely been examined thoroughly.

i. Bacterial treatment

Binnie California, Inc., a subsidary of Binnie and Partners from London, a private engineering consulting firm has proposed and conducted demonstration projects to treat selenium contaminated drainage water. Proprietary considerations have clouded complete and full disclosure of the precise methodology. A generalized description of the process is presented here. Basically, the process involves anoxic packed bed microbial reactors into which contaminated drainage water is introduced. A carbon source is introduced, such as locally available molasses, which stimulates microbiological activity resulting in dissolved selenium being taken up into the living cells of the bacteria in the reactors. The reactors retain this mixture for a specified time, it is passed into a holding tank, and then the bacteria are filtered thereby carrying much of the selenium with them (Letey et al., 1986; Fraley et al., 1987).

The effectiveness of this process is dependent on many basic factors, some of which have not been fully studied. For example, the characteristics of drainage water are highly variable with time of year and drainage source. A wide range of chemical factors and concentrations of dissolved ions including heavy metals and salts can alter the effectiveness of the process. Of particular importance are nitrates, sulfates, total organic carbon, and pH. In addition, the bacterial species mix introduced into the system may change over time, compromising effectiveness. The basic processes still need to be better understood in order to effectively manage the system in a cost effective-manner.

While initial results are promising, other similar processes are currently under study, such as using aerobic bacteria instead of anaerobic bacteria. A preliminary report showed that the Binnie California, Inc. process dramatically reduced selenium concentration from 400 mg/L to below 10 mg/L - the EPA drinking water standard for selenium (Letey et al., 1986). The Binnie test plant has (1988) been closed because it was unable to meet anticipated performance goals (Benson, 1988).

ii. Cyanobacteria (blue-green algae) treatment

Cyanobacteria (blue-green algae) are currently being investigated in the laboratory by Dr. W. Oswald at the University of California, Berkeley. It has been reported that these microorganisms can concentrate selenium from water ten-fold (Packer et al., 1986). The process requires light and oxygen, but because of rapid and expansive growth, it could be effective. The bioconcentrated selenium could be easily harvested mechanically through centrifugation and filtration. Food supplements have been suggested as a potential end use and income generator. A complete laboratory report is due out in the fall of 1987. A prototype facility under field conditions will investigate this process further.

iii. Wet flexible response plan ("Wet-flex")

This method has application for the wet ponds at Kesterson Reservoir and for on-farm evaporation ponds. The Lawrence Berkeley Laboratory at the University of California at Berkeley has reported that saline waters which promote the growth of the large algae *Nitella* can be used to isolate selenium in the biomass of the *Nitella* and cattails for removal through harvesting as long as the water is kept saline and no additional selenium is added. Maintaining this ecosystem is basic to the success of this method. More research is needed to verify its effectiveness and effect on wildlife. An "Immobilization Plan" alternative has also been proposed. This includes a more aggressive management of the *Nitella* and cattails to control selenium movement in food chains by modifying the ecosystems with various methods.

iv. Microbial Volatilization

Selenium contaminated soils and sediments can also be treated by encouraging indigenous aerobic soil fungi by providing a carbon source and added metal catalysts which increases selenium volatilization for release to the atmosphere. Laboratory tests have been promising and field trials are currently underway to determine field rates. More time is needed to determine the effectiveness of this treatment, but it shows considerable promise (Frankenberger et al., 1987). Although soil and sediment treatment is only applicable to exposed field surfaces up to 20 cm in depth (aerated) as opposed to deeper soil profiles; it may also be of value for treatment of soils and sediments from on-farm evaporation ponds and wet lands of the Grasslands area. Much more basic reseach is needed to explore the fundamental factors affecting this microbial process, its effectiveness in field applications, as well as the potential for the volatilization of arsenic, mercury, and tellurium from soil and sediments.

v. Accumulation of selenium by plants

Plants, including some species from the genera *Astragalus, Atriplex, Grindelia, Grayia, Stanleya, Scirpus* (bulrush), and *Typha* (cattails), have been shown to accumulate selenium (Carlisle and Cleveland, 1958; Kingsbury, 1964. However, as Izbicki and Harms (1986) showed, selenium accumulation may be lower than expected for some of these species.

