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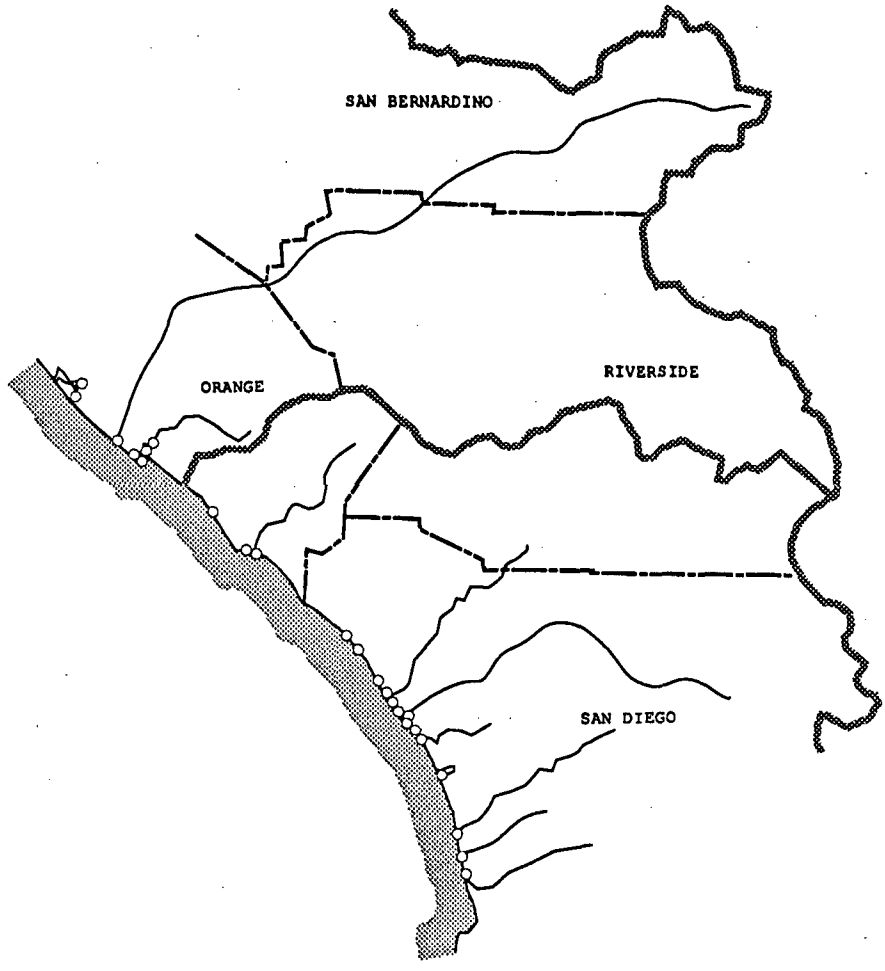

Technical Proposal for a Cooperative Agreement between the California State Water Resources Control Board and the U.S. Environmental Protection Agency Environmental Monitoring and Assessment Program

December 1993

STATE WATER RESOURCES CONTROL BOARD
CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

MEASURES OF BIOEFFECTS ASSOCIATED WITH TOXICANTS IN SMALL BAYS AND ESTUARIES OF SOUTHERN CALIFORNIA

PILOT STUDY

Proposed Cooperative Agreement Between the:

California State Water Resources Control Board

and the

U.S. Environmental Protection Agency
Environmental Monitoring and Assessment Program

December 1993

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MEASURES OF BIOEFFECTS ASSOCIATED WITH TOXICANTS IN SMALL BAYS AND ESTUARIES OF SOUTHERN CALIFORNIA

I. INTRODUCTION

The State Water Resources Control Board (State Water Board) and the U.S. EPA Environmental Monitoring and Assessment Program (EMAP) propose a Cooperative Agreement to conduct a pilot study for the assessment of adverse biological effects in small bays and estuaries of Southern California. In FY 1993-94 and FY 1994-95, EMAP will contribute $150,000, the State Water Board will contribute $100,000 and the National Oceanic and Atmospheric Administration (NOAA) will contribute $110,000 in contract funding to support monitoring of Southern California small bays and estuaries. The State Water Board and NOAA funding will be coordinated through a cooperative agreement between these two agencies (please refer to Appendix 1). The combined amount ($360,000) will be used to determine sediment toxicity, benthic community composition and abundance, and sediment chemistry in small bays and estuaries located between Huntington Harbour and Mission Bay in Southern California (Figure 1).

This workplan for the proposed 1994 pilot study is divided into several sections including Background, Purpose and Objectives, Technical Approach, Project Management, and References.

A. Background

EMAP is designed to respond to the growing demand for information characterizing the condition of the Nation's environment and the type and location of changes in it. It was created in response to the EPA Science Advisory Board's recommendation and stresses long-term assessment, probability-based sampling, and use of multiple indicators. The estuaries component of EMAP (EMAP-E) is a joint EPA/NOAA program that is designed to complement and, perhaps, eventually merge with NOAA's existing National Status and Trends Program (NS&T). Its goals are as follows:

1. Provide a quantitative assessment of the regional extent of estuarine environmental problems by measuring pollution exposure and ecological condition,

2. Measure changes in the regional extent of environmental problems for the Nation's estuarine ecosystems,

3. Identify and evaluate associations between the ecological condition of the Nation's estuarine ecosystems and pollutant exposure, as well as other factors known to affect ecological condition, and

4. Assess the effectiveness of pollution control actions and environmental policies on a regional scale and nationally.

In addition to meeting the overall goals of EMAP, EMAP-E is addressing specific environmental problems such as chemical and biological contamination, habitat modification, low dissolved oxygen, eutrophication, and cumulative impacts.

The State Water Board and seven California Regional Water Quality Control Boards (Regional Water Boards) are mandated by the Porter-Cologne Act (California Water Code, Division 7, Section 13390 et seq.) to implement the Bay Protection and Toxic Cleanup Program (BPTCP). The program has three primary activities: (1) the identification of "Toxic Hot Spots," (2) planning for the remediation of these sites, and (3) development of sediment quality standards. Monitoring activities will contribute to all three activities, whether by locating hot spots using a combination of bioeffects and chemical data; defining the chemical, biological, spatial, and temporal dimensions of known toxic hot spots; identifying sources of contaminants that add to or create hot spots; evaluating the effectiveness of remediation efforts; or providing information for the field data component of the sediment quality standards development effort.

The toxic hot spot identification effort is well underway throughout California's enclosed bays and estuaries (SWRCB, 1993). The BPTCP is taking a weight-of-evidence approach where a range of bioeffects data (toxicity testing, benthic community analysis, biomarkers, and bioaccumulation) will be combined with chemistry results. Sites are first screened for bioeffects and then revisited for confirmation as known toxic hot spots (this monitoring activity includes careful selection of reference sites, analysis of sediment chemistry as well as bioeffects measures, and field replication). To make a strong case for the identification of a

known hot spot, the program intends to carefully select reference sites to match out the effect of such confounding variables as grain size and Total Organic Carbon (TOC) so that the effects of chemical contamination can be better understood. The intent is to provide more convincing evidence than simply the association of bioeffects with chemical constituents.

B. Purpose and Objectives of the Proposed Project

Given this broad background, the purpose of the proposed pilot study is to both provide data useful for attainment of each program's objectives and aid the State Water Board's transition to eventual involvement in EMAP's full-scale monitoring program in 1995. To achieve these purposes the following objectives will form the foundation for data collection and analysis:

1. Estimate with known confidence the percent of degraded area in Southern California small bays and estuaries as measured by toxicity, benthic community analysis, and chemistry.

2. Identify and evaluate associations between the ecological condition of California's estuarine and coastal ecosystems and pollutant exposure, as well as other factors known to affect ecological condition (e.g., grain size and depositional events).

3. Compare advantages and disadvantages of alternate measures of bioeffects (e.g., Ampelisca vs. Rhepoxynius and two- vs. five-replicate benthic sampling) and specify preferred approaches.

4. Specify necessary changes in quality assurance procedures for the State Water Board's participation in EMAP's demonstration program.

II. TECHNICAL APPROACH
TOXICITY TESTING, BENTHIC COMMUNITY ANALYSIS, AND SEDIMENT CHEMISTRY

A. Overview

The pilot study areas are a number of small enclosed bays and estuaries located between Huntington Harbour and Mission Bay in southern California (Figure 1). The existing Cooperative Agreement between NOAA and the State Water Board (Appendix 1) stipulates that 42 stratified random sites varying from highly impacted to unimpacted will be sampled within these water bodies. Toxicity testing is to be performed at all 42 sites while chemical analysis is to be conducted at approximately 20 (to be selected after the results of toxicity testing become available). To satisfy the needs of the State Water Board, NOAA and EMAP, these data will be supplemented with 8 more sites, a third toxicity test, and benthic community analysis, as well as chemical analysis at the other 30 sites.

B. Sampling Design

The majority of sites will be sampled using EMAP assessment approaches including a stratified random sampling design. Maps 1 through 14 of Appendix 2 illustrate the individual strata or blocks for each of the small bays and estuaries. The list of waterbodies identified for sampling in Appendix 2 includes all enclosed bays in the study area. Estuaries considered too small for sampling include San Juan Creek, San Onofre Creek, Las Flores Creek Estuary, and Loma Alta Slough. Buena Vista Lagoon will not be sampled because a dam at its mouth prevents tidal influence.

Strata have been chosen to reflect high, medium, and low probability of contamination based on the results of previous testing and judgement regarding likely sites that are polluted. Generally, shoreline facilities in Newport Bay are expected to have a high probability of contamination while the open bay and dredged channels are expected to have medium to low levels. The other small bays and estuaries in the study are difficult to classify due to the absence of information but it is believed that some of these may provide sites relatively free of pollution or contamination.

Eight randomly selected candidate sites in each stratum will be provided by EMAP after initiation of the pilot project. Sampling will progress sequentially through the candidate sites in each stratum until the required site is located that meets the following criteria:

1. The site is predominantly depositional rather than erosional (i.e., the site has sediment of finer grain size).

2. The site is accessible (i.e., the site is of sufficient depth to perform sample collection; nonrestricted for military purposes; unobstructed by vessels, booms, and other physical features; etc.).

The small estuaries (coastal lagoons) will be sampled more than one time. The following eight strata will be sampled twice: Z, CC, FF, GG, HH, NN, OO, PP (please refer to Appendix 2 for maps).

C. Sample Collection and Processing

All pilot project sample collection is scheduled for mid to late summer of 1994 and will be performed in two or three separate trips spaced two to three weeks apart. The procedures to be followed in collecting samples and conducting field measurements are described in the BPTCP QAPP (Appendix 3). Full implementation of the entire array of EMAP quality assurance procedures will not be completed as part of this pilot study. In anticipation of participation in the EMAP demonstration project (in 1995) the California Department of Fish and Game will upgrade and test their Quality Assurance procedures during the pilot.

D. Laboratory Analysis

Three independent tests of sediment toxicity will be performed on each site: (1) a ten-day solid phase amphipod test using either Rhepoxynius abronius or Eohaustorius estuarius (this species will be used if salinity levels are lower than the acceptable range for R. abronius), (2) a pore water urchin fertilization or development test using Strongylocentrotus purpuratus, and (3) a ten-day solid phase amphipod test, using Ampelisca abdita. Laboratory methods for the Ampelisca test and benthic analysis have been published by EMAP (USEPA, 1992). Methods for the remaining toxicity tests appear in the BPTCP QAPP (Appendix 3). Any

artifacts of pore water toxicity testing will have to be corrected or their direction and magnitude documented before the test can be performed.

Additionally, benthic community structure (species composition and abundance) will be determined for five samples collected at each site.

The chemical analyses to be performed are listed in Table 1. The methods that will be used are listed in Appendix 3.

E. Quality Assurance

The draft QAPP for the pilot study consists of a blend of the QAPPs for EMAP and BPTCP. As stated above, full implementation of EMAP's quality assurance procedures will not be instituted until the start of the full-scale demonstration program in 1995. The pilot study QAPP is included as Appendix 3. The QAPP will be finalized as one of the first phases of the pilot project. The changes in the QAPP that are necesary to meet EMAP QA requirements will be identified (Study Objective 4).

F. Data Analysis

Analyses for the pilot project will address the questions of greatest concern to each of the participating agencies. The critical questions for Project Objectives 1 and 2 will fall into two general categories:

1. Ranking spatial subpopulations (e.g., comparing the spatial extent of pollution in the developed portions of the small bays to the open portions or undeveloped locations in the small bays), and

2. Ranking types of pollution exposure (e.g., comparing the spatial extent of organic or metal pollution that exceeds some critical value [e.g., Long and Morgan, 1990; MacDonald et al., 1993).

Most of the analyses will fall into the first category because the sampling design will be enhanced for spatial subpopulations of interest. For example, the pilot project will compare

locations with known sources of pollutants (boatyards or marinas) to areas that have no known sources of pollutants (deep channels or back bays).

For the purposes of EMAP comparisons, most questions to be addressed in the pilot project will be similar to: "For a specific indicator, what percent of the area of a specific subpopulation differs from reference conditions?" These types of questions will be approached in two steps. The first step will be to develop cumulative distribution functions (CDF) that describe the range of values for each parameter in each subpopulation. CDFs provide essential information about the central tendency (e.g., median) and extreme values of indicators. The second step will be to select the critical value that can be used to classify the condition of several subpopulations of interest.

Based on the CDFs, areas within subpopulations will be classified as meeting or not meeting reference conditions. The reference conditions that will be used are identified in the draft site ranking criteria developed for the BPTCP (SWRCB, 1993). Sediment pollutants will be compared to the sediment values developed by Long and Morgan (1990) and MacDonald et al. (1993). The threshold value for toxicity will be less than 80 percent survival or significant toxicity relative to a control. The benthic invertebrate assemblage data will be converted to either a linearly scaled index (Weisberg pers. comm.) and compared to a threshold or compared to a threshold based on the "reference envelope" approach (SCCWRP and EcoAnalysis, 1993).

Treatment of the data for the Cooperative Agreement between NOAA and the State Water Board will be largely descriptive, consisting of graphs, maps, and tabulated values for bioeffects measures and chemistry. Correlations will be performed on raw and normalized toxicity and chemical data.

To aid the BPTCP in following up toxic and degraded benthic community sites, these results will be tabulated separately. Toxicity will be arrayed in descending order, from most to least toxic; benthic results will be grouped into impacted, unimpacted, and intermediate sites. Independently of this cooperative agreement, the State Water Board will conduct followup investigations (which will include field replicates and careful selection of reference sites) to confirm sites as Toxic Hot Spots.

Data analysis for the comparison of the relative advantages of toxicity tests (Objective 3) will be accomplished by a simple comparison of the relative sensitivity of the toxicity tests, availability of reference sites, and concordance of response with benthic community structure. The question being addressed for the benthic community (in Objective 3) is: "Can sites be characterized using two replicate sampling?" The need for multiple replicates in benthic community analysis will be assessed by comparison of the within site variation characterized by 2 and 5 replicate samples at sites.

G. Database Management System

The data generated in this pilot study will be stored on the BPTCP statewide database. The BPTCP database management system, currently in the final stages of development, consists of a database server at Teale Data Center (TDC) in Sacramento with clients at the State and Regional Water Boards. The State Water Board and San Francisco Bay Regional Water Board have UNIX workstations while the remaining boards have 486 modem-equipped PCs. GIS capability includes a network connection to TDC, a subscription to the TDC GIS library, and ARC/INFO GIS software. The network connections include a dedicated line from TDC to the State Water Board and modem connections to the Regional Water Boards and the DFG's Marine Pollution Studies Laboratory (MPSL). BPTCP analytical results will be sent from individual laboratories (toxicity, benthic community, metals, organics, and TOC/grain size) for compilation at MPSL and forwarded to the State Water Board. Development of individual laboratory and MPSL capability is aided by EcoAnalysis, Inc. As of December, 1993 hardware procurement has been completed, Oracle has been installed, and a prototype database is in operation.

III. PROJECT MANAGEMENT

A. Organization

The Small Bays and Estuaries Pilot Study will be a cooperative effort of EMAP-E, NOAA, and the State Water Board. The California Department of Fish and Game, through a contract with the State Water Board, will provide sample collection, laboratory services, data analysis, and development of a draft final report. Review of the draft report will be conducted jointly by the three cooperating agencies, which will each receive a disk containing all the data. Overall coordination of the project will be the responsibility of the State Water Board, with the support of other participants. The management structure of the project is presented in Figure 2.

An Advisory Committee composed of representatives of the various participating organizations will assist in project management. The committee will meet as necessary to review the progress and results of the pilot project. The advisory committee will have the following members:

1. Ed Long, NOAA
2. Terry Fleming, EPA Region IX
3. Kevin Summers, Technical Director of EMAP-Estuaries
4. Michael Perrone, Chief of the Monitoring and Assessment Unit of the State Water Board
5. Michael Sowby, Chief of Research Investigations of the DFG Oil Spill Prevention and Response Program
6. Bruce Thompson, Project Manager of the San Francisco Estuary EMAP Pilot Project
7. Jeff Cross, Project Manager of the Southern California EMAP Pilot Project
8. Craig J. Wilson, Program manager for the Bay Protection and Toxic Cleanup Program at the State Water Board.

B. Schedule and Deliverables

The Small Bays and Estuaries Pilot Project will begin upon approval of this Cooperative Agreement. The steps in the project include preparation for field collection, field work, laboratory analysis, data analysis, and preparation of the final report. Figure 3 presents the proposed schedule for completing these activities.

C. Budget

Contract funding is being provided by the State Water Board, NOAA, and EMAP. The budgeted amounts for the tasks presented in the Cooperative Agreement are presented in Table 2. The total funding for contract activities is $360,000. We also anticipate at least $180,000 of in-kind services from the State Water Board, NOAA, EPA Region 9, and DFG (Table 3).

IV. REFERENCES

Long, E.R. and L.G. Morgan. 1990. The potential biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. National Oceanic and Atmospheric Administration, Rockville, MD.

MacDonald, D.D., K. Brydges, and M.L. Haines. 1993. Development of an approach to the assessment of sediment quality in Florida coastal waters. Prepared for the Florida Coastal Management Program, Florida Department of Environmental Regulation.

U.S. Environmental Protection Agency. 1992. EMAP Laboratory Methods Manual: Estuaries. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, Ohio (in revision).

Southern California Coastal Water Research Project and EcoAnalysis, Inc. 1993. The reference envelope approach in regional monitoring off Southern California. Report to EPA Region 9. SCCWRP, Westminster, CA.

State Water Resources Control Board. 1993. Status of the Bay Protection and Toxic Cleanup Program: Staff Report (Draft). Sacramento, CA.

TABLE 1: Chemicals Substances Currently Measured by the BPTCP.

Polyaromatic Hydrocarbons (PAHs)

Acenaphthylene
Anthracene
Benz(a)anthracene
Benzo(a)pyrene
Benzo(e)pyrene
Biphenyl
Chrysene
Dibenz(a,h)anthracene
2,6-dimethylnaphthalene
Fluoranthene
Fluorene
2-methylnaphthalene
1-methylnapthalene
1-methylphenanthrene
Naphthalene
Perylene
Phenanthrene
Pyrene
Benzo(b)fluoranthene
Acenaphthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Indeno(1,2,3-c,d)pyrene
2,3,5-trimethylnaphthalene

18 PCB Congeners:

PCB No.	Compound name
8	2,4'-dichlorobiphenyl
18	2,2',5-trichlorobiphenyl
28	2,4,4'-trichlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl
66	2,3',4,4'-tetrachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
128	2,2',3,3',4,4'-hexachlorobiphenyl
138	2,2',3,4,4',5'-hexachlorobiphenyl
153	2,2',4,4',5,5'-hexachlorobiphenyl
170	2,2',3,3',4,4',5-heptachlorobiphenyl
180	2,2',3,4,4',5,5'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl
195	2,2',3,3',4,4',5,6-octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

DDT and its metabolites

2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4,4'-DDT

Chlorinated pesticides other than DDT

Endrin
Aldrin
Alpha-Chlordane
Endosulfan I
Trans-Nonachlor
Dieldrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (gamma-HCH)
Mirex

Major Elements

Aluminum
Iron
Manganese

Trace Elements

Antimony
Arsenic
Cadmium
Chromium
Copper
Lead

TABLE 1 (continued): Chemicals Substances Currently Measured by the BPTCP.

Other measurements	Trace Elements (continued)
	Mercury
Total organic carbon	Nickel
Tributyltin	Selenium
Grain size	Silver
	Tin
	Zinc

Additional compounds recently added:

1) DDT and its metabolites--

DDMS,p,p'	DDMU,p,p'

2) Chlorinated pesticides other than DDT--

Chlorbenside	Cis-chlordane
Trans-chlordane	Oxychlordane
Cis-nonachlor	gamma-chlordene
Chlorpyrifos	Dacthal
Dichlorobenzophenone	Endosulfan II
Endosulfan sulfate	Ethion
HCH, alpha	HCH, beta
HCH, delta	alpha-chlordene
Methoxychlor	Oxadiazon
Toxaphene	

TABLE 2: Contract Budget for the Small Bays and Estuaries Pilot Project.

Task	*State Water Board*	*NOAA*	*EMAP*
Sample Collection	$ 21,600	$ 31,600	$ 18,050
Toxicity Testing			
Rhepoxynius	$ 25,000		
Urchin fertilization		$ 25,000	
Ampelisca			$ 25,000
Benthic Analysis			$ 55,250
Chemical Analysis	$ 23,400	$ 23,400	$ 42,700
Biomarkers[1]	$ 25,000	$ 25,000	
Report Writing	$ 5,000	$ 5,000	$ 5,000
Other[2]			$ 4,000
Total	$100,000	$110,000	$150,000

[1]Please refer to Appendix 1 for a discussion of work to be performed. This line item is included for informational purposes only.

[2]This funding will most likely be used to expand quality assurance requirements.

TABLE 3: Estimated In-Kind Budget for the Small Bays and Estuaries Pilot Project

Task	*State Water Board*	*DFG*	*NOAA*	*EPA, Region 9*	*Others*
Planning	$24,000		$4,000	$4,000	
Project Tracking	$24,000		$8,000	$4,000	
Information Management	$24,000				
Analysis and Reporting	$24,000		$8,000	$4,000	$8,000
Review and QA	$5,000	$40,000	$4,000	$4,000	$8,000
Total	$100,000	$40,000	$24,000	$12,000	$16,000

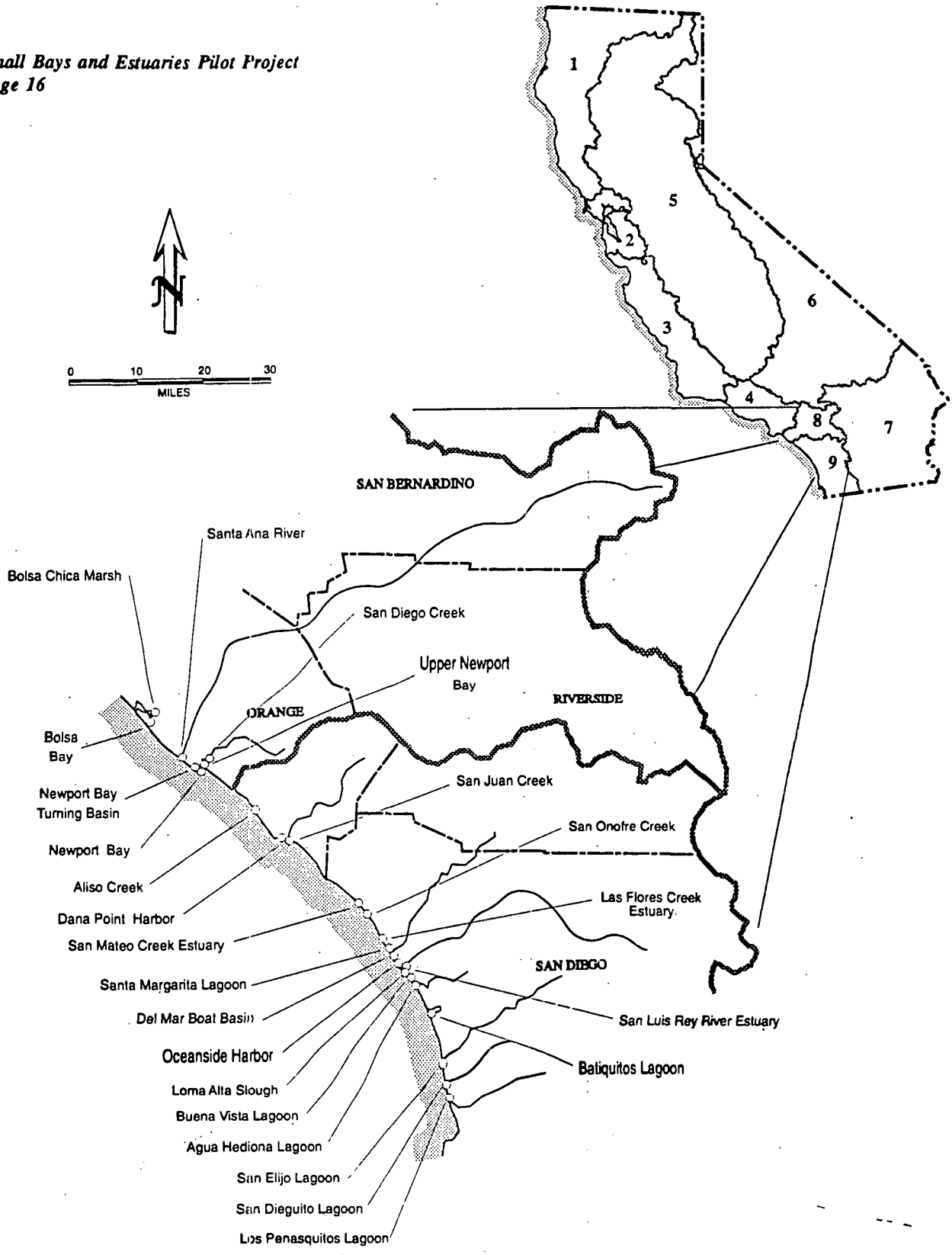


Figure 1: Southern California Small Bays and Estuaries

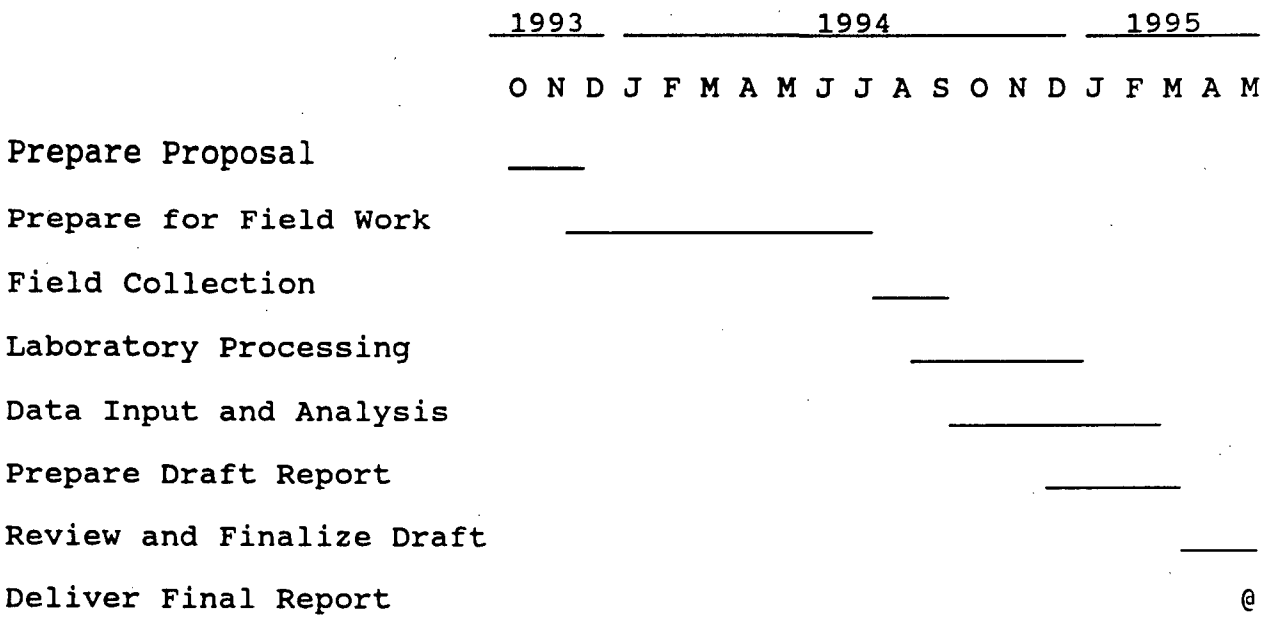


Figure 2: Small Bays and Estuaries Pilot Project Schedule

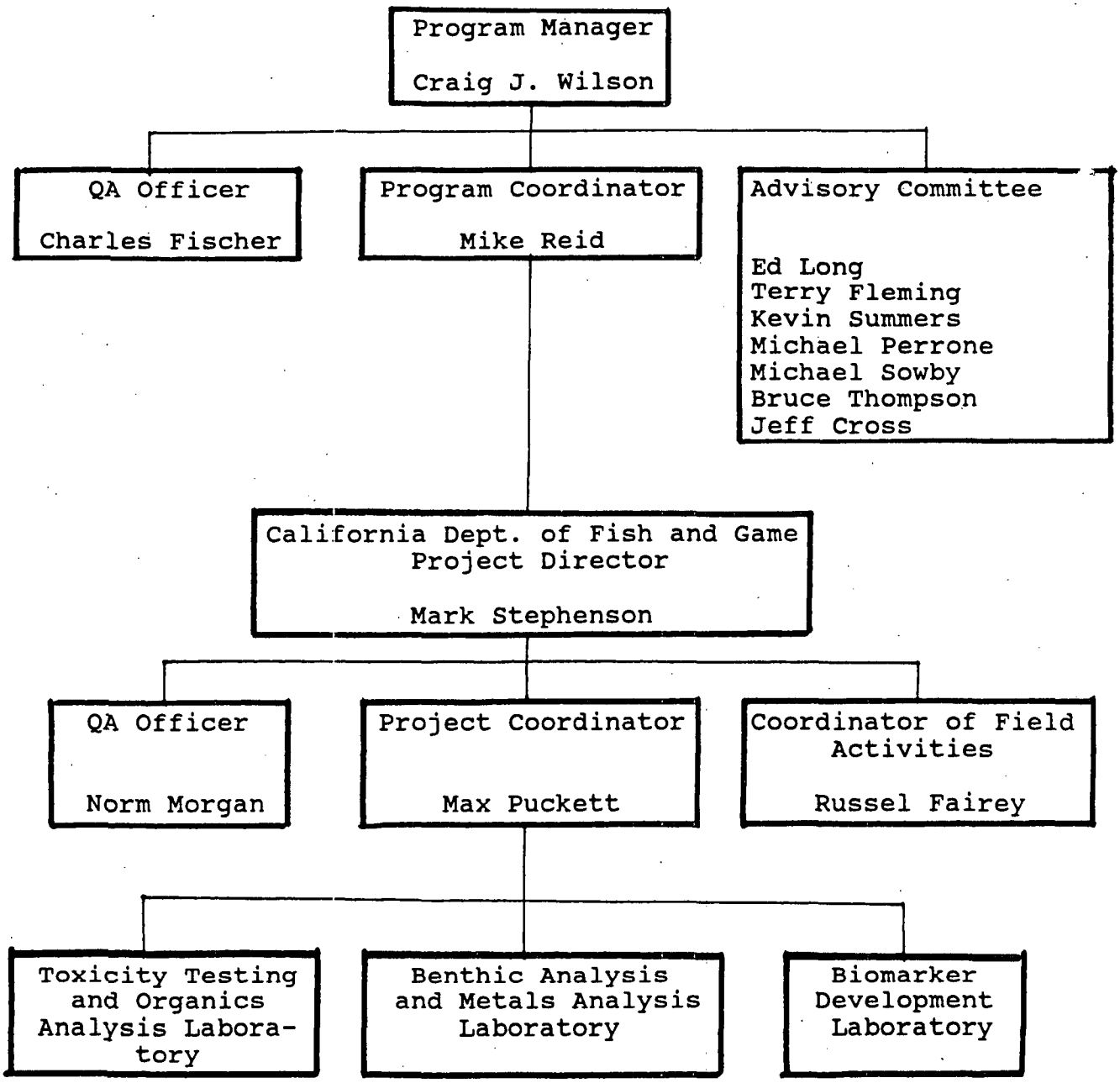


Figure 3. Management Structure of Small Bays and Estuaries Pilot Project

APPENDIX 1

State Water Board and NOAA

Cooperative Agreement (Third Year)

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
AND
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

MEASURES OF BIOEFFECTS ASSOCIATED WITH TOXICANTS IN SOUTHERN CALIFORNIA

YEAR THREE

PROPOSAL TO CONTINUE A COOPERATIVE AGREEMENT

JUNE 15, 1993

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
AND
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD
PROPOSAL TO CONTINUE A COOPERATIVE AGREEMENT

MEASURES OF BIOEFFECTS ASSOCIATED WITH TOXICANTS IN SOUTHERN CALIFORNIA

YEAR THREE

A. INTRODUCTION. The State Water Resources Control Board (State Water Board) and the National Oceanic and Atmospheric Administration (NOAA propose to continue a Cooperative Agreement to assess adverse biological effects in the inshore waters of southern California. The program began in FY 1991-92 and this proposal is for FY 1993-94 (year three). In FY 1993-94, NOAA will provide $110,000 to the State Water Board. The State Water Board will provide $100,000 for the program from the Bay Protection and Toxic Cleanup fund. These funds will be used to determine the sediment toxicity of sites in enclosed bays and coastal lagoons in southern California, continue development of one of the two biomarker tests, and measure sediment chemistry on a limited number of samples.

This workplan is divided into several sections including Background, Rationale, Research Tasks for FY 1993-94, Reports, Benefits of the Research to NOAA, Benefits of the Research to California, Proposed Cooperative Agreement, Costs, and References.

B. BACKGROUND. NOAA is mandated by several acts of Congress to conduct a program of research and monitoring on marine pollution. Much of this research is being conducted through the National Status and Trends (NS&T) Program. The NS&T Program performs regional intensive studies of the magnitude and extent of toxicant-associated bioeffects in selected coastal embayments and estuaries. The areas chosen for these regional studies are those in which the contaminant concentrations indicate the greatest potential for biological effects. These biological studies augment the regular chemical monitoring activities of the Program and provide answers to the proverbial "So what?" question regarding toxicants. NOAA and the State of California have begun to conduct one of these intensive programs in Southern California over a three-year period. This workplan describes the cooperative research effort to be conducted in the third year.

The State Water Board and seven California Regional Water Quality Control Boards (Regional Water Boards) are mandated by the Porter-Cologne Act (California Water Code, Division 7, Section 13390 et seq.) to implement the Bay Protection and Toxic Cleanup Program (BPTCP). One activity of the BPTCP is to develop sediment quality objectives. The intent of the sediment quality objectives is to protect the beneficial uses of bays and estuaries, including protection of human health and aquatic life. The objectives are to be based upon scientific information, including but not limited to chemical monitoring, bioassays, or established modeling procedures, and are intended to provide adequate protection for the most sensitive aquatic organisms. A

strategy was approved for developing these objectives in July 1991. The strategy includes the collection of new data from California to verify toxicity thresholds previously determined in research performed in California and elsewhere. Matching, paired chemical and biological data will be collected in studies performed in California for analysis and evaluation. The BPTCP is also required to conduct monitoring for the purposes of (1) following up existing monitoring to determine whether these sites qualify as toxic hot spots and (2) sampling in previously untested areas to determine whether additional toxic hot spots exist. The program has begun to implement this aspect of the BPTCP through a contract with the California Department of Fish and Game (DFG).

C. RATIONALE. The proposed research will be performed in Southern California coastal bays. A considerable amount of research has been performed on toxicants and measures of effects associated with them in Southern California. Most of this work has focused upon Santa Monica Bay and the continental shelf off the large municipal treatment plants in the Los Angeles, Orange County, and San Diego metropolitan areas. A considerable amount of sediment chemistry data exist for the Los Angeles/Long Beach Harbor, parts of San Pedro Bay, and parts of San Diego Bay, the major embayments of Southern California. These data have been collected mostly as prerequisites to dredging projects. Sediment toxicity has been determined to a lesser extent in these embayments in a number of small predredging studies, but not in any large synoptic surveys. In Los Angeles/Long Beach Harbor, most of the sediment toxicity data are available for specific maritime berths and navigation channels. In San Diego Bay, much of the available data were generated in predredging studies or in studies performed with relatively insensitive species. No data are available from coastal lagoons in the Southern California Bight.

A program of cooperative research by NOAA and the State of California was initiated in March 1992 with FY 1991 NOAA funds. It focuses upon the Los Angeles/Long Beach portion of the Southern California study area. That research included tests of sediment toxicity and toxicant-associated biomarkers in resident fish. In the second year (FY 1992-93), sediment survey work was conducted in the San Diego area with FY 1992 NOAA funds. This statement of work focuses in the enclosed bays and coastal lagoons between Los Angeles/Long Beach Harbor and San Diego Bay.

Objectives. The objectives of the research are to:

1. Determine the presence or absence of adverse biological effects in selected inshore and coastal areas of Southern California;

2. Determine the relative degree of severity of toxicant effects;

3. Determine the spatial distribution of toxicant-associated effects in selected areas of Southern California;

4. Determine the relationships between toxicants and measures of effects in Southern California; and

5. Continue development of either the mussel or fish biomarker.

Scope of Study. The study area extends from the Palos Verdes Peninsula south to the Mexico/USA border. It extends from approximately the 60 m isobath to the upper limit of tidal-influenced saltwater; however, most of the work will focus upon selected coastal bays and lagoons. In the first year, samples were collected in Los Angeles/Long Beach Harbor, San Pedro Bay, Anaheim Bay, Alamitos Bay, and Huntington Harbour.

In the second year, samples were collected in Tijuana Slough, San Diego Bay, San Diego Harbor, and Mission Bay. In the third year, it is anticipated that samples will be collected in Newport Bay, Bolsa Chica, Oceanside Harbor, and the numerous coastal lagoons located in the study area.

The research will involve biological and chemical analyses of sediments and resident demersal fish or mussels. Biological tests and chemical analyses will be performed with portions of each sample medium resulting in matching, paired data.

D. RESEARCH TASKS FOR FY 1993-94. Two research tasks are to be implemented in FY 1993-94: (1) measures of sediment contamination and toxicity and (2) measures of bioaccumulation and bioeffects in mussels or resident demersal fish. The details of the technical approaches and methods to be used in these two tasks will be described by the State of California. Specific details of sampling schedules will be determined jointly by NOAA and the State of California.

Samples will be collected at sites in each embayment that will serve at least two purposes: (1) to characterize the magnitude and spatial extent of toxicant-associated bioeffects in Southern California inshore areas; and (2) to determine relationships between concentrations and mixtures of sediment-associated toxicants, bioavailability and uptake of these chemicals, and the occurrence and severity of bioeffects. It follows that the grid of sampling sites selected to fulfill these two purposes must meet the following criteria: (1) the sites must be depositional (muddy) and, therefore, should represent recently deposited toxicants; (2) half of the sites must represent the integrated accumulation of toxicants from multiple nearby sources, while the other half must represent contamination in further need of assessment for toxic hot spot status; (3) the grid of sediment sampling sites must be representative of conditions throughout the study area; (4) the grid of sampling sites must be suitable for estimating the spatial extent of toxicant-associated bioeffects; and (5) a subset of the sediment sampling sites must have marsh or demersal fish available. Based upon these criteria and the programmatic goals of NOAA's NS&T Program and the State Water Board's Bay Protection and Toxic Cleanup Program, a balanced sampling strategy for sites in potentially highly toxic areas, in potentially moderately toxic areas, and in potentially reference (non-toxic) areas will be selected. Final selections will be performed jointly by NOAA and the State of California.

The data from the three years of research will be merged to form a synopsis of conditions in the study area. These data, in turn, will be compared with those from other parts of the study area that have been previously studied with similar methods. Data evaluations will be conducted jointly by NOAA and the State of California.

Task 1. Survey of Sediment Contamination and Toxicity

Rationale. Sediment toxicity tests provide a direct means of determining the relative biological significance of sediment-associated contaminants. Sediment-associated toxicants can be assumed to be bioavailable and concentrated to unacceptable levels when toxicity tests demonstrate that the sediments are toxic. Standardized methods have been developed and are available for use in these tests.

