# CHEMICAL AND BIOLOGICAL MEASURES OF SEDIMENT QUALITY AND TISSUE BIOACCUMULATION IN THE NORTH COAST REGION FINAL REPORT

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California State Water Resources Control Board

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#### **EXECUTIVE SUMMARY**

This report describes and evaluates chemical and biological data collected from North Coast Region between November, 1992 and December, 1996. The study was conducted as part of the ongoing Bay Protection and Toxic Cleanup Program (BPTCP), a legislatively mandated program designed to assess the degree of chemical pollution and associated biological effects in California's bays and harbors. This Study was designed by the North Coast Regional Water Quality Control Board (RWQCB) staff. It was managed and coordinated by the State Water Resources Control Board's (SWRCB) Bays and Estuaries Unit and the California Department of Fish and Game's (CDFG) Marine Pollution Studies Laboratory. Funding was provided through the SWRCB by fees assessed by the BPTCP.

The purposes of the present study were to:

- 1. Determine presence or absence of statistically significant toxicity effects in representative areas of the North Coast Region;
- 2. Determine relative degree or severity of observed effects, and distinguish more severely impacted sediments from less severely impacted sediments;
- 3. Determine relationships between pollutants and measures of effects in these water bodies.
- 4. Identify stations where pollution may impact biological resources.

This study involved chemical analysis of sediments and tissues, benthic community analysis, and toxicity testing of sediments and sediment pore water. Chemical analyses and bioassays were performed using aliquots of homogenized sediment samples collected synoptically at each station. Analyses of the benthic community structure and tissue samples were made on a subset of the total number of stations sampled.

The program design resulted in 65 samples collected from 31 station locations in the Humboldt, Arcata, and Bodega Bay region. Analyses performed most consistently at a station were solid phase amphipod bioassays (n=57), grain size (n=54), and total organic carbon (n=54). Trace metal analysis and trace synthetic organic analyses were performed on 34 and 33 sediment samples, respectively. Eight sediment samples were analyzed for PAH, PCB, BTEX or TPH analyses only. Ten tissue samples were analyzed for trace metals and trace synthetic organics, and an additional ten tissue samples were analyzed for PAH, PCB, BTEX, and TPH analyses only. Benthic community analysis was performed on 14 stations with 3 replicate cores per station. One relatively "unpolluted" station had sediment and pore water collected as a control for bioassay tests.

Sediment quality guideline values were used for comparison with chemical concentrations found within the North Coast Region. Chromium, nickel, PAHs, and lindane were found most often to exceed ERM or PEL guideline values. Due to relatively low chemical concentrations within the

region, ERL and TEL guideline values also were used to provide more relevant comparisons to the chemical composition of the North Coast Region. Copper, mercury, and zinc were found most often to exceed ERL and TEL guideline values. Although ERL and TEL values are considerably lower than ERM and PEL guidelines, multiple exceedances of ERL and TEL guidelines may indicate possible impacts on the relatively unpolluted environment of the North Coast Region.

The upper 90<sup>th</sup> percentiles, for sediment summary quotient ranges, for the North Coast Region were ERMQ>0.201 and PELQ>0.422. These values are significantly lower than other summary quotient values calculated for the state (i.e., San Diego's 90<sup>th</sup> percentile ERMQ>0.85 and PELQ>1.29). Nevertheless, these lower values are to be expected because the North Coast is not as heavily populated or industrialized as much of California. It should be noted that lower summary quotient values should not be used to infer chemical pollution does not exist at discrete locations within the region.

Tissue samples were collected from 10 stations and were analyzed for a variety of chemicals. Samples included both resident and transplanted mussels, oysters, crabs and polychaete worms. When applicable, corresponding State Mussel Watch Program (SMWP) stations also were assessed for chemical contamination and provided supplemental information about stations. Tissue chemical concentrations were evaluated based on recommended U.S. EPA human health risk screening values and additional criteria used in SMWP reports, such as, Elevated Detection Levels (EDLs) and Maximum Tissue Residual Levels (MTRLs). In general, measured tissue concentrations of organic contaminants, such as pesticides, BTEX and TPH, were below detection limits, indicating relatively low levels of tissue contamination in the North Coast Region. However, some trace metals were detected in patterns similar to those found in sediments. Metals that were detected in both sediments and tissues included chromium, nickel, copper, and mercury.

Toxicity within the region was examined using a variety of bioassays. Twenty-nine of 31 stations sampled were tested using solid phase amphipod survival tests. Of these stations, 9 were toxic at least once using either *Eohaustorius* or *Rhepoxynius*. Amphipod survival ranged from 38-99%. Stations shown to be toxic were scattered along the northern section of the Eureka waterfront, at the northern most station in Arcata Bay, and at the three marinas in Bodega Bay. All samples that were toxic, and had synoptic chemical analysis performed on them, had at least one ERM or PEL exceedance and at least 3 ERL or TEL exceedances. However, multiple regression analysis of data from throughout the region showed no significant relationships between amphipod toxicity and chemical concentrations.

In addition to amphipod bioassays, several supplemental bioassays were performed on selected samples from the North Coast Region. One of four sediment-water interface sea urchin development tests was found to be toxic; three out of seven *Mytilus* spp. embryo-larval development tests conducted in pore water were toxic, however, none of the *Mytilus* spp. subsurface water samples were toxic. None of the thirty-seven samples on which polychaete survival and growth tests were performed were toxic. No results from sea urchin porewater fertilization tests were used in station analysis due to methodology concerns with collection and storage of porewater samples.

Benthic community structure within the North Coast Region was analyzed using a Relative Benthic Index (RBI). The low and high ranges of the index indicate the relative "health" or pollution impact of a station compared to other stations within the data set. These ranges were used to classify 14 stations as degraded, transitional and undegraded. The RBI for the North Coast ranged between 0.4 and 0.9 and none were classified as degraded. Nine stations were classified as having transitional benthic communities. These stations were scattered throughout the study area, particularly in Bodega Bay. The three undegraded stations were located on the central portion of the Eureka Waterfront. Due to the relatively low pollution levels in this region, and the small benthic community sample size, distinct patterns or relationship between sediment chemistry and RBI values were not found.

Five stations, Porto Bodega Marina, Mason's Marina, H Street, J Street, and Humboldt Bay Coal Gas and Oil Plant were distinguished as stations of concern or interest for the region. These stations exhibited greater chemical concentrations, levels of toxicity, or biological impacts relative to the other stations analyzed in the region.

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#### LIST OF ABBREVIATIONS

AA Atomic Absorption

ASTM American Society for Testing Materials

AVS Acid Volatile Sulfide

BTEX Benzene, Toluene, Ethylbenzene, Xylene
BPTCP Bay Protection and Toxic Cleanup Program
CDFG California Department of Fish and Game

CH Chlorinated Hydrocarbon

COC Chain of Custody
COR Chain of Records
EDL Elevated Data Levels
ERL Effects Range Low
ERM Effects Range Median

ERMQ Effects Range Median Summary Quotient EqP Equilibrium Partitioning Coefficient FAAS Flame Atomic Absorption Spectroscopy

GC/ECD Gas Chromatograph Electron Capture Detection
GFAAS Graphite Furnace Atomic Absorption Spectroscopy

HCl Hydrochloric Acid

HDPE High-density Polyethylene

HMW PAH High Molecular Weight Polynuclear Aromatic Hydrocarbons

HNO3 Nitric Acid

HPLC/SEC High Performance Liquid Chromatography Size Exclusion

H<sub>2</sub>S Hydrogen Sulfide

IDORG Identification and Organizational Number

KCL Potassium Chloride

LC50 Lethal Concentration (to 50 percent of test organisms)

LMW PAH Low Molecular Weight Polynuclear Aromatic Hydrocarbons

MDL Method Detection Limit
MDS Multi-Dimensional Scaling

MLML Moss Landing Marine Laboratories
MPSL Marine Pollution Studies Laboratory
MTRL Maximum Tissue Residual Level

NH3 Ammonia

NIST National Institute of Standards and Technology NOAA National Oceanic and Atmospheric Administration

NOEC No Observed Effect Concentration NS&T National Status and Trends Program PAH Polynuclear Aromatic Hydrocarbons

PCB Polychlorinated Biphenyl PEL Probable Effects Level

PELO Probable Effects Level Summary Quotient

PPE Porous Polyethylene PVC Polyvinyl Chloride

#### List of Abbreviations (cont.)

kilogram = 1 kg

1 part per thousand (ppt) = 1 mg/g

1 part per million (ppm) = 1 mg/kg, 1  $\mu$ g/g 1 part per billion (ppb) = 1  $\mu$ g/kg, 1 ng/g

QA **Quality Assurance Quality Assurance Project Plan** OAPP **Quality Control** OC Relative Benthic Index RBI Reference REF RWQCB Regional Water Quality Control Board **SMWP** State Mussel Watch Program Scientific Planning and Review Committee **SPARC** Sediment Quality Criteria SQC **SWRCB** State Water Resources Control Board T Temperature Tributyltin TBŢ TEL Threshold Effects Level Tefzel Teflon® TFE Total Organic Carbon TOC Trace Organics Facility TOF University of California Santa Cruz **UCSC** U.S. Environmental Protection Agency USEPA Whole Core Squeezing WCS **Units** liter = 11milliliter = 1 ml $microliter = 1 \mu l$ gram = 1 gmilligram = 1 mg $microgram = 1 \mu g$ nanogram = 1 ng

#### I. INTRODUCTION

#### Purpose

The California Water Code, Division 7, Chapter 5.6, Section 13390 mandates the State Water Resources Control Board (SWRCB) and the Regional Water Quality Control Boards to provide the maximum protection of existing and future beneficial uses of bays and estuarine waters, and to plan for remedial actions at those identified toxic hot spots where the beneficial uses are being threatened by toxic pollutants.

In response to this mandate, the Bay Protection and Toxic Cleanup Program (BPTCP) investigated populated areas along California's northern coast. BPTCP has four major goals: provide protection of present and future beneficial uses of the bay and estuarine waters of California; identify and characterize toxic hot spots; plan for toxic hotspot cleanup or other remedial or mitigation actions; develop prevention and control strategies for toxic pollutants that will prevent creation of new toxic hot spots or the perpetuation of exiting ones within the bays and estuaries of the state. This report presents results from data collected in Region 1, which includes the area between Humboldt to Marin counties in Northern California.

The purposes of the present study were to:

- 1. Determine presence or absence of statistically significant toxic effects in representative areas of the North Coast Region;
- 2. Determine relative degree or severity of observed effects, and distinguish more severely impacted sediments from less severely impacted sediments;
- 3. Determine relationships between pollutants and measures of effects in these water bodies.
- 4. Identify stations where pollution may impact biological resources.

#### Programmatic Background and Needs

Due to a variety of human activities throughout northern California's bays and estuaries, there is a need to assess if any environmentally detrimental effects have been associated with those human activities. This study was designed to investigate these environmental effects by evaluating the biological and chemical state of northern California coastal sediments. The methods used to assess possible environmental impacts include sediment and interstitial water bioassays, sediment and tissue chemistry analysis, and benthic community analysis. This study was conducted along the coastal boundaries of Region 1, from Crescent City south to Estero de San Antonio. Although these water bodies are separated physically, and are different in character, for simplicity they often will be referred to collectively as the "North Coast Region" in this report (Figure 1).