Prosopis glandulosa var. Torreyana (mesquite) may also prove of value for selenium concentration and collection (Bainbridge and Mikkelsen, unpubl.). The pericarp portion of the *P. glandulosa* bean may have six times as much selenium as the seed and whole mesquite beans are apparently rich in selenium (Zolfaghari and Harden, 1982).

Selenium accumulating plants could be grown on selenium contaminated soils or wetlands or irrigated with water with elevated selenium levels and then harvested. The harvested plants could then be used as

selenium supplemented feed (Cervinka et al., 1987) or chemically treated or burned in a power plant.

b. Chemical treatments for selenium contamination

i. Ion exchange

The use of selective ion exchange resins to remove selenium ions from water has been evaluated by several investigators (Herrmann, 1985; Maneval et al, 1985; Boegel and Clifford, 1985; Klein, 1986). A private firm, Boyle Engineering is currently conducting exploratory studies with currently available resins and with manufacturers who are developing new resins for selenium removal.

An ion exchanger contains a solid matrix with fixed charged functional groups which behave much like a filter. The counterions attached to these functional groups allow target species of ions (i.e. selenate) to be trapped or collected on the ion exchanger surfaces (Paterson, 1970; Ma et al., 1982; Janauer, 1986; Naden and Streat, 1984; Vermeulen et al., 1984; Rodiquez, 1986). These attached ions can then be flushed out and isolated.

Much more research is needed to investigate the effectiveness of this treatment especially in light of the varying and complex chemical nature of drainage water. These factors could complicate ion exchange performance and cost.

ii. Reverse osmosis (membrane separation)

Reverse osmosis (RO) uses a thin membrane which separates water from a selective ion or ions using principles of diffusion and applying pressure (200-1500 pounds per square inch) to overcome osmotic pressures developed by solute concentrations (Considine and Considine, 1983). The removed portion of a solute is called solute rejection.

The rejection of selenium by reverse osmosis will depend on selenium speciation, composition of the predominant salts, product water flux, product water recovery, and many other factors including pH (Sorg and Logsdon, 1976; Burns and Roe, 1979; Hild, 1983; Hoornart, 1984; Eisenberg and Middlebrook, 1986; Marinas and Sellect, 1986). The removal of selenate should be more or less independent of pH. Selenite removal should increase with pH. High sulfate concentrations can drastically reduce the effectiveness of RO processes.

Removal of selenate and selenite was about 97 percent in municipal water spiked with a known quantity of selenium (Sorg and Logsdon, 1976). Low molecular weight uncharged organic species of selenium will probably pass through an RO membrane (Marinas and Selleck, 1986).

Selenium may act as a weak electrolyte in aqueous solution. Weak electrolytes do not carry a sufficient charge at low pH and may pass through the RO membrane. This may influence the choice of pretreatment options for RO plants. pH could be manipulated

chemically or biologically to improve RO performance. Solution pH and halogen disinfectants affect the stability and performance of RO membranes and pretreatment must be chosen carefully to ensure continued performance of the RO membrane (McCay et al., 1981). Chemical and biological pretreatment may be used to lower sulfate levels and improve RO operation.

Pretreatment was found essential for successful RO operation with agricultural drain water (CH_2M-Hill, 1986). Pretreatment required for a 10 million gallons per day RO plant would include multi-media filtration, chlorination, and dechlorination. Lime soda ash appeared to have the lowest cost per gallon of pretreatment. RO recovery of 83-87 percent appeared feasible. Estimated cost ranged from $21-28 million for 8,700 acre-feet per year. Major disadvantages include high cost, energy requirements, and need for extensive pretreatment (Longley and Hanna, 1986).

A RO plant may also be operated to desalinize water. This has been explored for a number of purposes, including agricultural wastewater and seawater (Johnson and Loeb, 1966; Antioniuk and McCutchen, 1983; Scott, 1981; Yamamoto, 1983). Pretreatment may be of value for these applications as well (Strenstrom, 1983).

iii. Activated alumina

Activated alumina will selectively remove forms of arsenic, fluoride, phosphate, silica and other anions from water with little interference from other cations and anions commonly present at higher concentrations (Kreft and Trussell, 1986). Activated alumina has recently been tested as a treatment for selenium removal from water (Trussell et al., 1980; Ghosh and Yuam-Pan, 1985).