Sample Collections. In this task, surficial sediments (upper 2 cm) representative of selected bays will be collected for chemical analyses and toxicity testing. The number of sampling sites in each embayment will be tailored to the size and configuration of that bay. For comparative purposes, selected sampling sites along the coast seaward of the selected bays and comparable to the study sites in grain size and organic content also will be sampled. Only fine-grained, depositional sediments will be collected. Half of the sampling sites will represent integrated conditions from multiple nearby sources of toxicants; the other half will represent contamination in further need of assessment for toxic hot spot status, regardless of the variety and source of toxicants. A Kynar-lined, modified Van Veen grab, or box core will be used to collect sediments using methods that will not contaminate the samples.

Multiple deployments of the sampler will be required to obtain sufficient material at each station for the battery of toxicity tests and chemical analyses. Care will be taken to ensure that cross-contamination between samples does not occur. After completing sampling at each station, the sampling devices and utensils will be thoroughly washed with seawater and hexane.

A total of 42 samples will be sampled within the third year study area, including the reference and control sediments. NOAA and the State of California will jointly select the number and final locations of the sampling sites.

The sampling sites will be sampled in multiple legs. The reference sediments will be collected from locations in California that are relatively unpolluted, not toxic, and comparable to the study sites in grain size and organic content. Control sediments will be collected from locations such as the home sediments of the amphipod test animals that are also unpolluted and not toxic.

The chain of custody will be documented during sample handling and shipment. Sediments will be kept cool (4°C) during shipping and not held for more than ten days before toxicity tests are initiated. All procedures will comply with the NS&T Program QA/QC requirements.

Toxicity Tests. Two independent tests of sediment toxicity will be performed with each sample: Ten-day solid phase tests of the survival of amphipods (Rhepoxynius abronius or Eohaustorius estuarius (if reduced salinity renders R. abronius unusable); and pore water tests of sea urchin egg fertilization (e.g., Strongylocentrotus purpuratus, Dendraster sp., or Lytechinus pictus), or abalone development (Haliotis sp.). The sediment from each station will

be tested in the laboratory with five replicates. Each test will be accompanied with equivalent tests of a positive control chemical (e.g., cadmium chloride).

The amphipod tests will follow the protocols prepared by ASTM (1991) for performance of sediment toxicity tests with marine and estuarine amphipods. The end-point of survival will be reported. The urchin egg fertilization tests will be performed with the pore water (or interstitial water), which will be recovered using the protocols reported by Carr et al. (1989), and dilution series used by the NS&T study in Tampa Bay, Florida. End-points of the urchin tests will include fertilization success (Dinnel et al., 1987). During the tests, the concentrations of dissolved oxygen, ammonium, and hydrogen sulfide tests, the concentrations of dissolved oxygen, ammonium, and hydrogen sulfide will be determined along with pH, temperature, and salinity. The concentration of unionized ammonia will be calculated, based upon the pH and ammonium data, and reported.

Chemical Analyses. Portions of each of the sediment samples will be set aside and frozen for chemical analyses. Chemical analyses will be performed with as many of the samples as possible and feasible. Those samples that prove to be of interest to NOAA and the State of California following a review of the toxicity data will be analyzed for contaminant concentrations. The sediments from a minimum of twenty (20) samples will be analyzed. Chemical analyses will be performed for the trace metals, pesticides, hydrocarbons, and selected normalizers (e.g., grain size, total organic carbon) that are routinely quantified by the NS&T Program, plus TBT. Analytical procedures will comply with NS&T Program QA/QC requirements and will include those for analyses of blanks and standard reference materials.

Data Evaluations. The data will be evaluated to determine:

1. Which stations and sites were statistically significantly more toxic than controls;
2. Spatial patterns in toxicity;
3. Relative degree of toxicity among the sites;
4. Relationships between the toxicity and chemical data; and
5. Relative sensitivity of the two toxicity tests.

Statistical methods to be used for identification of significantly toxic sites will be chosen jointly by NOAA and the State of California. The relative degree of toxicity will be determined according to the mean results for each station and site and reported graphically and in tabular formats. The relationships between the toxicity and chemical data will be determined in regression analyses, cluster analyses, concordance tests, and other methods to be specified. In addition, the bioassay and chemical data will be entered into a project data base and accumulated in that data base. As each leg of the study plan is completed, the new data will be added to this data base.

Reports. The final report will include the descriptions of methods, the raw data in tabular spreadsheet format, the results of the five data evaluations listed above, and textual descriptions of the results.

Task 2: Bioaccumulation and Biomarkers Study

Based upon the results of the year one and year two analyses, the State Water Board and NOAA will jointly select the specific focus of the year three work. Depending on year one and year two results, a determination will be made to proceed with Tasks 2.a. (mussels) or 2.b. (marsh and/or demersal fish).

The biomarker tests to be performed will be selected jointly by NOAA and the State of California. The approaches for mussels and fish studies are described separately below. Only one of the approaches will be implemented under this cooperative agreement. The selection will be made jointly by NOAA and the State Water Board using factors that are agreed upon by both agencies. After a subtask is selected, a specific proposal will be solicited describing the study design and a timeline for completion of the tasks.

a. Bioaccumulation and Biomarkers in Mussels.

Rationale. Mussels (Mytilus californianus) are collected from Bodega Head, transplanted to selected coastal sites, retrieved several months later, and analyzed for the occurrence of selected toxicants by the State of California Mussel Watch (CMW) Program. Also, NOAA performs similar analyses annually of the tissues of resident mussels (M. edulis/galloprovincialis in bays or M. californianus along the coast) collected from many locations in California as a part of the NS&T Program. The concentrations of some chemicals in the tissues are sufficiently high in some sites to warrant concern that adverse effects are occurring but very little effort has been expended to determine if these animals are suffering any adverse effects.

Along with the evaluations of reproductive success and biomarkers in mussels (M. edulis) in Buzzards Bay/Boston Harbor (J. Cappuzzo, WHOI) and in oysters in Tampa Bay, (W. Fisher, EPA) supported by the NS&T Program, we will evaluate the performance of selected biomarkers in M. edulis/galloprovincialis or M. californianus in Southern California where the mixtures of toxicants may differ from those in the other two areas. Mussels are valuable biomonitoring organisms since they are sessile. Therefore, the data from analyses of mussels can be attributed to the specific sampling sites.

In year two, a study was begun by the California State University at Long Beach (Dr. Sanders) to evaluate the relationship between selected biomarkers response to heat stress proteins, DNA strand breakages, a reproduction index and growth) and mussel tissue chemical concentrations. This study has begun and the researchers have found differences in growth between polluted and reference sites (Sanders, pers. comm.). We await the results of the other analyses so a decision can be made on whether to continue the research.

Sample Collections. In this task, either M. californianus from Bodega Head (or some other suitable reference area) will be transplanted to a selected subset of the sediment sampling sites or resident bay mussels (M. edulis/ galloprovincialis) will be collected at these sites. In these analyses of biological effects, emphasis will be placed upon resident mussels since they are most likely to represent long-term conditions at the sampling sites. At those sites in which resident mussels are not available for collection, mussels will be transplanted. Portions of the samples will be analyzed for toxicant concentrations and portions will be tested for selected biomarkers.

Sufficient numbers of mussels will be sampled at each site to allow determination of statistically significant differences among sites, based upon the site means. The tissues of a sufficient number of animals will be composited from each site to provide the minimum amount needed for the full suite of chemical analyses.

Mussels will be collected, handled, and transplanted using standard, non-contaminating methods of the CMW Program. All biomarker and chemical analyses performed on transplanted mussels also will be conducted on control mussels collected at Bodega Head.

The number and final locations of sampling sites will be determined jointly by NOAA and the State of California. Mussels will be transplanted to and retrieved from these sites in the same sequence. Portions of the samples will be allocated for the biomarker and chemical analyses and transported to the participating laboratories as quickly as possible.

Biological Tests. The biomarker for the third year of the program is heat stress protein induction, DNA strand damage, a condition index, reproduction index, growth, or other measurements deemed appropriate by both the State Water Board and NOAA.

Chemical Analyses. Tissues from mussels collected at each site and from Bodega Head will be analyzed for the trace metals, pesticides, hydrocarbons, and normalizers quantified by the NS&T Program. Standard methods that comply with the NS&T Program QA/QC requirements, including analyses of blanks and standard reference materials, will be used during the analyses.

Data Evaluations. The data will be evaluated to determine:

1. The concentrations of toxicants in transplanted or resident mussels;
2. The quantification of mean biomarker results at each site and the identification of significant differences among sites and between the study sites and the controls;
3. The geographic patterns in the incidence of the measured biological effects; and
4. The relationships between the biological and chemical data.

The statistical methods to be used in the data evaluations will be determined jointly by NOAA and the State of California. The chemical signatures and absolute concentrations of contaminants in the sediments at each site will be compared with those in the mussels collected at the same sites. The relative sensitivity, range in response, within-site variability, and concordance with the tissue chemistry will be evaluated. Analyses will be performed to identify at which sites, if any, the mean results were significantly different from those in Bodega Head controls. The mean results will be evaluated to identify spatial patterns in results among the sites. The chemical data from the tissue analyses and the sediment analyses (from Task 1) will be compared with the biomarker data to identify any relationships and to confirm concentrations predicted by sediment-water and water-tissue equilibrium partitioning models.

Reports. The final report will include detailed descriptions of methods, the raw data in tabular spreadsheet format, the results of the data evaluations listed above, and textual descriptions of the results.

b. Bioaccumulation and Biomarkers in Demersal Fish.

Rationale. The tests of sediment toxicity will provide some information on the relative bioavailability and toxicity of sediment-associated toxicants to benthic animals. The analyses of mussels will provide information on uptake and bioeffects in immobile, transplanted mollusks whose recent history has been documented. But neither task will provide information on uptake and effects in resident, demersal, animals closely associated with sediments.

In the first year of the program, a contract was developed with the University of California, Davis (Dr. Hinton) to study demersal gobies at selected sites and to analyze for selected biomarkers and chemical concentrations in these fish. Candidate species include Lepidogobius lepidus, Ilypnus gilberti, and Clevelandia ios. These species burrow into sediments and are territorial. Often, they are abundant. Beginning in mid-1993, a methods evaluation step is scheduled to be conducted in the Los Angeles area (first-year funds), candidate biomarker tests will be performed and the results evaluated. Based upon the results of the evaluation step, a survey of several sites will be conducted using the selected biomarker tests (if appropriate). The results of the work will be evaluated jointly by NOAA and the State of California to prepare a follow-up survey plan for the third year of preliminary research is promising.

Sample Collections. Fish will be collected at selected sites plus a pristine control site to be specified. They will be caught with trawls as specified in the first year. At least the minimum number of fish necessary to perform the biological and chemical analyses listed below will be captured at each site. Portions of the fish will be allocated for each of the analyses. The gall bladders of the fish will be shipped to NOAA/NMFS in Seattle for possible analyses of PAH metabolites in the bile.

Biological Tests. The biomarkers being considered for the third year of the program are:

1. Condition index;
2. Gonadal/somatic index;
3. Cytochrome P-450 and EROD induction in livers; and
4. Neoplasms and other histopathological disorders in the livers and kidneys.

Chemical Analyses. The liver and perhaps other tissues of the fish will be analyzed for the trace metals, pesticides, hydrocarbons, and normalizers routinely quantified in the NS&T Program.

Data Evaluations. The data will be evaluated to determine:

1. Relative bioaccumulation of sediment-associated toxicants in the tissues of the fish;
2. The presence/absence of statistically significant results among sites and between sites and reference or control sites.
3. The relative degree or severity of effects observed in each site; and
4. The relationships between the chemistry and biological data.

The statistical procedures to be used in the data evaluations will be determined jointly by NOAA and the State of California. The relative sensitivity, range in response, within-site variability, and concordance with tissue chemistry data will be determined. Sampling sites at which mean results are significantly different than controls will be identified. Mean results will be used to determine spatial patterns in response among the sampling sites.

E. REPORTS

- Cruise report which will consist of station locations with longitude and latitude readings for each station and site, a chart indicating the location of all stations and sites, and field notes regarding the sampling success and visual condition of the samples.

- A draft and final technical report of third year work which will include description of methods, raw data in tabular form, the results of the data evaluations, and textual descriptions of the results.

- Draft and final summary and overview report of years one through three work. This report will be prepared jointly by NOAA and the State Water Board in cooperation with DFG.

F. BENEFITS OF THE RESEARCH TO NOAA

This research program in Southern California will provide a number of programmatic benefits to NOAA. They include:

1. Presence or absence of adverse biological effects in areas known to have relatively high chemical concentrations;
2. Data to assess the degree or severity of toxicant effects;
3. Spatial distribution of toxicant-associated effects in Southern California;
4. New data with which to supplement existing data on the relationships between toxicants and toxic effects in Southern California;
5. Matching biological and chemical data with which to perform statistical analyses;
6. Biological data with which to assess the significance of chemical data from the NS&T Program's monitoring activities; and
7. Evaluations of the relative performance of a battery of biomarkers.

G. BENEFITS OF THE RESEARCH TO CALIFORNIA

The benefits of this program to the State of California would be similar to those for NOAA:

1. Presence or absence of adverse biological effects in areas known to have relative high chemical concentrations;
2. Data to assess the degree or severity of toxicant effects;
3. Spatial distribution of toxicant effects in Southern California;
4. New data with which to supplement existing data on the relationships between toxicants and toxic effects in Southern California;
5. Matching biological and chemical data with which to perform statistical analyses;
6. Biological data with which to assess the significance of chemical data from the Mussel Watch monitoring activities;
7. Evaluations of the relative performance of a battery of biomarkers; data to be used in a research program to develop State sediment quality objectives; and
8. Data to be used in a regulatory program to identify toxic hot spots.

H. PROPOSED COOPERATIVE AGREEMENT. This research will be implemented through a Cooperative Agreement between NOAA and the State of California. NOAA will transfer $110,000 to the State Water Board and the State Water Board will provide $100,000 for a total budget of $210,000.

Responsibilities for overall programmatic and technical direction will be shared by both NOAA and the State Water Board. The State Water Board will disperse the merged funds to their prime contractor, DFG, for task implementation. If needed, either the State Water Board or DFG will acquire certain skilled services from investigators at other State universities, agencies, and laboratories for implementation of the research. DFG will be the principal subcontractor to NOAA for the project. Research results and products will be developed for review and access by all three agencies. All three agencies will provide technical staff support for program planning, determination of technical scope and methods, logistics planning and facilitation, data evaluation, report review, and agency interface.

Collaboration with other NOAA components and other federal agencies will be handled by NOAA staff while State of California interagency arrangements will be handled by the State Water Board.

I. COST ESTIMATES FOR FY 1993-94 COOPERATIVE AGREEMENT

Task 1. Survey of Sediment Contamination and Toxicity

Sample Collection	
42 study sites @ $1425	$ 59,800
Toxicity Testing (2 tests)	
42 study stations @ $1000	42,000
Chemical Analysis	
20 study stations	
full organic scan + PAH @ $1180	23,600
full metal scan @ $900	18,000
TBT @ $170	3,400
TOC @ $50	1,000
Grain size @ $40	800
Reports	
5 Cruise @ $500	2,500
4 Quarterly @ $1250	2,000
1 Data report @ $1250	1,250
Miscellaneous Services, expendables	5,600
	$160,000
Task 2. Bioaccumulation and Biomarkers Study Sample collections, biomarker tests, chemical analyses, data evaluations, etc. please refer to text for explanation.)	$ 50,000
	$210,000

J. REFERENCES

American Society for Testing Materials. 1991. Standard guide for conducting solid phase ten-day static sediment toxicity tests with marine and estuarine amphipods. Method E18-67. ASTM, Philadelphia, PA. Annual Book of Standards Vol. 11.04.

Dinnel, P.A., J.M. Link, and Q.J. Stober. 1987. Improved methodology for a sea urchin sperm cell bioassay for marine waters. Arch. Environ. Contam. Toxicol. 16:23-32.

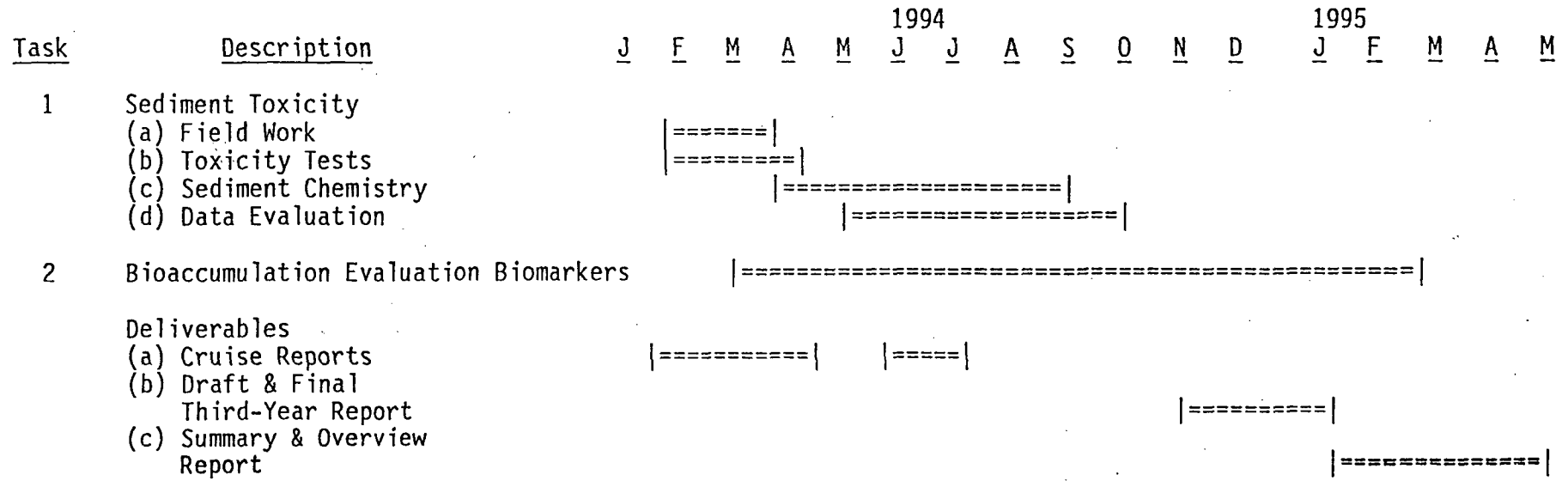
Hose, J.E. 1985. Potential uses of sea urchin embryos for identifying toxic chemicals: Description of a bioassay incorporating cytologic, cytogenetic, and embryologic endpoints. J. Appl. Toxicol. 5:245-254.

Hose, J.E., J.F. Cross, S.G. Stevens, and D. Diehl. 1987. Elevated circulating erthrocyte micronuclei in fishes from contaminated sites off southern California. Mar. Envir. Res. 22:167-176.

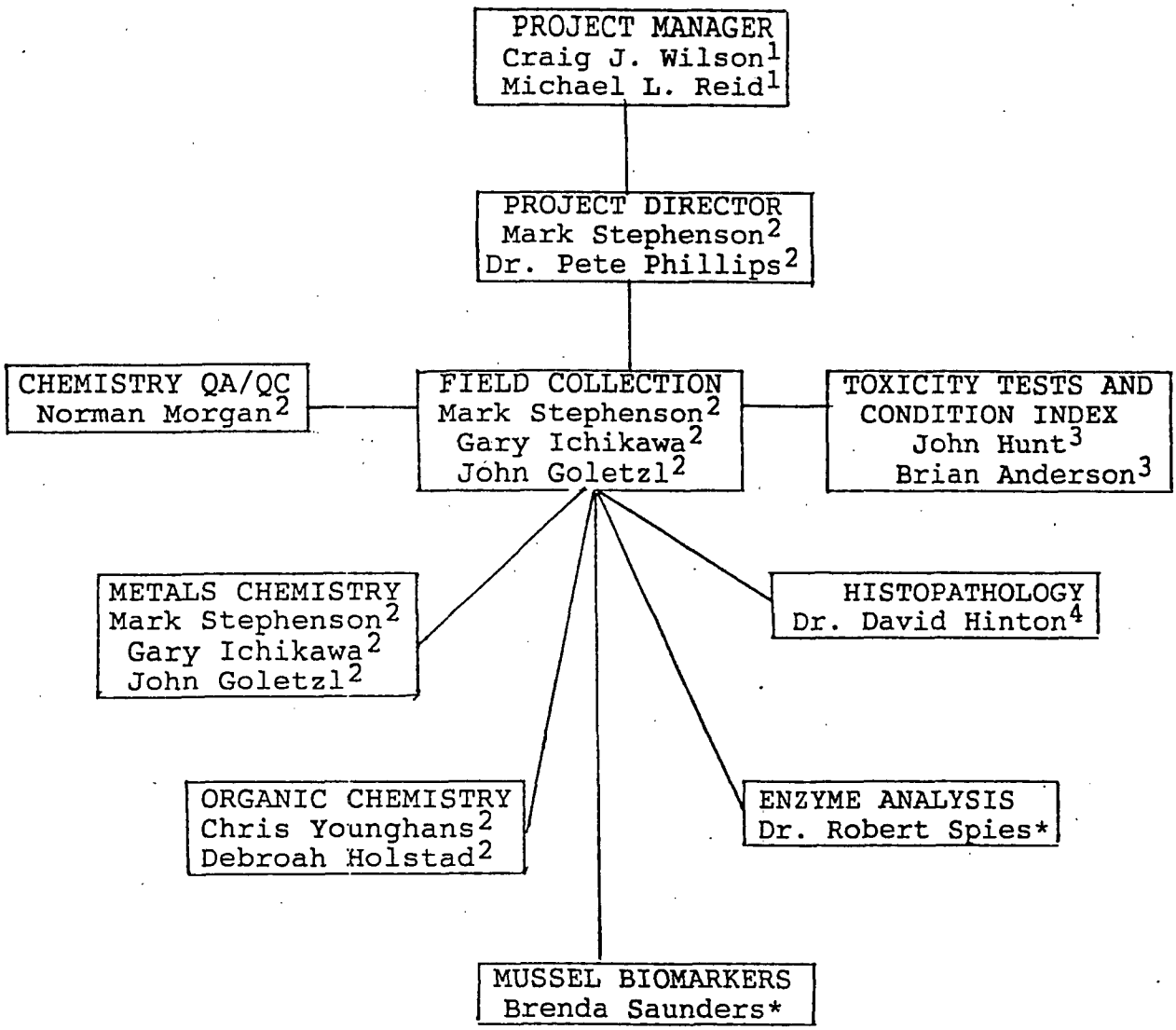
Long, E.R. et al. 1990. Comparative evaluation of five toxicity tests with sediments from San Francisco Bay and Tomales Bay, CA. Envir. Toxicol. and Chem. 9:1193-1214.

Malins, D.C. et al. 1987. Toxic chemicals including aromatic and chlorinated hydrocarbons and their derivatives, and liver lesions in white croaker (Genyonemus lineatus) from the vicinity of Los Angeles. Envir. Sci. and Technol. 21(8):765-770.

TENTATIVE TIME SCHEDULE



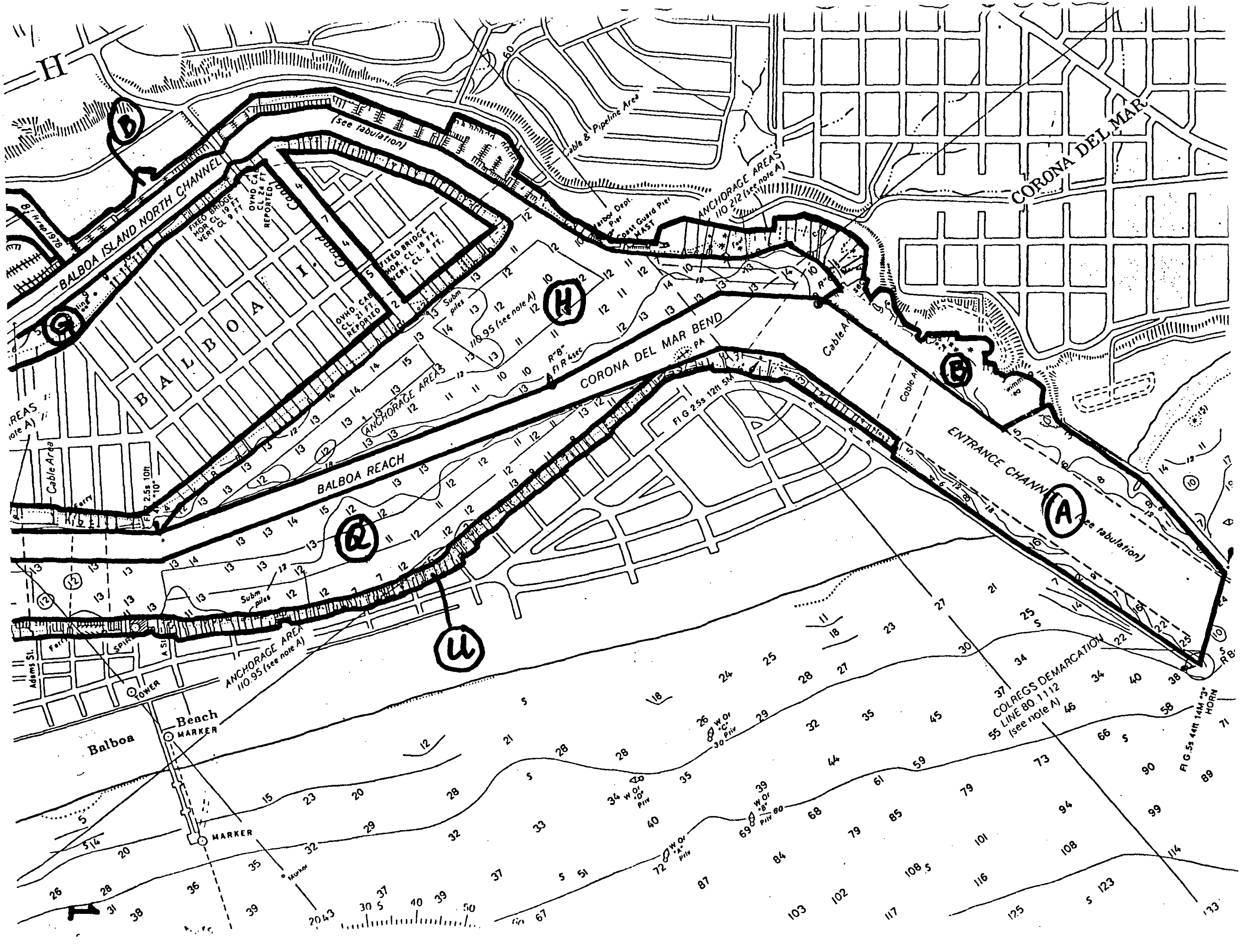
PROPOSED PROJECT ORGANIZATION CHART

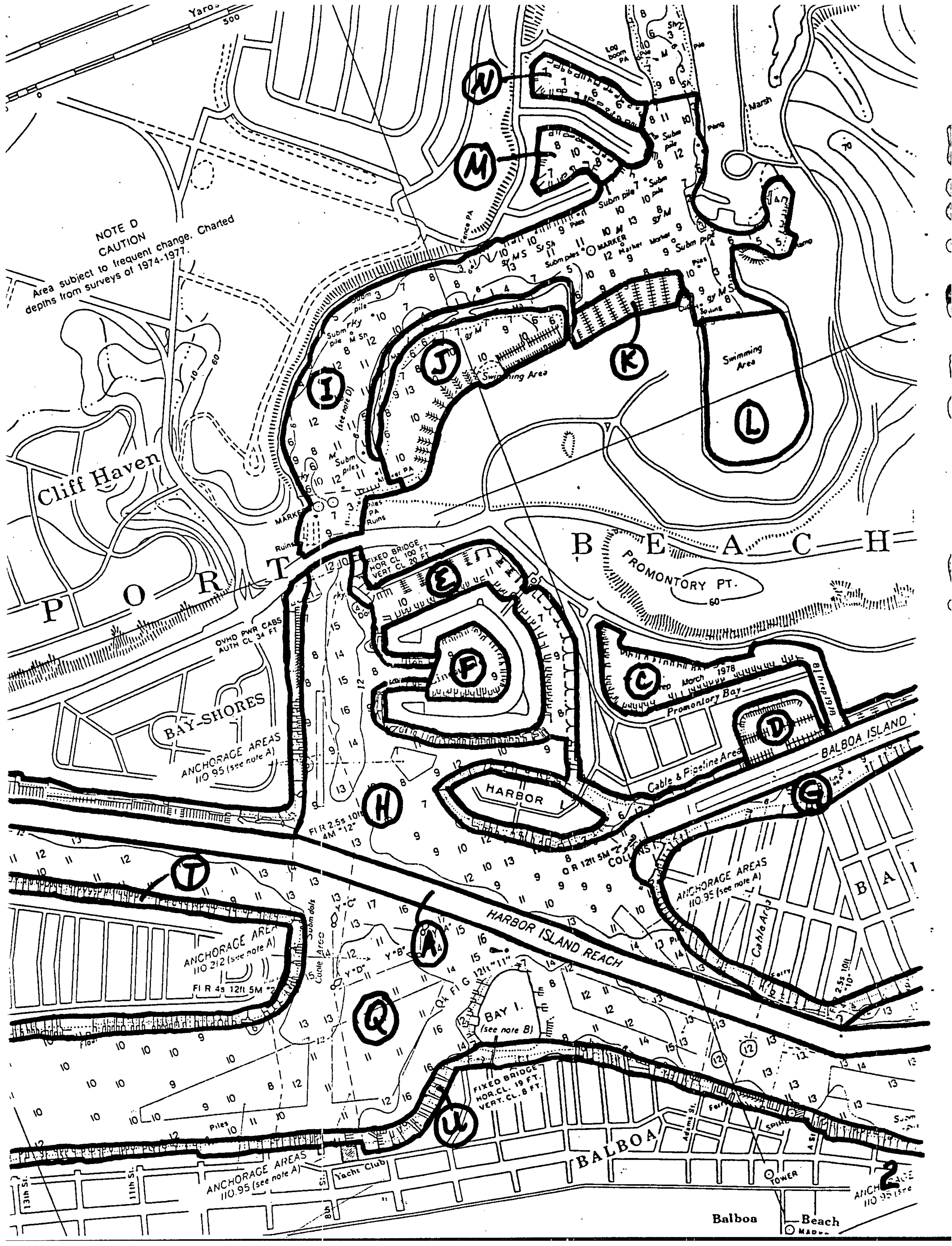


1 State Water Resources Control Board
2 California Department of Fish and Game
3 University of California at Santa Cruz
4 University of California at Davis
* Proposed Researcher

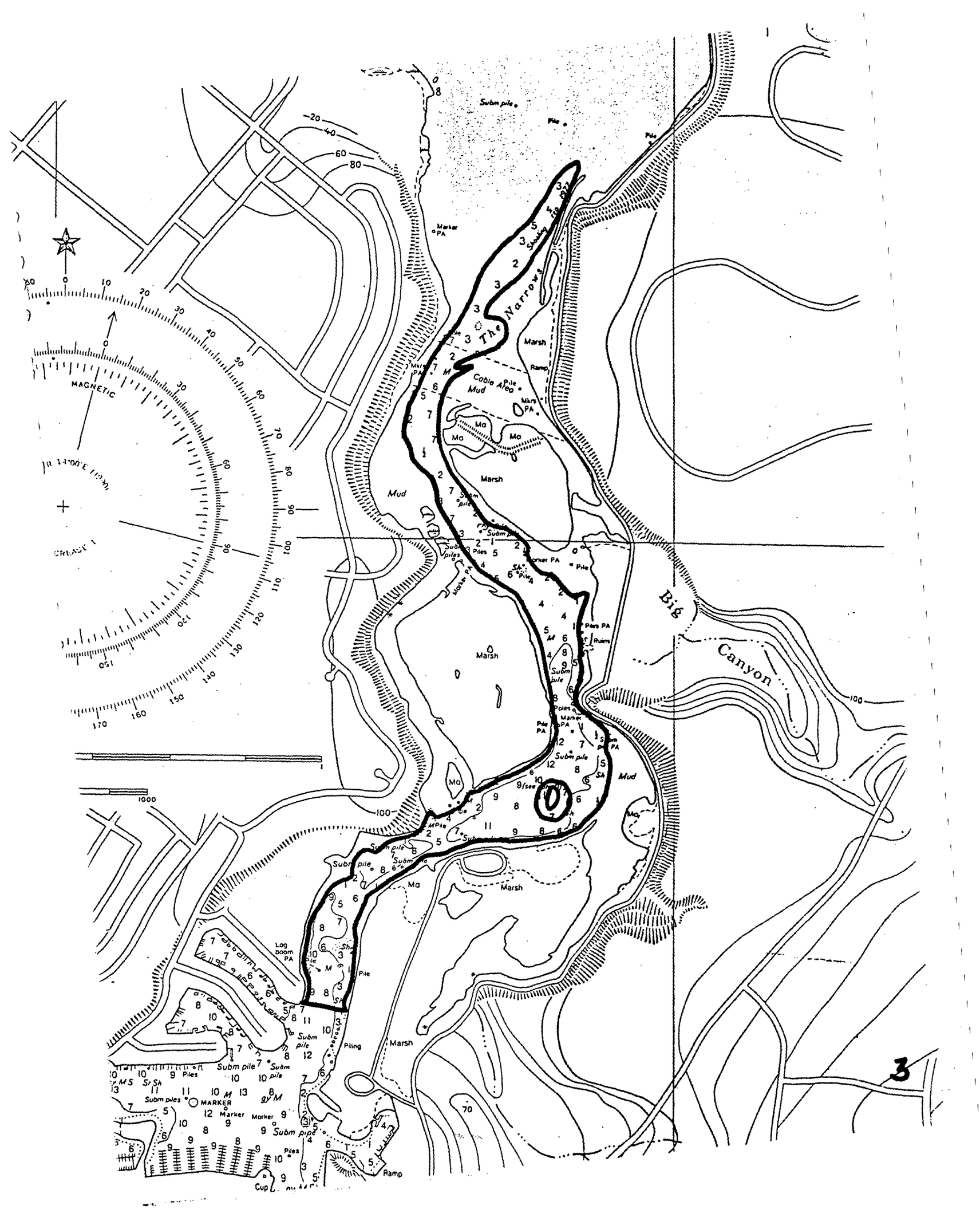
APPENDIX 2

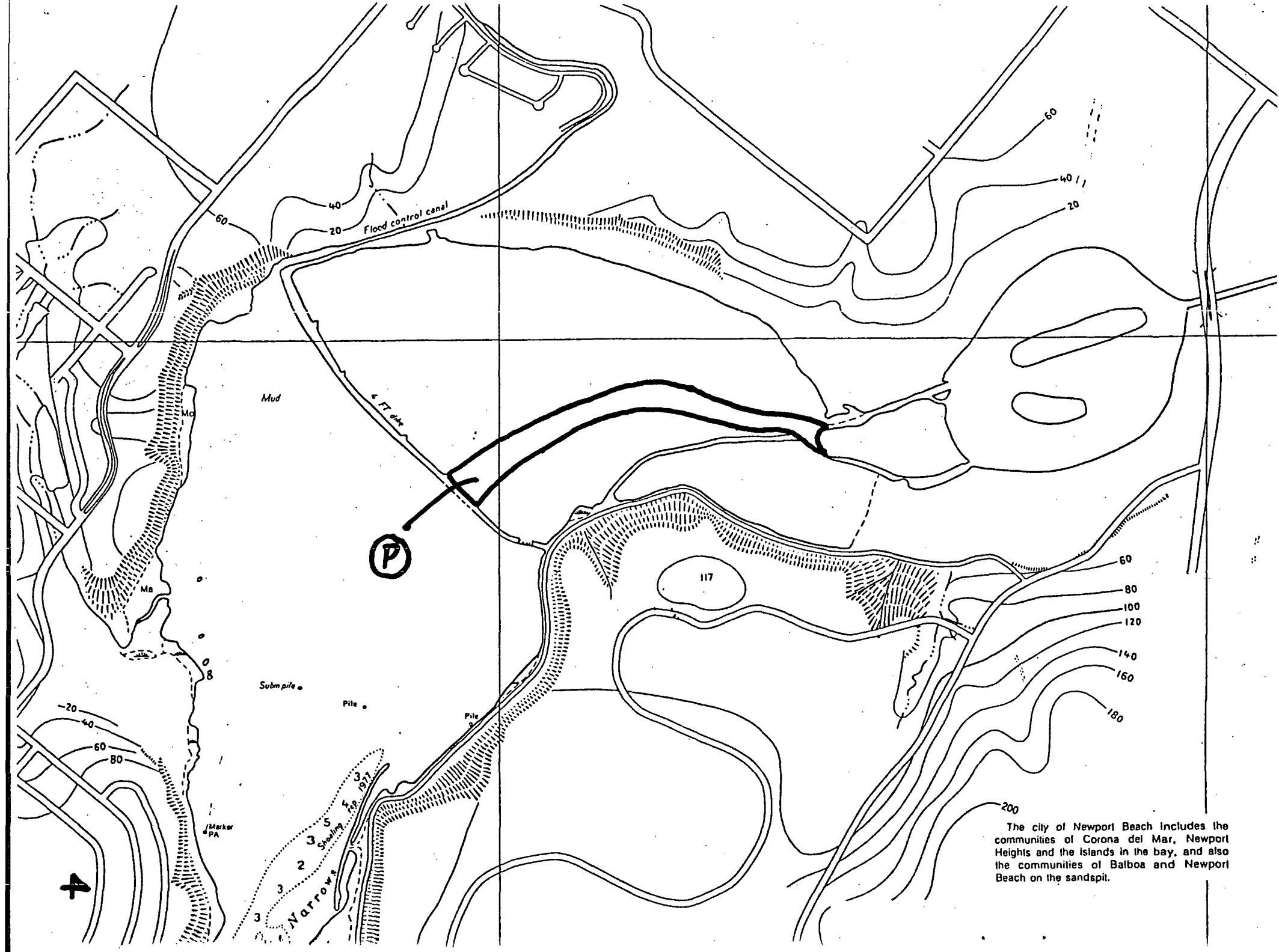
Maps Illustrating Sampling Strata


BALBOA ISLAND NORTH CHANNEL
FIXED BRIDGE HOR CL 19 FT VERT CL 9 FT
OVHD CAB CL 24 FT REPORTED
FIXED BRIDGE HOR. CL. 18 FT. VERT. CL. 4 FT.
OVHD CAB CL 21 FT REPORTED
BALBOA I
(see tabulation)
Cable & Pipeline Area
Harbor Dept. Pier
Coast Guard Pier
MAST
ANCHORAGE AREAS 110.212 (see note A)
CORONA DEL MAR
CORONA DEL MAR BEND
R "8" Fl R 4sec
Subm piles
110.95 (see note A)
ANCHORAGE AREAS
BALBOA REACH
Fl G 2.5s 12ft 5M
ENTRANCE CHANNEL
(see tabulation)
Cable Area
ANCHORAGE AREA 110.95 (see note A)
Adams St.
TOWER
Beach
Balboa
MARKER
COLREGS DEMARCATION LINE 80.1112 (see note A)
Fl G 5s 44ft 14M "3" HORN
A
B
G
H
Q
U