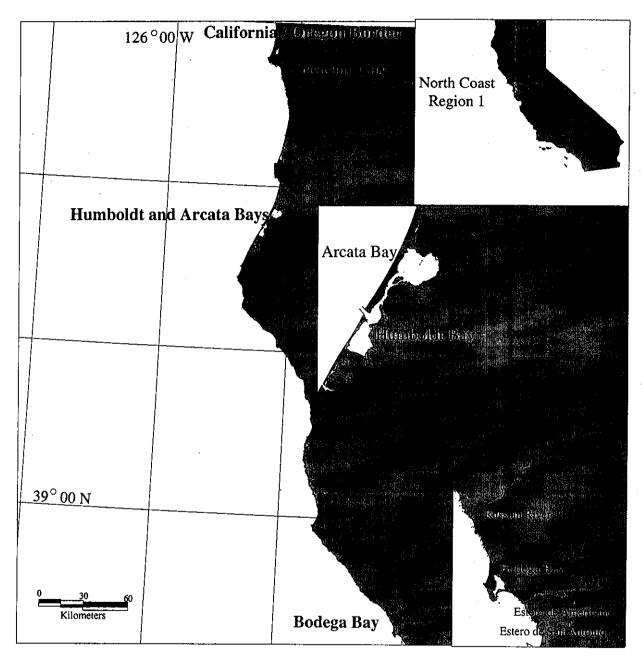


Figure 1. North Coast (Region 1) study area.

Sediment characterization approaches currently used by the BPTCP range from chemical or toxicity monitoring only, to monitoring designs that attempt to generally correlate the presence of pollutants with toxicity or benthic community degradation. Studies were designed, managed, and coordinated by the SWRCB's Bays and Estuaries Unit, and the California Department of Fish and Game's (CDFG) Marine Pollution Studies Laboratory (MPSL). Funding was provided by SWRCB through BPTCP assessed fees.

Sampling for the North Coast Region involved toxicity testing and chemical analysis of sediments, sediment pore water, and tissue samples, as well as, benthic community analysis. Toxicity tests and chemical analysis were performed using aliquots of homogenized sediment samples collected synoptically from each station, resulting in paired data. Analysis of benthic community structure, pore water, and tissue samples also were made on a subset of the total number of stations sampled.

Field and laboratory work was accomplished under interagency agreement with the CDFG. Staff of the San Jose State University Foundation at Moss Landing Marine Laboratories (MLML) performed sample collections. CDFG personnel at the MLML facility performed trace metals analyses. Synthetic organic pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) were analyzed at the University of California at Santa Cruz (UCSC) trace organics analytical facility at Long Marine Laboratory in Santa Cruz, California. Benzene, toluene, ethylbenzene, xylene (BTEX) and total Petroleum hydrocarbon (THP) analysis was performed by PACE Inc. Environmental Lab. MLML staff also performed total organic carbon (TOC) and grain size analyses, as well as benthic community analyses. Toxicity testing was conducted by the UCSC staff at the CDFG toxicity testing laboratory at Granite Canyon.

#### Study Area

The North Coast Region, as described by RWQCB (1992), is summarized in the following paragraphs. This region comprises all of Del Norte, Humboldt, Trinity, and Mendocino Counties, major portions of Siskiyou and Sonoma Counties, and small portions of Glenn, Lake, and Marin Counties. The North Coast Region is divided into two natural drainage basins, the Klamath River Basin and the North Coastal Basin. Total area encompassed by the North Coast Region is approximately 19,390 square miles, including 340 miles of scenic coastline and remote wilderness areas, as well as urbanized and agricultural areas.

This study included five main water bodies: Humboldt Bay, Bodega Harbor, Russian River estuary, Estero de Americano, and Estero de San Antonio. The following paragraphs will provide a brief description of the extent of each water body, as well as human activities of concern and are based upon the Regional Monitoring Plan (RWQCB 1992).

The Humboldt Bay water body includes Arcata Bay and three segments of Humboldt Bay. This area encompasses approximately 15,000 acres and is considered a shipping port, industrial center, and northern California population hub. The northern and central portions of the Bay are encircled by two cities and several small, unincorporated communities. Along with these communities there are associated industrial activities, such as pulp mills, bulk petroleum plants, fossil fuel and nuclear power plants, lumber mills, boat repair facilities and fish processing plants. Small commercial and sport marinas have been constructed in the Bay and agricultural

lands surround much of the Bay. Two large landfills are located adjacent to the Bay. Coal and oil gasification plants historically have been operated at various locations on the edge of the Bay. Municipal wastewater, industrial wastes and stormwater runoff have been discharged into the Bay throughout its 150 year history. Because there is a very narrow opening connecting Humboldt Bay to the Pacific Ocean, circulation and flushing are severely restricted, resulting in a high potential for sediment and pollutant deposition.

Two previous studies indicated there may be areas of concern within Humboldt Bay. State Mussel Watch Reports showed accumulation of heavy metals, pentachlorophenol, and tetrachlorophenol in tissues from transplanted mussels (Rasmussen, 1995). Also a draft report of a US Army Corps of Engineers (1991) study on sediments in the Eureka shipping channel described mortality of flatfish and oyster larvae in sediment bioassays. For these reasons 15 stations were examined within Humboldt Bay.

The second major water body within this study is Bodega Harbor. Bodega Harbor is a wide shallow bay with extensive mud flats, which are exposed at low tide. It encompasses approximately 700 acres and the harbor is largely undeveloped. A small fishing village and agricultural community have developed along the easterly shore. The Bodega Harbor subdivision began development in 1970 and consists of scattered lots around a golf course and open space. This subdivision, as well as the town of Bodega Bay, are sewered with treated wastewater being discharged inland. Bodega Harbor, like Humboldt Bay, has a narrow opening between two jetties severely restricting circulation and flushing of the Harbor, therefore creating a high potential for sediment and pollutant deposition. Of primary interest are the harbor's three large boat mooring facilities and associated boat repair and refueling facilities. State Mussel Watch reports (Rasmussen 1995, 1996) and a winter 1990-1991 study by the University of California, Bodega Marine Laboratory (BML) indicated there were areas of potential concern. The BML study conducted short-term oyster spat bioassays and found spat mortality at these three marinas. Based on these two reports four stations were examined within Bodega Harbor.

The Russian River Estuary is the third major water body included in this study. This estuary is the deep and broad terminus of the Russian River and encompasses approximately 150 acres. Flushing and tidal exchange occur only during and after periods of rainfall, otherwise natural sandbars obstruct the mouth for much of the year. While the Russian River Estuary is largely undeveloped, it is an area of potential concern for various reasons. There are municipal discharges which enter into the Russian River Estuary from several communities, including those of the densely populated Santa Rosa Plain. In addition there are historic industrial discharges, urban runoff from Sonoma and Mendocino counties, and agricultural runoff. All of these factors have created a potential for sediment and pollutant deposition in this water body.

Estero de Americano and Estero de San Antonio are the two remaining major water bodies included in this study. Estero de Americano is the terminus of the coastal Americano Creek. It encompasses approximately 370 acres and is largely undeveloped. Estero de San Antonio is the terminus of the coastal Stemple Creek. It encompasses approximately 255 acres and like Estero de Americano is largely undeveloped. The land surrounding both Esteros is extensively grazed by livestock. For this reason, there are numerous confined animal discharges that generate high ammonia and low dissolved oxygen levels within the Esteros. These factors create a potential for pollutant deposition thus these areas were examined as part of this study.

#### II. METHODS

#### Sampling Design

Station selection was based upon a directed point sampling design and was used to address SWRCB's need to identify specific areas of concern. This sampling design required a two step process for station selection. First, Regional and State Board staff identified areas of interest for sampling during an initial "screening phase". Station locations (latitude & longitude) were predetermined by agreement with the SWRCB, RWQCB, and CDFG personnel. Changing of the station location during sediment collection was allowed only under the following conditions:

- 1. Lack of access to predetermined station,
- 2. Inadequate or unusable sediment (i.e. rocks or gravel)
- 3. Unsafe conditions
- 4. Agreement of appropriate staff

This screening phase was intended to give a broad assessment of toxicity throughout the North Coast Region's five main water bodies. Chemical analysis was performed on selected samples in which toxicity results prompted further analysis. Stations that met certain criteria during the screening phase, then were selected for a second round of sampling, termed the "confirmation phase". During this phase, the sampling was replicated and chemical analysis of samples was more extensive. In addition, benthic community analysis was performed on all confirmation stations sampled during 1996. Results from this two step process were used to establish a weight of evidence or higher level of certainty for stations that later may be identified as "toxic hot spots" or areas of concern.

The program design resulted in 65 samples collected from 31 station locations in the Humboldt, Arcata, and Bodega Bay Region (Figures 2, 3), between November, 1992 and December, 1996. Station locations that were sampled more than once were always resampled at the original location using navigational equipment and lineups. Analyses done most consistently at a station were solid phase amphipod survival (n=57), grain size (n=54), and total organic carbon (TOC) (n=54). Trace metal analysis and trace synthetic organic analyses were performed on 34 and 33 sediment samples, respectively. Eight sediment samples were analyzed for PAH, PCB, benzene, toluene, ethylbenzene, xylene (BTEX) and total petroleum hydrocarbon (TPH) analyses only. Ten tissue samples were analyzed for trace metals and trace synthetic organics, and an additional ten tissue samples were analyzed for PAH, PCB, BTEX and TPH analyses only. Benthic community analysis was performed on 14 stations with 3 replicate cores per station. One relatively "unpolluted" station had sediment and pore water collected as a control for bioassay tests.



Figure 2. Humboldt and Arcata Bays sampling stations.

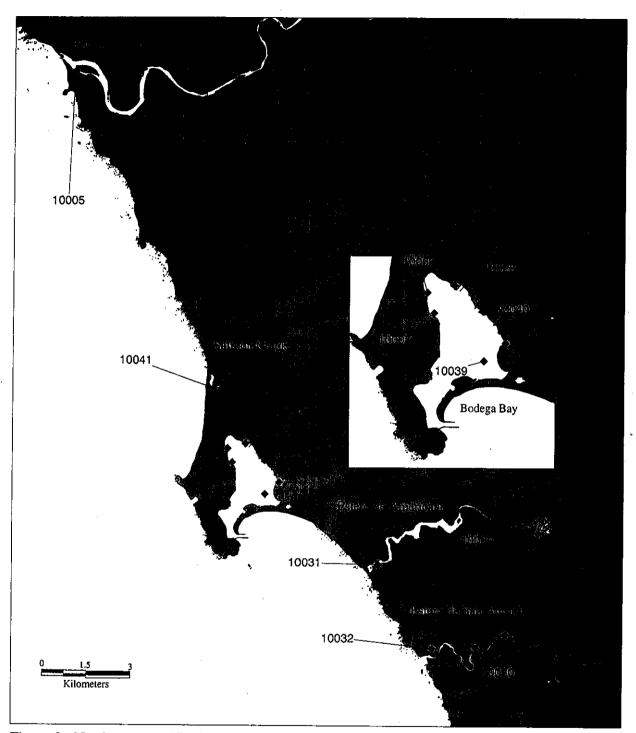


Figure 3. North coast and Bodega Bay sampling stations.