Sulfate and bicarbonate interfere with selenate adsorption. Reducing the alkalinity in the solution will increase capacity for selenate removal. Selenate, being lower in the selectivity series than selenite, is more susceptible to interference and competition from other ions (Kreft and Trussell, 1986). Selenate removal by alumina is not as efficient as selenite removal.

No methods have been developed to chemically reduce selenate to selenite economically although microbiological methods are promising. Agricultural drainage water with very high sulfate levels. e.g., up to 4,500 mg/L at Kesterson (Longley and Hanna, 1986), would probably not be treatable with the activated alumina process because the majority of the selenium is selenate. If a significant proportion of the selenium could be converted to selenite, this process could provide effective treatment. Chemical or biological treatment might be used to change selenate to selenite or to lower the sulfate level, thereby improving the operation of the activated alumina treatment process.

iv. Coagulation - alum or lime softening proceses

Selenium salts can be removed from water by coagulation. Selenate salts are generally more soluble than the corresponding selenite salts. As a result more selenite than selenate should be removed by both conventional coagulation and lime softening. Because selenate and sulfate chemistry is similar, both processes should be ineffective for selenate removal, due to high sulfate contents of the contaminated waters.

Little data exist on selenium removal by conventional water treatment and lime softening processes. Although these results do not apply directly to selenium contaminated water treatment, the work is related and provides some insight into the potential value of these water treatment processes (Sorg, 1986). These studies show that selenite is more readily absorbed than selenate and that selenite adsorption is pH dependent. The laboratory and pilot plant studies that have been conducted suggest that conventional coagulation and lime softening treatment process methods are ineffective for selenate removal and only moderately effective for selenite removal (Sorg, 1986).

The general conclusions drawn from the drinking water and wastewater studies are that: conventional water treatment techniques are ineffective for selenate removal; no more than 10 percent removal is achieved by alum or lime softening; lime softening can achieve 20-40 percent removal of selenite; increasing pH increases removal (pH 11 was better than pH 9); alum is least effective for selenite removal, with only 10-20 percent removal efficiency; and selenite can be oxidized to selenate by chlorine, so pre-chlorinization will decrease the removal of selenium (Longley and Hanna, 1986; Sorg, 1986).

v. Iron filings

Harza Engineering Co., a Chicago firm, has completed initial studies of selenium removal through their patented iron filing process. These included four months of small pilot operation at the Panoche Water District, bench scale tests, and analyses of data to develop design conditions and to develop planning level costs. A larger pilot plant is under construction (Harza, 1986; Letey et al., 1986).

Agricultural drainage water is pumped through a layer of iron filings to which the selenium is adsorped on surfaces. Water containing 160 mg/Se/L was treated for up to 6 hours with selenium decreases of up to 90 percent of the original concentration. Treatment facilities can be designed for various levels of selenium contamination, desired reduction efficiences, life span, and volume of drainage water to be treated. More results will be forthcoming from the second pilot plant.

vi. Iron coagulation

Iron coagulation is the most effective conventional water treatment method for the removal of selenite from water with removals of 60-80 percent. Selenium removal increases

as the pH of the treated water decreases, with best results at pH 7 or lower (Olson and Jensen, 1940; Plotnikov, 1958; Plotnikov, 1960; Plotnikov, 1964). This poses problems for high pH drainage waters. Removal of selenate by iron coagulation is much lower, on the order of 10 percent (Sorg, 1986).

vii. Iron hydroxide

Laboratory bench studies have been conducted by the United States Bureau of Reclamation Engineering and Research Center in Denver on the reduction and removal of selenates from water using iron hydroxides. Batch reactor studies are ongoing. Future studies include a site investigation at Murrieta Farms in late 1987. Much more work is proposed and necessary to test effectiveness.

viii. Chemical attenuation

Initial studies on the chemical attenuation of selenium in soil systems are beginning at the University of California at Riverside by Dr. G. Sposito. The use of laboratory soil columns is the first phase of the research which will then move into field plots to examine the effectiveness of reducing selenium loads from irrigated farming practices.

ix. Other methods

Many other ideas and theories are being tested for potential selenium removal from water, soils, and sediments. A few show environmental potential but usually only in combination with one or more of the above mentioned processes. Many studies involve desalting technologies which are modifications of reverse osmosis and ion exchange. Other applications of technology are attempting to combine treatments with potential economic benefits such as power generation in solar salt gradient ponds.

c. Disposal

Another option for dealing with selenium wastes is physical removal and disposal. This might involve scraping up contaminated soils and sediments for burial in a sealed waste dump (on- or off-site) or use in a selenium deficient area. It could also include collecting selenium-enriched water and transporting it to off-site disposal areas, or injecting it into deep wells.