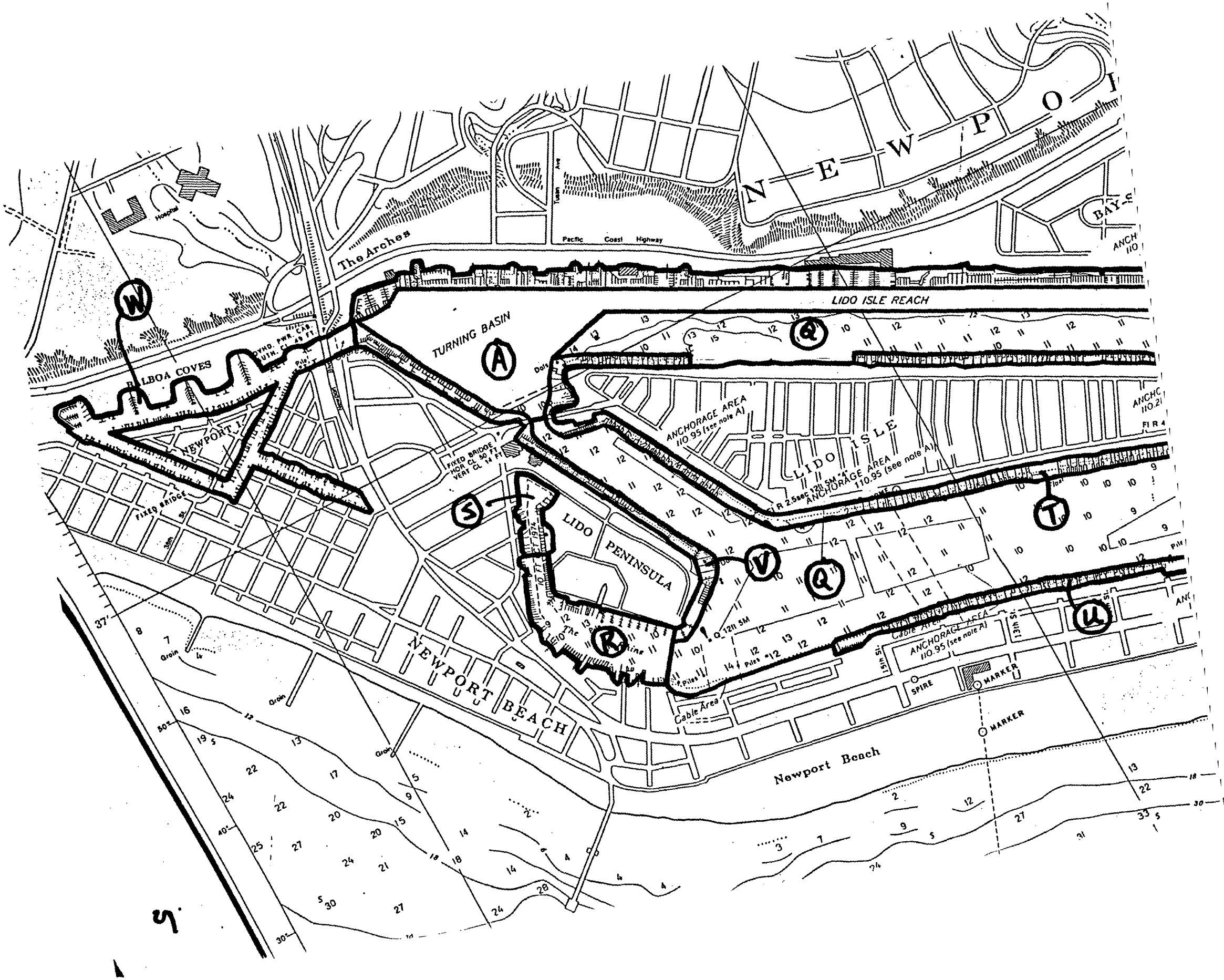


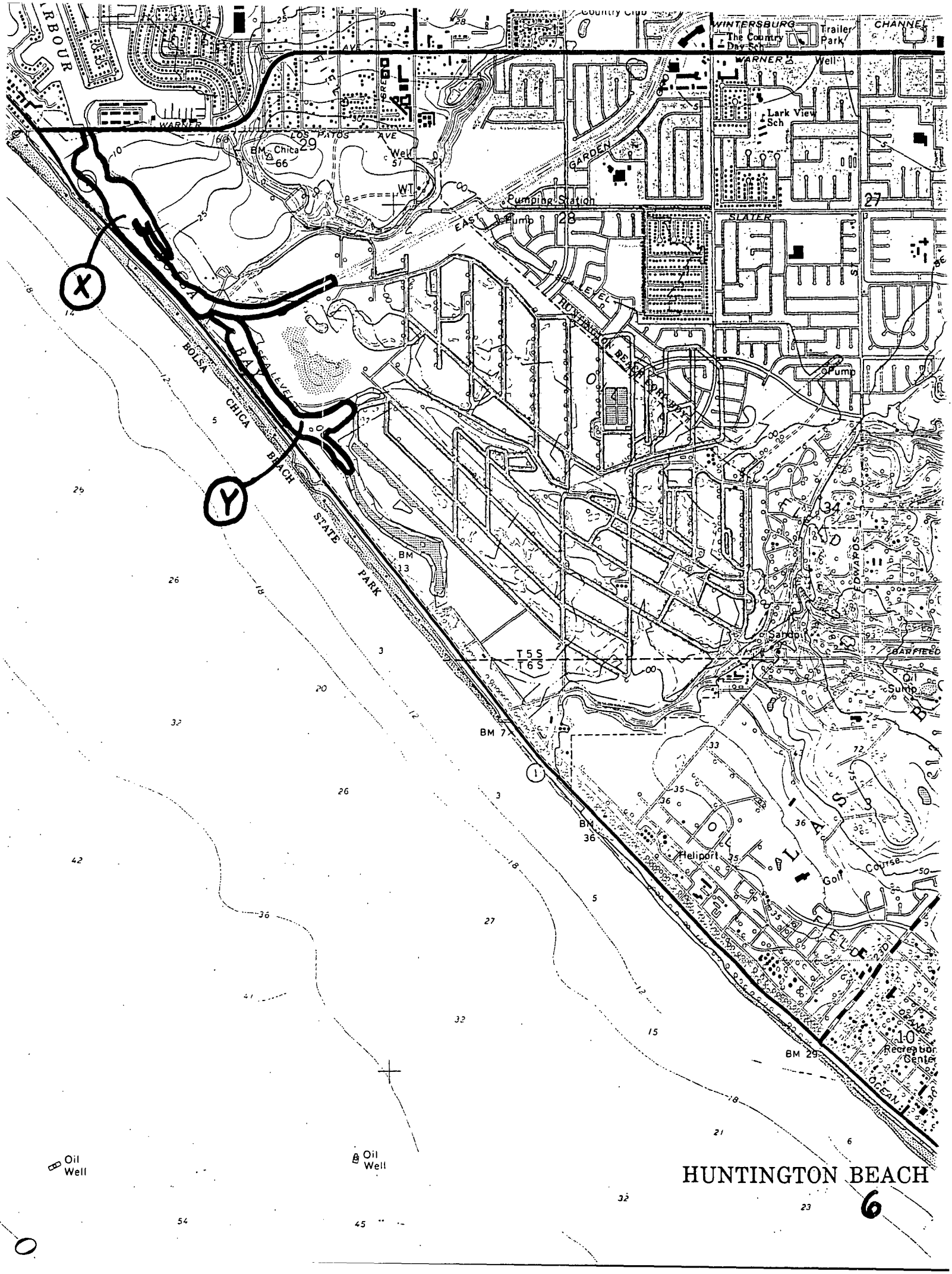
NOTE D
CAUTION
Area subject to frequent change. Charted depths from surveys of 1974-1977.
Cliff Haven
PORT
BEACH
BAY SHORES
PROMONTORY PT.
Promontory Bay
BALBOA ISLAND
HARBOR
HARBOR ISLAND REACH
BAY I. (see note B)
BALBOA
Balboa
Beach
Swimming Area
Marsh
FIXED BRIDGE HOR CL 100 FT VERT CL 20 FT
OVHD PWR CABS AUTH CL 34 FT
FIXED BRIDGE HOR.CL. 19 FT. VERT.CL. 8 FT.
ANCHORAGE AREAS 110.95 (see note A)
ANCHORAGE AREAS 110.212 (see note A)
Cable & Pipeline Area
Cable Area
Yacht Club
TOWER
MARKER
Ruins
Subm piles
Log boom PA
Fence PA
Dep March 1978
FI R 2.5s 10ft 4M "12"
FI R 4s 12ft 5M "2"
Qk FI G 12ft "11"
Q R 12ft 5M "2"
COLLINS
Yards
500
13th St.
11th St.
Adams St.
A
C
D
E
F
G
H
I
J
K
L
M
N
Q
T
U

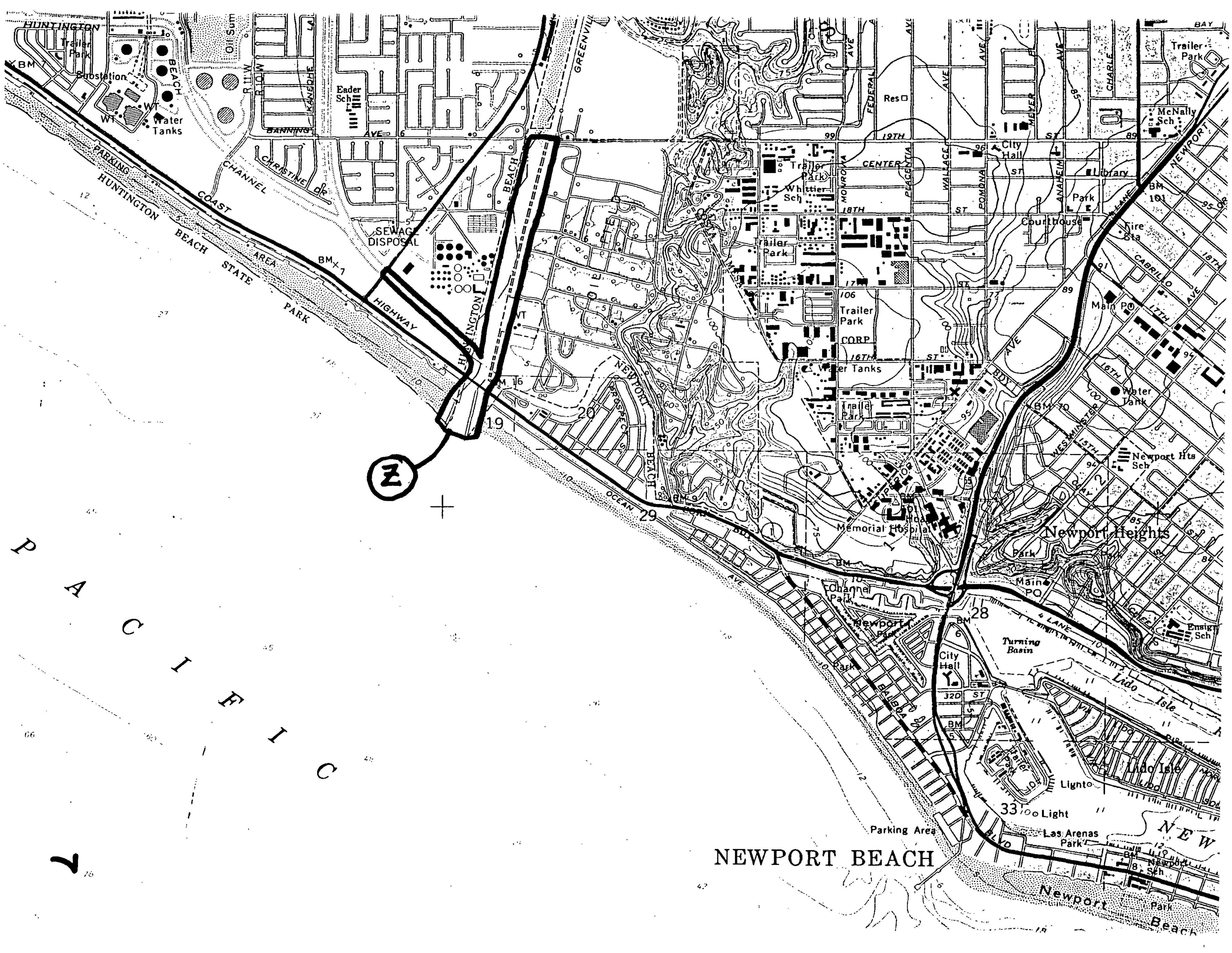

The Narrows
Big Canyon
Marsh
Mud
Ma
Subm pile
Piles
Pile
Marker PA
Cable Area
Ramp
Piling
Log boom PA
Subm pipe
MARKER
Piers PA
Ruins
MAGNETIC
3

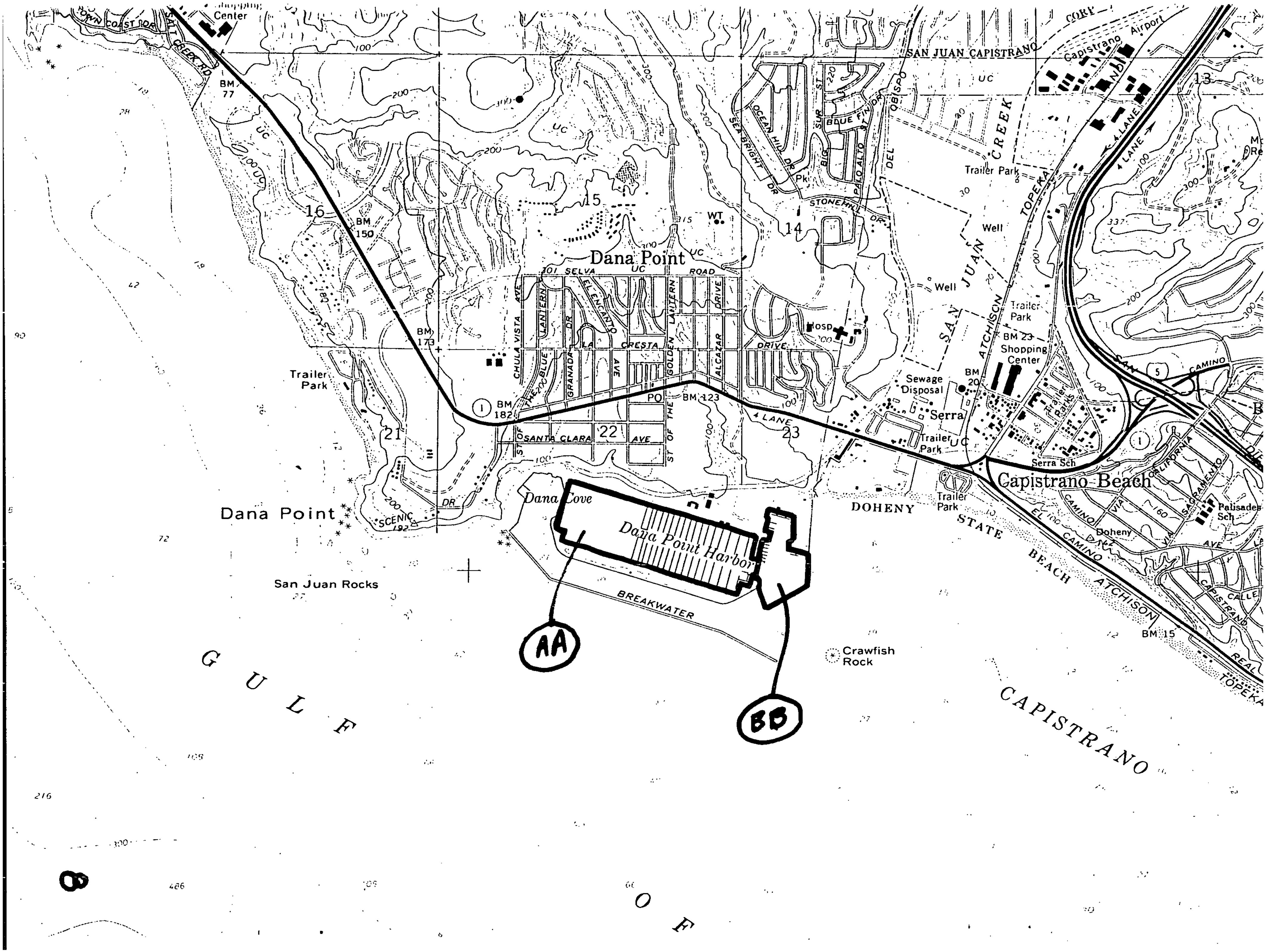


The city of Newport Beach includes the communities of Corona del Mar, Newport Heights and the islands in the bay, and also the communities of Balboa and Newport Beach on the sandspit.

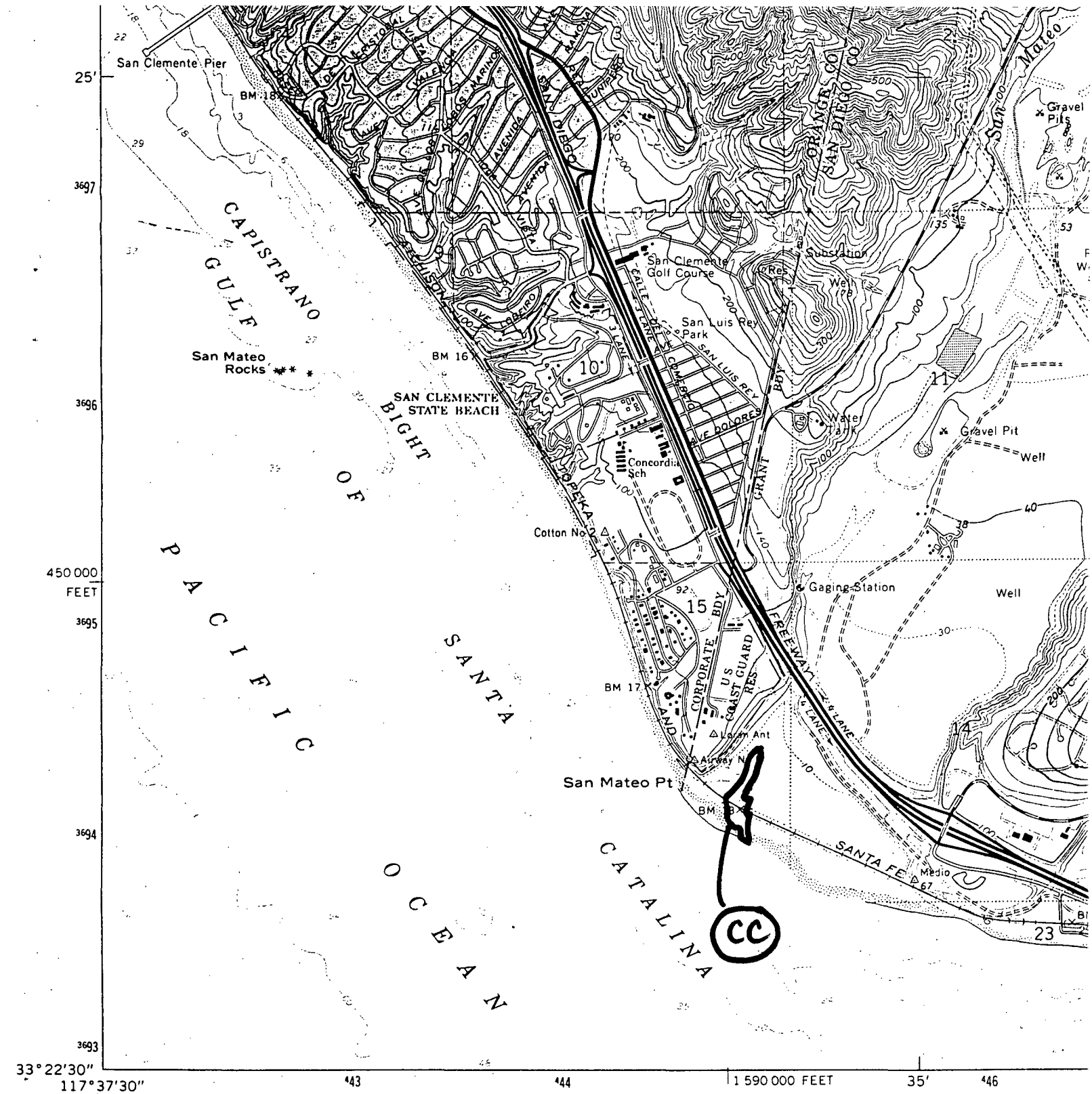

N E W P O
BAY-S
The Arches
Pacific Coast Highway
Tustin Ave
Hospital
W
BALBOA COVES
NEWPORT J
FIXED BRIDGE
TURNING BASIN
A
LIDO ISLE REACH
Q
ANCHORAGE AREA
110.95 (see note A)
LIDO ISLE
FIXED BRIDGE
HOR CL 50 FT
VERT CL 14 FT
S
LIDO
PENINSULA
V
Q'
T
L
K
NEWPORT BEACH
Cable Area
SPIRE
MARKER
Newport Beach
Groin
37th St
15th St
13th St


WINTERSBURG
Trailer Park
The Country Day Sch
CHANNEL
WARNER
Well
Lark View Sch
GARDEN
LOS PATOS AVE
BM Chica 66
29
Well 57
WT
Pumping Station
28
EAST
SLATER
27
SEA LEVEL
HUNTINGTON BEACH FREEWAY
Pump
BOLSA CHICA
BEACH
STATE PARK
BM 13
T5S
T6S
Sump
BM 7
BM 36
Heliport
Golf Course
BM 29
Recreation Center
OCEAN
Oil Well
Oil Well
HUNTINGTON BEACH
6


HUNTINGTON BEACH STATE PARK
PARKING AREA
COAST HIGHWAY
HUNTINGTON BEACH
CHANNEL
SEWAGE DISPOSAL
BANNING AVE
CHRISTINE DR
Eader Sch
Trailer Park
Substation
Water Tanks
Oil Sum
GREENVILLE
NEWPORT BLVD
OCEAN BLVD
19TH ST
CENTER ST
18TH ST
17TH ST
16TH ST
15TH ST
City Hall
Library
Courthouse
Fire Sta
Whittier Sch
McNally Sch
Reservoir
CORP
Water Tanks
Memorial Hospital
Main PO
Water Tank
Newport Hts Sch
Newport Heights
WESTMINSTER AVE
CABRILLO AVE
Channel Park
Newport Park
City Hall
32D ST
Turning Basin
Lido Isle
Light
Las Arenas Park
Newport Sch
Parking Area
NEWPORT BEACH
PACIFIC
Newport Beach Park
Ensign Sch
BALBOA
7



Dana Point
Dana Point
Dana Cove
Dana Point Harbor
BREAKWATER
AA
BB
San Juan Rocks
Crawfish Rock
G U L F
O F
CAPISTRANO
Capistrano Beach
DOHENY
STATE
BEACH
SAN JUAN CAPISTRANO
Capistrano Airport
SAN JUAN CREEK
Trailer Park
Trailer Park
Shopping Center
Sewage Disposal
Serra
Hosp
Serra Sch
Palisades Sch
Doheny
Well
SELVA ROAD
LA CRESTA DRIVE
SANTA CLARA AVE
STONEHILL DR
ATCHISON
TOPEKA
EL CAMINO REAL
SCENIC DR
4 LANE



Mapped, edited, and published by the Geological Survey

Control by USGS, USC&GS, and USCE

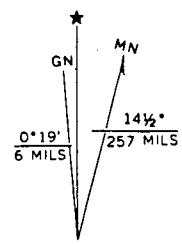
Topography by photogrammetric methods from aerial photographs taken 1946. Field checked 1947–48. Revised from aerial photographs taken 1967. Field checked 1968

Selected hydrographic data compiled from USC&GS surveys (1934) This information is not intended for navigational purposes

Polyconic projection. 1927 North American datum
10,000-foot grid based on California coordinate system, zone 6
1000-meter Universal Transverse Mercator grid ticks, zone 11, shown in blue

Red tint indicates areas in which only landmark buildings are shown
Fine red dashed lines indicate selected fence lines
Dotted land lines established by private survey

Purple tint indicates extension of urban areas



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Revisions shown in purple compiled from aerial photographs taken 1975. This information not field checked

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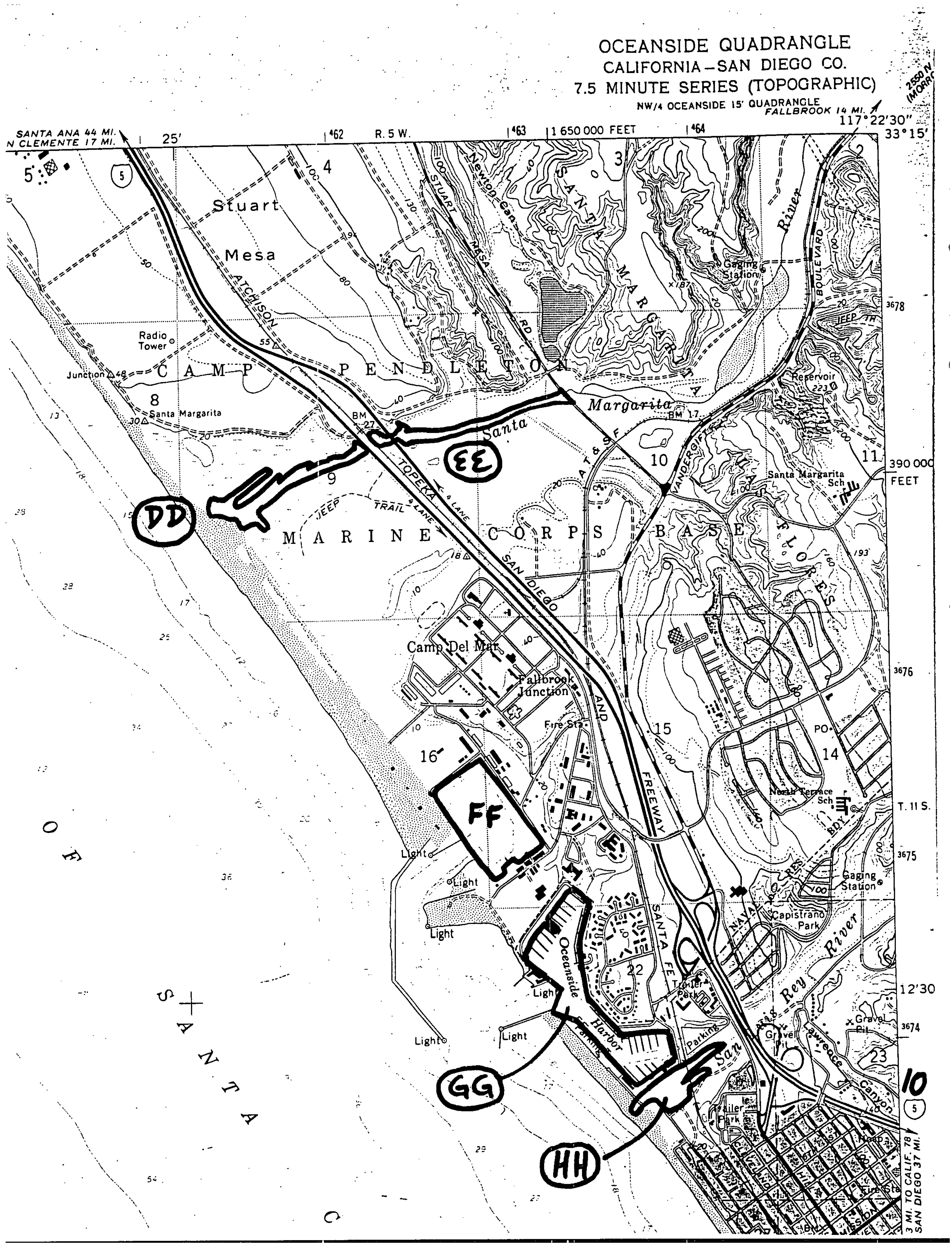
OCEANSIDE QUADRANGLE
CALIFORNIA - SAN DIEGO CO.
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Camp Del Mar
Fallbrook Junction
Fire Sta
North Terrace Sch
Capistrano Park
Oceanside Harbor
Trailer Park
Parking
Light
San Luis Rey River
Gravel Pit
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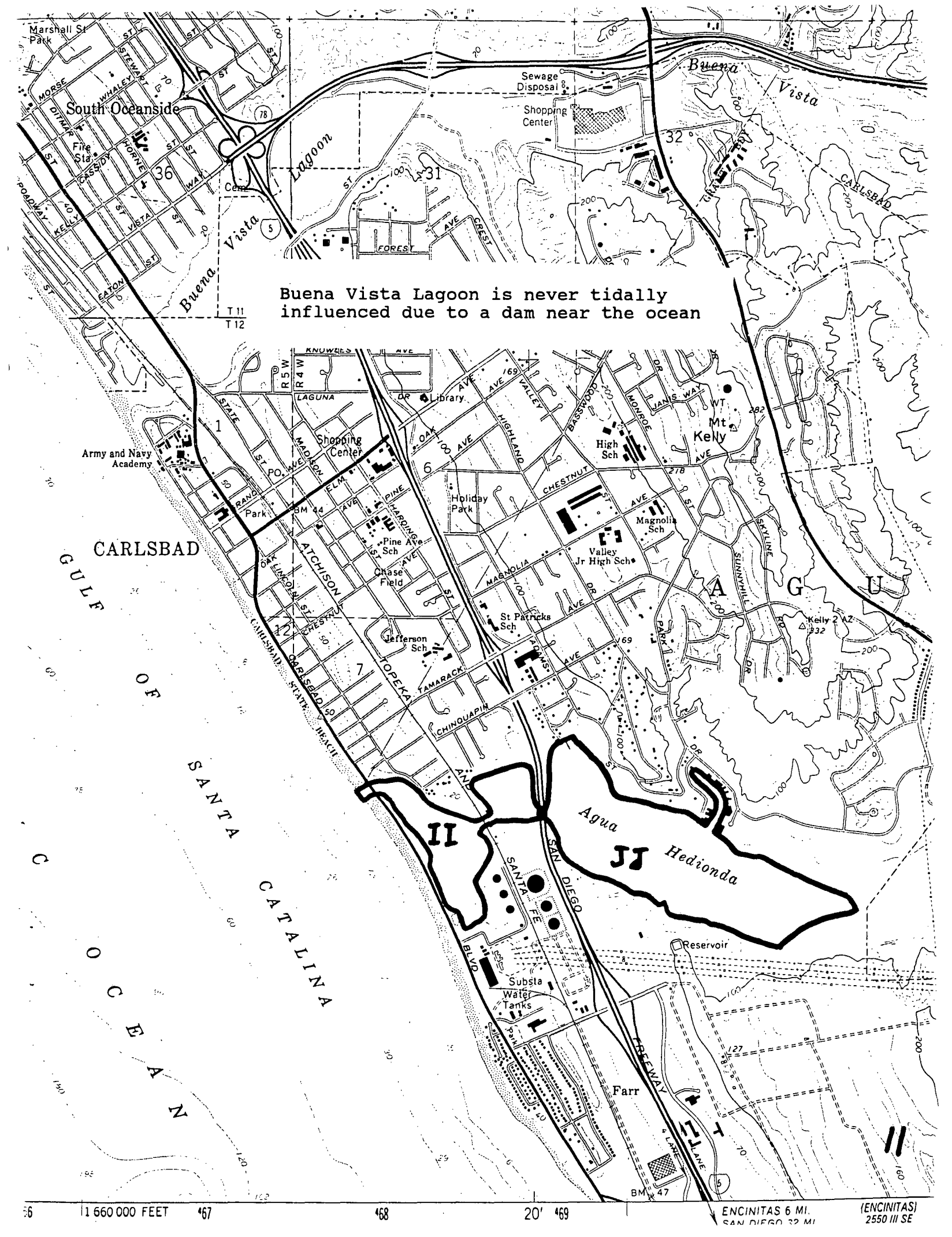
Buena Vista Lagoon is never tidally influenced due to a dam near the ocean
Marshall St Park
South Oceanside
Fire Sta
Sewage Disposal
Shopping Center
Buena Vista Lagoon
Buena Vista
Cem
FOREST
CARLSBAD
Army and Navy Academy
Shopping Center
Library
Holiday Park
Pine Ave Sch
Chase Field
Jefferson Sch
St Patricks Sch
Valley Jr High Sch
Magnolia Sch
High Sch
Mt Kelly
Kelly 2 AZ
Agua Hedionda
Reservoir
Substa
Water Tanks
Farr
GULF OF SANTA CATALINA OCEAN
ATCHISON
TOPEKA
SANTA FE
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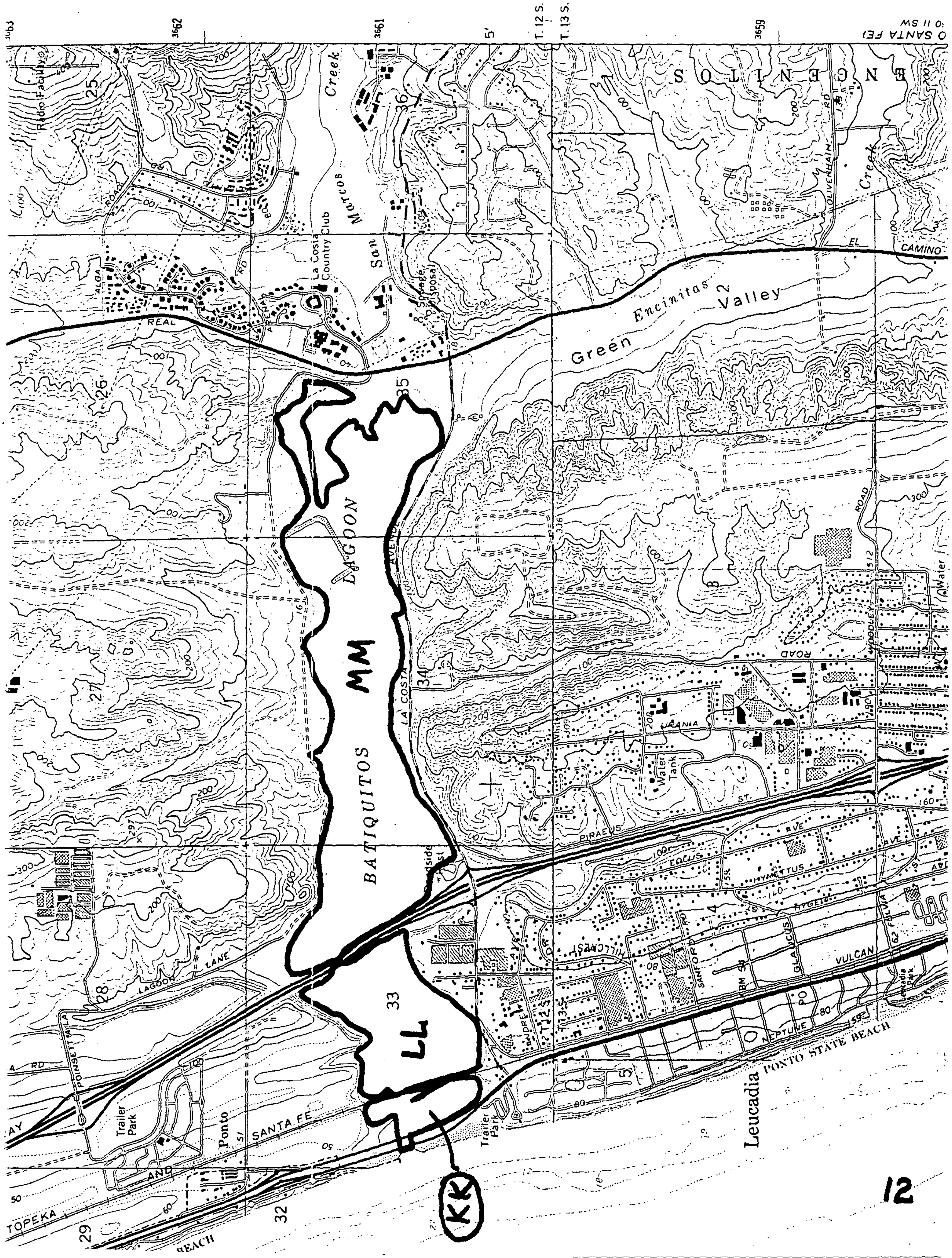
BATIQUITOS
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EL CAMINO
REAL
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Trailer Park
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Leucadia
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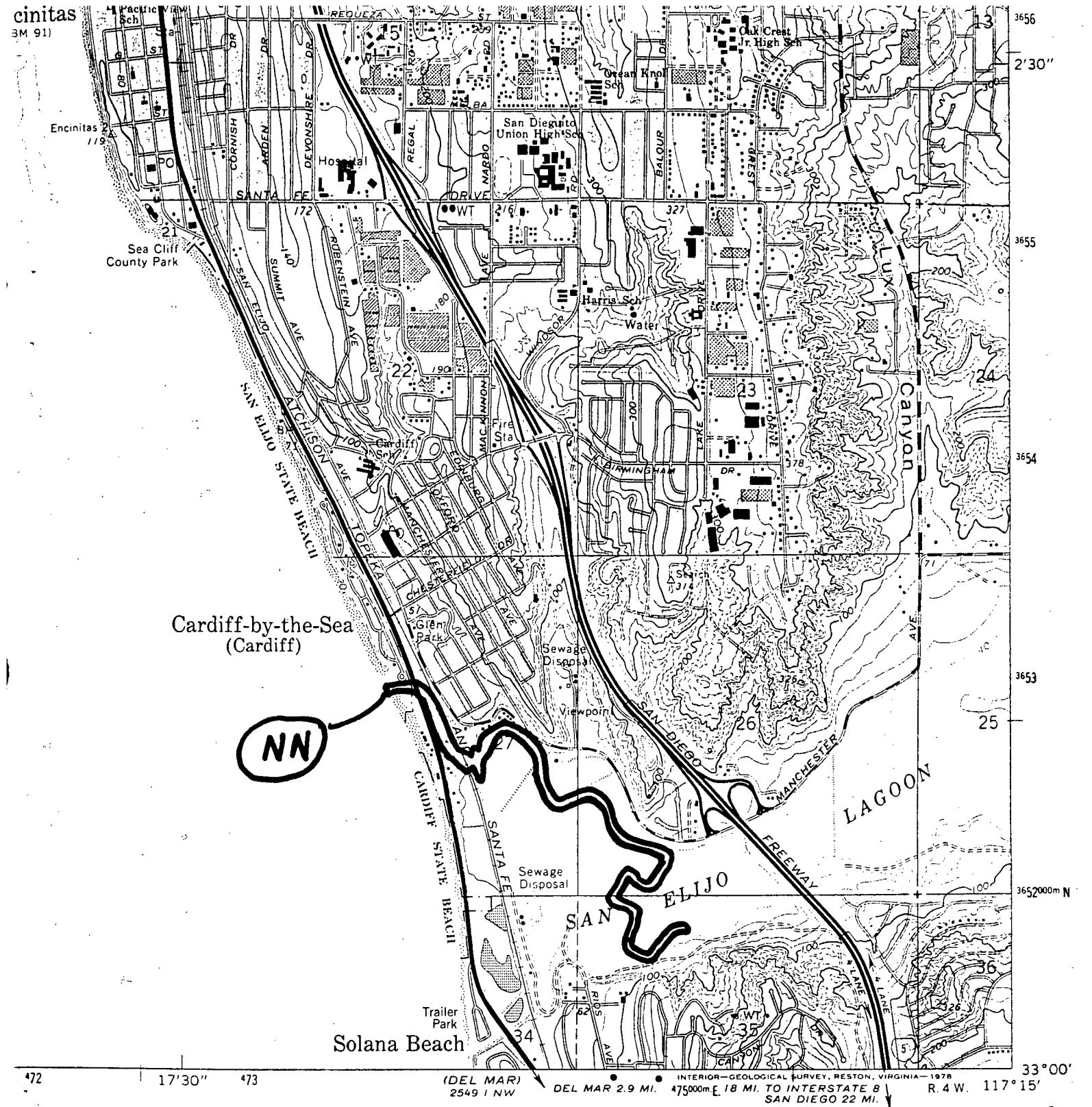
T. 13 S.



ENCINITAS, CALIF.