#### Sample Collection and Processing

#### **Summary of Methods**

Specific techniques used for collecting and processing samples are described in this section. Because collection of sediments influences the results of all subsequent laboratory and data analyses, it was important that samples be collected in a consistent and conventionally acceptable manner. Field and laboratory technicians were trained to conduct a wide variety of activities using standardized protocols to ensure comparability in sample collection among crews and across geographic areas. Sampling protocols in the field followed the accepted procedures of NS&T and ASTM, and included methods to avoid cross-contamination; methods to avoid contamination by the sampling activities, crew, and vessel; collection of representative samples of the target surficial sediments; careful temperature control, homogenization and subsampling; and chain of custody procedures.

#### **Cleaning Procedures**

All sampling equipment (i.e., containers, container liners, scoops, water collection bottles) was made from non-contaminating materials and was precleaned and packaged protectively prior to entering the field. Sample collection gear and samples were handled only by personnel wearing non-contaminating polyethylene gloves. All sample collection equipment (excluding the sediment grab) was cleaned by using the following sequential process:

Two-day soak and wash in Micro® detergent, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl, three ASTM Type II Milli-Q® water rinses, air dry, three petroleum ether rinses, and air dry.

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

The sediment grab was cleaned prior to entering the field and between sampling stations, by utilizing the following sequential steps: a vigorous Micro® detergent wash and scrub, a seawater rinse, a 10% HCl rinse, and a methanol rinse. The sediment grab was scrubbed with seawater between successive deployments at the same station to remove adhering sediments from contact surfaces possibly originating below the sampled layer.

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

Plastic containers (HDPE or TFE) for trace metal analysis media (sediment, archive sediment, porewater, and subsurface water) were cleaned by: a two-day Micro® detergent soak, three tapwater rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO<sub>3</sub>, three Type II Milli-Q® water rinses, and air dry.

Glass containers for total organic carbon, grain size or synthetic organic analysis media (sediment, archive sediment, porewater, and subsurface water), and additional teflon sheeting cap-liners were cleaned by: a two-day Micro® detergent soak, three tap-water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO<sub>3</sub>, three Type II Milli-Q® water rinses, air dry, three petroleum ether rinses, and air dry.

#### **Sediment Sample Collection**

All sampling locations (latitude & longitude), whether altered in the field or predetermined, were verified using a Magellan NAV 5000 Global Positioning System, and recorded in the field logbook. The primary method of sediment collection was by use of a  $0.1 \text{m}^2$  Young-modified Van Veen grab aboard a sampling vessel. Modifications included a non-contaminating Kynar coating, which covered the grab's sample box and jaws. After the filled grab sampler was secured on the boat gunnel, the sediment sample was inspected carefully. The following acceptability criteria were met prior to taking sediment samples. If a sample did not meet all the criteria, it was rejected and another sample was collected.

- 1. Grab sampler was not over-filled (i.e., the sediment surface was not pressed against the top of the grab).
- 2. Overlying water was present, indicating minimal leakage.
- 3. Overlying water was not excessively turbid, indicating minimal sample disturbance.
- 4. Sediment surface was relatively flat, indicating minimal sample disturbance.
- 5. Sediment sample was not washed out due to an obstruction in the sampler jaws.
- 6. Desired penetration depth was achieved (i.e., 10 cm).
- 7. Sample was muddy (>30% fines), not sandy or gravelly.
- 8. Sample did not include excessive shell, organic or man-made debris.

It was critical that sample contamination be avoided during sample collection. All sampling equipment (i.e., siphon hoses, scoops, containers) was made of non-contaminating material and was cleaned appropriately before use. Samples were not touched with un-gloved fingers. In addition, potential airborne contamination (e.g., from engine exhaust, cigarette smoke) was avoided. Before sub-samples from the grab sampler were taken, the overlying water was removed by slightly opening the sampler, being careful to minimize disturbance or loss of finegrained surficial sediment. Once overlying water was removed, the top 2 cm of surficial sediment was sub-sampled from the grab. Sub-samples were taken using a pre-cleaned flat bottom scoop. This device allowed a relatively large sub-sample to be taken from a consistent depth. When subsampling surficial sediments, unrepresentative material (e.g., large stones or vegetative material) was removed from the sample in the field. Such removals were noted on the field data sheet. Small rocks and other small foreign material remained in the sample. Determination of overall sample quality was determined by the chief scientist in the field. For the sediment sample, the top 2 cm was removed from the grab and placed in a pre-labeled polycarbonate container. Between grabs or cores, the sediment sample in the container was covered with a teflon sheet, and the container covered with a lid and kept cool. When a sufficient amount of sediment was collected, the sample was covered with a teflon sheet assuring no air bubbles. A second, larger teflon sheet was placed over the top of the container to ensure an air tight seal, and nitrogen was vented into the container to purge it of oxygen.

If water depth did not permit boat entrance to a station (e.g. <1 meter), personnel sampled that station using sediment cores (diver cores). Cores consisted of a 10 cm diameter polycarbonate tube, 30 cm in length, including plastic end caps to aid in transport. Samplers entered a study location from one end and sampled in one direction, so as to not disturb the sediment with feet. Cores were taken to a depth of at least 15 centimeters. Sediment was extruded out of the top end of the core to the prescribed depth of 2 cm, removed with a polycarbonate spatula and deposited into a cleaned polycarbonate tub. Additional samples were taken with the same seawater rinsed core tube until the required total sample volume was attained. Diver core samples were treated the same as grab samples, with teflon sheets covering the sample and nitrogen purging. All sample acceptability criteria were met as with the grab sampler.

# Sediment Sample Collection for Bioassay Controls

In order to have a reference point, or sediment control for bioassay tests, three 12 L replicates of sediment were collected from a location that was considered to be relatively "unpolluted". The replicates were located at least 50 m from one another and locations were verified using a Magellan NAV 5000 Global Positioning System, and then recorded in the field logbook. Due to the large volume of sediment needed, these samples were collected using the diver core method described above. The top 2 cm of sediment was extruded out of the top end of the diver core, removed with a polycarbonate spatula and deposited into a pre-cleaned 12 L polycarbonate tub. The sediment then was covered with teflon sheets and purged with nitrogen as per the regularly collected sediment samples.

Interstitial water also was collected at this location in order to be used as a reference or control for porewater bioassays. Interstitial water was collected by using a pre-cleaned polycarbonate spatula to dig a shallow hole in sediments exposed at low tide. This hole then was allowed to fill with interstitial water, which was collected using pre-cleaned polycarbonate turkey basters and placed in trace clean teflon bottles.

#### Transport of Samples

Six-liter or 12 L sample containers were packed (two or three to an ice chest) with enough ice to keep them cool for 48 hours. Each container was sealed in pre-cleaned, large plastic bags closed with a cable tie to prevent contact with other samples or ice or water. Ice chests were driven back to the laboratory by the sampling crew or flown by air freight within 24 hours of collection.

#### Homogenization and Aliquoting of Samples

Samples remained in ice chests (on ice, in double-wrapped plastic bags) until the containers were brought back to the laboratory for homogenization. All sample identification information (station numbers, etc.) was recorded on Chain of Custody (COC) and Chain of Record (COR) forms prior to homogenizing and aliquoting. A single container was placed on plastic sheeting while also remaining in original plastic bags. The sample was stirred with a polycarbonate stirring rod until mud appeared homogeneous.

All pre-labeled jars were filled using a clean teflon or polycarbonate scoop and stored in freezer/refrigerator (according to media/analysis) until analysis. The sediment sample was aliquoted into appropriate containers for trace metal analysis, organic analysis, pore water extraction, and bioassay testing. Samples were placed in boxes sorted by analysis type and leg number. Sample containers for sediment bioassays were placed in a refrigerator (4°C) while sample containers for sediment chemistry (metals, organics, TOC and grain size) were stored in a freezer (-20°C).

#### **Procedures for the Extraction of Sediment Pore water**

The BPTCP primarily used whole core squeezing to extract sediment pore water. The whole core squeezing method, developed by Bender et al. (1987), utilizes low pressure mechanical force to squeeze pore water from interstitial spaces. The following squeezing technique was a modification of the original Bender design with some adaptations based on the work of Fairey (1992), Carr et al. (1989), and Long and Buchman (1989). The squeezer's major features consist of an aluminum support framework, 10 cm i.d. acrylic core tubes with sampling ports and a pressure regulated pneumatic ram with air supply valves. Acrylic subcore tubes were filled with approximately 1 liter of homogenized sediment and pressure was applied to the top piston by adjusting the air supply to the pneumatic ram. At no time during squeezing did air pressure exceed 200 psi. A porous prefilter (PPE or TFE) was inserted in the top piston and used to screen large (> 70 microns) sediment particles. Further filtration was accomplished with disposable TFE filters of 5 microns and 0.45 microns in-line with sample effluent. Sample effluent of the required volume was collected in TFE containers under refrigeration. Porewater was subsampled in the volumes and specific containers required for archiving, chemical or toxicological analysis. To avoid contamination, all sample containers, filters and squeezer surfaces in contact with the sample were plastics (acrylic, PVC, and TFE) and cleaned with previously discussed clean techniques.

#### **Bioaccumulation Samples**

Bioaccumulation in resident organisms was investigated by analyzing mussels, oysters, crabs, and polychaete worms from several stations. Transplanted mussels also were collected using State Mussel Watch Program (SMWP) deployment and retrieval procedures (CDFG, 1992). Samples were frozen and taken back to the laboratory for dissection and distribution to the appropriate analytical laboratory. As with sediment samples, tissue samples were collected using trace clean techniques (CDFG, 1992).

#### **Benthic Samples**

Replicate benthic samples (n=3) were obtained from separate deployments of the sampler at predetermined stations. The coring device was 10 cm in diameter and 14 cm in height, enclosing a 0.0075 m<sup>2</sup> area. Corers were placed into sediment with minimum disruption of the surface sediments, capturing essentially all surface-active fauna as well as species living deeper in the sediment. Corers were pushed about 12 cm into the sediment and retrieved by digging along one side, removing the corer and placing the intact sediment core into a PVC screening device. Sediment cores were sieved through a 0.5 mm screen and residues (e.g., organisms and remaining

sediments) were rinsed into pre-labeled storage bags and preserved with a 10% formalin solution. After 3 to 4 days, samples were rinsed and transferred into 70% isopropyl alcohol and stored for future taxonomy and enumeration.

#### Chain of Records & Custody

Chain-of-records documents were maintained for each station. Each form was a record of all sub-samples taken from each sample. IDORG (a unique identification number for only that sample), station numbers and station names, leg number (sample collection trip batch number), and date collected were included on each sheet. A Chain-of-Custody form accompanied every sample so that each person releasing or receiving a subsample signs and dates the form.

#### Authorization/Instructions to Process Samples

Standardized forms entitled "Authorization/Instructions to Process Samples" accompanied the receipt of any samples by any participating laboratory. These forms were completed by DFG personnel, or its authorized designee, and were signed and accepted by both the DFG authorized staff and the staff accepting samples on behalf of the particular laboratory. The forms contain all pertinent information necessary for the laboratory to process the samples, such as the exact type and number of tests to run, number of laboratory replicates, dilutions, exact eligible cost, deliverable products (including hard and soft copy specifications and formats), filenames for soft copy files, expected date of submission of deliverable products to DFG, and other information specific to the lab/analyses being performed.

#### Trace Organic Analysis (PCBs, Pesticides, and PAHs)

#### **Summary of Methods**

Analytical sets of 12 samples were scheduled such that extraction and analysis will occur within a 40 day window. Methods employed by UCSC-TOF were modifications of those described by Sloan *et al.* (1993). Tables 1-5 indicate the pesticides, PCBs, and PAHs currently analyzed, and list method detection limits for sediments and tissues on a dry weight basis.