The recommended treatment option for the selenium contaminated soils at Kesterson Reservoir was on-site disposal in a sealed dump (SWRCB, 1987). However, as a result of a recent reevaluation of the issue, the areas at Kesterson thought most likely to pose future food chain problems will now be buried to isolate the selenium contaminated soils from the environment (SWRCB, 1988).

The original plan for the drainage waters of the San Joaquin Valley had been to transport them to the Delta (Letey et al., 1986). This plan was first abandoned because of rising costs and the subsequent discovery of the selenium problems at Kesterson Reservoir (Tanji et al., 1986). The possibility of transporting these drainage waters to the

Pacific Ocean was also discussed, but high costs and political pressure have probably eliminated this option. The use of deep well injection is currently being evaluated (Letey et al., 1986), but this is also costly and not without risks. Similar disposal of wastes in the Denver area led to a series of earthquakes (Healy et al., 1986). Site conditions and operating conditions must also be carefully reviewed to prevent groundwater contamination.

d. Isolation

The solution chosen for a previous problem with seleniferous soils in the western U.S. was the purchase of these lands by the Federal government and relocation of the residents (Anderson et al., 1961). Over 115,000 acres were purchased in south central South Dakota in the 1930's. Use of these lands are limited to appropriate levels of grazing.

e. Integrated treatment

It is possible several of these options will be used together in an integrated approach to deal with current and future selenium contamination problems in California. The best choice or choices for a given area will depend on a number of ecological and economic factors.

2. Prevention of future selenium pollution through agricultural water management and conservation

There are many combinations of water management and treatment options in agriculture that can significantly reduce the movement of selenium into the environment. The diversity of problem situations requires that these options be selected at the regional level or even on a farm by farm basis. For example, only a relatively small percentage of the soils in the San Joaquin Valley are highly contaminated with selenium. These areas contribute a disproportionately high percent of the total selenium load into the environment.

There is widespread non-uniformity of soils in a cropped field with respect to their capacity to allow water infiltration. This results in water applications in excess of that needed for most of a field in order to insure that adequate water enters those portions of a field with slower water infiltration capacities. This excess water can then percolate subsurface into drainage systems, into groundwater supplies, and/or into surface waters. There are numerous ways to reduce drainage water flows through management. The opportunities for drainage reductions is especially viable with gravity flow (surface or furrow) irrigation sytems, the most widespread irrigaton practice in the San Joaquin Valley.

There are complicating factors which affect water management options for reductions in selenium loads into the environment from agriculture. Water applications in excess of crop needs are necessary to some extent to

manage salinity problems. However, this leaching fraction is only a few percent of the applied water. Deep-rooted salt tolerant crops vary from shallow-rooted salt-sensitive crops in their water use and requirements both in terms of amounts applied, frequency of application and ability to use saline shallow groundwater. While water management can be effective in reducing selenium flows into the environment, there are associated costs which escalate in proportion to the level of selenium load reductions set as objectives.

While agricultural management options to reduce selenium loading for the land draining into the San Joaquin River (the northern area) are becoming clearer, the southern agricultural areas in the valley have fewer management options. Currently, on-site evaporation ponds receive most of the drainage water. The drainage reduction incentive is to limit the land area sacrificed for pond construction and operation by reducing drainage volumes. The management options for both areas should be similar, although the northern area with surface drainage may have a little more flexibility.

a. Drainage water reduction

Drainage water volume reductions from farms have been proposed to reduce selenium loading into the San Joaquin River from agricultural sources. While the volume of drainage water can be effectively reduced, it is uncertain whether the total selenium load entering the river can be reduced substantially.