SE/4 OCEANSIDE 15' QUADRANGLE
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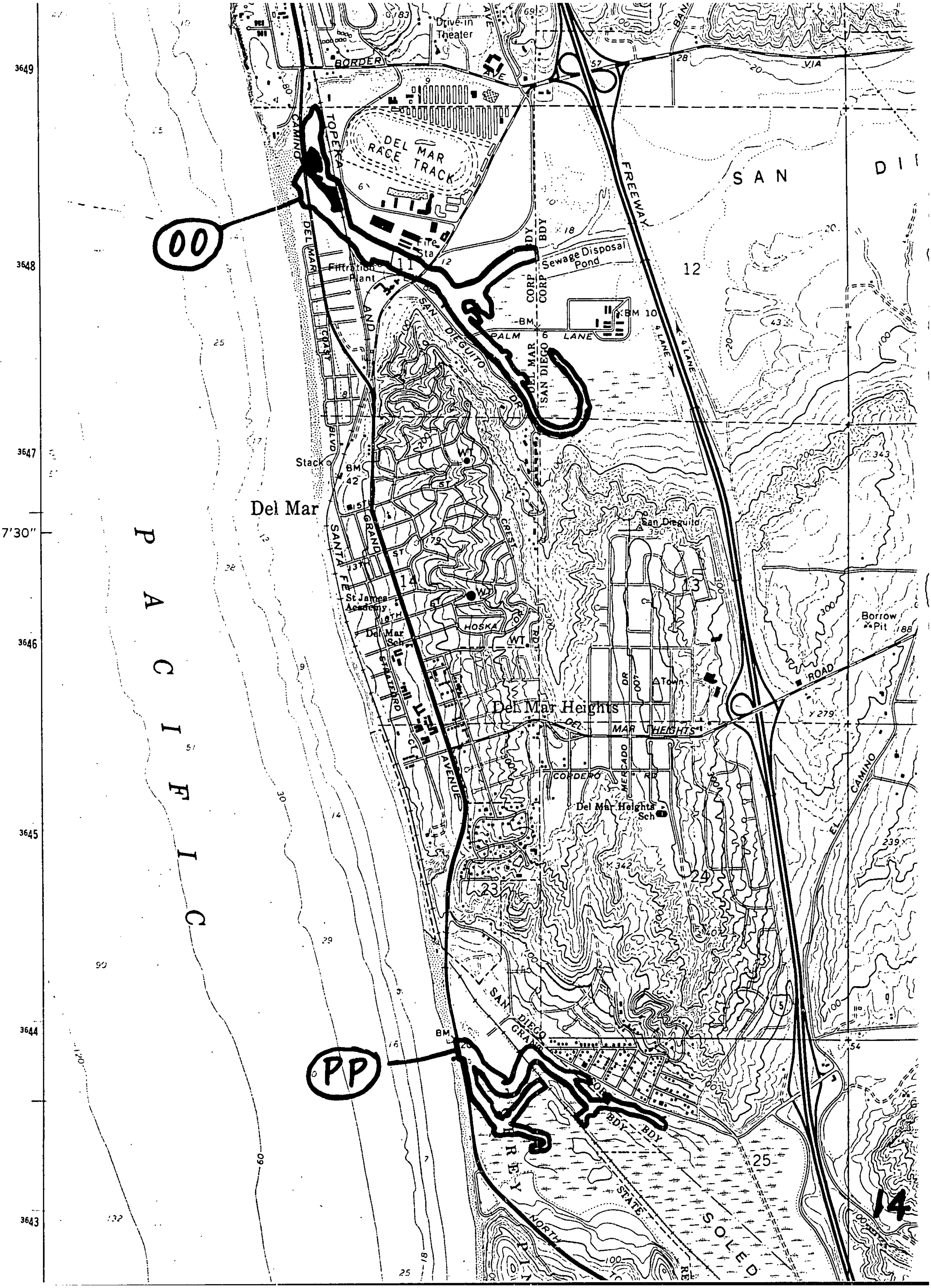

Drive-in Theater
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PALM LANE
BM 10
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DEL MAR
COAST BLVD
Stack
BM 42
Del Mar
GRAND ST
SANTA FE
CREST
San Dieguito
P A C I F I C
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St James Academy
Del Mar Sch
HOSKA
WT
Borrow Pit
ROAD
STRATFORD
Del Mar Heights
DEL MAR HEIGHTS
CORDERO RD
MERCADO
AVENUE
Del Mar Heights Sch
EL CAMINO
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APPENDIX 3

Quality Assurance Project Plan

for the

Bay Protection and Toxic Cleanup Program

DRAFT

BAY PROTECTION AND TOXIC CLEANUP PROGRAM

QUALITY ASSURANCE PROJECT PLAN

by

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Moss Landing Marine Laboratories
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and

Mike Reid
Bay Protection and Toxic Cleanup Program
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Sacramento, CA 94244-2130

Bay Protection and Toxic Cleanup Program
State Water Resources Control Board
Sacramento, CA 94244

December 1993

DRAFT

QUALITY ASSURANCE PROJECT PLAN APPROVAL

This Quality Assurance Project Plan (QAPP) was developed to assure that all environmental data generated for the State Water Resources Control Board's (SWRCB) Bay Protection and Toxic Cleanup Program (BPTCP) are scientifically valid and of acceptable quality to achieve the program's objectives. The signatures of key technical and management personnel indicate approval or concurrence with the procedures specified in this plan. These approvals and concurrences also represent a commitment to disseminate the plan, as well as the philosophy of total quality, to all project participants.

Craig J. Wilson — Date
BPTCP Contract/Project Manager for SWRCB
Bay Protection and Toxic Cleanup Program
State Water Resources Control Board
Sacramento, CA

Charles Fischer — Date
BPTCP Quality Assurance Officer for SWRCB
State Water Resources Control Board
Sacramento, CA

Mark Stephenson — Date
BPTCP Project Manager for DFG
California Department of Fish and Game
Marine Pollution Studies Laboratories
Moss Landing, CA.

Norman Morgan — Date
BPTCP Quality Assurance Officer for DFG
Department of Fish and Game
Marine Pollution Studies
Moss Landing, CA

PREFACE

This Quality Assurance Project Plan (QAPP) was prepared jointly by the California Department of Fish and Game (DFG) and the California State Water Resources Control Board (SWRCB) to insure quality in the scientific components of the Board's Bay Protection and Toxic Cleanup Program (BPTCP). The QAPP was prepared in large part by utilizing many elements, both format and content, of the QAPP for the Environmental Monitoring and Assessment Program (EMAP-Estuaries) for the 1993 Virginian Province, a U.S. Environmental Protection Agency (EPA) program. EMAP's QAPP, and thus the BPTCP's QAPP, follows the general guidelines and specifications provided by the Quality Assurance Management Staff of the U.S. EPA Office of Research and Development and guidelines provided in the EMAP Quality Assurance Management Plan. Because this QAPP will also be used for EMAP monitoring activities in California, a number of tasks or analyses supplemental to the methods necessary for the BPTCP are included in this QAPP. These additional methods are printed in **bold** type.

The primary objective of this QAPP is to maximize the probability that environmental data collected by the BPTCP will meet or exceed the objectives established for data quality. The QAPP presents a systematic approach that will be implemented within each major data acquisition and data management component of the program. Basic requirements specified in the QAPP are designed to: (1) ensure that collection and measurement procedures are standardized among all participants; (2) monitor the performance of the various measurement systems being used in the program to maintain statistical control and to provide rapid feedback so that corrective measures can be taken before data quality is compromised; (3) assess the performance of these measurement systems and their components periodically; and, (4) verify that reported data are sufficiently complete, comparable, representative, unbiased, and precise so as to be suitable for their intended use. These activities will provide data users with information regarding the degree of uncertainty associated with the various components of the BPTCP database.

This QAPP has been submitted in partial fulfillment of SWRCB Contract No. 1-165-250-0 from the California State Water Resources Control Board to the California Department of Fish and Game.

The proper citation of this document is:

Stephenson, M., M. Puckett, N. Morgan, and M. Reid. 1993. Bay Protection and Toxic Cleanup Program: Quality Assurance Project Plan. Bay Protection and Toxic Cleanup Program, State Water Resources Control Board, Sacramento, CA.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the contributions of the following individuals in the development and review of this document: Charles Fischer and Craig J. Wilson--California State Water Resources Control Board; Gary Ichikawa, Kim Paulson, Jon Goetzl--California Department of Fish and Game; Rusty Fairey, Carrie Bretz, and Pat Iampietro--San Jose State University Foundation; and Brian Anderson, John Hunt, Hilary McNulty, Deborah Holstad, and John Newman--University of California, Santa Cruz. Ray Valente--U.S. Environmental Protection Agency, EMAP program, kindly provided us with EMAP's 1993 Virginian Province QAPP documents that were used as a model, in both format and content, for this BPTCP QAPP.

TABLE OF CONTENTS

SECTION 1

INTRODUCTION

1.1 OVERVIEW OF THE BAY PROTECTION AND TOXIC CLEANUP PROGRAM

In 1989 the California Water Code was amended (Sections 13390 through 13396) to create the Bay Protection and Toxic Cleanup Program (BPTCP). The three primary goals of the program are to 1) identify toxic hot spots, 2) develop sediment quality objectives, and 3) remediate hot spots, either through cleanup efforts, mitigation, or prevention. The monitoring which forms a necessary component of each of these goals and the statutory requirements for standard procedures requires the development of a Quality Assurance Project Plan (QAPP). The remainder of this section provides the necessary project description for development of the QAPP's objectives and specific contents. It is organized into subsections covering the working definition of a toxic hot spot, methods for distinguishing natural from human-caused impacts, sampling design, and analysis of results. More details regarding such aspects of the program as indicator and site selection are described in the first status report of the program (SWRCB, 1993).

1.1.1 Hot Spot Definition

A detailed working definition of a known toxic hot spot has been developed that consists of the following five conditions (the full definition is included in Appendix 1):

1. Exceedance of water or sediment quality objectives,
2. Water or sediment toxicity associated with toxic pollutants,
3. Exceedance of tissue contaminant levels established by various agencies for the protection of human health or wildlife,
4. Impairment of resident organisms associated with toxic pollutants, and
5. Degradation of populations or communities associated with toxic pollutants.

(The definition also includes potential hot spots which are determined by concentrations of toxic pollutants above background levels, screening or other test toxicity, elevated tissue levels, or levels in excess of sediment or water quality criteria. Because a conservative approach was adopted in the development of the known toxic hot spot definition, rather stringent criteria have been included. For example, the mere presence of contamination was determined to be insufficient for qualification as a hot spot unless the level is high enough to exceed regulatory standards. Likewise, bioeffects are required to be demonstrated in relation to properly selected reference sites and to occur in association with chemical contamination. Furthermore, several of the criteria require a demonstration of recurrent effects.

Underlying this definition is a weight-of-evidence approach to the combination of the mixture of chemical and bioeffects measures. Since the presence of correlations between many of these measures is unknown at this time, it is conceivable that some sites may qualify as hot spots for some criteria but not for others. Consequently, sites for which a number of criteria are satisfied (e.g., sediment toxicity, benthic degradation, and a positive biomarker test accompanied by high contaminant levels in sediment and tissue) will be considered the highest priority for remediation. It will be necessary, therefore, to monitor some sites for the full mix of chemical and bioeffects measures.

1.1.2 Natural vs. Human-Caused Impacts

Prevention or remediation of hot spots resulting from human activity requires the ability to distinguish between those of natural and human origin. Monitoring designs can produce data that range from the purely correlational (i.e. the simple presence of pollutants in concert with bioeffects) to the carefully performed sediment TIE (or equivalent study for other bioeffects) whereby a specific causal relationship is convincingly established. For the purposes of BPTCP monitoring neither of these extremes was deemed acceptable - simple correlation studies would result in too many false positives (resulting in excessive remediation

expenditures) while sediment TIEs or their equivalents would be too time-consuming and would require excessive use of funds from public sources rather than responsible parties.

A compromise between these two extremes settled on the identification and use of reference sites matched for various confounding natural variables. For example, sediment toxicity reference sites were matched for sediment grain size and TOC, the latter being presumed to covary with other possible confounding factors. Similarly, benthic analysis reference sites will be matched for these variables as well as others thought to be relevant (e.g., dissolved oxygen content, salinity, temperature, Ph, and natural toxins). In this way, demonstrated bioeffects at a site (relative to a matched reference) will be determined to be associated with toxic chemicals if chemical analysis demonstrates significantly higher levels compared to the reference sites. Because a strict determination of cause-and-effect will not have been achieved (due to its extreme expense), we anticipate that responsible parties will have the opportunity to conduct Toxicity Identification Evaluations as an initial step in site remediation.

1.1.3 Sampling Design

The current design consists of site selection followed by a four-phase sample collection and analysis effort. Sites are selected because of previous evidence of contamination, previous evidence of a lack of contamination, or the probability of contamination or its absence based on knowledge of polluting activities in the waterbody; other sites are selected randomly within strata.

Once sites have been selected, sediment is sampled and tested with a suite of bedded sediment and pore water toxicity tests (referred to as "toxicity screening"). Nontoxic sites are resampled (referred to as a "reference site survey") in an effort to identify a group of potential reference sites that encompass the full range of characteristics (e.g., grain size and TOC) likely to occur among the sites to be retested for toxic hot spot status. "Confirmation" is then performed by means of which the sites with the highest toxicity from screening are

sampled in conjunction with the most appropriate potential reference sites. This third phase of sampling is more intensive than screening, including field replication as well as careful matching with reference sites. Chemical analysis is also emphasized, consisting of a full range of conventional metals and organics analyses on the confirmation sites that emerge as reference and toxic within each stratum (see below for explanation of data analysis methods to distinguish reference from toxic sites). Attention is also given to the role of unknown chromatographic peaks as well as naturally occurring toxins. Finally, the fourth phase of sampling consists of benthic collection and, if deemed appropriate, mussel or fish tissue for biomarker analysis (defined as biochemical changes or cell, tissue, or organism pathology). Chemical analysis of sediment will also be performed on sites judged to be impacted and unimpacted using these additional bioeffects measures and similar statistical analysis techniques. The four phases of sample collection are summarized in Table 1-1.

1.1.4 Statistical Analysis

As indicated in Table 1-1, statistical analysis to identify toxic hot spots is a multistage process that relies heavily on ordination analysis (see examples in EcoAnalysis et al., 1992 and Anderson et al., 1988). First, each separate bioeffect measure (toxicity, benthic composition, and biomarker status) is analyzed within relevant strata to determine whether reference and impacted sites can be distinguished. Next, using similar techniques, an effort is made to evaluate whether differences in toxins (conventionally measured, naturally occurring, and unknowns) are associated with the distinction between reference and impacted sites. Finally, the bioeffect-specific analyses are repeated on the combined bioeffects measures to address the weight-of-evidence approach and as an aid in prioritization of remediation efforts. As a result, sites with multiple bioeffects impacts receive more attention.

Table 1-1. Four Phases of Sample Collection for Toxic Hot Spot Identification

1. Toxicity Screening

- Suite of toxicity tests
  - Solid phase (bedded sediment) tests
    - *Rhepoxynius abronius* survival for salinity above 25 ppt
    - *Eohaustorius estuarius* survival for salinity below 25 ppt
    - *Neanthes arenaceodentata* growth for salinity above 25 ppt
  - Liquid phase tests
    - Interstitial water (pore water) tests
      - *Strongylocentrotus purpuratus* fertilization and development for salinity above 25 ppt
      - *Mytilus edulis* larval shell development for salinity below 25 ppt
    - Subsurface water (overlying water) tests
      - *Haliotis rufescens* embryo/larval shell development for salinity above 25 ppt
      - *Mytilus edulis* larval shell development for salinity below 25 ppt
- Five laboratory replicates with controls (three replicates for a dilution series of pore water)
- Ammonia, hydrogen sulfide, grain size, and TOC measured
- Metals and organics analysis of most and least toxic sites

2. Reference Site Survey

- Sites selected from screening phase that tested nontoxic for a variety of tests
- Nontoxic and toxic sites matched for grain size and TOC
- Repeat sample collection and toxicity testing of these potential reference sites

3. Toxicity Confirmation

- Sites selected from screening phase that tested toxic for any test
- Nontoxic sites from reference site survey (i.e. "reference sites") and toxic sites from screening matched for grain size and TOC

Table 1-1. Continued

- Repeat sample collection and toxicity testing of reference sites and toxic sites
  - Repeat of toxicity screening tests which were positive
  - Three field replicates in addition to five laboratory replicates with controls (three laboratory replicates for pore water dilution series)
  - Ammonia, hydrogen sulfide, grain size, and TOC measured
  - Statistical analysis to distinguish reference from toxic sites within strata
  - Pesticides, PCB, PAH, TBT, metals, and natural toxins measured on sediment from clearly distinguished reference and toxic sites
  - Additional statistical analysis to assess relative chemical contamination of reference and toxic sites (includes unknown peaks)

4. Field Bioeffects Assessment

- Benthic community analysis
  - Site sampling (reference, toxic, random, and other) during the same season each year
  - Five field replicates
  - Field measurement of other factors capable of influencing benthic composition
  - Ordination analysis to distinguish reference from impacted sites within strata (the analysis is conducted on a continually enlarging database as more sites are assessed)
  - Pesticides, PCB, PAH, TBT, metals, and natural toxins measured on sediment from clearly distinguished reference and impacted sites
  - Additional ordination analysis to assess relative chemical contamination of reference and impacted sites within strata (includes unknown peaks)
- Tissue Biomarker Analysis
  - Field and laboratory replicates
  - Field measurement of other factors capable of influencing the biomarker
  - Statistical analysis
  - Chemical analysis
  - Statistical analysis

1.2 QUALITY ASSURANCE PROGRAM FOR BPTCP

The State Water Resources Control Board's Bay Protection and Toxic Cleanup Program will conform with all requirements specified in the EPA mandatory QA guidelines (40 CFR Part 30.500, Stanley and Verner 1983). As part of this program, every environmental monitoring and measurement project is required to have a written and approved Quality Assurance Project Plan (QAPP).

The QAPP for the State Water Resources Control Board's Bay Protection and Toxic Cleanup Program (this document) describes the quality assurance and quality control activities and measures that will be implemented to ensure that the data will meet all quality criteria established for the project. All project personnel will be familiar with the policies, procedures, and objectives outlined in this quality assurance plan to assure proper interactions among the various data acquisition and management components of the project. This document will be revised, as appropriate, as changes are made to the existing QA program, and as additional data acquisition activities are implemented.

EPA guidance (Stanley and Verner, 1983) states that the 15 items shown in Table 1-2 should be addressed in the QAPP.

TABLE 1-2. Sections in this report that address the 15 subjects required in a Quality Assurance Project Plan.

Quality Assurance Subject	BPTCP QAPP (this document)
Title page	Title page
Table of contents	Table of contents
Project description	Section 1
Project organization and responsibility	Section 2
QA objectives	Section 4
Sampling procedures	Section 3A
Sample custody	Section 3A
Calibration procedures	Section 3B
Analytical procedures	Section 3B
Data reduction, validation, and reporting	Section 9
Internal QC checks	Section 5
Performance and system audits	Section 4
Preventive maintenance	Section 3B
Corrective action	Section 4
QA reports to management	Section 10

SECTION 2

PROJECT ORGANIZATION

2.1 MANAGEMENT STRUCTURE

Overall management of BPTCP monitoring activities will be provided by the Bays and Estuaries Unit of the State Water Resources Control Board. Expertise in specific research and monitoring components will be provided by the Department of Fish and Game (DFG) and their contracted organizations. DFG's Marine Pollution Studies Laboratories, with headquarters at Moss Landing Marine Laboratories (MLML), has been designated as the principal laboratory for the BPTCP, and therefore will provide direction, coordination, and support for all activities. DFG's scientific and technical services are primarily supplemented through subcontracts with the following organizations: 1) San Jose State University Foundation -- to conduct sample collection, sample preparation, metal analyses, benthic analyses, total organic carbon analyses, and grain size analyses, 2) University of California at Santa Cruz -- to conduct toxicity testing (performed at DFG's Granite Canyon Marine Pollution Studies Laboratory) and trace organic analyses (performed at UCSC's Long Marine Laboratory), and 3) EcoAnalysis, Inc. -- to aid in data management and the statistical design and analysis of monitoring and research efforts. Additional subcontracting services are provided by California State University Long Beach, University of California at San Diego, and University of California at Davis for the development of biomarker tests. Figure 2-1 illustrates the management structure for BPTCP monitoring while key personnel are listed in Table 2-1.

FIGURE 2-1. **Management structure for the Bay Protection and Toxic Cleanup Program's scientific component (contracted to the California Department of Fish and Game).**

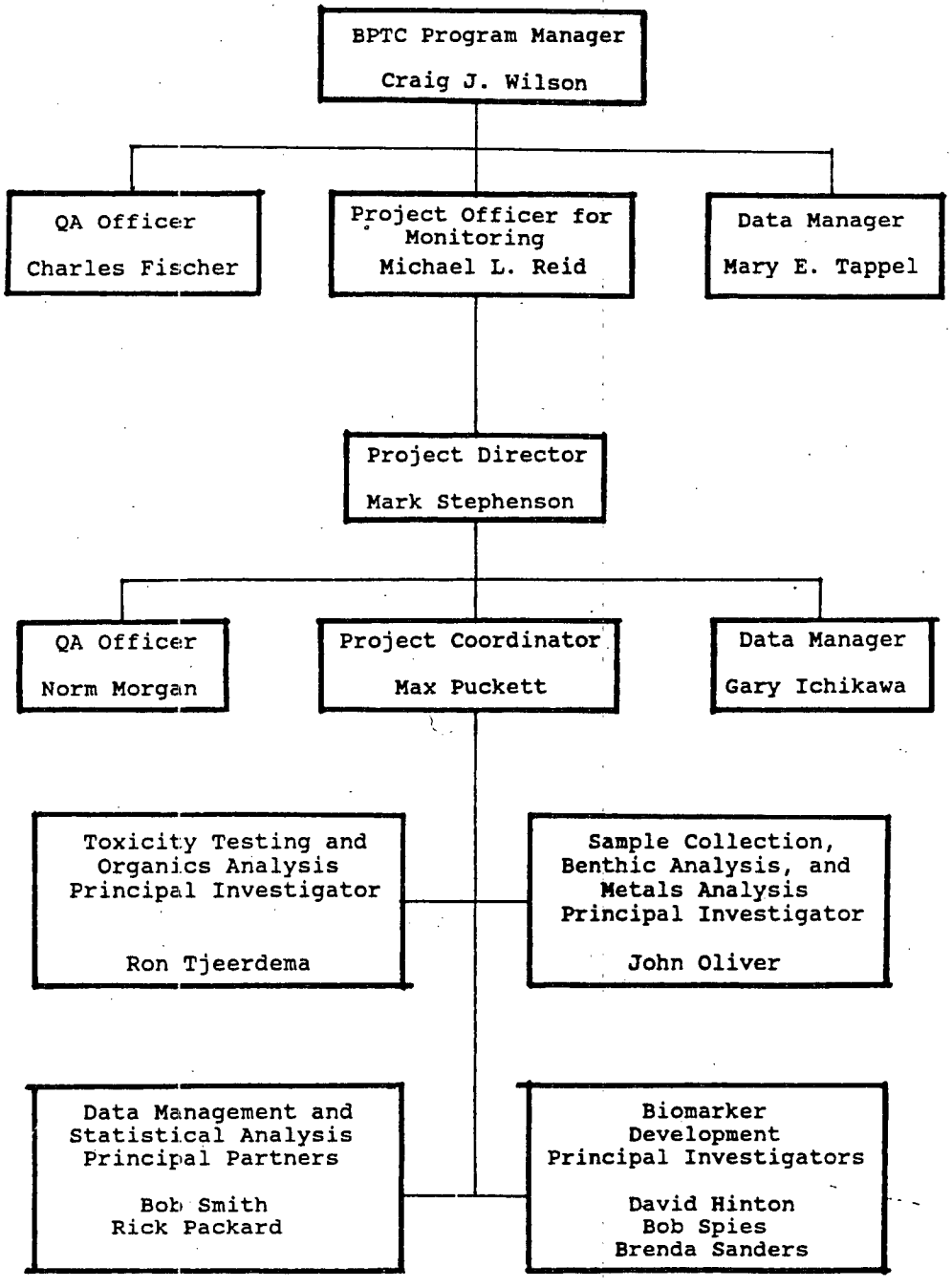

TABLE 2-1. List of key personnel, affiliations, and responsibilities for the BPTCP.

NAME	AFFILIATION (LOCATION)	RESPONSIBILITY
Craig J. Wilson	SWRCB (Sacramento)	SWRCB Program Manager
Mike Reid	SWRCB (Sacramento)	SWRCB Project Off. Monitoring
Charles Fischer	SWRCB (Sacramento)	SWRCB QA Officer
Mary Tappel	SWRCB (Sacramento)	SWRCB Data Manager
Mark Stephenson	DFG-MLML (Moss Landing)	DFG Project Manager
Max Puckett	DFG-GC (Monterey)	DFG Project Coordinator
Norman Morgan	DFG-WPCL (Nimbus)	DFG Project QA Officer
Gary Ichikawa	DFG-MLML (Moss Landing)	DFG Project Data Officer
Kim Paulson	DFG-MLML (Moss Landing)	TBT and Flame Metal Analyses
Jon Goetzl	DFG-MLML (Moss Landing)	Furnace Metal Analyses
Dave Crane	DFG-WPCL (Nimbus)	Metal Analyses
John Oliver	SJSUF-MLML (Moss Landing)	SJSUF Principal Investigator
Rusty Fairey	SJSUF-MLML (Moss Landing)	SJSUF Project Manager
Shelley Lamar	SJSUF-MLML (Moss Landing)	Project Admin./Data Librarian
Cassandra Roberts	SJSUF-MLML (Moss Landing)	Statistical Analyses/Field Crew
Eric Johnsen	SJSUF-MLML (Moss Landing)	Field Crew Supervisor
Jim Oakden	SJSUF-MLML (Moss Landing)	Grain Size, TOC, & Benthic QA
Pat Iampietro	SJSUF-MLML (Moss Landing)	Grain Size and TOC
Carrie Bretz	SJSUF-MLML (Moss Landing)	Benthic Analyses
Mike Gordon	SJSUF-MLML (Moss Landing)	Pore water metals analyses
Ron Tjeerdema	UCSC-LML (Santa Cruz)	UCSC Principal Investigator
John Hunt	UCSC-GC (Monterey)	UCSC Toxicity Project Co-manager
Brian Anderson	UCSC-GC (Monterey)	UCSC Toxicity Project Co-manager
Shirley Tudor	UCSC-GC (Monterey)	Toxicity Testing Data Officer
Hilary McNulty	UCSC-GC (Monterey)	Toxicity Testing QA Officer
Deborah Holstad	UCSC-LML (Santa Cruz)	Organic Analyses Project Manager
John Newman	UCSC-LML (Santa Cruz)	Organic Analyses & QA Officer
Ed Long	NOAA (Seattle)	BPTCP/NOAA Coop. Agreement
David Hinton	UCD	UCD Principal Investigator
Brenda Sanders	CSULB	CSULB Principal Investigator

Table 2.1 Continued

Abbreviations

SWRCB = California State Water Resources Control Board
DFG = California Department of Fish and Game
MLML = Moss Landing Marine Laboratories
GC = Granite Canyon Marine Pollution Studies Laboratory
SJSUF = San Jose State University Foundation
UCSC = University of California at Santa Cruz
LML = Long Marine Laboratory
NOAA = National Oceanic and Atmospheric Administration
UCD = University of California Davis
CSULB = California State University Long Beach

SECTION 3

GENERAL FIELD AND LABORATORY OPERATIONS

PART A: SAMPLE COLLECTION AND PROCESSING

3.1 INTRODUCTION

Currently the BPTCP is focused on the identification of Toxic Hot Spots. Later editions of the QAPP will be modified to address both the remediation of hot spots and the development of sediment quality objectives. Part A of this section describes the sampling design for hot spot identification as well as the specific techniques for collection and processing of samples. Because the collection of sediments influences the results of all subsequent laboratory and data analyses, it is important that samples be collected in a consistent and conventionally acceptable manner. However, because conventional methods may yet be insufficiently tested for the presence of artifacts (as regards toxicity testing in particular), the program will include a systematic effort to identify their presence (via comparison with field validation techniques) and subsequently determine their origins.

3.2 SAMPLING DESIGN

Hot Spot identification consists first of locating sites with the potential for hot spot status followed by more thorough testing to confirm the site as a hot spot. Several strategies are applied to locating sites for followup. First, existing monitoring data is reviewed to identify tissue contaminant sites (principally State Mussel Watch data), sediment contaminant sites (most often associated with waste discharge practices), and, less frequently, bioeffect sites (e.g., toxicity, benthic composition, and biomarkers). An important component of this and other site-location options is the identification of relatively clean sites that can be tested for use as reference sites. A second option is the examination of previously unsampled sites

which are suspected of being either contaminated or clean based on a knowledge of polluting activities. Finally, other sites are sampled in a stratified random manner to allow generalizations regarding the hot spot status of entire waterbodies. For all three options, specific site location information is detailed in contract task orders. With extension of the BPTCP, it is anticipated that a second round of such task orders will eventually be released.

Once sites have been identified for sampling, field collection of sediment is then scheduled. Because toxicity resulting from human activity is not presumed to be heavily influenced by seasonality, collection for this purpose is scheduled throughout the year. In contrast, benthic sampling is scheduled for a relatively small window during the summer due to its seasonal dependence. Because both of these measures will be linked to chemical contamination to qualify for hot spot status, sampling for this purpose will accompany both scheduled events even though this may result in some duplication. Scheduling of biomarker sampling will probably follow that of toxicity testing, but a decision on this will await completion of biomarker development efforts.

Site locations (latitude & longitude) will be pre-determined by agreement with the SWRCB, NOAA, Regional Water Quality Control Boards, and DFG personnel. Changing of the site locations during sediment collection will be allowed only under the following conditions;

1. lack of access to predetermined site,
2. inadequate or unusable sediment (i.e. rock or gravel)
3. unsafe conditions
4. agreement of appropriate staff

All site locations (latitude & longitude), whether altered in the field or pre-determined, will be verified using a Magellan GPS NAV 5000, and the data will be recorded in the field logbook. Once the site location has been established, a temporary buoy may be deployed. If within-site replication is desired, three samples (stations) will be taken at each site, one sample per station. A triangle with the buoy as the center point, with approximately 10-

meter sides will be visually mapped. The three samples will be taken, one at each point of the triangle, and a separate data sheet including latitude and longitude information will be completed. The boat may be anchored at each point to reduce drifting from position.

3.3 RECORD KEEPING

3.3.1 Field Logbook

A designated person will be responsible for recording data in a waterproof field logbook. The field logbook will include;

- date and time of start of sampling
- name of personnel, name of boat
- location of station (latitude & longitude)
- station description (DFG number, photos)
- type of grab used
- field observations (weather, water conditions)
- station depth
- number of grabs necessary and amount sampled
- type of analyses to be performed
- salinity and temperature
- visual characteristics (texture, benthos, odor, sheens)

3.3.2 Chain-of-custody

Chain-of-custody documents and procedures will also be followed and maintained. A chain-of- custody form will accompany every sample. Each person releasing a sample will sign and date the form and get the receiver's signature, with date and time, keeping one copy and giving one copy to receiver.

3.3.3 Chain-of-records

Chain-of-records documents will be maintained for each station. Each form will be a record of all samples taken for each station. IDORG, DFG station numbers and station names, leg

number (sample collection trip batch number), and date collected will be included on each sheet.

3.3.4 Labels

Labels will be fastened to outside and/or inside sample container. No jars will contain handwritten labels. As an extra check on proper labeling, all jars will be pre-labeled before samples are aliquoted. Labels will contain the following information:

-IDORG number

-DFG station number

-station name

-leg sampled

-date sampled

3.4 COLLECTION OF SAMPLES AND FIELD MEASUREMENTS

3.4.1 Training Program and Field QA/QC Audits

Proper training of field personnel represents a critical aspect of quality control. Field technicians are trained to conduct a wide variety of activities using standardized protocols to ensure comparability in data collection among crews and across geographic areas. Each crew consists of a boat captain, chief scientist, and a minimum of one technician. Minimum qualifications for chief scientists will include an M.S. degree in biological/ecological sciences and three years of experience in field data collection activities, or a B.S. degree and five years experience. The remaining crew members generally are required to hold B.S. degrees and, preferably, at least one year's experience. The captain will be an experienced boat handler, preferably holding a captain's license.

All the sampling equipment (*e.g.*, boats, instruments, grabs, nets, etc.) will be used extensively during "hands-on" training sessions (actual field sample collection trips), and by the end of the sampling trip, all crew members will demonstrate proficiency in all the required sampling activities.

In addition to in-field and in-laboratory training, all crews will be evaluated on their field performance during an annual field QA/QC audit conducted by BPTCP personnel. If any deficiencies within a crew are noted during this QA/QC audit, they will be remedied prior to continued field sampling. This can be accomplished by additional training or by changing the crew composition. It is the responsibility of the QA Coordinator to develop training certification and QA/QC audit "checklists" and maintain copies of all training certifications and QA/QC audit reports in a central file.

3.4.2 Collection of grab-deployed samples

Devices for subtidal surficial sampling vary greatly. The primary criterion for an acceptable sampling device is that it consistently collect undisturbed samples to a depth of 2-cm below the sediment surface without contaminating the samples. The size of the device will depend upon the amount of sediment needed and the size of the boat used. Other criteria for acceptable samples for collection of undisturbed sediment include:

- create a minimal bow wake when descending
- form a leak proof seal when the sediment sample is taken
- prevent winnowing and excessive sample disturbance when ascending
- allow easy access to the sample surface

For this study the primary method of sediment collection will be a modified Van Veen grab. Modifications include a teflon coat covering the sample box and jaws. Approximately 20 to 30 sites will be sampled every sampling trip (a "leg"). Trips will be spaced 2-3 weeks apart to allow for toxicity tests to be run. Replicate quality control samples for sediment chemistry will be taken at 5% of the total sites sampled.

3.4.3 Field Measurements

[Supplement to be added in early 1994 for the following:

- Dissolved oxygen
- Sulfides

- Stratification
- Secchi depth
- Ph
- Redox potential discontinuity depth]

3.5 SAMPLE ACCEPTABILITY CRITERIA

After the filled sampler is secured on the transom, or gunnel, or deck, the sediment sample will be carefully inspected. The following acceptability criteria will be met:

- o Sampler is not over-filled (i.e., the sediment surface is not pressed against the top of the sampler).
- o Overlying water is present, indicating minimal leakage.
- o Overlying water is not excessively turbid, indicating minimal sample disturbance.
- o Sediment surface is relatively flat, indicating minimal sample disturbance.
- o Desired penetration depth is achieved (i.e., 20 cm).
- o Sample has a sufficient oxic layer.
- o Sample is muddy (>30% fines), not sandy or gravelly.
- o Sample does not include excessive shell and organic debris.

If a sample does not meet all the above criteria, it will be rejected.

3.6 CLEANING PROCEDURES

This section describes cleaning of sediment sampling equipment, sediment storage containers, and sediment sampler.

3.6.1 Field equipment

All sampling equipment (i.e., containers, container liners, scoops, water collection bottles) will be made of non-contaminating materials and will be pre-cleaned and protectively

packaged prior to entering the field. Sample collection gear and samples will only be handled by personnel wearing non-contaminating polyethylene gloves. All sample collection equipment (excluding the sediment sampler) will be cleaned by using the following sequential process:

> Two-day soak and wash in Micro (brand) detergent, three tap-water rinses, three deionized water rinses, a three-day soak in 10% Hcl or HNO3, three Milli-Q (brand) water rinses, air dry, three petroleum ether rinses, and air dry.

All cleaning after the Micro (brand) detergent step is performed in a positive pressure "clean" room to prevent airborne contaminants from contacting sample collection equipment. Air supplied to the clean room is filtered.

The sediment sampler is cleaned prior to entering the field by utilizing the following sequential steps: a vigorous Micro (brand) detergent wash and scrub, a tap-water rinse, air dry, application of a PTFE teflon aerosol coating, a 10% Hcl or HNO3 rinse, and a petroleum ether rinse.

3.6.2 Sample storage containers

Sample storage containers are cleaned in accordance with the type of analysis to be performed upon its contents. All containers will be cleaned in a positive pressure "clean" room with filtered air to prevent airborne contaminants from contacting sample storage containers.

Containers for trace metal analysis media (sediment, archive sediment, pore water, and subsurface water) are cleaned by: a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Milli-Q (brand) water rinses, and air dry.

New containers for synthetic organic analysis media (sediment, archive sediment, pore water, and subsurface water) and additional teflon sheeting cap-liners are cleaned by: a two-day

Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Milli-Q (brand) water rinses, air dry, three petroleum ether rinses, and air dry.

Acid volatile sulfide analysis sediment containers are cleaned by: a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Milli-Q (brand) water rinses, and air dry.

Total organic carbon and grain size analysis sediment containers are cleaned by a two-day Micro (brand) detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO_3, three Milli-Q (brand) water rinses, three rinses with petroleum ether, followed by air drying.

3.6.3 In-field cleaning

To avoid cross-contamination, all equipment used in sample handling will be thoroughly cleaned before processing any sample or portion thereof. The sediment sampler will be cleaned prior to sampling a site by: rinsing all surfaces with seawater, scrubbing all sediment sample contact surfaces with Micro (brand) detergent, rinsing all surfaces with seawater, rinsing sediment sample contact surfaces with 10% HCl or HNO_3, and rinsing all sediment sample contact surfaces with methanol. If sites have multiple stations, the sediment sampler will be scrubbed and cleaned between stations in the same manner as it is between sites.

The sediment sampler will be scrubbed with seawater between successive deployments to remove adhering sediments from contact surfaces possibly originating below the sampled layer, thus preventing contamination from areas of non-interest. Sampling procedures will attempt to avoid exhaust from any engine aboard any vessel involved in sample collection. An engine will be turned off when possible during portions of the sampling process where contamination from engine exhaust may occur.

Trace metal-free and synthetic organic-free polystyrene scoops are used to transfer sample mud from the grab to the sample holding container. The sample holding container will be composed of noncontaminating polyethylene or polycarbonate.

3.7 SEDIMENT SAMPLE COLLECTION

3.7.1 Sediment sample collection utilizing grab sampler

Before sub-samples of the grab sample are taken, the overlying water will be removed. One method of removing this water is by slowly siphoning it off or using a turkey baster to pipette out overlying water. Other methods, such as decanting the water or slightly opening the sampler to allow the water to escape, will be done slowly and with care to minimize disturbance or loss of fine-grained surficial sediment.

Once the overlying water has been removed, the top 2 cm of surficial sediment can be sub-sampled from the grab. Sub-samples are taken using a pre-cleaned flat bottom scoop. This device allows a relatively large sub-sample to be taken accurately. Because accurate and consistent subsampling requires practice, an experienced person performs this task.

When subsampling surficial sediments, unrepresentative material (e.g., large stones or vegetative material) will be removed from the sample in the field. The smaller rocks and other foreign material remain in the sample. The criteria used to determine representativeness of sample material will be established by the chief scientist prior to sampling. Such removals will be noted on the field log sheet.

It is critical that sample contamination be avoided during sample collection. All sampling equipment (i.e., siphon hoses, scoops, containers) will be made of non-contaminating material and will be appropriately cleaned before use. Samples will not be touched with un-gloved fingers. In addition, potential airborne contamination (e.g., from engine exhaust, cigarette smoke) will be avoided.

3.7.2 Sediment sample collection utilizing diver cores

If water depth does not permit boat entrance to a site (e.g.. < 8ft.), divers will sample that site using sediment cores (diver cores). Cores consist of a four-inch diameter polycarbonate tube, one-foot in length, including plastic end caps to aid in transport. A plunger covered with a plastic laboratory glove is used to extrude the mud for collection. All sample acceptability criteria will be met.

Divers will enter a study site from one end and sample in one direction so as to not disturb the sediment with feet or fins. Cores will be taken to a depth of at least six inches. Cores will be removed and a plunger will be placed on the bottom of the core. The sample will be extruded through the top of the core, allowing surface water to run off slowly, as stated for the grab sample procedure. The mud will be pressed out of the top end of the core to the prescribed depth of 2-cm and cut with a polycarbonate spatula, and will be deposited into the cleaned polyethylene tub. Additional samples will be taken with the same core tube until the six-liter volume is attained. Sediment samples will be treated similar to grab samples, with teflon sheets covering the sample and nitrogen vented.

Data sheets will be completed including latitude and longitude, salinity, temperature, etc. If sub-surface water samples are requested, they will be taken in an area of the site not yet disturbed by samplers.

If replicate samples are required, new core tubes will be used and new laboratory gloves will be placed over the plunger. Sampling will be conducted far enough apart to ensure no disturbance by the samplers during the previous replicate.

3.7.3 Transport of sample containers

Six-liter sample containers will be packed (three to an ice chest) with enough ice to keep them cool for 48 hours. Each tub will be sealed in a pre-cleaned, large plastic bag closed

with a cable tie to prevent contact with other samples or ice or water. Ice chests will be driven back to the lab by the samplers or flown by air freight within 24 hours of collection.

3.8 HOMOGENIZATION AND ALIQUOTING OF SAMPLES

3.8.1 In-field sampling

For the sediment sample, the top 2-cm is removed from the grab and placed in the 6-liter polyethylene container. Between grabs or cores, the sediment in the container will be covered with a teflon sheet and the container covered with a lid and kept cool. When an adequate amount of sediment has been taken, the sample is covered with a teflon sheet assuring no air bubbles. A second, larger teflon sheet is placed over the top of the container to ensure an air tight seal, and nitrogen is vented into the container to rid it of oxygen.