#### **Sediment Extraction**

Samples were removed from the freezer and allowed to thaw. A 10 gram sample of sediment was removed for chemical analysis and an independent 10 gram aliquot was removed for dry weight determinations. The dry weight sample was placed into a pre-weighed aluminum pan and dried at 110°C for 24 hours. The dried sample was reweighed to determine the sample's percent moisture. The analytical sample was extracted 3 times with methylene chloride in a 250 mL amber Boston round bottle on a modified rock tumbler. Prior to rolling, sodium sulfate, copper, and extraction surrogates were added to the bottle. Sodium sulfate dehydrates the sample allowing for efficient sediment extraction. Copper, which was activated with hydrochloric acid, complexes free sulfur in the sediment. After combining the three extraction aliquots, the extract was divided into two portions, one for chlorinated hydrocarbon (CH) analysis and the other for polycyclic aromatic hydrocarbon (PAH) analysis.

#### Tissue Extraction

Samples were removed from the freezer and allowed to thaw. A 5 gram sample of tissue was removed for chemical analysis and an independent 5 gram aliquot was removed for dry weight determinations. The dry weight sample was placed into a pre-weighed aluminum pan and dried at 110°C for 24 hours. The dried sample was reweighed to determine the sample's percent moisture. The analytical sample was extracted twice with methylene chloride using a Tekmar<sup>TM</sup> Tissumizer. Prior to extraction, sodium sulfate and extraction surrogates were added to the sample and methylene chloride.

The two extraction aliquots were combined and brought to 100ml. A 25 ml aliquot was decanted through a Whatmann 12.5 cm #1 filter paper into a pre-weighed 50 ml flask for lipid weight determination. The filter was rinsed with ~15 ml of methylene chloride and the remaining solvent was removed by vacuum-rotary evaporation. The residue was dried for 2 hours at 110°C and the flask was re-weighed. The change in weight was taken as the total methylene chloride extractable mass. This weight then was used to calculate the samples "percent lipid".

#### Organic Analysis

The CH portion was eluted through a silica/alumina column, separating the analytes into two fractions. Fraction 1 (F1) was eluted with 1% methylene chloride in pentane and contained > 90% of p,p'-DDE and < 10% of p,p'-DDT. Fraction 2 (F2) analytes were eluted with 100% methylene chloride. The two fractions were exchanged into hexane and concentrated to 500  $\mu$ L using a combination of rotary evaporation, controlled boiling on tube heaters, and dry nitrogen blow downs.

F1 and F2 fractions were analyzed on Hewlett-Packard 5890 Series gas chromatographs utilizing capillary columns and electron capture detection (GC/ECD). A single 2 µl splitless injection was directed onto two 60 m x 0.25 mm i.d. columns of different polarity (DB-17 & DB-5; J&W Scientific) using a glass Y-splitter to provide a two dimensional confirmation of each analyte. Analytes were quantified using internal standard methodologies. The extract's PAH portion was eluted through a silica/alumina column with methylene chloride. It then underwent additional cleanup using size-exclusion high performance liquid chromatography (HPLC/SEC). The collected PAH fraction was exchanged into hexane and concentrated to 250 µL in the same manner as the CH fractions.

# **Analytes and Detection Limits**

Table 1. Dry Weight Detection Limits of Chlorinated Pesticides.

	Database	MDL, ng/g dry	MDL, ng/g dry
Analytes	Abbreviation	Sediment	Tissue
Fraction #1 Analytes †			:
Aldrin	ALDRIN	0.5	1.0
alpha-Chlordene	ACDEN	0.5	1.0
gamma-Chlordene	GCDEN	0.5	1.0
o,p'-DDE	OPDDE	1.0	3.0
o,p'-DDT	OPDDT	1.0	4.0
Heptachlor	HEPTACHLOR	0.5	1.0
Hexachlorobenzene	HCB	0.2	1.0
Mirex	MIREX	0.5	1.0
Fraction #1 & #2 Analytes <sup>†,‡</sup>			
p,p'-DDE	PPDDE	1.0	1.0
p,p'-DDT	PPDDT	1.0	4.0
p,p'-DDMU	PPDDMU	2.0	5.0
trans-Nonachlor	TNONA	0.5	1.0
Fraction #2 Analytes ‡		0.0	*.0
cis-Chlordane	CCHLOR	0.5	1.0
trans-Chlordane	TCHLOR	0.5	1.0
Chlorpyrifos	CLPYR	1.0	4.0
Daethal	DACTH	0.2	2.0
o,p'-DDD	OPDDD	1.0	5.0
p,p'-DDD	PPDDD	0.4	3.0
p,p'-DDMS	PPDDMS	3.0	20
p,p'-Dichlorobenzophenone	DICLB	3.0	25
Methoxychlor	METHOXY	1.5	15
Dieldrin	DIELDRIN	0.5	1.0
Endosulfan I	ENDO_I	0.5	1.0
Endosulfan II	ENDO_II	1.0	3.0
Endosulfan sulfate	ESO4	2.0	5.0
Endrin	ENDRIN	2.0	6.0
Ethion	ETHION	2.0	NA
alpha-HCH	НСНА	0.2	1.0
beta-HCH	НСНВ	1.0	3.0
gamma-HCH	HCHG	0.2	0.8
delta-HCH	HCHD	0.5	2.0
Heptachlor Epoxide	HE	0.5	1.0
cis-Nonachlor	CNONA	0.5	1.0
Oxadiazon	OXAD	6	NA
Oxychlordane	OCDAN	0.5	0.2

The quantitation surrogate is PCB 103.

The quantitation surrogate is d8-p,p'-DD

\*\*\*Note that all tissue MDLs are reported in dry weight units because wet weight MDLs are based on percent moisture of the individual sample.

Table 2. Dry Weight Detection Limits of NIST PCB Congeners.

•		MDL, ng/g	MDL, ng/g
Analytes <sup>†</sup>	Database	dry	dry
	Abbreviation	Sediment	Tissue
2,4'-dichlorobiphenyl	PCB8	0.5	1.0
2,2',5-trichlorobiphenyl	PCB18	0.5	1.0
2,4,4'-trichlorobiphenyl	PCB28	0.5	1.0
2,2',3,5'-tetrachlorobiphenyl	PCB44	0.5	1.0
2,2',5,5'-tetrachlorobiphenyl	PCB52	0.5	1.0
2,3',4,4'-tetrachlorobiphenyl	PCB66	0.5	1.0
2,2',3,4,5'-pentachlorobiphenyl	PCB87	0.5	1.0
2,2',4,5,5'-pentachlorobiphenyl	PCB101	0.5	1.0
2,3,3',4,4'-pentachlorobiphenyl	PCB105	0.5	1.0
2,3',4,4',5-pentachlorobiphenyl	PCB118	0.5	1.0
2,2',3,3',4,4'-hexachlorobiphenyl	PCB128	0.5	1.0
2,2',3,4,4',5'-hexachlorobiphenyl	PCB138	0.5	1.0
2,2',4,4',5,5'-hexachlorobiphenyl	PCB153	0.5	1.0
2,2',3,3',4,4',5-heptachlorobiphenyl	PCB170	0.5	1.0
2,2',3,4,4',5,5'-heptachlorobiphenyl	PCB180	0.5	1.0
2,2',3,4',5,5',6-heptachlorobiphenyl	PCB187	0.5	1.0
2,2',3,3',4,4',5,6-octachlorobiphenyl	PCB195	0.5	1.0
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	PCB206	0.5	1.0
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	PCB209	0.5	1.0

<sup>†</sup> PCB 103 is the surrogate used for PCBs with 1 - 6 chlorines per molecule. PCB 207 is used for all others.

\*\*\* Note that all tissue MDLs are reported in dry weight units because wet weight MDLs are based on percent moisture of the individual sample.

Table 3. Additional PCB Congeners and Their Dry Weight Detection Limits.

Analytes <sup>†</sup>	Database Abbreviation	MDL, ng/g dry Sediment	MDL, ng/g dry Tissue
2,3-dichlorobiphenyl	PCB5	0.5	1.0
4,4'-dichlorobiphenyl	PCB15	0.5	1.0
2,3',6-trichlorobiphenyl	PCB27	0.5	1.0
2,4,5-trichlorobiphenyl	PCB29	0.5	1.0
2,4',4-trichlorobiphenyl	PCB31	0.5	1.0
2,2,'4,5'-tetrachlorobiphenyl	PCB49	0.5	1.0
2,3',4',5-tetrachlorobiphenyl	PCB70	0.5	1.0
2,4,4',5-tetrachlorobiphenyl	PCB74	0.5	1.0
2,2',3,5',6-pentachlorobiphenyl	PCB95	0.5	1.0
2,2',3',4,5-pentachlorobiphenyl	PCB97	0.5	1.0
2,2',4,4',5-pentachlorobiphenyl	PCB99	0.5	1.0
2,3,3',4',6-pentachlorobiphenyl	PCB110	0.5	1.0
2,2',3,3',4,6'-hexachlorobiphenyl	PCB132	0.5	1.0
2,2',3,4,4',5-hexachlorobiphenyl	PCB137	0.5	1.0
2,2',3,4',5',6-hexachlorobiphenyl	PCB149	0.5	1.0
2,2',3,5,5',6-hexachlorobiphenyl	PCB151	0.5	1.0
2,3,3',4,4',5-hexachlorobiphenyl	PCB156	0.5	1.0
2,3,3',4,4',5'-hexachlorobiphenyl	PCB157	0.5	1.0
2,3,3',4,4',6-hexachlorobiphenyl	PCB158	0.5	1.0
2,2',3,3',4,5,6'-heptachlorobiphenyl	PCB174	0.5	1.0
2,2',3,3',4',5,6-heptachlorobiphenyl	PCB177	0.5	1.0
2,2',3,4,4',5',6-heptachlorobiphenyl	PCB183	0.5	1.0
2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB189	0.5	1.0
2,2',3,3',4,4',5,5'-octachlorobiphenyl	PCB194	0.5	1.0
2,2',3,3',4,5',6,6'-octachlorobiphenyl	PCB201	0.5	1.0
2,2',3,4,4',5,5',6-octachlorobiphenyl	PCB203	0.5	1.0

PCB 103 is the surrogate used for PCBs with 1 - 6 chlorines per molecule. PCB 207 is used for all others.

Table 4. Dry Weight Detection Limits of Chlorinated Technical Grade Mixtures.

Analyte	Database Abbreviation	MDL, ng/g dry Sediment	MDL, ng/g dry Tissue
Toxaphene <sup>‡</sup>	ТОХАРН	50	100
Polychlorinated Biphenyl Aroclor 1248	ARO1248	5	100
Polychlorinated Biphenyl Aroclor 1254	ARO1254	5	50
Polychlorinated Biphenyl Aroclor 1260	ARO1260	5	50
Polychlorinated Terphenyl Aroclor 5460 <sup>†</sup>	ARO5460	10	100

<sup>†</sup> The quantitation surrogate is PCB 207.

<sup>\*\*\*</sup>Note that all tissue MDLs are reported in dry weight units because wet weight MDLs are based on percent moisture of the individual sample.

<sup>†</sup> The quantitation surrogate is d8-p,p'-DDD

\*\*\* Note that all tissue MDLs are reported in dry weight units because wet weight MDLs are based on percent moisture of the individual sample.