The following methods can be used to reduce the volume of drainage effluent from irrigated lands.

i. Controlled irrigation

a. Surface or gravity flow non-pressurized systems

Currently surface irrigation methods in California including furrow and border strip are used on approximately 80% of the irrigated lands. Improvement in these systems can have the largest impact on drainage water volume reduction. Water enters the field at a high end and flows to the opposite end by gravity. The amount of water needed to meet irrigation requirements depends on the length of the field, the rate of water applications, the duration of the application period, and soil infiltration characteristics (Letey, 1986). Water applications resulting in uniform infiltration and with exact amounts of water are almost impossible. However, improvements in application efficiency can be realized with associated costs for equipment, management time, and scheduling. For example, field (furrow or basin) length can be shortened, higher water application rates can be used for a shorter time period, and timing of applications can be modified. Laser leveled basins with borders that are extremely flat can enable large volumes of water to be moved quickly and then allow for more uniform infiltration in a shorter time period. A predetermined amount of water can be applied in this manner, but construction costs and laser levelling are expensive.

Improving flow control in surface irrigation can reduce water application volumes. "Surge" irrigation uses specialized gated pipe systems to intermittently deliver or pulse water to furrows thereby speeding water travel across the field, increasing application uniformity, and reducing deep percolation and tail water run-off. Another modification of the surge system is "cablegation" which automates the intermittent flow of water down a field.

b. Pressurized systems

In the San Joaquin Valley as a whole, about 10.7 percent of the land irrigated in 1980 was irrigated with hand-moved sprinkler systems and only 1.6 percent with mechanically moved systems. Drip irrigation amounted to only 2.5 percent (Calif. DWR, 1984). Using pressurized pipes to sprinkle water on fields allows sloping lands, lands with non-uniform soil texture, or uneven lands to be irrigated. Much higher irrigated efficiences and uniformity of application may be achieved than those afforded by conventionally managed furrow irrigation systems, thereby affording opportunities to somewhat reduce application volumes and hence drainage volumes. There are substantial capital investment costs, maintenance costs, and labor costs involved in pressurized pipe irrigation systems.

Drip systems also provide high uniformity of application and control, but have much higher initial costs. Design and operational problems encountered in older drip systems can be corrected. Drip systems can be installed both on the surface and subsurface.

Other modifications of pressurized irrigation systems that show promise in reducing drainage volumes include side roll sprinklers, linear move sprinklers, modified continuous move sprinklers and center pivot sprinklers.

ii. Irrigation management and scheduling

The highest drainage flows occur during preplant irrigations before planting and through the period just after planting of crops. This involves both infiltrated water which drains out and also surface run-off. Surface run-off usually has little selenium, but subsurface drainage water can have elevated selenium levels. In many drainage systems currently the two are eventually mixed.

Much of the excess water is used to wet soil profiles and to leach salts. Although there is some disagreement about the amount required for leaching salt, some estimates suggest that as little as 5 percent of the applied water is actually required (Letey et al., 1986).

Partial control of drainage volumes is possible through methods of irrigation scheduling. In these methods water applications are timed to correspond to the needs of the crop as they occur during the growing season. By limiting applications to the amount calculated to be necessary, excess applications can be minimized. Extensive information is necessary for these methods and include regular climatic data, crop needs, soil water status, and established mathematical

relationships to predict estimated water needs. Computerized systems of data input and data processing have been developed and can be used to enhance management and scheduling.

The use of elevated shallow water tables as an alternative summer water source for irrigation can help in water conservation efforts.

b. Drainage water reuse

Drainage water usually contains some selenium and also considerable salt. However, Rhoades (1984) suggested using crop rotations of salt-sensitive and salt-tolerant crops combined with a rotation of saline and non-saline waters. When used properly no yield losses would occur. This plan may require readily available supplies of both types of water on demand. Separate water delivery systems may be required for this.