3.8.2 In-laboratory homogenization and aliquoting

3.8.2.1 Homogenization

Samples will remain in ice chest (on ice) until the containers are brought back to the lab for homogenization. All sample identification information (station numbers, etc.) will be recorded on COC and COR forms prior to homogenizing and aliquoting. A single container will be placed on plastic sheeting while also remaining in original plastic bag. The sample will be stirred with a polycarbonate stirring rod for at least 5 minutes, or until mud appears homogeneous.

3.8.2.2 Aliquoting and Storage

All pre-labeled jars will be filled using a clean teflon scoop, and will be stored in freezer/refrigerator (according to media/analysis) until analysis. Samples will be placed in boxes sorted by analysis type and leg number. The first sample taken is for acid volatile sulfide (AVS) if applicable. The remainder of the sediment sample is then aliquoted into appropriate containers for trace metal chemistry, organic chemistry, porewater extraction, and bioassay testing containers. The sample containers for sediment bioassays are then placed on ice or in a refrigerator (4°C). Sample containers for sediment chemistry (metals

and organics) are stored in a freezer (-20°C). Any excess sediment sample will be archived in a clean ziplock bag placed in a refrigerator until the next leg.

3.8.2.3 Sample Storage Temperature and Holding Time

Sample storage temperatures and holding times are described in Section 5 of this QAPP.

3.9 PROCEDURES FOR THE EXTRACTION OF PORE WATER

3.9.1 Introduction

Simple pore water (interstitial water, or water which exists between sediments) extraction techniques can be used to collect and evaluate sediment pore waters during bio-geochemical and toxicological studies. These techniques are also necessary to determine pollutant profiles with sufficient resolution to model benthic fluxes. The whole core squeezing method, developed by Bender et al. (1987), utilizes mechanical force to squeeze pore water from interstitial spaces. It has been used for examination of nutrients and particle-unreactive ions in superficial sediments, with promising results. Tracer experiments and comparisons with other pore water extraction techniques agree favorably and support the validity of this method. The following squeezing technique is a modification of the original Bender design with some adaptations based on the work of Carr et al.(1989) and Long and Buchman (1989). These modifications allow the squeezing technique to be useful in evaluating not only pollutant levels in pore waters of homogenized sediments, but allows profiling and determination of other important chemical redox characteristics in the sediments as well. This can be accomplished by whole core sampling and placing oxygen, Ph or ion selective electrodes in-line with sample effluent during sample squeezing (Fairey et al., submitted).

3.9.2 Sediment sampling for pore water extraction purposes

The whole core squeezer (WCS) was developed for laboratory or field use in conjunction with standard coring techniques. It is most effective when used with coring devices which preserve the sediment-water interface and the overlying water, or by diver coring. When

using coring devices, it is recommended that all surfaces in contact with sediment samples be manufactured or coated with non-contaminating surfaces (PPE, PEE or TFE) and be thoroughly cleaned (see section 6.0). Divers will minimize surface disturbance during sampling and also be aware of contamination problems.

3.9.3 Instrument description

The squeezer's major features consist of an aluminum support framework, 10 cm i.d. acrylic core tubes with sampling ports, a pressure regulated pneumatic ram with air supply valves, and Ph and oxygen electrodes placed in-line with sample effluent. Subcore tubes are easily placed in the support framework by release of the coupler pin. Upon return to the framework, pressure is applied to the top piston by adjusting the air supply to the pneumatic ram. Initially an air pressure of $\approx$ 20 psi is sufficient to maintain a steady flow of sample effluent through the top piston. At no time during squeezing will air pressure exceed 200 psi. A porous pre-filter (PPE or TFE) is inserted in the top piston and used to screen large ($>$ 70 microns) sediment particles. Further filtration is accomplished with disposable TFE filters of 5 microns and 0.45 microns in-line with sample effluent. Filter clogging and sediment compaction during the course of squeezing will slow effluent flow, so air pressure is slowly raised to compensate. This is easily accomplished with a fine adjustment pressure regulator on the air supply.

3.9.4 Pore water samples and handling

To avoid trace metal contamination, all sample containers, filters and WCS surfaces in contact with the sample are plastics (acrylic, PVC, and TFE) and cleaned with Micro, 10% HCl Millipore Milli-Q water and Methanol (see section 6.0). One to two liters of homogenized sediment sample are placed in the squeezer tube for pore water extractions. Sample effluent of the required volume is collected in TFE containers under refrigeration. Pore water is then subsampled in the volumes and specific containers required for archiving, chemical or toxicological analysis. Samples to be analyzed for trace metals will be acidified to an approximate pH of 2-3 to minimize oxidation of the metal and adsorption to sample

container walls. Other subsamples may be refrigerated or frozen as required under normal holding time criteria for each specific analysis. Upon completion of a sediment squeezing run, all squeezer surfaces in contact with sample will be thoroughly cleaned to minimize metal or organic cross-contamination between samples.

Blanks of Millipore Milli-Q water will be substituted for sample and squeezed prior to and after the core tubes are used for sample extractions. This squeezer blank will be used as a QA step to test for possible contaminations.

3.9.5 Documentation

As with any sampling, careful documentation is necessary. Comments relating to starting and ending time of a squeezing run, volumes squeezed and salinity of pore water will be recorded in the laboratory notebook. If in-line electrodes are being used, data relevant to their use will be logged or recorded on the strip chart.

3.10 COLLECTION OF SAMPLES FOR BENTHIC COMMUNITY ANALYSIS

Sediment samples for benthic community analysis are collected from mid summer to early fall. At each site, five (5) mini-cores (7-cm diameter, 5-cm depth) are collected from five (5) separate deployments of the sampler (i.e. one mini-core per deployment). Samples are immediately sieved with a 0.5 mm screen and preserved with 10% formalin. Three days later the formalin is drained and rinsed and replaced with 50% isopropyl alcohol. Samples will be stored for at least two years or until taxonomic identifications are performed. The SWRCB will determine which samples will be examined for benthic community composition based on the results of toxicity testing and chemical analysis.

3.11 COLLECTION OF FISH SAMPLES

Fish will be captured using otter trawls, beach seines, gillnets, beam trawls, diver-deployed devices and other gear, as warranted by sample area: depth, accessibility, bottom-topography, and regulations and restrictions. Captured fish will be removed from the capture device and placed in a trace metal-free and synthetic organic-free container for sorting. Captured fish will be sorted by species and size then rinsed with ambient water to remove sediments and debris. Two or more species groupings will be retained as possible samples. The fish will be individually packaged in pre-cleaned ziplock bags and frozen using dry ice in the field. Species grouping fishes will be individually weighed to arrive at a mean weight, standard deviation, and range which will aide in choosing the most attractive species for analysis.

3.12 SAMPLE COLLECTION AND STORAGE FOR AVS (acid volatile sulfide) ANALYSIS

Samples for AVS analysis may be taken in the field and/or the laboratory. The sample will be taken from the top 2-cm of sediment from a box core or from the homogenized sample in the laboratory. Plastic sample containers will be filled completely with sediment assuring no air spaces and kept on ice till freezing is possible. Samples will be held frozen for up to twelve months, unless otherwise recorded. Sample volatilization and extraction will be completed in accordance with Boothman, W.S. and Helmstetter, A. 1992. Sediment sulfides will be measured using a colorimetric method, suggested to be more accurate than the electrode method (Allen et al., 1991).

SECTION 3 (continued)

PART B: GENERAL LABORATORY OPERATIONS FOR ALL ASPECTS OF BPTCP

3.13 LABORATORY OPERATIONS

This section addresses only general laboratory operations, while the sections on each biological indicator present specific QA/QC requirements and procedures associated with the processing of specific samples. All laboratories providing analytical support for chemical or biological analyses will have the appropriate facilities to store and prepare samples, and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. Laboratories are expected to conduct operations using good laboratory practices, including:

- A program of scheduled maintenance of analytical balances, microscopes, laboratory equipment and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (ASTM Class 3, NIST Class S-1, or equivalents).
- Checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons are < 2 percent of the previous value.
- Recording all analytical data in bound logbooks in ink.
- Monitoring and documenting the temperatures of cold storage areas and freezer units three time per week.
- Verifying the efficiency of fume hoods.
- Having a source of reagent water meeting American Society of Testing and Materials (ASTM) Type I specifications (ASTM 1984) available in sufficient quantity to support analytical operations. The conductivity of the reagent water will not exceed 18 megohm at 25° C.

- Labeling all containers used in the laboratory with date prepared, contents, and initials of the individual who prepared the contents.
- Dating and storing all chemicals safely upon receipt. Chemical are disposed of properly when the expiration date has expired.
- Using a laboratory information management system to track the location and status of any sample received for analysis.
- SOPs readily available to staff.

Laboratories will be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, control charts and summary data of internal QA/QC checks, and results from certified reference material analyses. Laboratories will also be able to provide analytical data and associated QA/QC information in a format and time frame specified by the Bptcp Manager and/or Information Manager.

3.13.1 Laboratory Personnel, Training and Safety

Each laboratory providing analytical support to BPTCP has a designated on-site QA Officer. This individual will serve as the point of contact for the BPTCP QA staff in identifying and resolving issues related to data quality. To ensure that the samples are analyzed in a consistent manner throughout the duration of the project, key laboratory personnel will participate in an orientation session conducted during an initial site visit or via communication with BPTCP staff. The purpose of the orientation session is to familiarize key laboratory personnel with the QA program. Laboratories may be required to demonstrate acceptable performance before analysis of samples can proceed, as described for each indicator in subsequent sections. Laboratory operations will be evaluated on a continuous basis through technical systems audits, performance evaluation studies, and by participation in interlaboratory round-robin programs.

Personnel in any laboratory performing BPTCP analyses will be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the particular laboratory manager and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. Each laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA), or equivalent state or local regulations. The safety manual will be readily available to laboratory personnel. Proper procedures for safe storage, handling and disposal of chemicals will be followed at all times; each chemical will be treated as a potential health hazard and good laboratory practices will be implemented accordingly.

3.13.2 Quality Assurance Documentation

All laboratories will have the latest revisions of the BPTCP QAPP. In addition, the following documents and information will be current, and they will be available to all laboratory personnel participating in the processing of BPTCP samples:

- Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory including personnel responsibilities, laboratory acceptance criteria for release of data, and procedures for determining the acceptability of results.

- Laboratory Standard Operating Procedures (SOPs) - Detailed instructions for performing routine laboratory procedures. In contrast to the Laboratory Methods Manual, SOPs offer step-by-step instructions describing exactly how the method is implemented in the laboratory, specific for the particular equipment or instruments on hand.

- Instrument performance information - Information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information usually is recorded in logbooks or laboratory notebooks.

- Control charts - Control charts will be developed and maintained throughout the project for all appropriate analyses and measurements (see section 3.2.5).

3.13.3 Analytical Procedures

Complete and detailed procedures for processing and analysis of samples in the field have been noted in previous portions of Section 3, and detailed procedures for processing and analysis of samples in the laboratory are provided in the respective laboratories SOP manual.

3.13.4 Laboratory Performance Audits

Initially, a QA performance audit will be performed by BPTCP QA staff to determine if each laboratory effort is in compliance with the procedures outlined in the DFG QAPP and to assist the laboratory where needed. Additionally, technical systems audits may be conducted by a team composed of the QA Coordinator and his/her technical assistants. Reviews may be conducted at any time during the scope of the study, but are not required every year. Furthermore, laboratory performance will be assessed on a continuous basis through the use of internal and external performance evaluation (PE) samples and laboratory intercomparison studies (round robins).

3.13.5 Preparation and Use of Control Charts

Control charts are a graphical tool to demonstrate and monitor statistical control of a measurement process. A control chart basically is a sequential plot of some sample attribute (measured value or statistic). The type of control chart used primarily by laboratory analysts is a "property" chart of individual measurements (termed an X chart).

Measured values are plotted in their sequence of measurement. Three sets of limits are superimposed on the chart: 1) the "central line" is the mean value calculated from at least 7 initial measurements and represents an estimate of the true value of the sample being measured, 2) upper and lower "warning limits" representing the 95 percent confidence limits around the mean value, within which most (95 percent) of the measured values will lie when the measurement process is in a state of statistical control, and 3) upper and lower "control limits" representing the 99 percent confidence limits around the mean, within which nearly

all (99 percent) of the measured values will lie when the measurement process is in a state of statistical control.

Control charts will be updated by laboratory personnel as soon as a control sample measurement is completed. Based on the result of an individual control sample measurement, the following course of action will be taken (Taylor 1987):

- If the measured value of the control sample is within the warning limits, all routine sample data since the last acceptable control sample measurement are accepted, and routine sample analyses are continued.

- If the measured value of the control sample is outside of the control limits, the analysis is assumed to no longer be in a state of statistical control. All routine sample data analyzed since the last acceptable control sample measurement are suspect. Routine sample analyses are suspended until corrective action is taken. After corrective action, statistical control will be reestablished and demonstrated before sample analyses continue. The reestablishment of statistical control is demonstrated by the results of three consecutive sets of control sample measurements that are in control (Taylor 1987). Once statistical control has been demonstrated, all routine samples since the last acceptable control sample measurement are reanalyzed.

- If the measured value of a control sample is outside the warning limits, but within the control limits, a second control sample is analyzed. If the second control sample measurement is within the warning limits, the analysis is assumed to be in a state of statistical control, and all routine sample data since the last acceptable control sample measurement are accepted, and routine sample analyses are continued. If the second sample measurement is outside the warning limits, it is assumed the analysis is no longer in a state of statistical control. All routine sample data analyzed since the last acceptable control sample measurement are suspect. Routine sample analyses are

suspended until corrective action is taken. After corrective action, statistical control will be reestablished and demonstrated before sample analyses continue. The reestablishment of statistical control is demonstrated by the results of three consecutive sets of control sample measurements that are in control (Taylor 1987). Once statistical control has been demonstrated, all routine samples since the last acceptable control sample measurement are reanalyzed.

Taylor (1987) also provides additional criteria for evaluating control chart data to determine if a measurement system is no longer in a state of statistical control. For X charts, these criteria include:

- Four successive points outside a range equal to plus or minus one-half the warning limits.
- Seven successive points on one side of the central line, even if all are within the warning limits.
- More than 5 percent of the points outside the warning limits.

Central line, warning limits, and control limits will be evaluated periodically by either the on-site QA coordinator or the BPTCP staff. Central lines, warning limits, and control limits for each analyte and sample type will be redefined based on the results of quality control and quality assessment sample measurements. Current control charts will be available for review during technical systems audits. Copies of charts will be furnished to the QA staff upon request. Such charts will contain both the points and their associated values.

SECTION 4

QUALITY ASSURANCE OBJECTIVES

4.1 MEASUREMENT QUALITY OBJECTIVES

The BPTCP is measuring a defined set of parameters that are considered to be reliable indicators of bay and estuarine environmental condition. Table 4.1 lists the parameters measured in this program. Additional indicators being evaluated for inclusion are contaminant concentrations in fish tissue and biomarkers in fish and mussels.

TABLE 4-1. Indicators measured in the BPTCP.

Category	Indicator
Biotic Condition	Benthic species composition
Abiotic Condition	Sediment contaminant concentrations
	Sediment, pore water and subsurface toxicity
	TOC
	Ammonia
	H_2S
Habitat	Salinity
	Temperature
	Depth
	Grain size

Measurement error is frequently emphasized in monitoring programs as an important source of uncertainty. In the BPTCP, measurement error may be a less significant contributor to total uncertainty than sample density. Measurement error is, however, a potentially important variable in controlling the regional responsiveness, and thus the acceptability, of individual indicators. In addition, external users of BPTCP data may find that measurement error is an important source of variability that will be accounted for. It is therefore important for the BPTCP laboratories and field crews to control measurement error, to the extent possible, when selecting sampling methods and establish measurement quality objectives (MQOs) for each sampling method and laboratory analysis procedure. MQOs essentially represent data quality objectives that are based on control of the measurement system. They are being used to establish criteria for data acceptability because reliable error bounds cannot, at present, be established for end use of indicator response data. As a consequence, management decisions balancing the cost of higher quality data against program objectives are not presently possible.

Measurement quality objectives for the various measurements being made in the BPTCP are expressed in terms of accuracy, precision, and completeness requirements in Table 4-2. These MQOs were established by obtaining estimates of the most likely data quality that is achievable based on either the instrument manufacturer's specifications, scientific experience or historical data.

The MQOs presented in Table 4-2 are used as quality control criteria both in field and laboratory measurement processes to set the bounds of acceptable measurement error. Usually, MQOs are established for five aspects of data quality: representativeness, completeness, comparability, accuracy, and precision (Stanley and Verner 1985). These terms are described in the following sections in terms of their overall applicability to the BPTCP and the specific measurement systems being employed for each indicator.

TABLE 4-2. Measurement quality objectives for BPTCP indicators. Accuracy requirements are expressed as either maximum allowable percent deviation (%) or absolute difference (± value) from the "true" value; precision requirements are expressed as maximum allowable relative percent difference (RPD) or relative standard deviation (RSD) between two or more replicate measurements. Completeness goals are the percentage of expected results to be obtained successfully.

Indicator/Data Type	Accuracy Requirement	Precision Requirement	Completeness Goal
Sediment/tissue contaminant analyses:			
Organics	30%	30%	100%
Inorganics	15%	15%	100%
Sediment toxicity	NA	NA	100%
Benthic species composition and biomass:			
Sorting	10%	NA	100%
Counting	10%	NA	100%
Taxonomy	10%	NA	100%
Sediment characteristics:			
Particle size (% silt-clay) analysis	NA	10%	100%
Total organic carbon	10%	10%	100%
Acid volatile sulfide	10%	10%	100%
Water Column Characteristics:			
Dissolved oxygen	± 0.5 mg/L	10%	100%
Salinity	± 1.0 ppt	10%	100%
Depth	± 0.5 m	10%	100%
pH	± 0.2 units	NA	100%
Temperature	± 0.5 °C	NA	100%
Total Suspended solids	NA	10%	100%
Gross pathology of fish	NA	10%	100%
Fish community composition:			
Counting	10%	NA	100%
Taxonomic identification	10%	NA	100%
Length determinations	± 5 mm	NA	100%
Fish histopathology	NA	NA	NA

4.2 REPRESENTATIVENESS

The data quality attribute of "representativeness" applies not only to the overall sampling design, but also to individual measurements and samples obtained as part of the BPTCP's monitoring efforts. Holding time requirements for different types of samples ensure that analytical results are representative of conditions at the time of sampling; these requirements are specified in the individual indicator sections of this document. In addition, use of QA/QC samples which are similar in composition to samples being measured provides estimates of precision and bias that are representative of sample measurements. Therefore, as a general program objective, the types of QA documentation samples (*i.e.*, performance evaluation material) used to assess the quality of analytical data will be as representative as possible of the natural samples collected during the project with respect to both composition and concentration.

4.3 COMPLETENESS

Completeness is defined as "a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement" (Stanley and Verner 1985). The BPTCP has established a completeness goal of 100% for the various indicators being measured (Table 4-3). The 100% completeness goal is established in an attempt to provide a comprehensive set of data for each site evaluated for toxic hot spot or reference site status. If only partial data for the full range of indicators exist at a site, firm classification as to hot spot status will be compromised. Failure to achieve this goal usually results from lost or destroyed samples. Therefore, established protocols for tracking samples during shipment and laboratory processing will be followed to minimize data loss following successful sample collection.

4.4 COMPARABILITY

Comparability is defined as "the confidence with which one data set can be compared to another" (Stanley and Verner 1985). Comparability of reporting units and calculations, data base management processes, and interpretative procedures will be assured if the overall goals of the BPTCP are to be realized. One goal of the BPTCP is to generate a high level of documentation for the above topics to ensure that future BPTCP efforts can be made comparable. For example, both field and laboratory methods are described in full detail in manuals which will be made available to all field personnel and analytical laboratories. Field crews will undergo intensive training prior to the start of field work. In addition, the comparability of laboratory measurements is monitored through the interlaboratory comparison exercises and the use of field split or duplicate performance evaluation samples. The results of this comparability monitoring will be presented and evaluated in a quality assurance report prepared by the program's QA personnel following each year's sampling effort. Comparability will be assessed through application of appropriate statistical tests (e.g., t-tests, ANOVA), and results will be considered comparable if there are no significant differences. Failure to achieve this comparability goal will result in corrective actions which may include, but are not limited to, changes in field and laboratory methodology and/or concomitant changes in the program's QA/QC requirements.

4.5 ACCURACY, PRECISION, AND TOTAL ERROR

The term "accuracy", which is used synonymously with the term bias in this plan, is defined as the difference between a measured value and the true or expected value, and represents an estimate of systematic error or net bias (Kirchner 1983; Hunt and Wilson 1986; Taylor 1987). Precision is defined as the degree of mutual agreement among individual measurements, and represents an estimate of random error (Kirchner 1983; Hunt and Wilson 1986; Taylor 1987). Collectively, accuracy and precision can provide an estimate of the total error or uncertainty associated with an individual measured value. Measurement quality

objectives for the various indicators are expressed separately as accuracy (*i.e.*, bias) and precision requirements (Table 4-2). Accuracy and precision requirements may not be definable for all parameters due to the nature of the measurement type. For example, accuracy measurements are not possible for toxicity testing because "true" or expected values do not exist for these measurement parameters (see Table 4-2). In order to evaluate the MQOs for accuracy and precision, various QA/QC samples will be collected and analyzed for most data collection activities. Table 4-3 presents the types of samples to be used for quality assurance/quality control for each of the various data acquisition activities except sediment and fish tissue contaminant analyses. The frequency of QA/QC measurements and the types of QA data resulting from these samples or processes are also presented in Table 4-4. Because several different types of QA/QC samples are required for the complex analyses of chemical contaminants in sediment and tissue samples, they are presented and discussed separately in Section 5 along with presentation of warning and control limits for the various chemistry QC sample types.

4.6 COMPATIBILITY WITH PROGRAM GOALS

Presently, the BPTCP's primary purpose is the identification of Toxic Hot Spots, including the demonstration of an association with anthropogenic pollution (i.e. evidence, in the form of a statistical association, has to be presented that contaminants rather than natural factors such as grain size and ammonia are responsible for the observed toxicity or benthic degradation). Achieving this goal requires careful selection of nondegraded reference sites that match suspect hot spots for these natural factors. Presently, reference sites must generally be chosen which have been demonstrated to be nontoxic in repeat testing, which are matched with suspect hot spots for grain size and TOC, and which are located in the same geographic region (San Francisco Bay area or north or south of Pt. Conception). Later editions of this document will present the statistical tests used to determine whether the association with contaminants exists independent of the effects of natural factors. Additional details will also be provided regarding the addition of benthic data, the process for selecting

reference sites, reference site selection criteria, and statistical issues concerning the numbers and types of reference sites to be included in each attempt to qualify a group of sites as hot spots.

As later editions of this document address the program's additional goals of developing sediment quality objectives and remediating hot spots, this section will be supplemented with the appropriate quality assurance objectives to achieve compatibility with these goals.

TABLE 4-3. Quality assurance sample types, frequency of use, and types of data generated for BPTCP monitoring (see Table 5-4 for chemical analysis QA/QC sample types).

Variable	QA Sample Type or Measurement Procedure	Frequency of Use	Data Generated for Measurement Quality Definition
Sediment toxicity tests	Reference toxicant	Each experiment	Variance of replicated tests over time
Benthic Species Composition and Biomass:			
Sorting	Resort of sample	10% of each tech's work	No. animals found in resort
Sample counting and ID	Recount and ID of sorted animals	10% of each tech's work	No. of count and ID errors
Sediment grain size	Splits of a sample	10% of each tech's work	Duplicate results
Organic carbon and acid volatile sulfide	Duplicates and analysis of standards	Each batch	Duplicate results and standard recoveries
Dissolved Oxygen conc. (CTD)	**Comparison of calibrated YSI and CTD values**	**Each CTD cast**	**Difference between CTD and YSI**
Dissolved Oxygen conc. (YSI)	**Comparison with Winkler value**	**Once per shift**	**Difference between YSI and Winkler value**

Table 4-3 (continued).

Variable	QA Sample Type or Measurement Procedure	Frequency of Use	Data Generated for Measurement Quality Definition
Salinity	Refractometer reading	Each CTD cast	Difference between CTD probe and refractometer readings
Temperature	Thermometer reading	Each CTD cast	Difference between probe and thermometer
Depth	Check bottom depth against depth finder	Each CTD cast	Difference from actual
pH	QC check with standard	Once each day	Difference from standard
Fish identification	Fish preserved for verification by taxonomist	Twice/crew for each species	Number of mis-identifications
Fish counts/length	Remeasured and recounted during field QA audits	One audit for each crew/season	Difference between original and recount/ remeasurement
Fish gross pathology	Specimens preserved for confirmation	At least once per crew shift	Number of mis-identifications
Fish histopathology	Confirmation by second technician	5% of slides	Number of confirmations

SECTION 5

ANALYSIS OF CHEMICAL CONTAMINANTS IN SEDIMENT AND FISH TISSUE SAMPLES

5.1 OVERVIEW

Quality assurance of chemical measurements has many diverse aspects. This section presents BPTCP's QA/QC protocols and requirements covering a range of activities, from sample collection and laboratory analysis to final validation of the resultant data. Much of the guidance provided in this section is based on protocols developed for the SWRCB Mussel Watch program, EPA's Puget Sound Estuary Program (U.S. EPA 1989), as well as those developed over many years on the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends (NS&T) Program. This guidance is applicable to low parts per billion analyses of both estuarine sediment and tissue samples unless otherwise noted. Detailed descriptions of the analytical techniques and laboratory standard operating procedures are reported elsewhere (DFG, 1992).

The BPTCP measures a variety of organic and inorganic contaminants in estuarine sediment and fish tissue samples (Table 5-1); these compounds include all those measured in the NOAA NS&T Program **except the BPTCP does not analyze for co--planar PCBs**. The BPTCP requires its laboratories to demonstrate comparability continuously through strict adherence to common QA/QC procedures, routine analysis of Certified Reference Materials[1], and regular participation in an on-going series of interlaboratory comparison

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[1] Certified Reference Materials (CRMs) are samples in which chemical concentrations have been determined accurately using a variety of technically valid procedures; these samples are accompanied by a certificate or other documentation issued by a certifying body (*e.g.*, agencies such as the National Research Council of Canada (NRCC), U.S. EPA, U.S. Geological Survey, etc.). Standard Reference Materials (SRMs) are CRMs issued by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). A useful catalogue of marine science reference materials has been compiled by Cantillo (1992).

TABLE 5-1. Chemicals to be measured in sediments in the BPTCP.

Polyaromatic Hydrocarbons (PAHs)

Acenaphthylene	1-methylnapthalene
Anthracene	1-methylphenanthrene
Benz(a)anthracene	Naphthalene
Benzo(a)pyrene	Perylene
Benzo(e)pyrene	Phenanthrene
Biphenyl	Pyrene
Chrysene	Benzo(b)fluoranthene
Dibenz(a,h)anthracene	Acenaphthlene
2,6-dimethylnaphthalene	Benzo(k)fluoranthene
Fluoranthene	Benzo(g,h,i)perylene
Fluorene	Indeno(1,2,3-c,d)pyrene
2-methylnaphthalene	2,3,5-trimethylnaphthalene

18 PCB Congeners:

PCB No.	Compound name
8	2,4'-dichlorobiphenyl
18	2,2',5-trichlorobiphenyl
28	2,4,4'-trichlorobiphenyl
44	2,2',3,5'-tetrachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl
66	2,3',4,4'-tetrachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
128	2,2',3,3',4,4'-hexachlorobiphenyl
138	2,2',3,4,4',5'-hexachlorobiphenyl
153	2,2',4,4',5,5'-hexachlorobiphenyl
170	2,2',3,3',4,4',5-heptachlorobiphenyl
180	2,2',3,4,4',5,5'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl
195	2,2',3,3',4,4',5,6-octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

DDT and its metabolites

2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4,4'-DDT

Chlorinated pesticides other than DDT

Endrin
Aldrin
Alpha-Chlordane
Endosulfan I
Trans-Nonachlor
Dieldrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Lindane (gamma-HCH)
Mirex

Major Elements

Aluminum
Iron
Manganese

Trace Elements

Antimony
Arsenic
Cadmium
Chromium
Copper
Lead

TABLE 5-1 (continued). Chemicals to be measured in sediments in the BPTCP.

Other measurements	Trace Elements (continued)
Acid volatile sulfide	Mercury
Total organic carbon	Nickel
Tributyltin	Selenium
Grain size	Silver
	Tin
	Zinc

Additional compounds recently added:

1) DDT and its metabolites--

DDMS,p,p'	**DDMU,p,p'**

2) Chlorinated pesticides other than DDT--

Chlorbenside	**Cis-chlordane**
Trans-chlordane	**Oxychlordane**
Cis-nonachlor	**gamma-chlordene**
Chlorpyrifos	**Dacthal**
Dichlorobenzophenone	**Endosulfan II**
Endosulfan sulfate	**Ethion**
HCH, alpha	**HCH, beta**
HCH, delta	**alpha-chlordene**
Methoxychlor	**Oxadiazon**
Toxaphene	

exercises (round-robins). This is a "performance-based" approach for quality assurance of low-level contaminant analyses, involving continuous laboratory evaluation through the use of accuracy-based materials (e.g., CRMs), laboratory fortified sample matrices, laboratory reagent blanks, calibration standards, and laboratory and field replicates. The definition and use of each of these types of quality control samples are explained in later sections.
No single analytical method has been approved officially for low-level (*i.e.*, low parts per billion) analysis of organic and inorganic contaminants in estuarine sediments and fish tissue.

Recommended methods for the BPTCP are those used in the NOAA NS&T Program (Lauenstein et al. 1993), as well as those documented in the DFG QAQC Manual (DFG, 1992). Under the BPTCP performance-based chemistry QA program, laboratories are not required to use a single, standard analytical method for each type of analysis, but rather are free to choose the best or most feasible method within the constraints of cost and equipment. Each laboratory will, however, continuously demonstrate proficiency and data comparability through routine analysis of accuracy-based performance evaluation samples and reference materials representing real-life matrices.

5.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING

Field personnel will strictly adhere to the BPTCP protocols to insure the collection of representative, uncontaminated sediment and fish tissue chemistry samples. These sample collection protocols are described in detail in this document (see Section 3). Briefly, the key aspects of quality control associated with chemistry sample collection are as follows: 1) field personnel will be thoroughly trained in the proper use of sample collection gear and will be able to distinguish acceptable versus unacceptable sediment grab samples or fish trawls in accordance with pre-established criteria, 2) field personnel will be thoroughly trained to recognize and avoid potential sources of sample contamination (e.g., engine exhaust, winch wires, deck surfaces, ice used for cooling), 3) samplers and utensils which come in direct

contact with the sample will be made of non-contaminating materials (e.g., glass, high-quality stainless steel and/or Teflon®) and will be thoroughly cleaned between sampling stations, 4) sample containers will be of the recommended type (Table 5-2) and will be free of contaminants (i.e., carefully pre-cleaned), and 5) conditions for sample collection, preservation and holding times will be followed (Table 5-2).

Table 5-2. Summary of chemistry sample collection, preservation, and holding time conditions to be followed for BPTCP monitoring.

Sample Parameter	Sample Container	Sample Volume	Max. Sample Size	Max. Extract Preservation	Hold Time[b]	Holding Time
Sediment Metals (except Hg)	250-ml HDPE wide mouth jar	100 to 150 ml	100 to 150 g (approx.)	Freeze, -18° C	6 months	-[a]
Sediment Hg and TOC	same as above	same as above	same as above	same as above	28 days	-[a]
Sediment Organics (including butyltins)	500-ml pre-cleaned glass wide-mouth jar	250 to 300 ml	300 g (approx.)	Freeze, -18° C	14 days	40 days
Sediment Acid Volatile Sulfide (AVS)	125-ml poly-propylene wide-mouth jar	125 ml[c]	125 g	Cool, 4°C	14 days	36 hours
Fish Tissue (Organics and In-organics)	Whole fish are placed in water-tight plastic bags	NA	NA	Freeze (-18°C)	1 year[d]	40 days

[a] No EPA criteria exist. Every effort will be made to analyze sample as soon as possible following extraction or, in the case of metals, digestion.

[b] Every effort will be made to analyze these samples as soon as possible. If extractions are not to be performed within 14 days (or 28 days with Mercury), these samples will be frozen (-18°C) and extracted within 1 year.

[c] AVS containers will be filled to the top to minimize or eliminate headspace; containers will be capped tightly. Every effort will be made to minimize contact of the sediment with air and to analyze these samples as soon as possible.

[d] No EPA criteria exists for holding times of tissue samples. This is a maximum suggested holding time.

5.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

5.3.1 Overview

The QA/QC requirements presented in the following sections are intended to provide a common foundation for each laboratory's protocols; the resultant QA/QC data will enable an assessment of the comparability of results generated by different laboratories and different analytical procedures. It should be noted that the QA/QC requirements specified in this plan represent the minimum requirements for any given analytical method. Additional requirements which are method-specific will always be followed, as long as the minimum requirements presented in this document have been met.

The performance-based protocols utilized in the BPTCP for analytical chemistry laboratories consists of two basic elements: 1) initial demonstration of laboratory capability (e.g., performance evaluation) and 2) ongoing demonstration of capability. Prior to the initial analysis of samples, each laboratory will demonstrate proficiency in several ways: written protocols for the analytical methods to be employed for sample analysis will be submitted to the Program for review, method detection limits for each analyte will be calculated, an initial calibration curve will be established for all analytes, and acceptable performance will be shown on a known or blind accuracy-based material. Following a successful first phase, the laboratory will demonstrate its continued capabilities in several ways: participation in an on-going series of interlaboratory comparison exercises, repeated analysis of Certified Reference Materials, calibration checks, and analysis of laboratory reagent blanks and fortified samples. These steps are detailed in the following sections and summarized in Table 5-3. The sections are arranged to mirror the elements in Table 5-3 to provide easy cross-reference for the reader.

The results for the various QA/QC samples will be reviewed by laboratory personnel immediately following the analysis of each sample batch. These results then will be used to

determine when warning and control limit criteria have not been met and corrective actions will be taken, before processing a subsequent sample batch. When warning limit criteria have not been met, the laboratory is not obligated to halt analyses, but the analyst(s) is advised to investigate the cause of the exceedance. When control limit criteria are not met, specific corrective actions are required before the analyses may proceed. Warning and control limit criteria and recommended frequency of analysis for each QA/QC element or sample type required in the BPTCP also are summarized in Table 5-3.

TABLE 5-3. Key elements of laboratory quality control for BPTCP chemical analyses (see text for detailed explanations).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
1) Initial Demonstration of Capability (Prior to Analysis of Samples):			
- Instrument Calibration	NA	NA	Initial and then prior to analyzing each batch of samples
- Calculation of Method Detection Limits	Must be equal to or less than target values (see Table 5-4)		At least once each year
- Blind Analysis of Accuracy-Based Material	NA	NA	Initial
2) On-going Demonstration of Capability:			
- Blind Analysis of Interlaboratory Comparison Exercise Samples	NA	NA	Regular intervals throughout the year
- Continuing Calibration Checks using Calibration Standard Solutions	NA	will be within ±15% of initial calibration on average for all analytes, not to exceed ±25% for any one analyte	At a minimum, middle and end of each sample batch

TABLE 5-3 (continued).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
- Analysis of Certified Reference Material (CRM) or Laboratory Control Material (LCM):			One with each batch of samples
Precision (see NOTE 1): NA		**Value obtained for each analyte to be within 3sd of control chart limits**	**Value plotted on control chart after each analysis of the CRM**
Relative Accuracy (see NOTE 2):			
PAHs	Lab's value will be within ±25% of true value on average for all analytes; not to exceed ±30% of true value for more than 30% of individual analytes	Lab's value will be within ±30% of true value on average for all analytes; not to exceed ±35% of true value for more than 30% of individual analytes	
PCBs/pesticides	same as above	same as above	
inorganic elements	Lab will be within ±15% of true value for each analyte or within published 95% confidence limits of true value	Lab will be within ±20% of true value for each analyte or within published 95% confidence limits of true value	

NOTE 1: The use of control charts to monitor precision for each analyte of interest will follow generally accepted practices (*e.g.*, Taylor 1987 and section 3.2.5 of this document). Upper and lower control limits, based on 99% confidence intervals around the mean, will be updated at regular intervals.

NOTE 2: "True" values in CRMs may be either "certified" or "non-certified" (it is recognized that absolute accuracy can only be assessed using certified values, hence the term relative accuracy). Relative accuracy is computed by comparing the laboratory's value for each analyte against either end of the range of values (*i.e.*, 95% confidence limits) reported by the certifying agency. The laboratory's value will be within ±35% of either the upper or lower 95% confidence interval value. Accuracy control limit criteria only apply for analytes having CRM concentrations ≥10 times the laboratory's MDL.

TABLE 5-3 (continued).

Element or Sample Type	Warning Limit Criteria	Control Limit Criteria	Frequency
- Laboratory Reagent Blank	Analysts will use best professional judgement if analytes are detected at <3 times the MDL	No analyte will be detected at >3 times the MDL	One with each batch of samples
- Laboratory Fortified Sample Matrix (Matrix Spike)	**NA**	**Recovery try to be within the range 50% to 120% for at least 80% of the analytes**	**At least 5% of total number of samples**

NOTE: Samples to be spiked will be chosen at random; matrix spike solutions will contain all the analytes of interest. The final spiked concentration of each analyte in the sample will be at least 10 times the calculated MDL.

- Laboratory Fortified Sample Matrix Duplicate (Mat. Spike Dup.)	**NA**	**RPD[1] will be ≤ 30 for each analyte**	**Same as matrix spike**
- Field Duplicates (Field Splits)	**NA**	**NA**	**5% of total number of samples**
- Internal Standards (Surrogates)	NA	Recovery will be within the range 30% to 150%	Each sample
- Injection Internal Standards	Lab develops its own	Lab develops its own	Each sample

[1] RPD = Relative percent difference between matrix spike and matrix spike duplicate results (see appropriate section for equation).

5.3.2 Initial Demonstration of Capability

5.3.2.1 Instrument Calibration

Equipment will be calibrated prior to the analysis of each sample batch, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended control limit criteria (Table 5-3). All calibration standards will be traceable to a recognized organization for the preparation and certification of QA/QC materials (*e.g.*, National Institute of Standards and Technology, U.S. Environmental Protection Agency, etc.). Calibration curves will be established for each element and batch analysis from a calibration blank and a minimum of three analytical standards of increasing concentration, covering the range of expected sample concentrations. The calibration curve will be well-characterized and will be established prior to the analysis of samples. Only data which results from quantification within the demonstrated working calibration range may be reported by the laboratory (*i.e.*, quantification based on extrapolation is not acceptable). Samples outside the calibration range will be diluted or concentrated, as appropriate, and reanalyzed.

5.3.2.2 Initial Documentation of Method Detection Limits

Analytical chemists have coined a variety of terms to define "limits" of detectability; definitions for some of the more commonly-used terms are provided in Keith *et al.* (1983) and in Keith (1991). In the BPTCP, the Method Detection Limit (MDL) will be used to define the analytical limit of detectability. The MDL represents a quantitative estimate of low-level response detected at the maximum sensitivity of a method. The Code of Federal Regulations (40 CFR Part 136) gives the following rigorous definition: "the MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." Confidence in the apparent analyte concentration increases as the analyte signal increases above the MDL.

Each BPTCP analytical laboratory will calculate and report an MDL for each analyte of interest in each matrix of interest (sediment or tissue) prior to the analysis of field samples for a given year. Each laboratory is required to follow the procedure specified in 40 CFR Part 136 (Federal Register, Oct. 28, 1984) to calculate MDLs for each analytical method employed. The matrix and the amount of sample (*i.e.*, dry weight of sediment or tissue) used in calculating the MDL will match as closely as possible the matrix of the actual field samples and the amount of sample typically used. In order to ensure comparability of results among different laboratories, MDL target values have been established for the BPTCP (Table 5-4). The initial MDLs reported by each laboratory will be equal to or less than these specified target values before the analysis of field samples may proceed. Each laboratory will periodically (*i.e.*, at least once each year) re-evaluate its MDLs for the analytical methods used and the sample matrices typically encountered.