Table 5: Dry Weight Detection Limits of Polyaromatic Hydrocarbons.

Analytes <sup>†</sup>	Database Abbreviation	MDL, ng/g dry Sediment	MDL, ng/g dry Tissue
Naphthalene	NPH	5	10
2-Methylnaphthalene	MNP2	5	10
1-Methylnaphthalene	MNP1	5	10
Biphenyl	ВРН	5	10
2,6-Dimethylnaphthalene	DMN	5	10
Acenaphthylene	ACY	5	10
Acenaphthene	ACE	5	10
2,3,5-Trimethylnaphthalene	TMN	. 5	10
Fluorene	FLU	5	10
Dibenzothiophene	DBT	5	10
Phenanthrene	PHN	5	10
Anthracene	ANT	5	10
1-Methylphenanthrene	MPH1	5	10
Fluoranthene	FLA	5	10
Pyrene	PYR	5	10
Benz[a]anthracene	BAA	5	10
Chrysene	CHR	5	10
Tryphenylene	TRY	5	10
Benzo[b]fluoranthene	BBF	5	10
Benzo[k]fluoranthene	BKF	5	10
Benzo[e]pyrene	BEP	. 5	10
Benzo[a]pyrene	BAP	5	10
Perylene	PER	5	10
Indeno[1,2,3-c,d]pyrene	IND	5	15
Dibenz[a,h]anthracene	DBA	5	15
Benzo[g,h,I]perylene	BGP	5	15
Coronene	COR	5	15

<sup>&</sup>lt;sup>†</sup> See OA report for surrogate assignments.

#### **BTEX** and **TPH** Analysis

Eight sediment and nine tissue samples were analyzed by PACE Incorporated Environmental Laboratories for BTEX and TPH (diesel extraction). The methods for this extended organic analysis are summarized below and detection limits are given in Table 6 (Pace Analytical, 1997).

Samples are prepared for analysis using Method 5030A. This method is used to determine the concentration of volatile organic compounds in a variety of liquid and solid waste matrices using a purge and trap gas chromatographic procedure. Five grams of solid sample is dispersed in methanol to dissolve the volatile constituents and a portion of the methanol extract is combined with contaminant-free laboratory water. Then inert gas is bubbled through the 5-mL or 25-mL aqueous sample aliquot at ambient temperature to transfer the volatile components to the vapor phase. The vapor is swept to a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is flash heated and backflushed with inert gas to desorb and transfer the volatile components onto the head of a GC column. The column is heated to elute the volatile components, which are detected by the appropriate detector for the analytical method used.

Aromatic volatile organics in samples are analyzed using method 8020A, which is a gas chromatography (GC) method using purge and trap sample introduction (method 5030A). An inert gas is bubbled through a water matrix to transfer volatile aromatic hydrocarbons from the liquid to the vapor phase. Volatile aromatics are collected on a sorbent trap, then flash thermally desorbed and transferred to a GC column. Target analytes are detected using a photoionization detector (PID). Sediment samples may be heat purged directly in reagent water or are extracted with methanol; if extracted with methanol an aliquot of sample extract is added to blank reagent water for purge and trap GC analysis. Positive results are confirmed by GC analysis using a second GC column of dissimilar phase or by GC/MS. When a second column analysis is performed, peak Retention Times (RTs) on both columns must match expected RTs within the calculated RT windows. Also, calculated quantitations from each column should be in agreement with one another (generally they should match within a factor of two) for the presence of an analyte to be considered confirmed.

Gasoline and volatile aromatic compounds, including benzene, toluene, ethylbenzene, and the xylenes (BTEX), are analyzed by a modified method 8015A using the direct purge technique described above for method 5030A. Analysis is performed on a GC equipped with a photoionization detector (PID) and a flame ionization detector (FID) connected in series. If BTEX compounds are found without the associated presence of gasoline, confirmation analysis is performed with a second GC column of dissimilar phase and retention characteristics in accordance with the requirements of method 8020K.

Aqueous samples analyzed for diesel, kerosene, jet fuel, and motor oil are prepared using method 3510B (separatory funnel liquid/liquid extraction) or method 3520B (continuous liquid/liquid extraction). Solid samples are prepared using method 3540B (Soxhlet extraction), method 3550 (sonication extraction), or wrist action shaker extraction (California LUFT method). Thirty grams of sample is extracted and concentrated to a volume of 1 mL. Analysis is performed by a modified method 8015A on a GC equipped with a capillary or megabore column and FID detector.

Table 6. Dry Weight Detection Limits of BTEX and TPH.

Analytes	Database Abbreviation	MDL, ng/g dry Sediment	MDL, ng/g dry Tissue
Benzene	Benzene	5	300
Toluene	Toluene	5	300
Ethylbenze ·	EthBenzene	5	300
Xylene	Xlene	15	800
Total Petroleum Hydrocarbons	TPH_Diesel	1000	1000

#### Trace Metal Analysis

#### **Summary of Methods**

Trace metals analyses were conducted at the CDFG Trace Metals Facility at Moss Landing, CA. Table 7 indicates the trace metals analyzed and lists method detection limits for sediments and tissues. These methods were modifications of those described by Evans and Hanson (1993), as well as those developed by the CDFG (1990).

Table 7. Dry Weight Trace Metal Detection Limits.

	MDL	MDL
Analytes	μg/g dry	μg/g dry
	Sediment	Tissue
Silver	0.002	0.01
Aluminum	1	1
Arsenic	0.1	0.25
Cadmium	0.002	0.01
Copper	0.003	0.1
Chromium	0.02	0.1
Iron	0.1	0.1
Mercury	0.03	0.03
Manganese	0.05	0.05
Nickel	0.1	0.1
Lead	0.03	0.1
Antimony	0.1	0.1
Tin	0.02	0.02
Selenium	0.1	0.1
Zinc	0.05	0.05

<sup>\*\*\*</sup>Note that all tissue MDLs are reported in dry weight units because wet weight MDLs are based on percent moisture of the individual sample.

#### **Sediment Digestion Procedures**

One gram aliquot of sediment was placed in a pre-weighed teflon vessel, and one ml concentrated 4:1 nitric:perchloric acid mixture was added. Vessels were capped and heated in a vented oven at 130° C for four hours. Three ml hydrofluoric acid were added to the vessel, recapped and returned to an oven overnight. Twenty ml of 2.5% boric acid were added to the vessel and placed in oven for an additional 8 hours. Weights of teflon vessels and solution were recorded, and solution was poured into 30 ml polyethylene bottles.

#### **Tissue Digestion Procedures**

A three gram aliquot of tissue was placed in a pre-weighed teflon vessel, and three mls of concentrated 4:1 nitric:perchloric acid mixture were added. Samples then were capped and heated on hot plates for five hours. Caps were tightened and samples were heated in a vented oven at 130°C for four hours. Samples were allowed to cool and 15 mls of Type II water were added to the vessels. The solution then was quantitatively transferred to a pre weighed 30 ml polyethylene (HDPE) bottle and taken up to a final weight of 20 g with Type II water.

#### Atomic Absorption Methods

Samples were analyzed by furnace AA on a Perkin-Elmer Zeeman 3030 Atomic Absorption Spectrophotometer, with an AS60 auto sampler, or a flame AA Perkin Elmer Model 2280. Samples, blanks, matrix modifiers, and standards were prepared using clean techniques inside a clean laboratory. ASTM Type II water and ultra clean chemicals were used for all standard preparations. All elements were analyzed with platforms for stabilization of temperatures. Matrix modifiers were used when components of the matrix interfere with adsorption. The matrix modifier was used for Sn, Sb and Pb. Continuing calibration check standards (CLC) were analyzed with each furnace sheet, and calibration curves were run with three concentrations after

every 10 samples. Blanks and standard reference materials, MESS1, PACS, BCSS1 or 1646 were analyzed with each set of samples for sediments.

#### Toxicity Testing

#### **Summary of Methods**

All toxicity tests were conducted at the California Department of Fish and Game's Marine Pollution Studies Laboratory (MPSL) at Granite Canyon. Toxicity tests were conducted by personnel from the Institute of Marine Sciences, University of California, Santa Cruz.

#### **Sediment Samples**

Bedded sediment samples were transported to MPSL from the sample-processing laboratory at Moss Landing in ice chests at 4°C. Transport time was one hour. Samples were held at 4°C, and all tests were initiated within 14 days of sample collection, unless otherwise noted in the Quality Assurance section. All sediment samples were handled according to procedures described in ASTM (1992) and BPTCP Quality Assurance Project Plan (Stephenson *et al.*, 1994). Samples were removed from refrigeration the day before the test, and loaded into test containers. Water quality was measured at the beginning and end of all tests. At these times, pH, temperature, salinity, and dissolved oxygen were measured in overlying water from all samples to verify that water quality criteria were within the limits defined for each test protocol. Total ammonia concentrations also were measured at these times. Samples of overlying water for hydrogen sulfide measurement were taken at the beginning and end of each toxicity test. Interstitial water sample measurements were taken at the beginning and end of each toxicity test after Leg 30. Hydrogen sulfide samples were preserved with zinc acetate and stored in the dark until time of measurement.

#### **Porewater Samples**

Once at MPSL, frozen porewater samples were stored in the dark at -12°C until required for testing. Experiments performed by the U.S. National Biological Survey have shown no effects of freezing pore water upon the results of toxicity tests (Carr and Chapman, 1995). Samples were equilibrated to test temperature (15°C) on the day of a test, and pH, temperature, salinity, and dissolved oxygen were measured in all samples to verify that water quality criteria were within the limits defined for the test protocol. Total ammonia and sulfide concentrations were also measured. Porewater samples with salinities outside specified ranges for each protocol were adjusted to within the acceptable range. Salinities were increased by the addition of hypersaline brine, 60 to 80‰, drawn from partially frozen seawater. Dilution water consisted of Granite Canyon seawater (32 to 34‰). Water quality parameters were measured at the beginning and end of each test.

# **Subsurface Water Samples**

Abalone and mussel tests were performed on water column samples collected with the modified Van Veen grab. A polyethylene water sample bottle was attached to the frame of the grab and a bottle stopper was pulled as the jaws of the grab closed for a sediment sample. The water sample was consequently collected approximately 0.5 meters above the sediment surface. Subsurface

water samples were held in the dark at 4°C until testing. Toxicity tests were initiated within 14 days of the sample collection date. Water quality parameters, including ammonia and sulfide concentrations, were measured in one replicate test container from each sample in the overlying water as described above. Measurements were taken at the beginning and end of all tests.

#### Measurement of Ammonia and Hydrogen Sulfide

Total ammonia concentrations were measured using an Orion Model 95-12 Ammonia Electrode. The concentration of unionized ammonia was derived from the concentration of total ammonia using the following equation (Whitfield 1974, 1978):

$$[NH_3] = [total ammonia] \times ((1 + antilog(pK_a^o - pH))^{-1}),$$

where  $pK_a^{\circ}$  is the stoichiometric acidic hydrolysis constant for the test temperature and salinity. Values for  $pK_a^{\circ}$  were experimentally derived by Khoo *et al.* (1977). Method detection limit for total ammonia was 0.1 mg/L.