Blending drainage water with fresh water is another possible option. This option was explained by Dinar et al. (1985). Current field research is ongoing with respect to drainage water reuse where selenium is present in elevated amounts. Preliminary results indicated that food crop contamination may not be a problem, but only short-term data exists from which long-term effects cannot be determined. No information on the long-term effects of recycling soil selenium and other metals on soils or subsequent drainage effluent is yet available (Burau et al., 1987). Many of the limitations of drainage water reuse pertain to salinity considerations and elevated amounts of other elements which may become available for plant uptake.

c. Tail-water reduction

Combinations of controlled irrigation methods and irrigation management scheduling should result in significant reductions in tail-water run-off, thereby reducing surface discharges from agricultural land into receiving waters or evaporation ponds. Where tail-water run-off does occur it can be diverted to other fields for irrigation rather than spilled into drainage ditches. Tail-water reuse should pose no serious threat to crop production.

d. Evaporation ponds

Evaporation ponds have been used in the southern San Joaquin Valley for the disposal of wastewaters for many years (Green, 1986). However, they may be used less frequently in the future because of high costs and environmental concerns (Letey et al., 1986). Evaporation ponds have been the main option used for oilfield and food processing brines, and more recently, agricultural drainage water. These wastes, typically with salinity greater than 3,000 mS, have been considered to have little or no potential for beneficial reuse. Chemically, the brines collected in these evaporation ponds have much in common. Oilfield brines and much of the agricultural drainage water is sodium/sulfate/ bicarbonate dominated, with an array of minor elements that vary from area to area. Food processing brines tend to be predominantly sodium

chloride, with the minor elements somewhat controlled in the process. Oil field and food processing brines have provided some experience that may be of value in improving and using evaporation facilities to treat agricultural drainage water.

The primary concerns for farmers are the cost of building ponds that meet the Central Valley Regional Water Quality Control Board design standards, the threat of future legal action as a result of groundwater pollution and damage to wildlife (Letey et al., 1986). Ponds may also cause saline seeps around the pond perimeter. Brine or sludge from evaporation ponds will require disposal or further treatment which is likely to be very costly.

Combined with drainage water reduction programs, evaporation ponds could provide some short term isolation of selenium from the environment, but their useful life is not certain. The size of evaporation ponds required for on-farm uses can be reduced by reducing the volume of drainage waters on those farms. This is of particular significance for farms in the southern area of the westside of the San Joaquin Valley.

The selenium in the reducing conditions of pond sediments is insoluble and relatively immobile (see Chapter 3). This is reflected in the low selenium in the groundwater beneath Kesterson Reservoir, although higher levels are found in areas where the underlying clay layer was breached. As long as this sediment does not contact air or plant roots the selenium will be relatively stable and remain out of circulation (Weres et al., 1985).

A management program to immobilize selenium by chemical reduction and isolation in anoxic pond sediment would be designed to do the following: minimize disturbance of the sediments; avoid creating a zone where air penetrates into the sediment; ensure that the selenium now contained in the water becomes immobilized in the reducing bottom sediment by allowing the ponded water to continue percolating into the sediment while less selenium laden water gradually replaces it; and if necessary, modifying the ecosytem to increase the stability of the selenium-contaminated sediment. It is uncertain whether they can be done in the field. Nitrate can prevent reduction and fertilization might have to be very carefully controlled.

Currently, not enough is known to determine if the selenium-sequestering mechanisms present in Kesterson Reservoir are at work in other evaporation ponds in the southern San Joaquin River basin and the Tulare Lake basin.

e. Discontinue irrigation

One alternative for reducing selenium movement into California water resources is to prohibit the irrigation of lands where selenium contamination poses a serious risk.

The environmental effects of an irrigation water cutoff are not certain but are likely to be beneficial. Field work would be required to more clearly establish the environmental impacts of irrigation water limitations. In large part the impact would depend on land use after the change. It might vary between simple

abandonment of the lower quality land to a return to dryland farming (the historic use) on better land, and the restoration of grasses, trees, and marsh vegetation in other areas.

Some lands would conceivably be abandoned if water prices rose substantially or if irrigation water is limited. This would lead to reestablishment of vegetation by natural processes of dispersal. This could reduce selenium movement within and out of the agricultural areas as irrigation applications are reduced. However, runoff from rainfall on these abandoned lands might concentrate selenium in drainage areas creating problems similar to Kesterson Reservoir. Removal of irrigaton water might in fact increase selenium concentrations in some localized areas because of reducing flushing (Letey et al., 1986). As the natural vegetation recovers over time and runoff is reduced the environmental impacts would more likely be positive.

Dryland farming of small grains might be reintroduced on some of the lands when irrigation is limited or when water prices rise. The short-term impacts from this might be more favorable than those from simple abandonment of the land because the tillage and crops could reduce runoff and selenium movement. Wheat and barley would possibly be economically viable.