TABLE 5-4. Target method detection limits for the BPTCP analytes.

INORGANICS (NOTE: concentrations in ug/g (ppm), dry weight)

	Tissue	Sediments
Aluminum	10.0	1500
Antimony	not measured	0.2
Arsenic	2.0	1.5
Cadmium	0.2	0.05
Chromium	0.1	5.0
Copper	5.0	5.0
Iron	50.0	500
Lead	0.1	1.0
Manganese	not measured	1.0
Mercury	0.01	0.01
Nickel	0.5	1.0
Selenium	1.0	0.1
Silver	0.01	0.01
Tin	0.05	0.1
Zinc	50.0	2.0

ORGANICS (NOTE: concentrations in ng/g (ppb), dry weight)

	Tissue	Sediments
PAHs	10.0	5.0
PCB congeners	2.0	1.0
Chlorinated pesticides	1.0 to 25	0.5 to 3.0
Toxaphene	100	10

5.3.2.3 Initial Blind Analysis of a Representative Sample

A representative sample matrix which is uncompromised, homogeneous and contains the analytes of interest at concentrations of interest will be provided to each analytical laboratory new to the BPTCP; this sample will be used to evaluate laboratory performance prior to the analysis of field samples. The sample used for this initial

demonstration of laboratory capability typically will be distributed blind (*i.e.*, the laboratory will not know the concentrations of the analytes of interest) as part of the interlaboratory comparison exercises. Based on results that have typically been attained by experienced NS&T laboratories, a new laboratory's performance generally will be considered acceptable if its submitted values are within <30% (for organic analyses) and <20% (for inorganic analyses) of the known concentration of each analyte of interest in the sample. These criteria apply only for analyte concentrations equal to or greater than 10 times the MDL established by the laboratory. If the results for the initial analysis fail to meet these criteria, the laboratory will be required to repeat the analysis until the performance criteria are met, prior to the analysis of real samples.

5.3.3 On-going Demonstration of Capability

5.3.3.1 Participation in Interlaboratory Comparison Exercises

Through an interagency agreement, NOAA's NS&T Program and EPA's EMAP-E program jointly sponsor an on-going series of interlaboratory comparison exercises (round-robins). All the BPTCP analytical laboratories are required to participate in intercalibration exercises, which are conducted jointly by the National Institute of Standards and Technology (NIST) and the National Research Council of Canada (NRCC). These exercises provide a tool for continuous improvement of laboratory measurements by helping analysts identify and resolve problems in methodology and/or QA/QC. The results of these exercises also are used to evaluate both the individual and collective performance of the participating analytical laboratories on a continuous basis. The BPTCP laboratories are required to initiate corrective actions if their performance in these comparison exercises falls below certain pre-determined minimal standards, described in later sections.

Typically, one exercise is conducted over the course of a year. In a typical exercise, either NIST or NRCC will distribute performance evaluation samples in common to each laboratory, along with detailed instructions for analysis. A variety of performance

evaluation samples have been utilized in the past, including accuracy-based solutions, sample extracts, and representative matrices (*e.g.*, sediment or tissue samples). Laboratories are required to analyze the sample(s) "blind" and will submit their results in a timely manner both to the BPTCP Coordinator, as well as to either NIST or NRCC (as instructed). Laboratories which fail to maintain acceptable performance may be required to provide an explanation and/or undertake appropriate corrective actions. At the end of each calendar year, coordinating personnel at NIST and NRCC hold a QA workshop to present and discuss the comparison exercise results. Representatives from each laboratory are requested to participate in the annual QA workshops, which provide a forum for discussion of analytical problems brought to light in the comparison exercises.

5.3.3.2 Routine Analysis of Certified Reference Materials or Laboratory Control Materials

Certified Reference Materials (CRMs) generally are considered the most useful QC samples for assessing the accuracy of a given analysis (*i.e.*, the closeness of a measurement to the "true" value). Certified Reference Materials can be used to assess accuracy because they have "certified" concentrations of the analytes of interest, as determined through replicate analyses by a reputable certifying agency using two independent measurement techniques for verification. In addition, the certifying agency may provide "non-certified" or "informational" values for other analytes of interest. Such values are determined using a single measurement technique, which may introduce unrecognized bias. Therefore, non-certified values must be used with caution in evaluating the performance of a laboratory using a method which differs from the one used by the certifying agency. A list of reference materials commonly used by BPTCP laboratories is presented in Table 5-5.

A Laboratory Control Material (LCM) is similar to a Certified Reference Material in that it is a homogeneous matrix which closely matches the samples being analyzed. A "true" LCM is one which is prepared (*i.e.*, collected, homogenized and stored in a stable condition) strictly for use in-house by a single laboratory. Alternately, the material may be prepared by

a central laboratory and distributed to others (so-called regional or program control materials). Unlike CRMs, concentrations of the analytes of interest in LCMs are not certified but are based upon a statistically valid number of replicate analyses by one or several laboratories. In practice, this material can be used to assess the precision (*i.e.*, consistency) of a single laboratory, as well as to determine the degree of comparability

Table 5-5. Certified Reference Materials commonly used by BPTCP laboratories. SRMs are available from NIST (phone 301-975-6776); all other reference materials listed are available from NRC (phone 613-993-2359).

Calibration Solutions:	
SRM 1491	Aromatic Hydrocarbons in Hexane/Toluene
SRM 1492	Chlorinated Pesticides in Hexane
SRM 1493	Chlorinated Biphenyl Congeners in 2,2,4-Trimethylpentane
SRM 2260	Aromatic Hydrocarbons in Toluene
SRM 2261	Chlorinated Pesticides in Hexane
SRM 2262	Chlorinated Biphenyl Congeners in 2,2,4-Trimethylpentane
Environmental Matrices (Organics):	
SRM 1941a	Organics in Marine Sediment
SRM 1974	Organics in Mussel Tissue (Mytilus edulis)
Environmental Matrices (Inorganics):	
SRM 1646	Estuarine Sediment
BCSS-1	Marine Sediment
MESS-1	Estuarine Sediment
PACS-1	Harbor Sediment
BEST-1	Marine Sediment
DORM-1	Dogfish Muscle
DOLT-1	Dogfish Liver
SRM 1566a	Oyster Tissue

among different laboratories. If available, LCMs may be preferred for routine (*i.e.*, day to day) analysis because CRMs are relatively expensive. However, CRMs still must be analyzed at regular intervals (*e.g.*, monthly or quarterly) to provide a check on accuracy.

Routine analysis of Certified Reference Materials or, when available, Laboratory Control Materials represents a particularly vital aspect of the "performance-based" BPTCP QA philosophy. At least one CRM or LCM must be analyzed along with each batch of 25 or fewer samples (Table 5-3). For CRMs, both the certified and non-certified concentrations of the target analytes will be known to the analyst(s) and will be used to provide an immediate check on performance before proceeding with a subsequent sample batch. Performance criteria for both precision and accuracy have been established for analysis of CRMs or LCMs (Table 5-3); these criteria are discussed in detail in the following paragraphs. If the laboratory fails to meet either the precision or accuracy control limit criteria for a given analysis of the CRM or LCM, the data for the entire batch of samples is suspect. Calculations and instruments will be checked; the CRM or LCM may have to be reanalyzed (*i.e.*, reinjected) to confirm the results. If the values are still outside the control limits in the repeat analysis, the laboratory is required to find and eliminate the source(s) of the problem and repeat the analysis of that batch of samples until control limits are met, before continuing with further sample processing. The results of the CRM or LCM analysis will never be used by the laboratory to "correct" the data for a given sample batch.

Precision criteria: Each laboratory is expected to maintain control charts for use by analysts in monitoring the overall precision of the CRM or LCM analyses. Upper and lower control chart limits (*e.g.*, warning limits and control limits) will be updated annually; control limits based on 99% percent confidence intervals around the mean are recommended. Following the analysis of all samples in a given year, an RSD (relative standard deviation, a.k.a. coefficient of variation) will be calculated for each analyte of interest in the CRM. Based on typical results obtained by experienced analysts, an overall RSD of less than 30% will be considered acceptable precision for each analyte having a CRM concentration >10 times the laboratory's MDL. Failure to meet this goal will result in a thorough review of the laboratory's control charting procedures and analytical methodology to determine if improvements in precision are possible.

Accuracy criteria: The "absolute" accuracy of an analytical method can be assessed using CRMs only when certified values are provided for the analytes of interest. However, the concentrations of many analytes of interest to BPTCP are provided only as non-certified values in some of the more commonly-used CRMs. Therefore, control limit criteria are based on "relative accuracy", which is evaluated for each analysis of the CRM or LCM by comparison of a given laboratory's values relative to the "true" or "accepted" values in the LCM or CRM. In the case of CRMs, this includes both certified and noncertified values and encompasses the 95% confidence interval for each value as described in Table 5-3.

Based on typical results attained by experienced analysts in the past, accuracy control limit criteria have been established both for individual compounds and combined groups of compounds (Table 5-3). There are two combined groups of compounds for the purpose of evaluating relative accuracy for organic analyses: PAHs and PCBs/pesticides. The laboratory's value will be within <30% of the true value on average for each combined group of organic compounds, and the laboratory's value will be within <35% of either the upper or lower 95% confidence limit for at least 70% of the individual compounds in each group. For inorganic analyses, the laboratory's value will be within <20% of either the upper or lower 95% confidence limit for each analyte of interest in the CRM. Due to the inherent variability in analyses near the method detection limit, control limit criteria for relative accuracy only apply to analytes having CRM true values which are >10 times the MDL established by the laboratory.

5.3.3.3 Continuing Calibration Checks

The initial instrument calibration performed prior to the analysis of each batch of samples is checked through the analysis of calibration check samples (*i.e.*, calibration standard solutions) inserted as part of the sample stream. Calibration standard solutions used for the continuing calibration checks will contain all the analytes of interest. At a minimum, analysis of the calibration check solution will occur at the start and at the end of each sample

batch. Analysts will use best professional judgement to determine if more frequent calibration checks are necessary or desirable.

If the control limit for analysis of the calibration check standard is not met (Table 5-4), the initial calibration will have to be repeated. If possible, the samples analyzed before the calibration check sample that failed the control limit criteria will be reanalyzed following the recalibration. The laboratory will begin by reanalyzing the last sample analyzed before the calibration standard which failed. If the relative percent difference (RPD) between the results of this reanalysis and the original analysis exceeds 30 percent, the instrument is assumed to have been out of control during the original analysis. If possible, reanalysis of samples will progress in reverse order until it is determined that there is less than 30 RPD between initial and reanalysis results. Only the re-analysis results will be reported by the laboratory. If it is not possible or feasible to perform reanalysis of samples, all earlier data (*i.e.*, since the last successful calibration control check) is suspect. In this case, the laboratory will prepare a narrative explanation to accompany the submitted data.

5.3.3.4 Laboratory Reagent Blank

Laboratory reagent blanks (also called method blanks or procedural blanks) are used to assess laboratory contamination during all stages of sample preparation and analysis. For both organic and inorganic analyses, one laboratory reagent blank will be run in every sample batch. The reagent blank will be processed through the entire analytical procedure in a manner identical to the samples. Warning and control limits for blanks (Table 5-3) are based on the laboratory's method detection limits as documented prior to the analysis of samples. A reagent blank concentration between the MDL and 3 times the MDL for one or more of the analytes of interest will serve as a warning limit requiring further investigation based on the best professional judgement of the analyst(s). A reagent blank concentration equal to or greater than 3 times the MDL for one or more of the analytes of interest requires definitive corrective action to identify and eliminate the source(s) of contamination before proceeding with sample analysis.

5.3.3.5 Internal Standards

Internal standards (commonly referred to as "surrogates", "surrogate spikes" or "surrogate compounds") are compounds chosen to simulate the analytes of interest in organic analyses. The internal standard represents a reference analyte against which the signal from the analytes of interest is compared directly for the purpose of quantification. Internal standards must be added to each sample, including QA/QC samples, prior to extraction. The reported concentration of each analyte will be adjusted to correct for the recovery of the internal standard, as is done in the NOAA National Status and Trends Program. The internal standard recovery data therefore will be carefully monitored; each laboratory must report the percent recovery of the internal standard(s) along with the target analyte data for each sample. If possible, isotopically-labeled analogs of the analytes will be used as internal standards.

Control limit criteria for internal standard recoveries are provided in Table 5-3. Each laboratory will set its own warning limit criteria based on the experience and best professional judgement of the analyst(s). It is the responsibility of the analyst(s) to demonstrate that the analytical process is always "in control" (*i.e.*, highly variable internal standard recoveries are not acceptable for repeat analyses of the same certified reference material and for the matrix spike/matrix spike duplicate).

5.3.3.6 Injection Internal Standards

For gas chromatography (GC) analysis, injection internal standards (also referred to as "internal standards" by some analysts) are added to each sample extract just prior to injection to enable optimal quantification, particularly of complex extracts subject to retention time shifts relative to the analysis of standards. Injection internal standards are essential if the actual recovery of the internal standards added prior to extraction is to be calculated. The injection internal standards also can be used to detect and correct for problems in the GC injection port or other parts of the instrument. The compounds used as injection internal standards will be different from those already used as internal standards. The analyst(s) will

monitor injection internal standard retention times and recoveries to determine if instrument maintenance or repair, or changes in analytical procedures, are indicated. Corrective action will be initiated based on the experience of the analyst(s) and not because warning or control limits are exceeded. Instrument problems that may have affected the data or resulted in the reanalysis of the sample will be documented properly in logbooks and internal data reports and used by the laboratory personnel to take appropriate corrective action.

5.3.3.7 Matrix Spike and Matrix Spike Duplicate

A laboratory fortified sample matrix (commonly called a matrix spike, or MS) and a laboratory fortified sample matrix duplicate (commonly called a matrix spike duplicate, or MSD) will be used both to evaluate the effect of the sample matrix on the recovery of the compound(s) of interest and to provide an estimate of analytical precision. A minimum of 5% of the total number of samples submitted to the laboratory in a given year will be selected at random for analysis as matrix spikes/matrix spike duplicates. Each MS/MSD sample is first homogenized and then split into three subsamples. Two of these subsamples are fortified with the matrix spike solution and the third subsample is analyzed as is to provide a background concentration for each analyte of interest. The matrix spike solution will contain all the analytes of interest. The final spiked concentration of each analyte in the sample will be at least 10 times the MDL for that analyte, as previously calculated by the laboratory.

Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the sediment samples analyzed during the project. If the percent recovery for any analyte in the MS or MSD is less than the recommended warning limit of 50 percent, the chromatograms and raw data quantitation reports will be reviewed. If an explanation for a low percent recovery value is not discovered, the instrument response may be checked using a calibration standard. Low matrix spike recoveries may be a result of matrix interferences and further instrument response checks may not be warranted, especially if the low recovery

occurs in both the MS and MSD and the other QC samples in the batch indicate that the analysis was "in control". An explanation for low percent recovery values for MS/MSD results will be discussed in a cover letter accompanying the data package. Corrective actions taken and verification of acceptable instrument response will be included.

Analysis of the MS/MSD also is useful for assessing laboratory precision. The relative percent difference (RPD) between the MS and MSD results will be less than 30 for each analyte of interest (see Table 5-4). The RPD is calculated as follows:

$$RPD = \frac{(C1 - C2)}{(C1 + C2)/2} \times 100$$

where: C1 is the larger of the duplicate results for a given analyte
C2 is the smaller of the duplicate results for a given analyte

If results for any analytes do not meet the RPD < 30% control limit criteria, calculations and instruments will be checked. A repeat analysis may be required to confirm the results. Results which repeatedly fail to meet the control limit criteria indicate poor laboratory precision. In this case, the laboratory is obligated to halt the analysis of samples and eliminate the source of the imprecision before proceeding.

5.3.3.8 Field Duplicates and Field Splits

For the BPTCP, sediment will be collected at each station using a grab sampler. Each time the sampler is retrieved, the top 2 cm of sediment (approximately) will be scraped off, placed in a large mixing container and homogenized, until a sufficient amount of material has been obtained. One blind sample will be collected per leg for analysis.

5.4 OTHER SEDIMENT MEASUREMENTS

The preceding sections presented QA/QC requirements covering laboratory analysis of sediment and fish tissue samples for organics (i.e., PAHs, PCBs and chlorinated pesticides) and inorganics (i.e., metals). In addition to these "conventional" contaminants, the BPTCP laboratories are required to measure several ancillary sediment parameters, such as total organic carbon (TOC), acid volatile sulfide (AVS), and tributyltin (TBT) concentrations. The laboratory QA/QC requirements associated with these "other sediment measurements" are presented in the following sections.

5.4.1 Total Organic Carbon

As a check on precision, each laboratory will analyze at least one total organic carbon (TOC) sample in duplicate for each batch of 25 or fewer samples. Based on typical results attained by experienced analysts, the relative percent difference (RPD) between the two duplicate measurements will be less than 20%. If this control limit is exceeded, analysis of subsequent sample batches will stop until the source of the discrepancy is determined and the system corrected.

At least one certified reference material (CRM) or, if available, one laboratory control material (LCM) will be analyzed along with each batch of 25 or fewer TOC samples. Any one of several marine sediment CRMs distributed by the National Research Council of Canada's Marine Analytical Chemistry Standards Program (*e.g.*, the CRMs named "BCSS-1", "MESS-1" and "PACS-1", see Table 5-6) have certified concentrations of total carbon and are recommended for this use. Prior to analysis of actual samples, it is recommended that each laboratory perform several total organic carbon analyses using a laboratory control material or one of the aforementioned CRMs to establish a control chart (the values obtained by the laboratory for total organic carbon will be slightly less than the certified value for total carbon in the CRM). The control chart then will be

used to assess the laboratory's precision for subsequent analyses of the LCM or CRM with each sample batch. In addition, a method blank will be analyzed with each sample batch. Total organic carbon concentrations will be reported as ug/g (ppm) dry weight of the unacidified sediment sample. Data reported for each sample batch will include QA/QC sample results (duplicates, CRMs or LCMs, and method blanks). Any factors that may have influenced data quality will be discussed in a cover letter accompanying the submitted data, both on paper and in electronic file format (i.e., text file).

5.4.2 Acid Volatile Sulfide

Quality control of acid volatile sulfide (AVS) measurements is achieved through the routine analysis of a variety of QA/QC samples. Prior to the analysis of samples, the laboratory must establish a calibration curve and determine a limit of reliable detection for sulfide for the analytical method being employed. Following this, laboratory performance will be assessed through routine analysis of laboratory duplicates, calibration check standards, laboratory fortified blanks (*i.e.*, spiked blanks), and laboratory fortified sample matrices (*i.e.*, matrix spikes).

One sample in every batch of 25 or fewer samples will be analyzed in duplicate as a check on laboratory precision. Based on typical results attained by experienced analysts, the relative percent difference (RPD) between the two analyses will be less than 20%. If the RPD exceeds 20%, a third analysis will be performed. If the relative standard deviation of the three determined concentrations exceeds 20%, the individual analyses will be examined to determine if non-random errors may have occurred. As previously discussed, field duplicates will also be collected for AVS determination to assess laboratory precision.

Due to the instability of acid volatile sulfides to drying and handling in air, CRMs have not been developed for assessing overall measurement accuracy. Therefore, each laboratory must analyze at least one calibration check standard, one laboratory fortified blank and one laboratory fortified sample matrix in each batch of 25 or fewer samples as a way of determining the accuracy of each step entailed in performing the analysis. The concentration of sulfide in each of these three types of accuracy check samples will be known to the analyst; the calculated concentration of sulfide in each sample will be within 15% of the known concentration.

If the laboratory is not within 15% of the known concentration for the calibration check solution, instruments used for AVS measurement must be recalibrated and/or the stock solutions redetermined by titration. If the laboratory fails to achieve the same accuracy (within 15% of the true value) for AVS in the laboratory fortified blank, sources of error (*e.g.*, leaks, excessive gas flows, poor sample-acid slurry agitation) will be determined for the analytical system prior to continuing. If AVS recovery falls outside the 85% to 115% range for the matrix spike, the system will be evaluated for sources of error and the analysis will be repeated. If recovery remains unacceptable, it is possible that matrix interferences are occurring. If possible, the analysis will be repeated using smaller amounts of sample to reduce the interferant effects. Results for all QA/QC samples (duplicates, calibration check standards, spiked blanks and matrix spikes) will be submitted by the laboratory as part of the data package for each batch of samples, along with a narrative explanation for results outside control limits.

5.4.3 Tributyltin

Assessment of the distribution and environmental impact of tributyltin requires its measurement in marine sediment and tissue samples at trace levels. Quality control of these measurements consists of checks on laboratory precision and accuracy. One laboratory reagent blank must be run with each batch of 25 or fewer samples. A reagent blank

concentration between the MDL and 3 times the MDL will serve as a warning limit requiring further investigation based on the best judgement of the analyst(s). A reagent blank concentration equal to or greater than 3 times the MDL requires corrective action to identify and eliminate the source(s) of contamination, followed by reanalysis of the samples in the associated batch.

One laboratory fortified sample matrix (commonly called a matrix spike) or laboratory fortified blank (*i.e.*, spiked blank) will be analyzed along with each batch of 25 or fewer samples to evaluate the recovery of the butyltin species of interest. The butyltins will be added at 5 to 10 times their MDLs as previously calculated by the laboratory. If the percent recovery for any of the butyltins in the matrix spike or spiked blank is outside the range 70 to 130 percent, analysis of subsequent sample batches will stop until the source of the discrepancy is determined and the system corrected.

The NRCC sediment reference material "PACS-1", which has certified concentrations of the three butyltin species of interest, also will be analyzed along with each batch of 25 or fewer sediment samples as a check on accuracy and reproducibility (*i.e.*, batch-to-batch precision). If values obtained by the laboratory for butyltins in "PACS-1" are not within 30% of the certified values, the data for the entire batch of samples is suspect. Calculations and instruments will be checked; the CRM may have to be reanalyzed to confirm the results. If the values are still outside the control limits in the repeat analysis, the laboratory is required to determine the source(s) of the problem and repeat the analysis of that batch of samples until control limits are met, before continuing with further sample processing.

5.5 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

5.5.1 Sample Tracking

The BPTCP information management personnel have developed a comprehensive system for recording sampling information in the field and tracking sample shipments. Each analytical

laboratory must designate a sample custodian, authorized to check the condition of and sign for incoming field samples, obtain documents of shipment and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the Project Coordinator. Laboratory personnel will be aware of the required sample holding times and conditions (see Table 5-2), and the laboratory must have clearly-defined and documented custody procedures for sample handling, storage, and disbursement.

5.5.2 Data Reporting Requirements

As previously indicated, laboratory personnel will verify that the measurement process was "in control" (i.e., all specified QA/QC requirements were met) for each batch of samples before proceeding with the analysis of a subsequent batch. In addition, each laboratory will establish a system for detecting and eliminating transcription and/or calculation errors prior to reporting data. It is recommended that an individual not involved directly in sample processing be designated as laboratory QA Officer to perform these verification checks independent of day-to-day laboratory operations.

Only data which has met QA requirements will be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed and only the results of the reanalysis will be submitted, provided they are acceptable. Each data package will consist of the following:

- A cover letter, both on paper and in electronic file format, providing a brief description of the procedures and instrumentation used (including the procedure(s) used to calculate MDLs), as well as a narrative explanation of analytical problems (if any) or failure(s) to meet quality control limits.

- Tabulated results in hard copy form, including sample size, wet weight, dry weight, and concentrations of the analytes of interest (reported in units identified to three

significant figures unless otherwise justified). Concentration units will be ng/g or ug/g (dry weight) for sediment or tissue. All data will be double entered to check for accuracy and the report signed by the laboratory manager or designee. The data shall conform to the approved BPTCP Data Base Description.

- Tabulated results in computer-readable form (e.g., diskette) included in the same shipment as the hard copy data, but packaged in a diskette mailer to prevent damage. The data will be submitted to the data processing manager in dBASE 4 format. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted.

- Tabulated method detection limits achieved for the samples.

- Results for all QA/QC samples (*e.g.*, CRMs, calibration check samples, blanks, matrix spike/matrix spike duplicates, etc.) must be submitted by the laboratory as part of the data package for each batch of samples analyzed. **The laboratory must provide a "batch number" as a way to link samples from a given batch or analytical set with their accompanying QA/QC samples. The batch number is described in the Data Base Description and is a field in the dBase database. Each type of analysis (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analyses, TOC and grain size, and AVS) will have it's own unique batch number. In addition, to the batch number field, another field will be included in all data sets (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analyses, TOC and grain size, and AVS) that lists the file names that contain the summarized QA data and any text describing the data (metadata) for that sample. This field is also described in the database. The laboratory will denote QA/QC samples using the codes (abbreviations) and reporting units specified in Table 5-6. This field is described in the database**

description and will be entered into each of the data sets by each of the laboratories.

Laboratories are responsible for assigning only two data qualifier codes or "flags" to the submitted data. If an analyte is not detected, the laboratory will report the result as **-8.** If a quantifiable signal is observed, the laboratory will report a concentration for the analyte; the data qualifier code -9 then will be used to flag any reported values which are below the laboratory's MDL. The -9 code has the following meaning: "The reported concentration is below or equal to the detection limit. The detection limit (MDL) is reported as a separate variable."

TABLE 5-6. Codes for denoting QA/QC samples in submitted data packages.

Code	Description	Unit of Measure
CLC	Continuing Calibration Check Sample	Percent recovery
LRB	Lab Reagent Blank	varies
LCM	Lab Control Material	ug/g or ng/g dry wt.
LCMPR	Lab Control Material % Recovery	Percent Recovery
LF1	Lab Spiked Sample- 1st Member	ug/g or ng/g dry wt.
LF1PR	Lab Spiked Sample- 1st Mem. % Rec.	Percent Recovery
LF2	Lab Spiked Sample- 2nd Member	ug/g or ng/g dry wt.
LF2PR	Lab Spiked Sample- 2nd Mem. % Rec.	Percent Recovery
MSDRPD	Rel % Difference: LF1 to LF2	Percent
LFB	Lab Fortified Blank	Percent Recovery
LSFPR	Lab Spiked Sample % Rec.	Percent Recovery
LDRPD	Lab Duplicate Relative % Diff.	Percent
MDL	**Method Detection Limit**	**ug/g or ng/g dry wt.**
FB	**Field Blank**	**ug/g or ng/g dry wt.**
FR	**Field Replicate**	**ug/g or ng/g dry wt.**

There may be a limited number of situations where sample re-analysis is not possible or practical (*i.e.*, minor exceedance of a single control limit criteria). The laboratory is expected to provide a detailed explanation of any factors affecting data quality or interpretation; this explanation will be in the form of a cover letter, both on paper and in electronic file format (i.e., text file) accompanying each submitted data package. The narrative explanation is in lieu of additional data qualifier codes supplied by the laboratory (other than the -8 and -9 codes). The QAQC tables are referenced in the data base containing the data for the program in a separate field. Each sample will have a separate entry (stored in the main database as a separate field) that links it to the QAQC summary database files for that sample.

5.5.3 Data Evaluation Procedures

It is the responsibility of the Project Coordinator to acknowledge initial receipt of the data package(s), verify that the four data evaluation steps identified in the following paragraph are completed, notify the analytical laboratory of any additional information or corrective actions deemed necessary as a result of the Project Coordinator's data evaluation and, following satisfactory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for a team of individuals (e.g., the Project Coordinator, the QAQC Officer, and/or analytical chemists) to assist the Project Coordinator in technical evaluation of the submitted data packages. While the Project Coordinator has ultimate responsibility for maintaining official contact with the analytical laboratory and verifying that the data evaluation process is completed, it is the responsibility of the Project QA Officer to closely monitor and formally document each step in the process as it is completed. This documentation will be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist will be supplemented with detailed memos to the project file outlining any

concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package will commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten and (if holding times have been exceeded) can sometimes limit options for reanalysis. The following steps are to be followed and documented in evaluating BPTCP chemistry data:

1) Checking data completeness (verification)
2) Assessing data quality (validation)
3) Assigning data qualifier codes
4) Taking final actions

The specific activities required to complete each of these steps are illustrated in Figure 5-1 and described in the following sections, which are adopted in large part from the document "A Project Manager's Guide to Requesting and Evaluating Chemical Analyses" (EPA 1991).

5.5.3.1 Checking Data Completeness

The first part of data evaluation is to verify that all required information has been provided in the data package. The steps to be followed in the assessment and evaluation of BPTCP chemistry data will be in accordance with EPA procedures (U.S. EPA, 1991). In the BPTCP, this will include the following specific steps:

- Project coordinator will verify that the package contains the following: narrative explanations signed by the laboratory manager, hard copies of all results (including QA/QC results), and accompanying computer diskettes.

- The electronic data file(s) will be parsed and entered into the BPTCP database to verify that the correct format has been supplied.

- Once the data have been entered into the DFG BPTCP database, automated checks will be run to verify that results have been reported for all expected samples and all analytes.

The Project Coordinator will contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory will provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

5.5.3.2 Assessing Data Quality

Data validation, or the process of assessing data quality, can begin after BPTCP personnel have determined that the data package is complete. Normally, the first major part of validation involves checking 100-percent of the data for any possible errors resulting from transcription of tabulated results, misidentification or miscalculations. However, BPTCP laboratories are expected to submit data which already has been tabulated and checked 100% for accuracy (by double entry or verification), and the raw data reports needed by BPTCP personnel to perform these checks (e.g., chromatograms, original quantitation reports) are not submitted as part of the data package. The laboratory is required to maintain this raw data in an orderly manner and to have these records available for review by BPTCP personnel upon request (i.e., the data may be audited at any time following appropriate notification of the laboratory). The first-step validation checks performed by BPTCP personnel will be limited to the following: 1.) a check to verify that all reporting units and numbers of significant figures are correct; 2.) a check to verify that all of the laboratory's calculated percent recovery values (for calibration check samples, Laboratory Control Materials, and matrix spikes) and relative percent difference values (for duplicates) are correct; and 3.) a check to verify that the reported concentrations for each analyte fall within "environmentally-realistic" ranges, determined from previous studies and expert judgement. In addition, past studies indicate that the different compounds in each class of chemicals

being measured in BPTCP samples (e.g., PAHs, PCBs, DDTs and other chlorinated pesticides) typically occur in the environment in somewhat fixed ratios to one another. For example, the DDT breakdown products p,p DDD and p,p DDE typically can be expected to occur at higher concentrations than p,p DDT in estuarine sediments of the East Coast. If anomalous departures from such expected ratios are found, it may indicate a problem in the measurement or data reduction process requiring further investigation.

The second major aspect of data validation is to compare the QA/QC data against established criteria for acceptable performance, as specified earlier in this plan. This will involve the following specific steps:

1) Results for QA/QC samples will be tabulated, summarized and evaluated. Specifically, a set of summary tables will be prepared from the BPTCP database showing the percent recovery values and relative percent difference values (where applicable) for the following QA/QC samples: continuing calibration check samples, laboratory control material(s), and **matrix spike/matrix spike duplicate samples.** The tables will indicate the percent recovery values for these samples for each individual batch of samples, as well as the average, standard deviation, coefficient of variation, and range for all batches combined. These tables are also supplied in a dBase format or spreadsheet format under a separate file name that is referenced in the main data base containing the raw data.

2) Similar summary tables will be prepared for the laboratory reagent blank QA/QC samples.

3) The summary results, particularly those for the Laboratory Control Material (i.e., Certified Reference Material), will be evaluated by comparing them against the QA/QC warning and control limit criteria for accuracy, precision, and blank contamination specified in Table 5-4.

4) Method detection limits reported by the laboratory for each analyte will be tabulated and compared against the target values in Table 5-5.

There are several possible courses of action to be taken if the reported data are found to be deficient (i.e., warning and/or control limits exceeded) during the assessment of data quality:

1) The laboratory's cover letter (narrative explanation) will be consulted to determine if the problems were satisfactorily addressed.

2) If only warning limits were exceeded, then it is appropriate for the laboratory to report the results. Exceedance of control limits, however, will result in one of the following courses of action: 1) all associated results will be qualified in the database as estimated values (as explained in the following section), or 2) the data will be rejected and deleted from the database because the analysis was judged to be out of control (based on the professional judgement of the reviewer). Rejection of data due to failure of the laboratory's quality control system could ultimately result in disqualification of the laboratory from further participation in the BPTCP program.

5.5.3.3 Assigning Data Qualifier Codes

Data qualifier codes are notations used by laboratories and data reviewers to briefly describe, or qualify, data and the systems producing data. As previously indicated, BPTCP laboratories are expected to assign only two data qualifier codes ("-8" and "-9") to data values before submitting them to the program. BPTCP data reviewers, in turn, will assign an additional data qualifier code in situations where there are exceedances of control limit criteria. The most typical situation is when a laboratory fails to meet the accuracy control limit criteria for a particular analyte in a Certified Reference Material or matrix spike sample. In these situations, the QA reviewer will verify that the laboratory did meet the control limit criteria for precision. If the lack of accuracy is found to be consistent (i.e., control limit criteria for precision were met), then it is likely that the laboratory experienced

a true bias for that particular analyte. In these situations, all reported values for that particular analyte will be qualified with a "-7" code. The "-7" code has the following meaning: "The reported concentration is considered an estimate because control limits for this analyte were exceeded in one or more quality control samples." The metal data qualifier field may have a code such as (-7, Pb) if some error in measurement is expected.

Because some degree of expert judgement and subjectivity typically is necessary to evaluate chemistry QA/QC results and assign data qualifier codes, data validation will be conducted only by qualified personnel. It is the philosophy of the program that data which are qualified as estimates because of minor exceedance of a control limit in a QA/QC sample ("-7" code) are still usable for most assessment and reporting purposes. However, it is important to note that all QA/QC data will be readily available in the database along with the results data, so that interested data users can make their own estimation of data quality.

5.5.3.4 Taking Final Action

Upon completion of the above steps, a report summarizing the QA review of the data package will be prepared, samples will be properly stored or disposed of, and laboratory data and accompanying explanatory narratives will be archived both in a storage file and in the database. Technical interpretation of the data begins after the QA review has been completed.

Reports documenting the results of the QA review of a data package will summarize all conclusions concerning data acceptability and will note significant quality assurance problems that were found. These reports are useful in providing data users with a written record on data concerns and a documented rationale for why certain data were accepted as estimates or were rejected. The following specific items will be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.
- Brief descriptions of analytical methods and the method(s) used to determine detection limits.

- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.
- Descriptions of initial and ongoing calibration results, blank contamination, and precision and bias relative to QA plan objectives (including tabulated summary results for Certified Reference Materials and matrix spike/matrix spike duplicates).

SECTION 6

SEDIMENT PARTICLE SIZE ANALYSIS

[Subject to Modification in early 1994]

6.1 OVERVIEW

Particle size is used to characterize the physical characteristics of sediments. Because particle size influences both chemical and biological variables, it can be used to normalize chemical concentrations according to sediment characteristics and to account for some of the variability found in biological assemblages and toxicity testing. For the BPTCP only the percent fines (silt+clay) will be determined for the particle size samples using the dry sieve method (DFG, 1992).

6.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING TIME

BPTCP protocols for collecting particle size samples are described in detail in the DFG QAQC manual. Samples will be from aliquots of the homogenate supplied to all laboratories. **A minimum sample size of 100 grams is recommended. Samples will be held and shipped on ice (NOT dry ice) and may be stored at 4°C for up to one year before analysis. Samples must not be frozen or dried prior to analysis, as either process may change the particle size distribution.**

6.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

Quality control of sediment particle size analysis is accomplished by strict adherence to protocol and documentation of quality control checks. Certain procedures are critical to the collection of high quality data. For example, it is essential that each sample be homogenized thoroughly in the laboratory before a subsample is taken for analysis. Laboratory

homogenization will be conducted even if samples were homogenized in the field. Furthermore, all screens used for dry sieving must be clean before conducting analysis, and all of the sample must be retrieved from them. To clean a screen, it should be inverted and tapped on a table, while making sure that the rim hits the table evenly. Further cleaning of brass screens may be performed by gentle scrubbing with a stiff bristle nylon brush. Stainless steel screens may be cleaned with a nylon or brass brush.

The analytical balance, drying oven, sieve shaker, and temperature bath used in the analysis will be calibrated at least monthly. Dried samples will be cooled in a desiccator and held there until they are weighed. If a desiccator is not used, the sediment will accumulate ambient moisture and the sample weight will be overestimated. A color-indicating desiccant is recommended so that spent desiccant can be detected easily. Also, the seal on the desiccator will be checked periodically, and, if necessary, the ground glass rims will be greased or the "O" rings will be replaced.

The most critical aspect of the pipet analysis is knowledge of the temperature of the silt-clay suspension. An increase of only 1°C will increase the settling velocity of a particle 50 μm in diameter by 2.3 percent. It is generally recommended that the pipet analysis be conducted at a constant temperature of 20°C. However, Plumb (1981) provides a table to correct for settling velocities at other temperatures. If the mass of sediment used for pipet analysis exceeds 25 g, a subsample will be taken as described by Plumb (1981). Silt-clay samples in excess of 25 g may give erroneous results because of electrostatic interactions between the particles. Silt-clay samples less than 5 g yield a large experimental error in weighing relative to the total sample weight. Thorough mixing of the silt-clay suspension at the beginning of the analysis also is critical. A perforated, plexiglass disc plunger is very effective for this purpose. Once the pipet analysis begins, the settling cylinders must not be disturbed, as this will alter particle settling velocities. Care must be taken to disturb the sample as little as possible when

pipet extractions are made. A supplemental analysis for percent clay and percent silt will be done on some samples using the pipet analysis technique (DFG, 1992).

Quality control for the sediment analysis procedures will be accomplished primarily by reanalyzing a randomly selected subset of samples from each batch. A batch of samples is defined as a set of samples of a single textural classification (*e.g.*, silt/clay, sand, gravel) processed by a single technician using a single procedure. **Approximately 10% of each batch completed by the same technician will be reanalyzed (*i.e.*, reprocessed) in the same manner as the original sample batch. Based on results typically attained by experienced technicians, if the absolute difference between the original value and the second value is greater than 10% (in terms of the percent of the most abundant sediment size class), then a third analysis will be completed by a different technician. The values closest to the third value will be entered into the database. In addition, all the other samples in the same batch must be re-analyzed, and the laboratory protocol and/or technician's practices will be reviewed and corrected to bring the measurement error under control. If the percent of the most abundant sediment size class in the original sample and the reanalyzed sample differs by less than 10, the original value will not be changed and the sediment analysis process will be considered in control.**

Additional quality control for particle size analyses will be accomplished by reanalyzing samples that fail either a range check or recovery check. For the range check, any sample results that fall outside expected ranges (i.e., any percentage that totals greater than 100%) will be reanalyzed. For the recovery check, if the total weight of the recovered sands is 10% (by weight) less or greater than the starting weight of sands, the sample must be reanalyzed.

6.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

6.4.1 Sample Tracking

The laboratory responsible for processing the sediment particle size samples must designate a sample custodian, authorized to check the condition of and sign for the incoming field samples, obtain documents of shipment and verify sample custody records. This individual is required, upon receipt of samples, to record and transmit all tracking information to the BPTCP project coordinator. Laboratory personnel will be aware of the required sample holding times and conditions for particle size samples, and there will be clearly-defined custody procedures for sample handling, storage, and disbursement in the laboratory.

6.4.2 Data Reporting Requirements and Evaluation Procedures

The weight of each sediment fraction will be reported to the nearest 0.01 gram dry weight. The laboratory will report the results for all samples analyzed (including QC duplicates) both in hard copy and in a computer-readable format specified by the BPTCP Project Coordinator. In addition, both the paper and electronic data packages will include a cover letter with a summary of all quality control checks performed and a narrative explanation of any problems that may have influenced data quality. The report submitted to the BPTCP coordinator shall include the following:

- A cover letter, both on paper and in electronic file format, providing a brief description of the procedures and instrumentation used as well as a narrative explanation of analytical problems (if any) or failure(s) to meet quality control limits.

- Tabulated results in hard copy form including concentrations of the analytes of interest (reported in units identified to three significant figures unless otherwise justified). Concentration units will be % (dry weight). All data will be double entered to check for accuracy and the report signed by the laboratory manager or designee. The data shall conform to the approved BPTCP Data Base Description.