Total sulfide concentrations were measured using an Orion Model 94-16 Silver/Sulfide Electrode, except samples tested after February, 1994, were measured on a spectrophotometer using a colorimetric method (Phillips *et al.* 1997). The concentration of hydrogen sulfide was derived from the concentration of total sulfide by using the following equation (ASCE 1989):

$$[H_2S] = [S^{2-}] \times (1 - ((1 + antilog(pK_a^{\circ} - pH))^{-1})),$$

where temperature and salinity dependent  $pK_a^{\circ}$  values were taken from Savenko (1977). The method detection limit for total sulfide was 0.1 mg/L for the electrode method, and 0.01 mg/L for the colorimetric method. Values and corresponding detection limits for unionized ammonia and hydrogen sulfide were an order of magnitude lower than those for total ammonia and total sulfide, respectively. Care was taken with all sulfide and ammonia samples to minimize volatilization by keeping water quality sample containers capped tightly until analysis.

#### Marine and Estuarine Amphipod Survival Tests

Solid-phase sediment sample toxicity was assessed using the 10-day amphipod survival toxicity test protocols outlined in EPA 1994. All *Echaustorius* and *Rhepoxynius* were obtained from Northwestern Aquatic Sciences in Yaquina Bay, Oregon. Animals were separated into groups of approximately 100 and placed in polyethylene boxes containing Yaquina Bay collection site sediment, then shipped on ice via overnight courier. Upon arrival at Granite Canyon, the *Echaustorius* were acclimated to 20% (T=15°C), and *Rhepoxynius* were acclimated to 28% (T=15°C). Once acclimated, the animals were held for an additional 48-hours prior to addition to the test containers.

Test containers were one liter glass beakers or jars containing 2-cm of sediment and filled to the 700-ml line with control seawater adjusted to the appropriate salinity using spring water or distilled well water. Test sediments were not sieved for indigenous organisms prior to testing although at the conclusion of the test, the presence of any predators was noted and recorded on the data sheet. Test sediment and overlying water were allowed to equilibrate for 24 hours, after

which 20 amphipods were placed in each beaker along with control seawater to fill test containers to the one-liter line. Test chambers were aerated gently and illuminated continuously at ambient laboratory light levels.

Five laboratory replicates of each sample were tested for ten days. A negative sediment control consisting of five lab replicates of Yaquina Bay home sediment for *Eohaustorius* and *Rhepoxynius* was included with each sediment test. After ten days, the sediments were sieved through a 0.5-mm Nitex screen to recover the test animals, and the number of survivors was recorded for each replicate.

Positive control reference tests were conducted concurrently with each sediment test using cadmium chloride as a reference toxicant. For these tests, amphipod survival was recorded in three replicates of four cadmium concentrations after a 96-hour water-only exposure. A negative seawater control consisting of one micron-filtered Granite Canyon seawater, diluted to the appropriate salinity was compared to all cadmium concentrations. Amphipod survival for each replicate was calculated as:

Number of surviving amphipods X 100 Initial number of amphipods

#### Haliotis rufescens Embryo-Larval Development Test

The red abalone (*Haliotis rufescens*) embryo-larval development test was conducted on subsurface water samples. Details of the test protocol are given in US EPA 1995a. A brief description of the method follows.

Adult male and female abalone were induced to spawn separately using a dilute solution of hydrogen peroxide in seawater. Fertilized eggs were distributed to the test containers within one hour of fertilization. Test containers were polyethylene-capped, seawater leached, 20-ml glass scintillation vials containing 10 milliliters of sample. Each test container was inoculated with 100 embryos (10/mL). Samples tested at multiple concentrations were diluted with one micron-filtered Granite Canyon seawater. Laboratory controls were included with each set of samples tested. Controls include a dilution water control consisting of Granite Canyon seawater, and a brine control with all samples that require brine adjustment. Tests were conducted at ambient seawater salinity (33±2‰). A 48-h positive control reference test was conducted concurrently with each porewater test using a dilution series of zinc sulfate as a reference toxicant.

After a 48-h exposure period, developing larvae were fixed in 5% buffered formalin. All larvae in each container were examined using an inverted light microscope at 100x to determine the proportion of veliger larvae with normal shells, as described in US EPA 1995a. Percent normal development was calculated as:

Number of normally developed larvae counted X 100 Total number of larvae counted

#### Mytilus spp. Embryo-Larval Development Test

The bay mussel (*Mytilus* spp.) embryo-larval development test was conducted on porewater and subsurface water samples. Details of the test protocol are given in US EPA 1995a. A brief description of the method follows.

Adult male and female mussels were induced to spawn separately using temperature shock by raising the ambient temperature by 10°C. Fertilized eggs were distributed to test containers within four hours of fertilization. Test containers were polyethylene-capped, seawater leached, 20-ml glass scintillation vials containing 10 milliliters of sample. Each test container was inoculated with 150 to 300 embryos (15-30/mL) consistent among replicates and treatments within a test set. Samples tested at multiple concentrations were diluted with one micron-filtered Granite Canyon seawater. Laboratory controls were included with each set of samples tested. Controls include a dilution water control consisting of Granite Canyon seawater, a brine control with all samples that require brine adjustment. Tests were conducted at 28±2‰. A 48-h positive control reference test was conducted concurrently with each test using a dilution series of cadmium chloride as a reference toxicant.

After a 48-h exposure period, developing larvae were fixed in 5% buffered formalin. All larvae in each container were examined using an inverted light microscope at 100x to determine the proportion of normal live prossidoconch larvae, as described in US EPA 1995a. Percent normal live larvae was calculated as:

Number of normal larvae X 100 Initial embryo density

#### Neanthes arenaceodentata Survival and Growth Test

The Neanthes test followed procedures described in Puget Sound Protocols (1991). Emergent juvenile Neanthes arenaceodentata (2-3 weeks old) were obtained from Dr. Donald Reish of California State University, Long Beach. Worms were shipped in seawater in plastic bags at ambient temperature via overnight courier. Upon arrival at MPSL, worms were allowed to acclimate gradually to 28% salinity (<2% per day, T=15°C). Once acclimated, the worms were maintained at least 48 hours, and no longer than 10 days, before the start of the test.

Test containers were one-liter glass beakers or jars containing 2-cm of sediment and filled to the 700-ml line with seawater adjusted to 28‰ using spring water or distilled well water. Test sediments were not sieved for indigenous organisms prior to testing, but the presence of any predators was noted and recorded on the data sheet at the conclusion of the test. Test sediment and overlying water were allowed to equilibrate for 24 hours, after which 5 worms were placed in each beaker along with 28‰ seawater to fill test containers to the one-liter line. Test chambers were aerated gently and illuminated continuously at ambient laboratory light levels. Worms were fed TetraMin® every 2 days, and overlying water was renewed every 3 days. Water quality parameters were measured at the time of renewals.

After 20 days, samples were sieved through a 0.5-mm Nitex screen, and the number of surviving worms recorded. Surviving worms from each replicate were wrapped in a piece of pre-weighed aluminum foil, and placed in a drying oven until reaching a constant weight. Each foil packet was then weighed to the nearest 0.1 mg. Worm survival and mean weight/worm for each replicate was calculated as follows:

Percent worm survival = Number of surviving worms X 100

Initial number of worms

Mean weight per worm = Total weight - foil weight X 100

Number of surviving worms

#### Strongylocentrotus purpuratus Embryo-Larval Development Test

The sea urchin (Strongylocentrotus purpuratus) larval development test was conducted on porewater samples. Details of the test protocol are given in US EPA 1995a. A brief description of the method follows.

Sea urchins were collected from the Monterey County coast near Granite Canyon, and held at MPSL at ambient seawater temperature and salinity (33±2%) until testing. Adult sea urchins were held in complete darkness to preserve gonadal condition. On the day of a test, urchins were induced to spawn in air by injection with 0.5M KCl. Eggs and sperm collected from the urchins were mixed in seawater at a 500 to 1 sperm to egg ratio, and embryos were distributed to test containers within 1 hour of fertilization. Test containers were polyethylene-capped, seawater leached, 20-ml glass scintillation vials containing 10 milliliters of sample. Each test container was inoculated with approximately 250 embryos (25/ml). All porewater samples were tested at three concentrations: 100, 50 and 25% pore water, with each concentration having three replicates. Porewater samples were diluted using one micron-filtered Granite Canyon seawater. Laboratory controls were included with each set of samples tested. Controls include a dilution water control consisting of Granite Canyon seawater, and a brine control with all samples that require brine adjustment. Tests were conducted at ambient seawater salinity (33±2‰). A 96-hour positive control reference test was conducted concurrently with each porewater test using a dilution series of copper chloride as a reference toxicant.

After a 96-hour exposure, larvae were fixed in 5% buffered formalin. Approximately 100 larvae in each container were examined under an inverted light microscope at 100x to determine the proportion of normally developed larvae as described in US EPA 1995a. Visual clues used to identify embryos as normal included development of skeletal rods (spicules) that extend beyond half the length of the larvae and normal development of a three-part gut. Embryos demonstrating retarded development were considered abnormal. Percent normal development was calculated as:

Number of normally developed larvae counted X 100 Total number of larvae counted

# Strongylocentrotus purpuratus Embryo-Larval Development Test using the Sediment-Water Interface Exposure System

The purple sea urchin (S. purpuratus) embryo/larval development test at the sediment-water interface was conducted on intact core sediment samples taken with minimal disturbance from the Van Veen grab sampler. Details of the test protocol are given in the MPSL Standard Operating Procedure, which follows the US EPA methods manual (1995a). A brief description of the method follows.

Sea urchins were collected from the Monterey County coast near Granite Canyon, and held at MPSL at ambient seawater temperature and salinity until testing. Adult sea urchins were held in complete darkness to preserve gonadal condition. On the day of the test, urchins were induced to spawn in air by injection with 0.5 mL of 0.5M KCl. Eggs and sperm collected from the urchins were mixed in seawater at a 500 to 1 sperm to egg ratio, and embryos were distributed to the test containers within one hour of fertilization. Sediment-water interface test containers consisted of a polycarbonate tube with a 25-µm screened bottom placed so that the screen was within 1-cm of the surface of an intact sediment core (Anderson et al. 1996). Seawater at ambient salinity was poured into the core tube and allowed to equilibrate for 24 hours before the start of the test. After inserting the screen tube into the equilibrated cores, each tube was inoculated with approximately 250 embryos. The laboratory control consisted of Yaquina Bay amphipod home sediment from Northwestern Aquatic Sciences. Tests were conducted at ambient seawater salinity ± 2‰. Ambient salinity at Granite Canyon is usually 32 to 34‰. A positive control reference test was conducted concurrently with the test using a dilution series of copper chloride as a reference toxicant.