Active restoration of vegetation on these lands and development of extensive marshlands and ponds is possible. Soil amendments to increase organic matter and acidity would be desirable and would help immobilize selenium. Costs would probably have to be assumed by the government either as cash payments or in the form of tax credits.

Economic impacts from a complete irrigation water cutoff have been estimated by several investigators (Wallace and Strong, 1985; Jones and Stokes, 1986). Estimates range from $63 million to more than $100 million. These studies have neglected the existing subsidies to the farmers in the area. The unreimbursed cost for irrigation has been estimated at over $750 million just for Westlands Water District (Le Veen, 1985). The subsidy for agricultural water is placed as high as $90 per acre foot by some investigators (Candee et al., 1985). These subsidies are substantial and strongly influence both what is grown and how irrigation is managed.

The cost of commodity price support programs which are well-utilized in many of the areas experiencing selenium problems also needs to be included. Without subsidies agriculture would be less profitable to the farmers and some of the more common, high water demand crops would not be grown. However the benefits to society might be higher if the subsidies and some of the farming in the area was discontinued or changed.

Cost benefit studies have also ignored the potential returns from dryland farming and recreational use of the land if it is retired from agricultural uses. A thorough review of the economics of alternative scenarios is needed.

There are currently no practical criteria for deciding which farms, clusters of farms or areas, pose serious selenium risks in their drainage water discharges. A farm by farm

analysis to determine "hot-spots" of potential selenium contamination could prove to be very expensive, scientifically complex and controversial. Identification of selenium sources can be confused by contamination from lateral subsurface flows, rising groundwater, past use of selenium contaminated groundwater drainage water, and the interactions with other factors. Yet this might help delineate some of the more serious sources of selenium contamination.

f. Agroforestry to manage groundwater

Some of the drainage systems in California are needed to keep otherwise seasonally high water tables low. This is necessary to maintain crop production without the ill effects of water-logging or upward salt migration during the growing season. Trees can help to keep these otherwise seasonally high water tables low either alone or in combination with other management programs. Trees might also be used to concentrate brines prior to other treatments and to reduce draingage flows.

Trees have been used to manage ground water for centuries in China and other countries. China has been one of the few countries to include this traditional treatment in their modern water management schemes. In recent years, large projects with trees have been completed in China. In Shangdong Province for example, 4 million trees and 2.5 million shrubs were planted on 13,000 hectares for drainage purposes (Robertson, 1985).

The Australians have also been working with trees to control ground water problems and the initial results have been encouraging. The provincial government of Victoria, for example, recently completed a million dollar tree planting program with ground water management as one of the primary goals (Oates 1983; May, 1986).

Trees may ultimately prove useful in the maintenance of farming on California's irrigated lands (Bainbridge, 1987; Cervinka, 1987). The benefits trees provide include both direct evapotranspiration of water by the tree and improved microclimatic conditions on surrounding lands, which reduces plant crop water demand and evaporation from the soil surface (hence less irrigation water is needed). Climatic improvement results from increased humidity, reduced wind speed, and shading. Irrigation demand may be reduced considerably as a result of the interaction of these factors. Trees can also reduce wind damage to crops if layouts are planned to provide wind breaks.

Ground water use can be substantial if phreatophytic trees are used. These may consume more than 6 feet of water a year per acre of trees (Sheridan, 1981; Virginia and Jarrell, 1983). Trees may provide additional benefits if they are chosen carefully. *Prosopis* spp. (mesquite), for example, is a phreatophyte with high salt tolerance. Some species will survive salinity higher than seawater (Felker et al., 1981). These trees are also drought and heat tolerant (Nilsen et al., 1983) and can maintain high productivity when sufficient water is available. Mesquite can produce 13 tons/hectare/year (Felker et al., 1983) of what has become a valued firewood (Bainbridge,

1986); edible pods suitable for fodder or human food (Meyer, 1985); and reasonably high nitrogen fixation rates >25 kgN/ha/yr (Rundel et al., 1982). Other trees might be of value for this work include carob, acacia, oak, poplar, and eucalyptus.