- Tabulated results in computer-readable form (e.g., diskette) included in the same shipment as the hard copy data, but packaged in a diskette mailer to prevent damage. The data will be submitted to the data processing manager in dBase 4 format. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted.

The Project Coordinator will acknowledge initial receipt of the data package(s), verify that the four data evaluation steps identified in the following paragraph are completed, notify the laboratory of any additional information or corrective actions deemed necessary as a result of the BPTCP's data evaluation and, following satisfactory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for the Project coordinator to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. The Project Coordinator will monitor and formally document each step in the data evaluation process as it is completed. This documentation will be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist will be supplemented with detailed memos to the electronic and paper project files outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package will commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten and (if holding times have been exceeded) can sometimes limit options for reanalysis. The first part of data evaluation is to verify that all required information has been provided in the data package. In the BPTCP, this will include the following specific steps:

- Project personnel will verify that the package contains a cover letter signed by the laboratory manager, hard copies of all results (including QA/QC results), and accompanying computer diskettes.

- The electronic data file(s) will be parsed and entered into the BPTCP project database to verify that the correct format has been supplied.

- Once the data have been transferred to the project database, automated checks will be run to verify that results have been reported for all expected samples and all analytes.

The Project Coordinator will contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory will provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Data validation, or the process of assessing data quality, will begin after project personnel have determined that the data package is complete. Data validation for particle size data will consist of the following: 1.) a check to verify that all reporting units and numbers of significant figures are correct; 2.) a check to verify that the cumulative percentage of each particle size fraction never exceeds 100% (i.e., a failed range check); 3.) a check to verify that the results for duplicate samples do not differ by more than 10%; and 4.) the relative standard deviation (RSD) for the three particle size samples obtained at each station will be calculated. For any station having an RSD greater than 20%, all raw data and calculations will be checked by the laboratory to ascertain that the difference truly reflects natural spatial variability among the three grab samples and not measurement error.

6.4.3 Assigning Data Qualifier Codes and Taking Final Action

Data qualifier codes are notations used by laboratories and data reviewers to briefly describe, or qualify, data and the systems producing data. All QA/QC data associated with particle size analyses will be readily available in the database along with the results data, so that interested data users can perform their own assessments of data quality.

Upon completion of all data evaluation steps, a report summarizing the QA review of the data package will be prepared, samples will be properly stored or disposed of, and laboratory data will be archived both in a storage file and in the database. Reports documenting the results of the QA review of the data package will summarize all conclusions concerning data acceptability and will note significant quality assurance problems that were found. These reports are useful in providing data users with a written record of data concerns and a documented rationale for why certain data were accepted as estimates or were rejected. The following specific items will be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.
- Brief descriptions of sample collection and analysis methods.
- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.

SECTION 7

MARINE TOXICITY TESTING

[Subject to Modification in early 1994]

7.1 OVERVIEW

The process for relying on toxicity assessment to identify Toxic Hot Spots is described briefly in the Introduction of this document. A more thorough discussion follows. First, existing data (State Mussel Watch, sediment chemistry, and toxicity) are reviewed for the likely presence and absence of toxicity. Screening of these sites (and others selected at random or likely to be degraded and nondegraded) follows and consists of application of a battery of toxicity tests (bedded sediment, pore water, and overlying water) on single replicates. Because determination of hot spot status using toxicity testing requires recurrent toxicity associated with chemical contamination, sediment chemistry analysis is also performed during screening. Once initial data review and screening are completed, a survey is performed to ensure that adequate numbers of nontoxic (reference) sites are available for each TOC/grain size stratum. Once sufficient numbers and types of reference sites are identified, confirmation sampling is performed on groups of reference and potential toxic hot spots (sediment chemistry is repeated and three field replicates are sampled). Subsequent statistical analysis is applied to these data to determine whether distinctions exist between reference sites and suspect hot spots and whether these distinctions are associated with chemical contamination within strata. The remainder of this section presents QA/QC protocols and requirements for toxicity testing, from sample collection and laboratory analysis to validation of the resultant data.

7.2 PROJECT DESCRIPTION

7.2.1 Objective and Scope Statement

Toxicity is assessed using a number of standardized solid-phase sediment, pore water, and elutriate toxicity tests. The Marine Pollution Studies Laboratory (MPSL) at Granite Canyon is conducting water and sediment toxicity tests using species specified by the Project Manager; candidate species are listed below. The test organisms are exposed to water or sediment samples in the laboratory, and any resulting detrimental effects are quantified, giving a numerical estimate of the sample toxicity.

7.2.2 Data Usage

Laboratory toxicity estimates give an indication of the potential threat to aquatic organisms posed by the contaminated water or sediments. Correlation of toxicity data with matching chemical data from split samples allows identification and measurement of contaminants that may be harmful to aquatic life. Potential hotspots identified by this project will be further investigated to determine the areal extent of contamination and to guide remediation efforts.

7.2.3 Technical Approach

Sediment toxicity testing at MPSL will follow standardized procedures for each organism, as specified in accepted published protocols.

7.2.3.1 Solid Phase Toxicity Tests

Solid phase toxicity tests will be conducted by placing test organisms in contact with whole sediments in test chambers filled with clean dilution water. Candidate test species and protocols for solid phase toxicity tests include:

Amphipods: *Rhepoxinius abronius* (ASTM, 1991)
Eohaustorius estuarius (DeWitt et al., 1989)
Hyalella azteca (Nebecker et al., 1984)
Ampelisca abdita (Valente and Strobel, 1993)

Polychaetes: *Neanthes arenaceodentata* (Johns et al., 1990)

7.2.3.2 Interstitial (Pore) Water Toxicity Tests

The toxicity of interstitial water has been shown to closely correlate with that of whole sediments. Interstitial waters contain the water soluble fractions of sediment contaminants, and are generally considered to be the primary route of exposure for aquatic organisms in contaminated sediments (although ingestion may be the primary route for some species). Interstitial water is extracted in small volumes by squeezing or centrifuging whole sediment. Toxicity tests on interstitial water use water column organisms with protocols modified for small test solution volumes. A number of test protocols using water column organisms have been identified for use in regulating discharges to marine water portions of bays and estuaries. These protocols are listed in the State Water Quality Control Plans for Enclosed Bays and Estuaries of California and are indicated with an asterisk* in the following lists. The following is a list of organisms that have either been used previously in interstitial water tests or are easily adaptable to small test solution volumes ($\leq$ 10 ml) for interstitial water testing. The citations refer to the protocols to be used at MPSL.

Bivalve larvae	**Crassostrea gigas* (ASTM, 1987; Tetra Tech, 1986; Chapman & Morgan, 1983)
	**Mytilus edulis* (ASTM, 1987)
Abalone larvae	**Haliotis rufescens* (Anderson et al., 1990)
Echinoderm fertilization	**Strongylocentrotus* spp. (Dinnel et al. 1987, with modifications by EPA, 1992)
Giant Kelp	**Macrocystis pyrifera* (Anderson et al, 1990)
Red Alga	**Champia* (Weber et al., 1988)
Fish Embryos	*Atherinops* (Anderson et al., 1990)

**Menidia* (Middaugh et al.,1988)

Pimephales (Spehar et al., 1982)

Cladocerans *Daphnia* (Nebecker et al., 1984)

Cereodaphnia (Mount and Norberg, 1984; Horning and Weber, 1985)

7.2.3.3 Ambient Water Toxicity Tests

Monitoring of toxic hotspots in the BPTCP includes evaluation of ambient water column toxicity. A number of test protocols using water column organisms have been identified for use in regulating discharges to marine water portions of bays and estuaries. These protocols are listed in the State Water Quality Control Plans for Enclosed Bays and Estuaries of California and are indicated with an asterisk* in the following list. The following are the organisms (and protocols) to be used at MPSL to test for ambient water column toxicity.

Bivalve larvae *Crassostrea gigas* (ASTM, 1987; Tetra Tech, 1986; Chapman and Morgan, 1983)

Mytilus edulis (ASTM, 1987)

Abalone larvae *Haliotis rufescens* (Anderson et al., 1990)

Echinoderm fertilization *Strongylocentrotus* spp. (Dinnel et al. 1987, with modifications by EPA, 1992)

Giant Kelp *Macrocystis pyrifera* (Anderson et al, 1991)

Red Alga *Champia* (Weber et al., 1988)

Mysid	*Holmesimysis* (Hunt et al., 1992)
Fish Embryos	*Atherinops* (Anderson et al., 1990)
	**Menidia* (Middaugh et al.,1988)
	Pimephales (Spehar et al., 1982)
Fish Larvae	*Atherinops* (Anderson et al., 1990)
	Menidia (Peltier and Weber, 1985; Weber et al., 1988)
	Pimephales (Peltier and Weber, 1985; Weber et al., 1988)
Cladocerans	*Daphnia* (Nebecker et al., 1984)
	Ceriodaphnia (Mount and Norberg, 1984; Horning and Weber, 1985)

7.2.4 Monitoring Parameters and Collection Frequency

The parameters to be measured, their frequency of measurement, references and other information are given in Table 1.

Table 7-1. Monitoring Parameters

Parameter	Sampling Frequency	Test Replicate Sampled	Immediate Processing or Measurement	Reference
Rhepoxinius				
Emergence	Daily	All Chambers	Record number emerged	Tetra Tech, 1986
Survival	Termination	All Chambers	Record	
Eohaustorius				
Emergence	Daily	All Chambers	Record number emerged	Tetra Tech, 1986
Survival	Termination	All Chambers	Record	
Hyalella				
Emergence	Daily	All Chambers	Record number emerged	Nebecker, 1984
Survival	Termination	All Chambers	Record	
Neanthes				
Survival	Termination	All Chambers	Record	Johns et al., 1990
Initial Ind. Wt.	Initiation	3 groups of 5	Record	
Final Total Wt.	Termination	All Chambers	Record and divide by # to get mean individual wt.	
Bivalve larvae				
Normal shell development	Termination	All chambers	Fix larvae in formalin, examine w/microscope, record number normal and abnormal	ASTM, 1987 Tetra Tech, 1986
Haliotis				
Normal shell development	Termination	All chambers	Fix larvae in formalin,	Anderson, 1990
Echinoderm Fertilization				
Presence of Fertilization Membrane	Termination	All Chambers	Fix eggs/embryos in formalin, examine microscopically, record number fertilized and unfertilized	Dinnel et al.1987 modified as in EPA, 1992
Macrocystis				
Germination	Termination	All Chambers	Examine microscopically and record	Anderson, 1990
Growth	Termination	All Chambers	Measure with ocular micrometer	
Champia				
Cystocarp production	Termination	All Chambers	Examine microscopically and record	Weber et al 1988
Holmesimysis				
Survival	Daily	All Chambers	Count and remove dead	Hunt et al., 1992
Growth	Termination	All Chambers	Examine microscopically and measure length	

Table 7-1. Monitoring Parameters (Continued)

Parameter	Sampling Frequency	Test Replicate Sampled	Immediate Processing or Measurement	Reference
Atherinops				
Survival	Daily	All chambers	Record number survive, remove dead.	Anderson, 1990
Dry weight	After 7 day	All chambers	Dry surviving larvae, weigh, record to nearest 0.1 mg	
Menidia beryllina				
Survival	Daily	All chambers	Record number survive, remove dead.	Weber et al 1988 Peltier and Weber
Dry weight	After 7 day	All chambers	Dry surviving larvae, weigh, record to nearest 0.1 mg	1985
Pimephales				
Survival	Daily	All chambers	Record number survive, remove dead.	Weber et al 1988 Peltier and Weber
Dry weight	After 7 day	All chambers	Dry surviving larvae, weigh, record to nearest 0.1 mg	1985
Daphnia				
Adult Survival	Daily	All Chambers	Record number survive, remove dead.	Nebecker, 1984
Number of live young	Daily	All Chambers	Record and remove.	
Total live young	Termination	All Chambers	Sum and Record	
Most young by any one adult	Termination	All Chambers	Sum and Record	
Cereodaphnia				
Adult Survival	Daily	All Chambers	Record number survive, remove dead.	Mount and Norberg, 1984;
Number of live young	Daily	All Chambers	Record and remove.	Horning and Weber, 1985
Total live young	Termination	All Chambers	Sum and Record	
Most young by any one adult	Termination	All Chambers	Sum and Record	
All Tests				
Reference Toxicant	Beginning and end of test	Stock solution and highest concentration	Pour into clean 30 ml polyethylene vial, acid. w/1% Q-dist. HNO_3	Anderson et al., 1990; Bruland et al., 1979

Table 7-1. Monitoring Parameters (Continued)

Parameter	Sampling Frequency	Test Replicate Sampled	Immediate Processing or Measurement	Reference
Total ammonia (unionized NH_3 can be calculated based on pH)	Test start & end	Overlying water in test chamber	Record nearest 1 mg/L (if between 1 and 10) Record nearest 0.1 mg/L (when < 1.0)	APHA, 1985 Sec. 417E
Dissolved oxygen	0, 48, 96, and 144 h	Overlying water, pore water, and elutriate; one replicate of each sample	Record to nearest 0.01 mg/L	APHA, 1985 Sec. 421F
pH	0, 48, 96, and 144 h	One replicate of each sample	Record to nearest 0.01 pH unit	APHA, 1985 Sec. 423
Salinity	0, 48, 96, and 144 h	One replicate of each sample	Record to nearest 1 ‰	Anderson et al., 1990
Temperature	0, 48, 96, and 144 h	One replicate of each sample, and water bath	Record to nearest 0.5°C	Anderson et al., 1990

7.3 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

This section describes methods used at MPSL to determine the precision, accuracy, representativeness, comparability, and completeness of data generated in toxicity studies. The primary data generated in toxicity testing is the degree of response observed in test organisms exposed to environmental samples or toxicant compounds, although secondary data such as dissolved oxygen concentration are also collected.

The degree to which toxicity test data can be used to adequately assess the effects of contaminants in the field is determined by study design, sample handling, measurement error, and appropriate statistical analysis. All field sites, regardless of contamination, vary in a number of characteristics, including sediment grain size, total organic carbon (TOC) content, oxidation state, and infaunal assemblage. In order to resolve differences due to contamination, the natural variation among uncontaminated reference sites must be determined. Samples from reference sites are tested to characterize inherent site variability, and to establish a benchmark against which to compare contaminated sites. In addition to reference samples, control samples are also tested. Tests conducted on control water or sediments serve to verify the health of the test organisms and assure the proper maintenance of test conditions such as lighting, temperature, organism handling, and cleanliness of test equipment. When amphipods are used as test organisms, control sediments (often called "home sediments") are collected at the same time and place as the test organisms. With other infaunal test organisms, control sediments may also be "artificial", such as silica particles of appropriate grain size, or they may be collected at remote sites with a well documented history of low toxicity. In aqueous tests, controls are samples of clean laboratory dilution water. Data from tests on control samples are used primarily for quality assurance purposes to determine whether the tests meet test acceptability criteria.

Outlined below are the quantitative data quality objectives (DQOs), and the equations used to calculate accuracy, precision, and completeness of the data.

7.3.1 Data Quality Objectives

7.3.1.1 Precision

Toxicity test precision can be estimated by comparing: 1) the variation among laboratory replicates of each sample, and 2) the results of multiple tests using reference toxicants. Depending on the protocol used and the goals of the study, three to five laboratory replicates are analyzed for each sample tested. There are no established criteria for acceptable levels of between-replicate variability, but standard deviations can be compared to those produced in similar studies to gauge the precision of test data.

Reference toxicant tests are used to verify the sensitivity of the test organisms by measuring their response to a dilution series of a toxicant for which there is sufficient previous information to establish an expected response. Since the toxicity of the reference material is assumed to be constant, the results of reference toxicant tests can be used to determine the precision of the test system, as described below. Reference toxicant tests will be performed for all tests, using water only as the test medium. (Solid phase reference toxicant tests are not conducted in this study because insufficient information is available on spiking techniques and expected responses of test organisms.)

For each reference toxicant test, a point estimate is generated which indicates the reference toxicant concentration corresponding to a given level of effect. For tests using a lethal endpoint, the trimmed Spearman-Karber method is used to generate a median lethal concentration (LC_{50}) as the point estimate. For tests using a sublethal dichotomous endpoint, such as percent normal larval shell development, the trimmed Spearman-Karber method is used to generate the median effective concentration (EC_{50}) as the point estimate. For tests using a sublethal continuous endpoint, such as growth inhibition, the EPA Inhibition Concentration percentage (ICp) statistical program is used to generate the median inhibition concentration (IC_{50}) as the point estimate. Toxicity test precision (P) is given as the coefficient of variation (CV) among repetitive reference toxicant test point estimates. The CV is the standard deviation (sd) divided by the mean (X) of multiple point estimates.

$$P = CV = \backslash|F(sd,X)\ (100\%).$$

Acceptability of reference toxicant test precision has not been specified for all test protocols to be used in this project. In general, toxicity test precision of 40% or less is considered acceptable (Rue, et al., 1988). The coefficient of variation for all reference toxicant tests performed as part of this project will be reported as an estimate of test precision.

Precision of dissolved oxygen, pH, salinity, and temperature will be determined as the CV of triplicate measurements. Triplicate measurements will be taken at the beginning of each series of measurements and on a minimum of 5% of all samples measured. If the CV exceeds 5% for any of the above parameters, the analyses conducted since the previous triplicate analysis will be repeated.

7.3.1.2 Accuracy

Toxicity test accuracy cannot be determined, because there is no "true" or "correct" response against which to compare the results of a toxicity test. All organisms are inherently different in their response to contaminants, and organisms cannot be calibrated against standards. There are no data quality objectives for toxicity test accuracy.

Accuracy of water quality parameter measurements will be assessed on a regular basis at the beginning and end of each set of measurements by comparing the measured value of a standard against the known value of the standard. Accuracy will be expressed in terms of the relative error as the percent deviation of the measured value from the known value. Accuracy is calculated as follows:

$$RPD = \backslash|F([V_m - V_k],V_k) \times 100\%$$

where: RPD = the relative percent difference

Vm = the measured value,

Vk = the known value.

If an RPD value for dissolved oxygen, pH, salinity, and temperature measurement exceeds 10%, the measurements conducted since the previous accuracy check will be repeated.

7.3.1.3 Representativeness

The degree to which laboratory toxicity measurements represent actual effects of contaminated sediments to exposed organisms in the field is determined by a number of factors, including: sampling design, number and characteristics of reference sites (see above), sampling gear, sample handling, test species used, and exposure time. All of these factors have been determined for this project by personnel external to the Marine Pollution Studies Laboratory.

7.3.1.4 Comparability

Comparability of toxicity data is based on knowledge of the species used, the test conditions, and the results of concurrent reference toxicant tests. Standard species and protocols will be used in this study, and test conditions of temperature, salinity, pH, and dissolved oxygen will be controlled and monitored during the course of the toxicity tests. Reference toxicant tests (positive controls) using standard toxicants will be conducted concurrently to assess the relative sensitivity of the test organisms. Control seawater and control sediments (negative controls) will be used to determine the "blank" response of the test organisms used. By generating and documenting the above information during this study, the toxicity of samples tested at MPSL can be compared to that of other samples elsewhere if the other samples are tested using the same standard species, protocols, and reference toxicants.

7.3.1.5 Completeness

We anticipate that all of the samples received at our laboratory will be tested. There are a number of components that must be successfully completed in order to generate acceptable toxicity data for each sample, including: acceptable control response, acceptable reference

toxicant test results, acceptable levels of variation in test conditions, and dependable supply of suitable test organisms. Since only some test species for this project are cultured at our facility (others are purchased commercially), and because of the vagaries of dealing with test organisms in the laboratory, we expect some level of test failure, which we estimate at 20%. For this reason we have requested an additional sample from each site to allow us to retest any samples that are not successfully tested initially. We anticipate a completeness percentage of 95% given sufficient sediment to allow one retest of each sample if necessary. Because of constraints on sample collection, retested sediments will be older than originals. We will test sediments only if they have been properly stored for a period of not longer than six weeks.

7.4 SAMPLING AND LABORATORY PROCEDURES

Sampling for this project is being conducted by others (see project organization chart, Section 2). General laboratory procedures are referenced in Section 3B. Standard operating procedures are on file or under development at the Marine Pollution Studies Laboratory at Granite Canyon.

7.5 SAMPLE CUSTODY PROCEDURES

Sample labelling and custody procedures have been developed by the State Mussel Watch sample collection team. Samples of chain of custody forms are available in the Quality Assurance Project Plan for sampling.

At the Marine Pollution Studies Laboratory, the QA/QC Officer is responsible for custody of all incoming samples. The QA/QC Officer maintains the chain of custody records, which are photocopied and maintained in separate original and back-up copy files. The QA/QC Officer maintains the sample tracking log that follows all samples through all stages of laboratory handling and analysis. The sample tracking log includes sample identification numbers, location and condition of storage, date and time of each removal and return to

storage, the signature of the person removing and returning samples, and the final disposition of samples. All custody forms and sample log entries are independently verified at the end of each test run. All sample custody information is cross checked before data is released in reports to DFG and the State Board. Original chain-of-custody records, sample tracking logs, data report sheets, and quality control records will be sent to DFG when data is reported. Copies will be kept at MPSL.

7.6 CALIBRATION PROCEDURES AND PREVENTATIVE MAINTENANCE

Calibration procedures at the Marine Pollution Studies Laboratory are necessary for five types of equipment used in the project. There are no preventative maintenance schedules for any analytical equipment used in the project.

7.6.1 Calibration

Dissolved oxygen and pH are measured using an Orion EA 940 expandable ion analyzer. The oxygen probe is zeroed electronically and calibrated against water-saturated air before each series of measurements, as recommended by the manufacturer. Manufacturer's stated relative accuracy for dissolved oxygen is $\pm$ 0.002 ppm, and repeatability is $\pm$0.002 ppm.The pH probe is calibrated against two pH buffers (7.0 and 10.0) before each series of measurements. Manufacturer's stated relative accuracy for pH is $\pm$ 0.002 pH units, and repeatability is $\pm$ 0.002 pH units.

An Atago refractometer is used to measure test solution salinity. It is calibrated at the beginning and end of each series of measurements using a seawater sub-standard that was measured to the nearest 0.001 ‰ on a Beckman salinometer calibrated to Wormley water. Measurement on the refractometer is accurate to $\pm$ 1‰.

Temperature is measured using standard mercury thermometers that are calibrated semiannually to an ASTM certified thermometer factory calibrated to NIST standards.

Temperature control units for constant temperature rooms, water baths and incubators are checked twice daily and adjusted when necessary to maintain correct temperature.

Reference toxicant stock solutions are prepared using a Mettler AE 163 balance. The balance is self calibrating by means of adjusting a calibration weight lever during an electronic calibration procedure. This calibration procedure is performed monthly.

7.6.2 Preventative Maintenance

There are no manufacturer's recommended preventative maintenance procedures for the instruments listed above. Probes are stored in their proper storage solutions, and probe membranes are changed according to manufacturer's recommendations.

7.7 DOCUMENTATION, DATA REDUCTION AND REPORTING

7.7.1 Documentation

Raw data is recorded in non-erasable ink on standardized printed data sheets. Test solution water quality measurement data is recorded on the back of the same sheet. Original data sheets are copied twice; then the three sheets are labeled as "original", "working copy", and "archive copy". Each is stored in a separate file cabinet. The original is submitted to the funding agency as part of the corresponding project report. The working copy is used to enter data into computer data base and statistics programs. The archived copy is stored in the archive file. Print outs of descriptive and comparative statistics are attached to the working copies for reference when compiling data interpretations for reports.

7.7.2 Data Reduction and Reporting

Raw data from data sheets will be entered into a data base programmed by Rick Packard of Ecoanalysis, the contractors responsible for data management on this project. Data will be entered by two people using a double entry program that automatically checks for errors in transcription.

Each site will be characterized by descriptive statistics indicating the mean response and variation among replicates for each sample. Statistically significant differences among sites will be determined by analysis of variance (ANOVA). Individual comparisons can be made using multiple range tests, such as the Student-Neuman-Keuls test for identifying groups of sites based on toxicity, or the Dunnett's test for comparing sites within gradients or against a control. These data analysis strategies will be based on the use of field replicates to determine the variance for estimating statistical significance. In some cases, where strict confirmation of toxicity results is not required, sites may be sampled without field replication. ANOVA techniques may be used in such cases only with the caveat that using laboratory replication underestimates the variance associated with field collected samples. In addition, some variability exists between sites regardless of the presence of toxicity. Use of multiple reference sites allows characterization of between site variation in the absence of toxicants. Further review of experimental designs by qualified statisticians is recommended to reconcile the logistical difficulties of sampling multiple reference sites with the formal data requirements for adequate analysis.

Data will be provided in a format that allows correlation with physical and chemical data gathered at other laboratories. This will allow analysis of correlation between toxicity and contaminant concentration, particle size, or other parameters. Data will be reported graphically where needed for data interpretation.

Reference toxicant data will be reported as means and standard deviations for each reference toxicant treatment, accompanied by the no observed effect concentration (NOEC), the median lethal, effective, or inhibition concentration (LC_{50}, EC_{50}, or IC_{50}), and the mean control response. Original data sheets will be included for all reported results.

7.8 DATA VALIDATION

All data reported for this project will be subject to a 100 percent check for errors in transcription, calculation, or computer input by the Project Officer, John Hunt.

Additionally, the Project QA/QC Officer, Hilary McNulty, will review all sample logs and data forms to ensure that requirements for sample holding times, sample preservation, sample integrity, data quality assessments, and equipment calibration have been met. At the discretion of the Project Officer, data which do not meet these requirements will either not be reported or will be reported with an explanation of associated problems.

In addition, reference toxicant tests (using water only exposures) will be conducted concurrently to all sediment tests using organisms from the same lot or shipment to determine the suitability of the organisms and test conditions. Data from sediment tests will be considered valid only if the reference toxicant tests meet test acceptability criteria. Responses of test organisms to negative controls, both clean (home) sediment and clean (laboratory) dilution seawater, will be reported to verify compliance with test acceptability criteria. If any of the test criteria are not met, then the sediment samples will be retested along with another reference toxicant test. Data will be compared to that from reference sites to determine significant differences (as stated above).

7.9 PERFORMANCE AND SYSTEM AUDITS

7.9.1 Internal Audits

A log is kept of every test conducted at the Marine Pollution Studies Laboratory with corresponding information about the result and disposition of samples and data. At bimonthly intervals, the QA/QC officer conducts an audit of sample storage areas and data files to determine whether these are in agreement with sample and data logs and records. The QA/QC officer will also conduct frequent checks of data sheets, calibration sheets, and accuracy and precision data sheets to make sure that persons conducting tests and taking measurements are doing so correctly.

7.9.2 External Audits

MPSL agrees to comply with and assist in any performance or system audits conducted by the DFG or SWRCB as part of this project. These audits will take place on the time

schedule determined by the DFG or SWRCB, and we anticipate an external audit at or near the time of project initiation by the SWRCB QA officer.

7.10 CORRECTIVE ACTION

Data quality objectives and validation procedures for this program have been designed to ensure that personnel will be able to quickly identify and correct analytical problems. Should the results of data validation measures indicate that the integrity of data associated with the sample set is questionable, the analyses would be repeated. Quality assurance audits of the program have been proposed in the work plan to ensure that work is performed by individuals who understand the objectives and methods to be used. Audit results will be documented and reported to the Project Officer who will be responsible for implementing all necessary corrective actions.

7.11 REPORTS

Not later than October 1, 1992, and quarterly thereafter, during the life of this project, the Marine Pollution Studies Laboratory University Project Officer will provide a written progress report to the University's Principle Investigator who will include it in a comprehensive report covering all aspects of sample analysis, to be submitted to the DFG Project Director. Progress reports will describe:

1. activities performed,
2. problems encountered and proposed solutions,
3. percent completion of each task,
4. preliminary data obtained, including raw data sheets, and
5. schedule for next quarter.

Data reports shall be submitted as specified in contract task orders. Data reports will include all data generated under the task order, descriptive and comparative statistics resulting from data analysis, any necessary graphics, and a written interpretation of the test results.

SECTION 8

MACROBENTHIC COMMUNITY ASSESSMENT

[Subject to Modification in early 1994]

8.1 OVERVIEW

Benthic assessment to identify Toxic Hot Spots proceeds in much the same fashion as toxicity assessment. Existing data (State Mussel Watch, sediment chemistry, toxicity, and benthic composition) are reviewed for the likely presence and absence of benthic degradation. Screening of these sites (and others selected at random or likely to be degraded and nondegraded) follows and consists of observations collected by diving or otherwise viewing the site (e.g., boat-based sediment collection). In contrast to toxicity assessment, benthic determination of hot spot status does not require repeat demonstration of degradation. Once initial data review and screening are completed, a survey is performed to ensure that adequate numbers of nondegraded (reference) sites are available for each stratum (e.g., grain size, TOC, dissolved oxygen, etc.). The full set of field measurements (see section 3.4.2) is taken at these sites to supplement this process. Once sufficient numbers and types of reference sites are identified, confirmation sampling is performed on groups of reference and suspect hot spots, field measurements are taken, field replicates are included, and sediment chemistry is performed. Subsequent statistical analysis is applied to these data to determine whether distinctions exist between reference sites and suspect hot spots and whether these distinctions are associated with chemical contamination within strata.

This section presents BPTCP QA/QC protocols and requirements for macrobenthic community assessment, from sample collection and laboratory analysis to validation of the resultant data and construction of a benthic index. Sampling is conducted from mid summer to early fall each year prior to the development of major winter storm events. Five (5) replicate benthic samples are obtained at each site from five (5) separate deployments of the sampler. Each sample is processed individually in the laboratory to obtain an accurate assessment of the number of individuals of each species present and their biomass.

8.2 QUALITY CONTROL PROCEDURES: SAMPLE COLLECTION, PRESERVATION AND HOLDING TIME

This is explained in detail in Section 3. In summary, sediment samples for macrobenthic community assessments will be collected at each station using a Young-modified Van Veen grab sampler. In order to be considered acceptable, each grab sample must be obtained following the protocols specified in this document. In particular, field personnel will be thoroughly trained in the proper techniques for sieving and sample preservation (using a buffered formalin solution). In addition, each sediment sample must be inspected carefully before being accepted for benthic community assessment. Each of the following acceptability criteria must be satisfied (from U. S. EPA 1991):

- Sediment will not be extruded from the upper face of the sampler such that organisms may be lost
- Overlying water will be present (indicates minimal leakage)
- The sediment surface should be relatively flat (indicates minimal disturbance or winnowing)
- The entire surface of the sample will be included in the sampler
- The grab sampler must have penetrated the sediment to a minimum depth of 7 cm

If a grab sample does not meet any one of these criteria, it will be rejected.

In the laboratory, catalogued and stored samples must be easily retrieved and protected from environmental extremes. Samples cannot be allowed to freeze and will be stored above 5 °C to prevent the formation of paraformaldehyde. Temperatures greater than 30 °C will be avoided so as to retard evaporative losses. Stored and archived samples will be checked once every three months for excessive evaporative losses due to loosely-fitting or cracked container lids, or inadequately sealed jars.

8.3 QUALITY CONTROL PROCEDURES: LABORATORY OPERATIONS

In the laboratory, QA/QC involves a series of check systems for organism sorting, counting and taxonomic identification. These checks are described in the following sections.

8.3.1 Sorting

The quality control check on each technician's efficiency at sorting (*i.e.*, separating organisms from sediment and debris) consists of an independent resort by a second, experienced sorter. A minimum of 10% of all samples sorted by each technician must be resorted (i.e., the sediment and debris remaining after the original sort is completely re-examined) to monitor performance and thus provide feedback necessary to maintain acceptable standards. (Note: BPTCP benthic analyses completed to date from the LA Harbor area included checking 100% of residues or resorts). These resorts will be conducted on a regular basis on at least one sample chosen at random from each batch of 10 samples processed by a given sorter. Inexperienced sorters require a more intensive QC check system. Experienced sorters or taxonomists will check each sample processed by inexperienced sorters until proficiency in organism extraction is demonstrated. Once proficiency has been demonstrated, the checks may be performed at the required frequency of one every ten samples. Bound laboratory logbooks must be maintained and used to record the number of samples processed by each technician, as well as the results of all sample re-sorts. Sorters are required to sign and date a Milestone Progress Checksheet for each replicate sample processed.

The results of sample resorts may require that certain actions be taken for specific technicians. Laboratory supervisors must be particularly sensitive to systematic errors (*e.g.*, consistent failure to extract specific taxonomic groups) which may suggest the need for further training. Sorting efficiencies below 90% will require resorting and recounting of all samples in the associated batch and continuous monitoring of that technician to improve efficiency. If specimens are discovered within sample residues, they will be removed by the Benthic QA Officer and placed in the appropriate vial. Once all quality control criteria associated with the sample resort have been met, the sample residue (e.g., sediment and debris) may be discarded.

8.3.2 Species Identification and Enumeration

Only senior taxonomists are qualified to perform re-identification quality control checks. A minimum of 10% of all samples (*i.e.*, one sample chosen at random out of every batch of ten samples) processed by each taxonomic technician must be checked by a second qualified taxonomist to verify the accuracy of species identification and enumeration. This control check establishes the level of accuracy with which identification and counts are performed and offers feedback to taxonomists in the laboratory so that a high standard of performance is maintained. Samples will never be re-checked by the technician who originally processed the sample.

Ideally, each batch of ten samples processed by an individual taxonomic technician will be from a similar habitat type (*e.g.*, all oligohaline stations). The recheck of one out of the ten samples in a batch will be done periodically and in a timely manner so that subsequent processing steps and data entry may proceed. As each taxon is identified and counted during the recheck, the results will be compared to the original data sheet. Discrepancies will be double-checked to be sure of correct final results. Following re-identification, specimens will be returned to the original vials, labelled with project, date collected, site and or station information, and IDORG.

All changes in species identification will be recorded on the original data sheet (along with the date and the initials of the person making the change) and these changes will be entered into the database. However, the numerical count for each taxonomic group will not be corrected unless the overall accuracy for the sample is below 90%. The results of all QC rechecks of species identification and enumeration will be recorded in a timely manner in a separate logbook maintained for this purpose.

Taxonomic identifications will be consistent within a given laboratory, and with the identifications of other regional laboratories. Consistent identifications are achieved by implementing the procedures described above and by maintaining informal, but constant, interaction among the taxonomists working on each major group. As organisms are

identified, a voucher specimen collection will be established. This collection will consist of representative specimens of each species identified in samples from Southern and Northern California. For some species, it may be appropriate to include in the voucher specimen collection individuals sampled from different geographic locations within the State. At the end of the year, the voucher specimen collection will be sent to recognized experts for verification of the laboratory's taxonomic identifications. The verified specimens will then be placed in a permanent taxonomic reference collection. Continued collection of verified species does not require additional expert verification, because the reference collection can be used to confirm the identification. In addition, the reference collection will be used to train new taxonomists. Participation of the laboratory staff in a regional taxonomic standardization program (if available) is recommended, to ensure regional consistency and accuracy of identification.

The laboratory is required to notify the project coordinator of any taxonomic identification errors discovered by outside experts, as this may necessitate database corrections. Such corrections will be made only after further consultation with the laboratory personnel and the outside expert(s) and will be supported by written documentation which clearly explains the nature of and rationale for the changes.

All specimens in the reference collection will be preserved in 70% ethanol in labeled vials that are segregated by species and sample. More than one specimen may be in each vial. The labels placed in these vials will be made of waterproof, 100-percent (at least) rag paper, pre-printed labels identifying the project, date collected, site/station information, and idorg. A separate label will identify the enclosed specimen(s) with the current nomenclature. Paper with less than a 100-percent rag content or that is not waterproofed will disintegrate in the 70-percent alcohol mixture. It is important to complete these labels, because future workers may not be familiar with the project, station locations, and other details of the work in progress. In addition, the reverse side of the label will contain information about the confirmation of the identification by experts in museums or other institutions (if appropriate). To reduce evaporation of alcohol, the lids of vials and jars can be sealed with parafilm

wrapped in a clockwise direction. The species (and other taxonomic designation) will be written clearly on the outside and on an internal label. Reference specimens will be archived alphabetically within major taxonomic groups. A listing of each species name, the name and affiliation of the person who verified the identification, the location of the individual specimen in the laboratory, the status of the sample if it has been loaned to outside experts, and references to pertinent literature will be maintained by the laboratory performing the identifications.

Reference collections are invaluable, and will be retained at the location where the identifications were performed. In no instance will this collection be destroyed. A single person will be identified as curator of the reference collection and will be responsible for its integrity. Its upkeep will require periodic checking to ensure that alcohol levels are adequate. When refilling the jars, it is advisable to use full-strength alcohol (i.e., 95 percent), because the alcohol in the 70-percent solution will tend to evaporate more rapidly than the water.

8.4 QUALITY CONTROL PROCEDURES: INFORMATION MANAGEMENT

8.4.1 Sample Tracking

BPTCP information management personnel have developed a comprehensive system for cataloguing and archiving sample containers. The laboratory responsible for processing the macrobenthic community samples must designate a sample custodian, authorized to check the condition of and sign for the incoming field samples, obtain documents of shipment and verify sample custody records. In addition, the laboratory must have clearly-defined custody procedures for sample handling, storage, and disbursement in the laboratory and must maintain accurate and timely records of the location and status of all samples.

8.4.2 Record Keeping and Data Reporting Requirements

It is mandatory for the laboratory responsible for processing the macrobenthic community samples to maintain thorough and complete records. All data generated in the laboratory will

be recorded directly onto standardized data forms. Preparation of data sheets prior to sample processing facilitates sample tracking, sample processing, QA/QC procedures, and data entry and helps to minimize transcription and other errors. Data forms will be designed so that all necessary information is recorded clearly and unambiguously; data will be recorded in ink and signed by the responsible person. Completed data sheets and QA/QC forms will be kept in bound notebooks arranged by type; these forms will be made available to the Project Coordinator upon request and will be inspected for adequacy during QA audits. The following information will be provided to the Project Coordinator:

- A cover letter, both on paper and in electronic file format, providing a brief description of the procedures used, as well as a narrative explanation of problems (if any) or failure(s) to meet quality control limits.

- Tabulated results in hard copy form including a field for sample identification that corresponds to the sample IDORG as described in the DFG BPTCP database description. All data will be double entered to check for accuracy and the report will be signed by the laboratory manager or designee. The data shall conform to the approved DFG BPTCP Data Base Description.

- Tabulated results in computer-readable form (e.g., diskette) included in the same shipment as the hard copy data, but packaged in a diskette mailer to prevent damage. The data will be submitted to the data processing manager in dBase 4 format. If data are not delivered in this format, the data package will be considered incomplete and will not be accepted.

- Results for all QA/QC samples must be submitted by the laboratory as part of the data package for each batch of samples analyzed. The laboratory must provide a **"batch number"** as a way to link samples from a given batch or analytical set with their accompanying QA/QC samples. The batch number is described in the Data Base Description and is a field in the dBase database. Each type of analysis (metals,

organics, toxicity testing, benthic analysis, toxicity testing chemical analysis, TOC and grain size, and AVS) will have it's own unique batch number. In addition, to the batch number field, another field will be included in all data sets (metals, organics, toxicity testing, benthic analysis, toxicity testing chemical analysis, TOC and grain size, and AVS) that lists the file names that contain the QA data for that sample. This field is also described in the database. The laboratory will denote QA/QC samples using the codes (abbreviations) and reporting units specified in Table 5-6. This field is described in the database and will be entered into each of the data sets by each of the laboratories.

Laboratory managers will verify that all specified QA/QC requirements are met for a given batch of samples, or, if not, that specified corrective actions are implemented and problems resolved, before a technician is permitted to proceed with sample processing. The laboratory must establish a comprehensive information management system that allows responsible personnel to detect and eliminate transcription and/or calculation errors prior to submission of the final data package in computer readable format. This includes, for example, data entry procedures that involve double entry of information from the laboratory data sheets into separate databases and subsequent comparison to ensure a high level of data transcription accuracy. Data transcription errors also can be minimized through the use of computer data entry forms that duplicate or closely mirror the format of the hard copy data sheets used in the laboratory. The laboratory's manager or QA Officer will perform manual checks on a random subset of all transcribed data sheets (at least 10% of the total) to verify transcription accuracy.

The laboratory will report the results for all samples both in hard copy and in a computer-readable format specified by the Project Coordinator. At a minimum, the following information will be included: BPTCP sample ID, laboratory sample ID (if applicable), numbers of individuals per sample for each species (i.e, abundance), and number of species per taxonomic grouping (i.e. polychaetes, crustaceans, molluscs, echinoderms, others).