After an exposure period of 96 hours, larvae were fixed in 5% buffered formalin. One hundred larvae in each container were examined under an inverted light microscope at 100x to determine the proportion of normally developed larvae as described in US EPA 1995a. Percent normal development was calculated as:

Number of normally developed larvae counted X 100 Total number of larvae counted

# Strongylocentrotus purpuratus Fertilization Test

The sea urchin (S. purpuratus) fertilization test was conducted on porewater samples. Details of the test protocol are described in Dinnel et al. (1987). Sea urchins were from the same stock described for the sea urchin larval development test. On the day of a test, urchins were induced to spawn in air by injection with 0.5M KCl. Sperm were exposed in test containers for sixty minutes before approximately 1000 eggs were added. After twenty minutes of fertilization, the test was fixed in a 5% buffered formalin solution. A constant sperm to egg ratio of 500 to 1 was used in all tests. This ratio maintained fertilization in the 70-90% range required by the test

protocol. Fertilization was determined by the presence or absence of a fertilization membrane. Test containers were polyethylene-capped, seawater leached, 20-ml glass scintillation vials containing 5 milliliters of pore water. Porewater samples were diluted with one micron-filtered Granite Canyon seawater. Laboratory controls were included with each set of samples tested. Controls included a dilution water control consisting of Granite Canyon seawater, a brine control with all samples that require brine adjustment. Tests were conducted at ambient seawater salinity (33±2 ppt). A positive control reference test (1-hour sperm exposure) was conducted concurrently with each porewater test using a dilution series of copper chloride as a reference toxicant. All eggs in each container were examined under an inverted light microscope at 100x, and counted as either fertilized or unfertilized. Percent fertilization was calculated as:

> Number of fertilized eggs Number of eggs observed

X 100

# Statistical Analysis of Toxicity Test Data

Samples were defined as significantly more toxic than laboratory controls if the following criteria were met: 1) a separate-variance t-test determined there was a significant difference (p<0.05) in mean toxicity test organism response (e.g., percent survival) between the sample and the laboratory control and 2) mean organism response in the toxicity test was lower than a certain percentage of the control value, as determined using the 90th percentile Minimum Significant Difference (MSD).

Statistical significance in t-tests is determined by dividing an expression of the difference between sample and control by an expression of the variance among replicates. We used a "separate variance" t-test that adjusted the degrees of freedom to account for variance heterogeneity among samples. If the difference between sample and control is large relative to the variance among replicates, then the difference is determined to be significant. In many cases, however, low between-replicate variance will cause a comparison to be considered significant, even though the magnitude of the difference can be small. The magnitude of difference that can be identified as significant is termed the Minimum Significant Difference (MSD) which is dependent on the selected alpha level, the level of between-replicate variation, and the number of replicates specific to the experiment. With the number of replicates and alpha level held constant, the MSD varies with the degree of between-replicate variation. The "detectable difference" inherent to the toxicity test protocol can be determined by identifying the magnitude of difference that can be detected by the protocol 90% of the time (Schimmel et al., 1994; Thursby and Schlekat, 1993). This is equivalent to setting the level of statistical power at 0.90 for these comparisons. This is accomplished by determining the MSD for each t-test conducted, ranking them in ascending order, and identifying the 90th percentile MSD, the MSD that is larger than or equal to 90% of the MSD values generated.

Current BPTCP detectable difference (90th percentile MSD) values are listed in Table 8. Samples with toxicity test results lower than the values given, as a percentage of control response, would be considered toxic if the results were also significantly different from the control in the individual t-test.

Table 8. Minimum significant differences used to calculate significant toxicity in the BPTCP toxicity test protocols (see text for complete MSD description).

Species	Name	MSD	% of Control	N
Ee	Eohaustorius	25	75	385
Hr	Abalone (all reps)	32	68	467
Me	Mytilus	20	80	223
Na Sv	Neanthes surv.	36	64	335
Na Wt	Neanthes wt.	56	44	335
Ra	Rhepoxynius	23	77	720
Sp Dev	Urchin dev.(all)	40	60	939
Sp Fert	Urchin fert.	12	88	79
SP SWI	Urchin SWI	41	- 59	109

# Test Acceptability and Evaluation

Quality Assurance/Quality Control (QA/QC) guidelines, for the toxicity tests used in the BPTCP project, are summarized in the BPTCP Quality Assurance Project Plan (Stephenson *et al.*, 1994). Test acceptability criteria from published protocols were evaluated for all tests. Quality assurance checklists were compiled that noted compliance for all tests with each of these criteria.

Evaluation codes were assigned to each deviation from QA/QC guidelines, and can be summarized as follows:

- -3: sample has minor exceedances of QA criteria that are unlikely to affect assessments.
- -4: sample meets or exceeds control criteria requirements.
- -5: data have exceedances, but are generally usable for most assessments and reporting purposes.
- -6: sample has major exceedances of control criteria requirements and the data are not usable for most assessments and reporting purposes.
- -7: sample has major exceedances of control criteria requirements and the data was not useable.
- -9: not analyzed

It is recommended if assessments are made that are especially sensitive or critical, that the QA evaluations be consulted before using the data. Test data judged to be unacceptable are not reported, and samples from unacceptable tests are retested if necessary.

# Total Organic Carbon Analysis of Sediments

#### Summary of Methods

Samples were received in the frozen state and allowed to thaw at room temperature. Source samples were gently stirred and sub-samples were removed with a stainless steel spatula and placed in labeled 20 ml polyethylene scintillation vials. Approximately 5 grams equivalent to dry weight of the wet sample was sub-sampled.

Sub-samples were treated with two, 5 ml additions of 0.5 N, reagent grade HCl to remove inorganic carbon (CO<sup>-3</sup>), agitated, and centrifuged to a clear supernate. Some samples were retreated with HCl to remove residual inorganic carbon. The evolution of gas during HCl treatment indicates the direct presence of inorganic carbon (CO<sup>-3</sup>). After HCl treatment and decanting, samples were washed with approximately 15 ml of deionized-distilled water, agitated, centrifuged to a clear supernate, and decanted. Two sample washings were required to remove weight determination and analysis interferences.

Prepared samples were placed in a 60° C convection oven and allowed to come to complete dryness (approx. 48 hrs.). Visual inspection of the dried sample before homogenization was used to ensure complete removal of carbonate containing materials (shell fragments). Two 61 mm (1/4") stainless steel solid balls were added to the dried sample, capped and agitated in a commercial available ball mill for three minutes to homogenize the dried sample.

A modification of the high temperature combustion method, utilizing a Weatstone bridge current differential was used in a commercially available instrument, (Control Equipment Co., 440 Elemental Analyzer) to determine carbon and nitrogen concentrations. The manufacture's suggested procedures were followed. The methods are comparable to the validation study of USEPA method MARPCPN I. Two to three aliquots of 5-10 mg of dried prepared sub-sample were used to determine carbon and nitrogen weight percent values. Calibration of the instrument was with known standards using Acetanilide or L-Cystine. Detection limits are 0.2 ug/mg carbon and 0.01 ug/mg nitrogen dry weight. The above methods and protocols are modifications of several published papers, reference procedures and analytical experimentation experience (Franson, 1981; Froelich, 1980; Hedges and Stern, 1983; MARPCPN I, 1992).

#### Quality Control/Quality Assurance

Quality control was tested by the analysis of National Research Council of Canada Marine Sediment Reference Material, BCSS-1 at the beginning and end of each sample analysis set (20-30 individual machine analyses). All analyzed values were within suggested criteria of  $\pm$  0.09% carbon (2.19% Average). Nitrogen was not reported on the standard data report, but was accepted at  $\pm$  0.008% nitrogen (0.195% Average) from the EPA study. Quality assurance was monitored by re-calibration of the instrument every twenty samples and by the analysis of a standard as an unknown and comparing known theoretical percentages with resultant analyzed percentages. Acceptable limits of standard unknowns were less than  $\pm$  2%. Duplicate or triplicate sample analysis variance (standard deviation/mean) greater than 7% is not accepted. Samples were re-homogenized and re-analyzed until the variance between individual runs fell below the acceptable limit of 7.0%.

#### Grain Size Analysis of Sediments

#### **Summary of Methods**

The procedure used combined wet and dry sieve techniques to determine particle size of sediment samples. Methods follow those of Folk (1974).

#### Sample Splitting and Preparation

Samples were thawed and thoroughly homogenized by stirring with a spatula. Spatulas were rinsed of all adhering sediment between samples. Size of the subsample for analysis was determined by the sand/silt ratio of the sample. During splitting, the sand/silt ratio was estimated and an appropriate sample weight was calculated. Subsamples were placed in clean, pre-weighed beakers. Debris was removed and any adhering sediment was washed into the beaker.

## Wet Sieve Analysis (separation of coarse and fine fraction)

Beakers were placed in a drying oven and sediments were dried at less than 55°C until completely dry (approximately three days). Beakers were removed from drying oven and allowed to equilibrate to room temperature for a least a half-hour. Each beaker and its contents were weighed to the nearest 0.01 g. This weight minus the empty beaker weight was the total sample weight. Sediments in beakers were disaggregated using 100 ml of a dispersant solution in water (such as 50 g Calgon/L water), and the sample was stirred until completely mixed and all lumps disappeared. The amount and concentration of dispersant used was recorded on the data sheet for each sample. Sample beakers were placed in an ultrasonic cleaner for 15 minutes for disaggregation. Sediment dispersant slurry was poured into a 63 µm (ASTM #230, 4 phi) stainless steel or brass sieve in a large glass funnel suspended over a 1L hydrometer cylinder by a ring stand. All fine sediments were washed through the sieve with water. Fine sediments were captured in a 1L hydrometer cylinder. Coarse sediments remaining in sieve were collected and returned to the original sample beaker for quantification.

# Dry Sieve Analysis (coarse fraction)

The coarse fraction was placed into a preweighed beaker, dried at 55-65°C, allowed to acclimate, and then weighed to 0.01 g. This weight, minus the empty beaker weight, was the coarse fraction weight. The coarse fraction was poured into the top sieve of a stack of ASTM sieves having the following sizes: No. 10 (2.0 mm), 18 (1.0 mm), 45 (0.354 mm), 60 (0.25 mm), 80 (0.177 mm), 120 (0.125 mm), and 170 (0.088 mm). The stack was placed on a mechanical shaker and shaken at medium intensity for 15 minutes. After shaking, each sieve was inverted onto a large piece of paper and tapped 5 times to free stuck particles. The sieve fractions were added cumulatively to a pretared weighing dish, and the cumulative weight after each addition determined to 0.01g. The sample was returned to its original beaker, and saved until sample computations were completed and checked for errors.

# **Analytical Procedures**

Fractional weights and percentages for various particle size fractions were calculated. If only wet sieve analysis was used, weight of fine fraction was computed by subtracting coarse fraction from total sample weight, and percent fine composition was calculated using fine fraction and total sample weights. If dry sieve was employed as well, fractional weights and percentages for the sieve were calculated using custom software on a Macintosh computer. Calibration factors were stored in the computer.

# Statistical Relationship Analysis

Relationships between toxicity (dependent) and chemistry (independent) were investigated in a two-step process. Pearson correlation coefficients were determined for chemical variables to screen for multicollinearity within each group of analytes (i.e., metals and organics) (Tabachnick and Fidell, 1996). Co-varying analytes (bivariate Pearson correlation >0.6) were removed. Multiple regression was then used to test the degree of dependence of amphipod toxicity on grain size, TOC and chemical concentrations. All data were transformed to meet assumptions of parametric tests by using log (x+1) or arcsin transformations when appropriate (Zar, 1984).

# Benthic Community Analysis

# **Summary of Methods**

Samples were selected for benthic community analysis by SWRCB staff based on results from toxicity tests. Each catalogued sample was processed individually in the laboratory to obtain an accurate assessment of species diversity and abundance. All macroinvertebrates were sorted from residues under a dissecting microscope, identified to lowest possible taxon, and counted. Laboratory processing of benthic cores consists of both rough and fine sorting. Initial sorting separates animals into large taxonomic groups such as polychaetes, crustaceans, mollusks and other (e.g., phoronids). Bound laboratory logbooks were maintained and used to record number of samples processed by each technician, as well as results of any sample resorts, if necessary. Sorters were required to sign and date a Milestone Progress Checksheet for each replicate sample processed. Specimens of similar taxonomic groups were placed in vials and labeled internally and externally with project, date collected, station information, and IDORG. In-house senior taxonomists and outside specialists processed and verified the accuracy of species identification and enumeration. An archived voucher specimen collection was established at this time.