The agroforestry option may not prove sustainable over the long term either. Evapotranspiration can lead to a buildup of salt and selenium in the root zone (Merwin, 1987). This may ultimately prove fatal to the plant. It may also lead to elevated trace element levels in plant tissue and seeds which could prove detrimental to wildlife if they are not carefully managed. Field trials are underway to determine the potential value and problems associated with agroforestry systems in the San Joaquin Valley (Cervinka et al., 1987).

At the moment, the comments of Letey et al. (1986) are summarize the status of selenium problems in California:

"Complete technical information to make sound water management decisions is lacking, and extensive research programs have been initiated by Federal agencies, state agencies, and the University of California. Unfortunately, critical decisions must be made before research findings are complete, and research alone is not likely to provide a solution to the problem. Indeed, a solution free of risk, significant and costly trade-offs, and deep seated value judgments is not probable. As such, the future will ultimately be decided in the political arena."

E. Summary

More extensive analyses of drainage water reduction options, water conservation, and drainage water treatments can be found in Calif. DWR (1984), Willey (1985a,b, 1987), Caswell and Zilberman (1986), Boyle Engineering (1986), Central Valley Water Use Study Committee (1986), University of Calif. Committee of Consultants (1987), Cervinka et al. (1987) San Joaquin Valley Drainage Program (1987) and State Water Resources Control Board (1987).

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Maximum permissible tissue concentration -- the maxium allowable concentration of a substance in the diet of a consumer (e.g. fish, waterfowl, human organism) that will not adversely affect growth, survival, reproduction or cause other sublethal effects.

Methylation -- introduction of a methyl group (CH_3-) to a molecule.

Myopathy -- progressive wasting of skeletal muscles.

Parenteral -- not by the intestines.

Particulate -- discrete minute particles.

Pelleting -- forming aggregates from powder, typically for ease of handling.

Peroral -- administered by mouth.

Phreatophyte -- a plant obtaining most of its water requirement from moist soil above permanent groundwater.

Prills -- pellets formed by melting and letting the drops of molten liquid cool while falling.

RWQCB -- Regional Water Quality Control Board.

Roasting -- heating in a furnace.

Salinity -- the salt content of a water sample measured by determining the concentration of total dissolved solids or electrical conductivity.

Scrubbed-- cleaned with water, chemical, or physical treatments.

Selenomethionine -- an amino acid (protein constituent) containing a selenium atom in place of the normal sulfur atom.

SARB -- State Air Resources Board.

SWRCB -- California State Water Resources Control Board.

Subcutaneous -- just below the skin.

Subsurface drains -- perforated pipe or open joint clay tile pipe installed about eight feet below the soil surface to intercept and convey soil moisture. Used in areas with poor natural drainage to prevent water buildup in the crop root zone.

Total dissolved solids (TDS) -- the amount of material remaining after evaporating a water sample at 103-105 degrees Celsius for one hour.

Unimpared runoff -- historic river flow taking out the effects of human activities, including storage, diversion, and return flows.

USBR -- United States Bureau of Reclamation.

USFWS -- United States Fish and Wildlife Service.

USGS -- United States Geological Survey, United States Dept. of Interior.

Volatilization -- conversion of solid or liquid to gaseous phase.

Vulcanism -- related to volcanic activity and events.

Waste load allocation -- the quantity of waste that may be discharged into a surface water body without excessive impairment of its beneficial uses.

Water quality criteria -- scientifically derived constituent concentrations in a water body which are thought to protect specific beneficial uses.

Water table -- the upper surface of the zone of saturation in soil (all pores filled with water), except where the surface is formed by an impermeable layer. The hydrostatic pressure equals atmospheric pressure at the water table.

Methylation -- introduction of a methyl group (CH_3-) to a molecule.
Myopathy -- progressive wasting of skeletal muscles.
Parenteral -- introduced other than by the intestines.
Particulate -- discrete minute particles.
Pelleting -- forming aggregates from powder, typically for ease of handling.
Peroral -- administered by mouth.
Phreatophyte -- a plant obtaining most of its water requirement from moist soil above permanent groundwater.
RWQCB -- Regional Water Quality Control Board.
Roasting -- heating in a furnace.
Salinity -- the salt content of a water sample measured by determining the concentration of total dissolved solids or electrical conductivity.
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