Tables summarizing the results of QC checks (e.g., resorts, recounts, and reidentifications) must be included as part of the data package, as well as a cover letter signed by the Laboratory Manager containing a narrative explanation of any problems that may have influenced data quality.

8.4.3 Data Evaluation Procedures

It is the responsibility of the DFG BPTCP Project Coordinator to acknowledge initial receipt of the data package(s), verify that the data evaluation procedures are completed, notify the laboratory of any additional information or corrective actions deemed necessary as a result of the BPTCP's data evaluation and, following satisfactory resolution of all "corrective action" issues, take final action by notifying the laboratory in writing that the submitted results have been officially accepted as a completed deliverable in fulfillment of contract requirements. It may be necessary or desirable for the Project Coordinator to delegate the technical evaluation of the data to the QA Coordinator or other qualified staff member. It is the responsibility of the Project Coordinator to monitor closely and formally document each step in the data evaluation process as it is completed. This documentation will be in the form of a data evaluation tracking form or checklist that is filled in as each step is completed. This checklist will be supplemented with detailed memos to the project file outlining the concerns with data omissions, analysis problems, or descriptions of questionable data identified by the laboratory.

Evaluation of the data package will commence as soon as possible following its receipt, since delays increase the chance that information may be misplaced or forgotten. The first part of data evaluation is to verify that all required information has been provided in the data package. First, BPTCP personnel will verify that the package contains the following: a cover letter in both electronic (i.e., computer text file) and paper formats (signed by the laboratory manager), hard copies of all results (including tables summarizing the results of

all QA/QC checks), and accompanying computer diskettes. Second, the electronic data file(s) will be parsed into the BPTCP database to verify that the correct format has been supplied.

The Project Coordinator will contact the laboratory and request any missing information as soon as possible after receipt of the data package. If information was omitted because required analyses were not completed, the laboratory will provide and implement a plan to correct the deficiency. This plan may include submittal of a revised data package and possible reanalysis of samples.

Data validation, or the process of assessing data quality, will begin after laboratory personnel have determined that the data package is complete. Data validation for the benthic community assessment will consist of a thorough review of the summarized QA/QC data submitted as part of the data package to verify that specified control limits for sample resorts, species recounts and reidentifications were not exceeded, or, if exceeded, that specified corrective actions were implemented and are explained in adequate detail in an accompanying cover letter. If all specified control limits were met during sample processing and/or problems adequately explained, the data can be accepted for use without qualification.

8.4.4 Data Quality Reports

All QA/QC data associated with the laboratory processing of benthic samples will be presented in BPTCP reports and publications along with the results data, so that interested data users can make their own assessment of data usability. Upon completion of all data evaluation steps, a report summarizing the QA review of the data package will be prepared, samples will be properly stored or disposed of, and laboratory data and associated commentary will be archived both in a storage file and in the database. Reports documenting the results of the review of the data package will summarize all conclusions concerning data acceptability and will note significant quality assurance problems that were found. These reports are useful in providing data users with a written explanation of why certain data

qualifier codes were assigned and/or why some data was rejected. The following specific items will be addressed in the QA report:

- Summary of overall data quality, including a description of data that were qualified.
- Brief descriptions of sample collection and testing methods, and changes made in sampling design, if appropriate.
- Description of data reporting, including any corrections made for transcription or other reporting errors, and description of data completeness relative to objectives stated in the QA plan.

SECTION 9

INFORMATION MANAGEMENT

9.1 SYSTEM DESCRIPTION

The Information Management System (IMS) developed for the Bay Protection and Toxic Cleanup Program (BPTCP) is designed to perform the following functions:

- o document sampling activities and standard methods,
- o document sample tracking and shipments,
- o process and organize both field, laboratory, and QAQC data,
- o perform range checks on selected numerical data,
- o facilitate the dissemination of information, and
- o archive the data.

9.2 QUALITY ASSURANCE/QUALITY CONTROL

Two general types of problems which must be resolved in developing QA/QC protocols for information and data management are: (1) correction or removal of erroneous individual values and (2) inconsistencies that damage the integrity of the data base. The following features of the BPTCP IMS will provide a foundation for the management and quality assurance of all data collected and reported during the life of the project.

9.2.1 Standardization

A systematic numbering system will be developed for unique identification of individual samples, sampling events, stations, analytical Batch numbers, shipments, equipment, and diskettes. The sample numbering system will contain codes which will allow the computer system to distinguish among several different sample types (*e.g.*, actual samples, quality control samples, sample replicates, etc.). This system will be flexible enough to allow

changes during the life of the project, while maintaining a structure which allows easy comprehension of the sample type. This unique numbering system is described in the DFG BPTCP Database Description.

9.2.2 Preprinted Labels for Sample Containers

Sample containers will be labeled with waterproof printed labels to eliminate potential confusion in the field and thereby reduce the number of incorrect or poorly-affixed labels. Containers with all the required preprinted labels, and sample sheets will be prepared from the sampling database that is created for the field crews prior to each sampling event (an event is defined as a single visit by a crew to a sampling site).

9.2.3 Data Entry, Transcription, Data Change and Transfer

In addition to paper data sheets, all data collected by field crews are recorded in a series of electronic forms after returning to the laboratory. Following the initial entry of data into the computer system, it is printed onto hard copy and checked 100% against the original paper data sheets. This check is performed by the field crew chief, who may correct transcription errors and ultimately is responsible for assigning an acceptance code to the entered data. Once the data have been checked and accepted by the crew chief, the field personnel no longer have the authority to make changes.

A cruise report is prepared within one week of returning to the laboratory. The cruise report documents the purpose of the cruise, task order authorizing field work, and field activities such as a log of daily activities, personnel involved, problems encountered, sites sampled, latitude and longitude of station locations, etc. The BPTCP Program Coordinator for DFG reviews the data after each cruise and suspicious data is flagged for further investigation. If a change to the data is required, the data librarian is required to complete a Data Revision/Correction Form (electronic file and hard copy form) indicating the data sheet, variable, and reason for change. This information is written to a dBase-4 file. The original database containing the raw data or QAQC data will have a data correction/revision field as

described in the DFG Database Description. When satisfied that the data is 100% correct, the Data Librarian assigns an acceptance code.

9.2.4 Automated Data Verification

Erroneous numeric data will be identified using automatic range checks and filtering algorithms. When data fall outside of an acceptable range, they will be flagged in a report for review by the Project Coordinator, the Project Quality Assurance Officer, or their designee. This type of report will be generated routinely and will detail the files processed and the status of the QA checks. The report will be generated both on disk and in hard copy for permanent filing. The Project Coordinator will review the report and release data which have passed the QA check for addition to the database. All identified errors must be corrected before flagged files can be added to a database, and as detailed above, a Data Revision/Correction Form must be completed if it is necessary to correct data. If it is found that the data check ranges are not reasonable, the values will be changed by a written request which includes a justification for the change.

Database entries which are in the form of codes will be compared to lists of valid values (*e.g.*, look-up tables) established by experts for specific data types. These lists of valid codes will be stored in a central data base for easy access by users. When a code cannot be verified in the appropriate look-up table, the observation will be flagged in a written report for appropriate corrective action (*e.g.*, update of the look-up table or removal of the erroneous code).

9.2.5 Sample Tracking and Instructions for Analyses

All samples will be hand delivered to the recipient laboratory by the BPTCP staff at MLML. Exceptions will have to be granted in writing by the Project Coordinator. If the samples are shipped the tracking of sample shipments from the MLML site to the analytical laboratories is extremely important in order to minimize loss of samples by the field crews, shipping carrier, receiving laboratory, or as a result of improper packaging. Shipment tracking is performed by the transfer of shipment and receipt information via daily telephone calls from

the MLML staff and receiving labs, and by the recording of shipping and receiving documents from the carrier such as UPS and Federal Express. All shipments will have the proper chain of record (COR) forms enclosed. The chain of custody information is computerized and is stored in hardcopy notebook by the BPTCP Field Crew at MLML in order to ease in the tracking of a particular sample. An electronic file (diskette) containing information regarding samples being transferred will also be delivered with the hard copy coc form to the respective laboratories receiving samples for analyses. This diskette is to be returned upon delivery of products and shall contain data in dBASE-4 database format as required by DFG.

Also included with chain-of-custody forms will be a checklist of analyses to be performed and expected delivery date of products, as well as any other details or instructions necessary to perform appropriate analyses. This checklist/coc package will also include the cruise report and accompanying station location maps for the sampling leg or event from which the samples originated. The checklist will also be signed and returned with the coc forms, verifying that the recipient laboratory understands and agrees to perform the analyses as outlined.

9.2.6 Reporting

Following analysis of the samples, the summary data packages transmitted from the laboratories will include results, QA/QC information, and accompanying text in a manner outlined in the coc/checklist package as detailed by CDFG. All data reports, as well as any other official BPTCP deliverable product will be submitted directly to DFG BPTCP personnel, and not to any other agency or project cooperators/funders. DFG is then responsible for timely submission of quality assured data to the SWRCB or its designees.

Any data reports not complying with all DFG data reporting criteria will be rejected and returned for correct format. All data must be submitted in previously determined dBase-4 format, and must be accompanied by an electronic file (diskette) and a hardcopy file. A

Data Accuracy Verification/Data Transmittal Form shall also accompany the data report, verifying that the data has complied with QA/QC criteria, and that it has been double-entered or double-verified according to protocol. This form will be signed by both the submitting laboratory and all appropriate DFG officials receiving/reviewing the data report and files.

If the laboratory has assigned internal identification numbers to the samples, the data report transmitted must include at a minimum the BPTCP sample identification number, the CDFG Station Number, Leg Number, and any internal number used by the laboratory. Specific data reporting requirements associated with each indicator are discussed in the corresponding section of this plan.

Analytical laboratories are responsible for permanent archiving of all raw data used in generating results for a minimum period of seven years.

9.2.7 Redundancy (Backups)

All files in the BPTCP IMS will be backed up regularly. The main IMS data management storage system will be at MLML. A backup will be kept at Granite Canyon MPSL and updated weekly to enable the information management team to reconstruct the database in the event that one system is destroyed or incapacitated. Backups will be sent to the SWRCB and Eco-Analysis at the same time they are sent to the Granite Canyon facility. All disks and files will be numbered uniquely and registered by the BPTCP Data Librarian. Any change in data will prompt a recall of all backup disks that are registered. A Data Revision/Correction Form will be completed on every occasion which data already entered into the database is corrected or revised for any purpose. This was detailed previously.

Updates (diskettes containing the newly revised data in a database) will be sent out to the SWRCB and any other users that have registered copies of the data. At all laboratories and the BPTCP IMS center at MLML, backups will be made daily to all working files that have been changed that day. In addition, backups of all BPTCP intermediate files or

correspondence files will be performed on a monthly basis and transmitted to the Data Librarian at MLML to provide a backup in the event of a complete loss of data or files at one of the laboratories.

All original data files will be saved on-line for at least two years, after which the files will be permanently archived. Archiving of data will be done at the SWRCB on a non-volatile medium such as an optical "WORM" disk. All original files, especially those containing the raw field data, will be protected so that they can be read only (*i.e.*, write and delete privileges will be removed from these files).

9.3 DOCUMENTATION AND RELEASE OF DATA

Comprehensive documentation of information relevant to users of the BPTCP IMS will be maintained and updated as necessary. Most of this documentation will be accessible by diskette. The documentation will include a database description, access control, and database directories (including directory structures), code tables, and continuously-updated information on field sampling events and their purpose, and data availability.

A limited number of personnel will be authorized to make changes to the BPTCP database. All changes will be carefully documented via the use of a BPTCP Data Revision/Correction Form (both electronic and hard-copy forms), and controlled by the Data Librarian at MLML. On-line databases which are accessible to outside authorized users will be available in "read only" form at the SWRCB at some time in the future. Access to data by unauthorized users will be limited through the use of standard security procedures. Information on access rights to all BPTCP directories, files, and data bases will be provided to all potential users.

The release of data from the BPTCP IMS to outside agencies (agencies/personnel not participating in the BPTCP) will occur on a graduated schedule, and will be made at the sole discretion of the SWRCB. Different classes of users will be given access to the data only after it has passed a specified level of quality assurance review. Each group will use the data

on a restricted basis, under explicit agreements with the BPTCP Project Manager at the SWRCB. The following four groups are defined for access to data:

I. DFG BPTCP group, including the information management team, the research team, the field coordinator, the Project Manager, the Project Coordinator, the Project QA Officer and the field crew chiefs.

II. SWRCB BPTCP group-including the Project Manager, Project staff and QA officer.

III. RWQCB BPTCP users

IV. Ecoanalysis group

V. General Public - University personnel, the research community, and Federal, state and municipal agencies.

Prior to release at level V (general public), all files will be checked and/or modified to assure that values contain the appropriate number of significant figures. The purpose is to assure that the data released do not imply greater accuracy than was realized. This will be especially important in files where data were summarized. In such cases additional figures beyond the decimal point may have been added by the statistical program during averaging or other manipulations. It will be the responsibility of the various laboratories to inform the DFG Project Coordinator of the appropriate number of significant figures for each measurement, and ultimately the DFG Project Coordinator's responsibility to ensure that the data submitted to DFG reflect that level of significant figures. Requests for premature release of BPTCP data will be submitted to the SWRCB through the Project Coordinator in writing. The Project Coordinator and the Quality Assurance Officer, in consultation with the Project Manager, will make a recommendation to the SWRCB regarding whether they feel the data should be released. The final authority on the release of all data is the SWRCB Project Manager and all releases must be authorized in writing. The long-term goal for the BPTCP Information Management Team will be to develop a user interface through which all data will be accessed directly on the computer. This will improve control of security and monitoring of access to the data, and it will help ensure that only the proper data files are being accessed.

SECTION 10

QUALITY ASSURANCE REPORTS TO MANAGEMENT

A quality assurance report will be prepared by the BPTCP Project Coordinator following each year's sampling efforts. This report will summarize the measurement error estimates for the various data types using the QA/QC sample data. Precision, accuracy, comparability, completeness, and representativeness of the data will be addressed in this document. A separate QA report will accompany each major sampling event and will address all QA concerns relevant to the data collected during the sampling event.

Within 30 days of each audit (field or laboratory), the QA Officer will submit a report to the DFG Project Manager (an audit form will be developed by DFG for this purpose). This report will describe the results of the audit in full detail and note any deficiencies requiring management action. The QA Officer will monitor the implementation of corrective actions in response to negative findings, and will make regular reports to the Project Manager in this regard.

In addition to the formal reports described above, the QA Officer will report regularly to the DFG Project Manager and Coordinator on an informal basis, through E-mail, conference calls, and/or direct contact. One of the primary responsibilities of the QA Officer is to keep the Project Manager informed of any issue or problem which might have a negative effect on the data collected.

The BPTCP Program QA Officer, with assistance from the Project Coordinator, will prepare a Quality Assurance Annual Report (QAAR). The QAAR summarizes the quality assurance activities conducted during the previous fiscal year, and describes activities planned for the upcoming fiscal year.

SECTION 11

REFERENCES

Adams, M., J. S. Rosen, H. Buffum, J. Beaulieu, and M. Hughes. 1991. Information Management Plan for the EMAP-Near Coastal Program. U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Gulf Breeze, FL.

Allen, H.E., G. Fu, W. Boothman, D. DiToro, J. Mahony. 1991 Determination of acid volatile sulfide and selected simultaneously extractable metals in sediment. EPA Draft, AVS and SEM Procedure, Dec. 2, 1991

American Society for Testing and Materials (ASTM). 1984. Annual Book of ASTM Standards, Vol. 11.01. Standard Specifications for Reagent Water D1193-77 (reapproved 1983). American Society for Testing and Materials, Philadelphia, PA.

American Society for Testing Materials (ASTM). 1987. Standard practice for conducting static acute tests with larvae of four species of bivalve molluscs. Procedure E 724-80. Annual book of ASTM standards; water and environmental technology. Vol 11.04: 382 - 388. American Society for Testing and Materials, Philadelphia, PA.

American Society for Testing and Materials (ASTM). 1991. Guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. ASTM Standard Methods Volume 1104, Method Number E-1367-90. American Society for Testing and Materials, Philadelphia, PA.

Anderson, B.S., J.W. Hunt, S.L. Turpen, A.R. Coulon, M. Martin, D.L. McKeown and F.H. Palmer. 1990. Procedures manual for conducting toxicity tests developed by the Marine Bioassay Project. California State Water Resources Control Board 90 - 10WQ. Sacramento, California. 113 p.

Anderson, J.W., S.M. Bay, and B.E. Thompson. 1988. Characteristics and effects of contaminated sediments from Southern California. Prepared for the State Water Resources Control Board, Sacramento, CA.

APHA. 1985. Standard Methods for the Examination of Water and Wastewater. 16th. Edition. American Public Health Association, Washington, DC. 1268 pp.

Baker, J. R. and G. D. Merritt. 1990. Environmental Monitoring and Assessment Program: Guidelines for Preparing Logistics Plans. EPA 600/4-91-001. U. S. Environmental Protection Agency, Las Vegas, Nevada.

Bender, M., Martin, W., Hess, J., Sayles, F., Ball, L. and Lambert, C. (1987) A whole core squeezer for interfacial pore water sampling. Limnol. Oceanogr., 32, 1214-1225

Boothman, W.S. and Helmstetter, A. 1992 Determination of acid-volatile sulfide and simultaneously-extracted metals in sediments using sulfide-specific electrode detection AVSSEM SOP Volume 2.0, 4 Sep 92.

Bruland, K.W., R.P. Franks, G.A. Knauer, and J.H. Martin. 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in seawater. Anal. Chem. Acta 150: 233 - 245.

Cantillo, A. Y. 1992. Standard and Reference Materials for Marine Sciences, Third Edition. NOAA Technical Memorandum NOS ORCA 68, National Ocean Service, Office of Ocean Resources Conservation and Assessment, Silver Spring, MD.

Carr, R.S., Williams, J.W., and Fragata, C.T.B. (1989) Development and evaluation of a novel marine sediment pore water toxicity test with the polychaete Dinophilus gyrociliatus. Env. Tox.Chem. 8: 533-543

Chapman, P.M. and J.D. Morgan. 1983. Sediment bioassays with oyster larvae. Bull. Environ. Contam. Toxicol. 31: 438-444.

Degraeve, G. M., N. G. Reichenbach, J. D. Cooney, P. I. Feder, and D. I. Mount. 1988. New developments in estimating endpoints for chronic toxicity tests. Abstract, Am. Soc. Test. Mater. 12th Symp. Aquat. Toxicol. Hazard Assess., Sparks, Nev.

Department of Fish and Game. 1992. Laboratory Quality Assurance Program Plan. Environmental Services Division. Sacramento, CA.

DeWitt, T.H., R.C. Swartz, J.O. Lamberson. 1989. Measuring the acute toxicity of estuarine sediments. Environ. Toxicol. and Chem. 8: 1035-1048.

Dinnell, P.J., J. Link, and Q. Stober. 1987. Improved methodology for sea urchin sperm cell bioassay for marine waters. Arch. Envir. Cont. and Toxicol. 16: 23-32.

EcoAnalysis, Inc., Southern California Coastal Water Research Project, and Tetra Tech, Inc. 1992. Analysis of ambient monitoring data for the Southern California Bight. Prepared for U.S. Environmental Protection Agency, Region IX, San Francisco, CA.

Fairey, W.R., Johnson, K.S., Coale, K.H., Berelson, W.B. and Elrod, V.A. (1992) Trace metal analysis of sediment interstitial waters: A transect through the oxygen minimum of the California margin. Submitted

Federal Register, Part VIII, EPA, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Proposed Rule. 40 CFR Part 136, Oct. 28, 1984.

Hamilton, M. A., R. C. Russo, and R. V. Thurston. 1977. Trimmed Spearman-Karber method for estimating median lethal concentrations in toxicity bioassays. Environ. Sci. Technol. 11:714-719; Correction 12:417 (1978).

Horning, W.B. II and C.I. Weber (eds.). 1985. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. Environmental Monitoring and Research Laboratory - Cincinnati Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/4-85/014.

Holland, A. F. (ed.). 1990. Near Coastal Program Plan for 1990: Estuaries. EPA 600/4-90/033. U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Narragansett, RI.

Hose, J.E. 1985. Potential uses of sea urchin embryos for identifying toxic chemicals: description of a bioassay incorporating cytologic, cytogenetic and embryological endpoints. J. Applied Tox. (5) 4: 245-254.

Hunt, J.W., B.S. Anderson, S.L. Turpen, H.R. Barber, D.L. McKeown, F.H. Palmer and M. Martin. (1991). Marine Bioassay Project Sixth Report: Interlaboratory comparisons and protocol development with four marine species. Report # 91 - 21 - WQ. State Water Resource Control Board, California.

Hunt, D. T. E., and A. L. Wilson. 1986. The Chemical Analysis of Water: General Principles and Techniques. 2nd ed. Royal Society of Chemistry, London, England 683 pp.

Jahnke, R.A. (1988) A simple reliable and inexpensive pore water sampler. Limnol. Oceanogr., **33**, 483-487

Johns, D.M., T.C. Ginn and D.J. Reish. 1990. The juvenile neanthes sediment bioassay. Puget Sound Notes, No. 24, U.S. EPA, Seattle, WA.

Keith, L. H., W. Crumett, J. Deegan, Jr., R. A. Libby, J. K. Taylor, and G. Wentler. 1983. Principles of environmental analysis. Anal. Chem. 55:2210-2218.

Keith, L. H. 1991. Environmental Sampling and Analysis: A Practical Guide. Lewis Publishers, Chelsea, MI, 143 pp.

Kirchner, C. J. 1983. Quality control in water analysis. Environ. Sci. and Technol. 17(4):174A-181A.

Kirkland, L., in preparation. Quality Assurance Management Plan for the Environmental Monitoring and Assessment Program. U.S. Environmental Protection Agency, Washington, D.C.

Lauenstein, G. L., A. Y. Cantillo, and S. Dolvin (eds.). 1993. A Compendium of Methods Used in the NOAA National Status and Trends Program. National Ocean Service, Office of Ocean Resources Conservation and Assessment, Silver Spring, MD (in press).

Long, E.R., S.M. Bay, R.J. Breteler, R.S. Carr, P.M. Chapman, J.E. Hose, A.L. Lissner, J. Scott, and D.A. Wolf. 1990. Comparative evaluation of five toxicity tests with sediment from San Francisco Bay and Tomales Bay, California. Environ. Toxicol. and Chem. 9: 1193-1214.

Long, E.R. and Buchman, M.F. (1989) An evaluation of candidate measures of biological effects for the National Status and Trends Program. NOAA Tech. Memo. NOS OMA 45.

Middaugh, D.P., M.J. Hemmer, and E.M. Lores. 1988. Teratological effects of 2,3-dinitrophenol, produced water, and naphthalene on embryos of the inland silverside *Menidia beryllina*. Dis. Aquat. Org., 4, 53 - 65.

Mount, D.I. and T.J. Norberg. 1984. A seven-day life-cycle cladoceran test. Environ. Toxicol. and Chem. 3: 425-434.

Nacci, D., Nelson, S., Nelson, W., and E. Jackim. 1992. Application of the DNA alkaline unwinding assay to detect DNA strand breaks in marine bivalves. Mar. Env. Res. (in press).

Nebecker, A.V., M.A. Cairns, J.H. Gakstatter, K.W. Maleug, G.S. Schuytema, and D.F. Krawezyk. 1984. Biological methods for determining toxicity of contaminated freshwater sediments to invertebrates. Environ. Toxicol. and Chem. 3: 617-630.

Olsen, A. R. (ed.). 1992. The Indicator Development Strategy for the Environmental Monitoring and Assessment Program. U. S. Environmental Protection Agency, Environmental Research Laboratory, Corvallis, OR.

Peltier, W.H., and C. I. Weber. 1985. Methods for measuring the acute toxicity of effluents to freshwater and marine organisms. Environmental Monitoring and Support Laboratory - Cincinnati Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/4-85/013.

Plumb, R. H., Jr. 1981. Procedures for handling and chemical analysis of sediment and water samples. Technical Report EPA\CE-81-1. U.S. Environmental Protection Agency/U.S. Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material, U.S. Army Waterways Experiment Station, Vicksburg, MS. 471 pp.

Reifsteck D., C. J. Strobel, and S. C. Schimmel. 1993. EMAP-Estuaries 1993 Virginian Province Field Operations and Safety Manual. U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Narragansett, RI.

Rosen, J. S. 1993. Documentation of the Calculation of the EMAP Estuaries Virginian Province Benthic Index. Unpublished manuscript, U.S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Narragansett, RI.

Rue, W.J., J.A. Fava, D.R. Grothe. 1988. A review of inter- and intra-laboratory effluent toxicity test method variability. Aquatic Toxicology and Hazard Assessment: 10th Volume, ASTM STP 971, W.J. Adams, G.A. Chapman, and W.G. Landis, Eds., American Society for Testing and Materials, Philadelphia, pp. 190-203.

Shugart, L.R. 1988. Quantitation of chemically induced damage to DNA of aquatic organisms by alkaline unwinding assay. Aquat. Tox., 13: 43-52.

Shugart, L.E., Bickman, J., Jackim, G., McMahon, G., Ridley, W., Stein, J., and S. Steinert. 1992. DNA alterations. In: "Biomarkers: Biochemical, Physiological, and Histological Markers of Anthropogenic Stress." edited by R.J. Huggett, R.A. Kimerle, P.M. Mehrle, Jr., and H.L. Bergman. SETAC special publication series. Lewis Publishers, Boca Raton, FL. p 125-154.

Singh, N, McCoy, M.T., Tice, R.R., and E.L. Schneider. 1988. A simple technique for quantification of low levels of DNA damage in individual cells. Exp. Cell Res. 175: 184-191.

Spehar, R.L., D.K. Tanner and J.H. Gibson. 1982. Effects of kelthane and pydrin on early life stages of fathead minnows (*Pimephales promelas*) and amphipods (*Hyalella azteca*). In J.G. Pearson, R.B. Foster and W.E. Bishop, eds., *Aquatic Toxicology and Hazard Assessment: Fifth Conference*. STP 766. American Society for Testing and Materials, Philadelphia, PA, pp. 234 - 244.

Stanley, T. W., and S. S. Verner. 1983. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. EPA/600/4-83/004. U.S. Environmental Protection Agency, Washington, D.C.

Stanley, T. W., and S. S. Verner. 1985. The U. S. Environmental Protection Agency's quality assurance program. pp 12-19 In: J. K. Taylor and T. W. Stanley (eds.). Quality Assurance for Environmental Measurements, ASTM STP 867. American Society for Testing and Materials, Philadelphia, Pennsylvania.

State Water Resources Control Board. 1993. Status of the Bay Protection and Toxic Cleanup Program. Staff Report. Sacramento, CA.

Soutar, A., Johnson, S., Fisher, K., and Dymond, J. (1981) Sampling the sediment-water interface for an organic rich surface layer. Trans. Am. Geophys. Union, **62**, 905 Plenum Press, New York

Swartz, M.H., W.A. DeBen, J.K.P. Jones, J.O. Lamberson and F.A. Cole. 1985. Phoxocephalid amphipod bioassay for marine sediment toxicity. In: 7th ASTM Aquatic Toxicology and Hazard Assessment Symposium. Special Technical Report 854 Milwaukee, WI, April 18, 1983. R.D. Purdy and R.C. Bahner, eds. Philadelphia, PA: American Society for Testing Materials, pp. 284-307.

Tetra Tech, 1986. Recommended Protocols for measuring selected environmental variables in Puget Sound. Prepared for the Puget Sound Estuary Program by: Tetra Tech Inc., 11820 Northup Way Bellevue, WA 98005. March, 1986.

Tice, R.R., Phillips, M.D., Croom, D.K., Andrew, P.W., and C.H. Nauman. 1991. Evaluation of DNA damage in Golden Mice (*Ochrotomys nuttalli*) inhabiting a hazardous waste site. Presented at Envir. Muta. Soc. Annual Meeting, April 6-11, 1991, FL.

Taylor, J. K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Inc., Chelsea, Michigan. 328 pp.

U.S. Environmental Protection Agency. 1992. EMAP Laboratory Methods Manual: Estuaries. U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, Ohio (in revision).

U.S. Environmental Protection Agency, in preparation. Statistical Summary: EMAP-Estuaries Virginian Province - 1991. U. S. Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development, Narragansett, RI.

U.S. Environmental Protection Agency. 1979a. Methods for chemical analysis of water and wastes. EPA-600/4-79/020. U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, Ohio (revised March 1983).

U.S. Environmental Protection Agency. 1979b. Handbook for analytical quality control in water and wastewater laboratories. U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA/600/4-79/019.

U.S. Environmental Protection Agency. 1989. Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound. U.S. Environmental Protection Agency, Puget Sound Estuary Program, Office of Puget Sound, Seattle, Washington.

U.S. Environmental Protection Agency. 1991. A Project Manager's Guide to Requesting and Evaluating Chemical Analyses. EPA 910/9-90-024. U.S. Environmental Protection

Agency, Puget Sound Estuary Program, Office of Coastal Waters, Region 10, Seattle, Washington.

U.S. Environmental Protection Agency. 1992. Sea urchin (Strongylocentrotus purpuratus) fertilization test method. Final Draft. Gary A. Chapman, U.S. Environmental Protection Agency. ERL - ', Pacific Ecosystems Branch, Newport, Oregon.

U.S. Environmental Protection Agency/Army Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material, "Ecological evaluation of proposed discharge of dredge material into Ocean Waters; Implementation Manual of Section 103 of Public Law 92-532 (Marine Protection and Sanctuaries Act 1972),". July 1977 (2nd printing April 1978). Environmental Effects Laboratory, U.S. Army Engineers, Waterways Experiment Station, Vicksburg, Mississippi.

Weber, C.I., W.B. Horning II, T.W. Newikeisel, P.A. Lewis, E.L. Robinson, J. Menkedick, and F. Kessler (eds.). 1988. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to marine and estuarine organisms. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA-600/4-87/028. National Technical Information Service, Springfield, VA.

Weisberg, S. B., J. B. Frithsen, A. F. Holland, J. F. Paul, K. J. Scott, J. K. Summers, H. T. Wilson, R. M. Valente, D. G. Heimbuch, J. Gerritsen, S. C. Schimmel, and R. W. Latimer. 1993. EMAP-Estuaries Virginian Province 1990 Demonstration Project Report. EPA 600/R-92/100. U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, RI.

Valente, R.M. and C.J. Strobel. 1993. EMAP-Estuaries Virginian Province: Quality Assurance Project Plan for 1993. EPA 600/X-93/XXX. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Narragansett, RI.

APPENDIX 1: Working Definition of a Toxic Hot Spot

The following draft definition provides the BPTCP with a specific working definition and a mechanism for identifying and distinguishing between "known" and "potential" toxic hot spots.

1. Known Toxic Hot Spot

A site meeting any one or more of the following conditions is considered to be a "known" toxic hot spot:

1. The site exceeds water or sediment quality objectives for toxic pollutants that are contained in appropriate water quality control plans.

   This finding requires chemical measurement of water or sediment, or measurement of toxicity using tests and objectives stipulated in water quality control plans. Determination of a toxic hot spot using this finding should rely on recurrent measures over time (at least two separate sampling dates). Suitable time intervals between measurements must be determined.

2. The water or sediment exhibits toxicity associated with toxic pollutants, based on toxicity tests acceptable to the BPTCP.

   To determine whether toxicity exists, recurrent measurements (at least two separate sampling dates) should demonstrate an effect. Appropriate reference and control measures must be included in the toxicity testing. The methods acceptable to and used by the BPTCP may include some toxicity test protocols

not referenced in water quality control plans (Table 8 in Chapter III). Toxic pollutants should be present in the media at concentrations sufficient to cause or contribute to toxic responses in order to satisfy this condition.

3. The tissue toxic pollutant levels of organisms collected from the site exceed levels established by the Office of Environmental Health Hazard Assessment (OEHHA), California Department of Health Services (DHS), United States Food and Drug Administration (FDA) for the protection of human health, or the National Academy of Sciences (NAS) for the protection of human health or wildlife. When health warning against the consumption of edible organisms has been issued by OEHHA or DHS, on a site, the site is automatically classified a "known" toxic hot spot.

   Acceptable tissue concentrations are measured either as muscle tissue (preferred) or whole body residues. Residues in liver tissue alone are not considered a suitable measure for known toxic hot spot designation. Animals can either be deployed (if a resident species) or collected from resident populations. Recurrent measurements are required. Residue levels established for the protection of human health can be applied to any consumable species.

   Shellfish: Except for existing information, each sampling episode should include a minimum of three replicates. The value of interest is the average value of the three replicates. Each replicate should be comprised of at least 15 individuals. For existing State Mussel Watch information related to organic pollutants, a single composite sample (20-100 individuals), may be used instead of the replicate measures. When recurrent measurements exceed one of the levels referred to above, the site is considered a known toxic hot spot.

3. Toxic pollutant levels in the tissue of resident or test species are elevated, but do not meet criteria for determination of the site as a known toxic hot spot, tissue toxic pollutant levels exceed maximum tissue residue levels (MTRLs) derived from water quality objectives contained in appropriate water quality control plans, or a health warning has been issued for the site by a local public health agency.

4. The level of pollutant at a site exceeds Clean Water Act Section 304(a) criterion, or sediment quality guidelines or EPA sediment toxicity criteria for toxic pollutants.

In summary, sites are designated as "known" hot spots after generating information which satisfies any one of the five conditions constituting the working definition. To use the working definition, a list of toxicity tests for BPTCP toxicity testing is provided in Table 8 (Chapter III). This list identifies toxicity tests for monitoring and surveillance activities described in regional monitoring plans and partially satisfies the Water Code requirement [Section 13392.5(a)(2)] for standardized analytical methods (Department of Fish and Game, 1993).

2. Potential Toxic Hot Spot

In addition to the identification of "known" toxic hot spots, the statute requires the identification of suspected or "potential" toxic hot spots (Water Code Section 13392.5). Sites with existing information indicating possible impairment, but without sufficient information to be classified as a "known" toxic hot spot are classified as "potential" hot spots. Four conditions sufficient to identify a "potential" toxic hot spot are defined below. If any one of the following conditions is satisfied, a site can be designated a "potential" toxic hot spot:

1. Concentrations of toxic pollutants are elevated above background levels, but insufficient data are available on the impacts associated with such pollutant levels to determine the existence of a known toxic hot spot;

2. Water or sediments which exhibit toxicity in screening tests or tests other than those specified by the BPTCP;

Abnormal Development: Abnormal development can be determined using measures of physical or behavioral disorders or aberrations. Evidence that the disorder can be caused by toxic pollutants, in whole or in part, must be available.

Histopathology: Abnormalities representing distinct adverse effects, such as carcinomas or tissue necrosis, must be evident. Evidence that toxic pollutants are capable of causing or contributing to the disease condition must also be available.

Biomarkers: Direct measures of physiological disruption or biochemical measures representing adverse effects, such as significant DNA strand breakage or perturbation of hormonal balance, must be evident. Biochemical measures of exposure to pollutants, such as induction of stress enzymes, are not by themselves suitable for determination of "known" toxic hot spots. Evidence that a toxic pollutant causes or contributes to the adverse effect are needed.

5. Significant degradation in biological populations and/or communities associated with the presence of elevated levels of toxic pollutants.

This condition requires that diminished numbers of species or changes in the number of individuals of a single species (when compared to a reference site) are associated with concentrations of toxic pollutants. The analysis should rely on measurements from multiple stations. Care should be taken to ensure that at least one site is not degraded so that a suitable comparison can be made.

Fin-fish: A minimum of three replicates is necessary. The number of individuals needed will depend on the size and availability of the animals collected; although a minimum of five animals per replicate is recommended. The value of interest is the average of the three replicates. Animals of similar age and reproductive stage should be used.

4. Impairment is associated with toxic pollutants found in resident individuals.

Impairment means reduction in growth, reduction in reproductive capacity, abnormal development, histopathological abnormalities, or identification of adverse effects using biomarkers. Each of these measures must be made in comparison to a reference condition where the endpoint is measured in the same species and tissue is collected from an unpolluted reference site.

Growth Measures: Reductions in growth can be addressed using suitable bioassays acceptable to the BPTCP or through measurements of field populations (please refer to Table 8).

Reproductive Measures: Reproductive measures must clearly indicate reductions in viability of eggs or offspring, or reductions in fecundity. Suitable measures include: pollutant concentrations in tissue, sediment, or water which have been demonstrated in laboratory tests to cause reproductive impairment, or significant differences in viability or development of eggs between reference and test sites.

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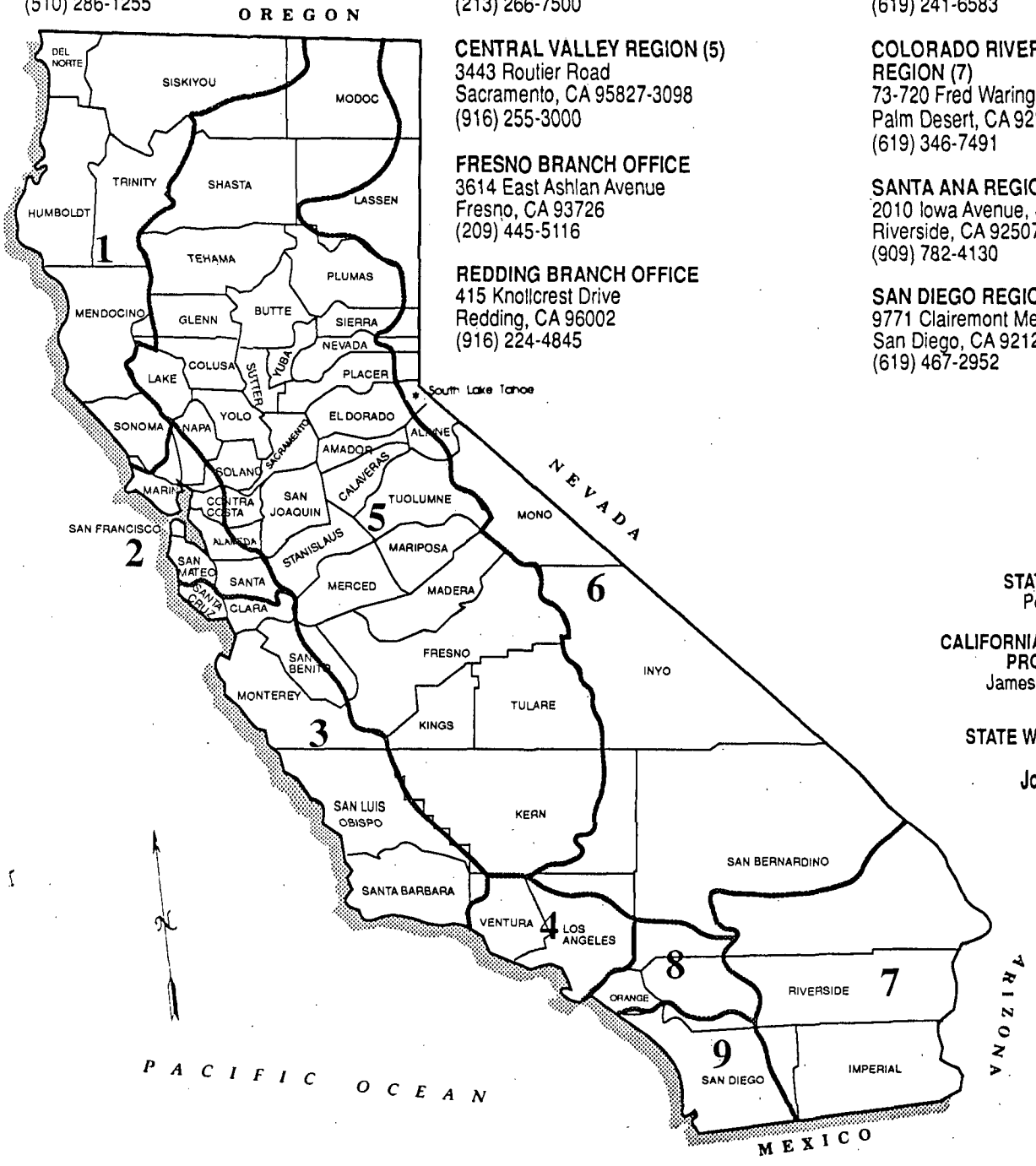

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