#### Relative Benthic Index

Benthic samples were sieved, sorted and the number of individuals of each species in each replicate core were identified. A number of summary statistics were calculated for each station, including summaries of total fauna, number of species, and the 4 major phyla (Polychaetes, Crustaceans, Molluscs, and Echinoderms).

The Relative Benthic Index (RBI) used in this study utilizes the above summarized fauna information in a refined version of the benthic index presented by Fairey et al. (1996). It is based on simple, realistic natural history concerning responses of marine benthic communities to anthropogenic and natural disturbances. Community patterns used in the index include number of species (all taxa, only molluses, and only crustaceans); and the number of individuals of crustaceans, the number of individuals of selected species that are indicators of relatively disturbed benthic habitats, and the number of individuals of selected species that are indicators of relatively undisturbed benthic habitats. The RBI is developed for particular areas by selecting different indicator species. It does not require the presence of unpolluted reference stations, and does not refer to data beyond that collected in each study. Often the evaluation of community degradation depends on comparisons to unpolluted reference stations which are difficult to locate and vary for reasons that are unknown and unrelated to pollution.

# **Number of Species**

The number of species often decreases with severe disturbances (Oliver et al. 1977, 1980; Lenihan and Oliver 1995) and is the best indicator of biodiversity, particularly when species are sampled in relation to habitat area (Hurlbert 1971; Jumars 1975, 1976; Abele and Walters 1979). Therefore, the first community parameter in the RBI is the total number of species found in a standard sample of habitat area. Among the more numerous large taxonomic groups, crustaceans are generally more sensitive to environmental contaminants and other anthropogenic disturbances than most other components of the infauna, particularly polychaetes (Pearson and Rosenberg 1978; Reish et al. 1980; Thistle 1981; Lenihan and Oliver 1995; Lenihan et al. 1995). Speciose and numerically abundant crustacean faunas on the Pacific coast of the United States generally are only found in uncontaminated environments (Barnard 1963), making the number of crustacean species an important indicator of overall environmental health. To a lesser degree, the number of mollusk species also increase with decreasing environmental stress (Stull et al. 1986; Swartz et al. 1986), and are thus also included in the RBI. Polychaetes, crustaceans, and molluses are the three dominate groups of benthic macro-invertebrates from many nearshore communities (Oliver et al. 1980), but unlike the crustaceans and molluscs many of the most opportunistic or weedy species are polychaete (Grassle and Grassle 1974; McCall 1977; Sanders et al. 1980; Santos and Simon 1980; Rhoads et al. 1978,). As a result, the number of polychaete species was not used in the RBI, because they do not indicate as clearly either a relatively disturbed habitat or a relatively undisturbed habitat.

#### Number of Individuals

An increase in the number of crustacean individuals also is indicative of relatively healthy environments (Stull et al. 1986; Swartz et al. 1986; Oliver et al. 1977; Lenihan and Oliver 1995). Although sometimes one or two crustacean species can be abundant in disturbed habitats (Vetter 1995; Okey 1997), but less so than for other major taxonomic groups, particularly polychaete worms (Pearson and Rosenberg 1978; Grassle and Grassle 1974; Oliver et al. 1977). Therefore, the number of individuals of crustaceans also is used in the RBI, but not the number of individuals in any other major taxonomic group.

# **Indicator Species**

The population sizes of selected indicator species are strongly associated with benthic habitats that are relatively disturbed or undisturbed (Grassle and Grassle 1974; Oliver et al. 1977; Davis and Spies 1980; Weston 1990; Lenihan and Oliver 1995; Okey 1997); even more so than the number of species or the number of crustacean individuals. Therefore, five species were used in the RBI as indicators of either highly disturbed or undisturbed benthic communities and habitats. The number and identity of indicator species can change from one regional study location to another. Selection of indicator species was based on known responses to anthropogenic and other disturbances (Grassle and Grassle 1974; McCall 1977; Oliver et al. 1977; Davis and Spies 1980; Sanders et al. 1980; Santos and Simon 1980; Thistle 1981) and related natural history such as life history traits (Grassle and Grassle 1974; Oliver et al. 1977; Rhoads and Boyer 1982; Lenihan and Oliver 1995) or abundance patterns along environmental gradients and among the study stations (Oliver et al. 1980; Stull et al. 1986; Swartz et al. 1986; Weston 1990). The 2 negative indicator species are highly opportunistic annelids which thrive in disturbed, polluted,

or marginal environments, and generally are not found in less disturbed communities. The 3 positive indicator species generally are not found in polluted habitats and are characteristic of regions where anthropogenic and other severe disturbances do not play major roles in structuring communities. Each indicator species is discussed below:

# Negative indicator species

#### Capitella capitata

The Capitella species complex is a cosmopolitan group which lives in a wide range of conditions: fouled or low oxygen, high organic matter, and fine sediments. They are abundant around outfalls discharging biological wastes, and have a rapid (1 to 2 month) life cycle. Capitella are capable of surviving for days with little or no oxygen, and they often are considered the best example of a "weedy", opportunistic species (Grassle and Grassle 1976; McCall 1977; Pearson and Rosenberg 1978; Lenihan and Oliver 1995; Okey 1997).

### Oligochaetes

Oligochaetes are a poorly known group which typically found in peripheral/disturbed habitats such as, under decaying algae on beaches, and in fouled or low oxygen muds of back bays, estuaries, and harbors (Brinkhurst and Simmons 1968; Pearson and Rosenberg 1978; Brinkhurst and Cook 1980). They often occur in large masses near no other macrofauna. In San Francisco Bay they may comprise 100% of the fauna where there is gross pollution (i.e. large amounts of organic material from sewage). If oxygen levels are sufficient, and there is little toxic waste and high bacterial levels, oligochaete densities become extremely high (Brinkhurst and Simmons, 1968). They are well known indicators of relatively degraded freshwater ecosystems (Pearson and Rosenberg 1978; Brinkhurst and Cook 1980).

### Positive Indicator Species

#### Ampelisca spp.

Ampelisca filter feed from vertical tubes which they build at the surface of clean, fine sediments. Tremendous densities of Ampelisca can form a dense carpet of tubes changing the physical structure of the sedimentary regime. The carpet also enhances habitat values and supports a very diverse fauna (Mills 1967; Oliver et al. 1983, 1984; Oliver and Slattery 1985a). Although Ampelisca can colonize open sediment patches (Mills 1967), they do not colonize disturbed locations as rapidly as the more motile and non-tube dwelling amphipod groups (Oliver and Slattery 1985b; Klaus et al. 1990).

# Macoma spp.

The clams *Macoma* and *Tellina*, both in the Tellinidae, are small and live shallowly under the sediment surface. *Macoma* generally favor finer sediment, including bays, more so than *Tellina* do. Some *Macoma* filter feed, while others deposit feed by vacuuming sediment surface with their incurrent siphon (Reid and Reid 1969). They are not known to be early colonists in disturbed sedimentary habitats (Oliver *et al.* 1977).

#### Tellina spp.

Tellina live in clean, well-oxygenated sands of shallow water (Oliver et al. 1980). Species in Southern California attain great enough densities to be a major component of the shallow water,

benthic infaunal community (Barnard 1963). They are not known to be early colonists in disturbed sedimentary habitats (Oliver et al. 1977).

#### Calculation of RBI

Previous versions of the Benthic Index have used individual impact thresholds for determination of degree of negative impact to Total Fauna and Number of Crustacean Species (Fairey et al. 1996). While these thresholds have been useful, the necessarily arbitrary nature of the selection process introduced potential artifacts for stations whose values for Total Fauna, Total Molluscs and Total Crustacea approached the threshold value. To address this problem, calculation of the Relative Benthic Index was revised to be based on percentages of the total range. The final threshold value for determination of impacted versus non-impacted stations was based on the overall Relative Benthic Index, and selected using best professional judgment. Justification for this critical threshold value of the RBI is discussed below.

For total fauna, number of mollusk species and number of crustacean species, the maximum and minimum values in these parameters over all the stations were determined. For each station, the total number of species, total mollusk species, and total number of crustacean species then were converted to the percentage of the total range for these parameters. Similarly, the number of crustacean individuals at each station is converted to a percentage of the total range, and is added to the total fauna, mollusk, and crustacean species numbers. The community numbers thus represent four-sixth of the Relative Benthic Index for each station.

For the positive and negative indicator indices, the final index was weighted towards presence and absence of key indicator species, with abundance of each species given additional incremental weight. Accordingly, the abundance of each indicator species was transformed using a double square-root transformation to compress the range of values. For each species, the transformed abundance was converted to a percentage of the total range. The transformed values of the negative indicator species were summed and subtracted from the sum of the values for the positive indicator species.

The overall Relative Benthic Index was calculated by summing the values of the Total Fauna, Total Molluscs, Crustacean Species, and Indicator Species, and standardizing it to the total range. This resulted in a range in values from 0.00 (Most Impacted) to 1.00 (Least Impacted).

#### Use of RBI

It is not possible to compare directly RBI values between different regions. The high and low ranges of values vary based on the extreme values within each data set. In addition, different indicator species often are used between regions. The RBI does however provide the relative "health" of each of the stations in a given data set compared to the other stations in the same data set.

The RBI does not indicate causality. While a low RBI value could be the result of chemical toxicity, it also could be the result of other types of anthropogenic disturbance, such as dredging. A low RBI also could result from a variety of natural disturbances, such as freshwater runoff, temperature stratification, or storm impacts.

It is not possible to test the RBI to determine significance levels or confidence levels, or to statistically determine what ranking indicates significant impact. However, since a degree of arbitrarity is incorporated into all determinations of significance, whether statistical or intuitive, this should not be considered a significant drawback. For this study, the threshold for significantly impacted benthic community structure was set at a Benthic Index less than or equal to 0.3. While this threshold is necessarily somewhat arbitrary, it is considered suitable based on the best professional judgment of the benthic ecologists who performed the analysis. Several factors were considered in deriving this threshold: the stations below the threshold have few overall species, few crustacean species, presence of negative indicator species, and absence of positive indicator species. These stations would be considered to be significantly degraded by the vast majority of naturalists familiar with the region's bays and estuaries. A Benthic Index of 0.4-0.6 was considered to be a transitional community. A transitional community did not show clear signs of community structure degradation however, these communities also were not clearly indicative of an undegraded community. An undegraded community was defined with a Benthic Index of 0.7-0.9. Undegraded communities have a greater number of species overall, several crustacean species, presence of positive indicator species, and the absence of negative indicator species. However, some degree of caution should be noted due to the arbitrary nature of using cutoffs from a condensed index to characterize a complex and dynamic benthic assemblage. The RBI can be used in combination with chemistry and toxicity test data to provide a "weight-ofevidence" for determination of the most impacted stations.

# Quality Assurance/Quality Control

# **Summary of Methods**

Summaries of quality assurance and quality control procedures are described under separate cover in the Bay Protection and Toxic Cleanup Program Quality Assurance Project Plan (QAPP)(Stephenson et al. 1994). This document describes procedures within the program, which ensure data quality and integrity. Quality assurance procedures follow those of the NS&T Program to ensure comparability with other NOAA survey areas nationwide. In addition, individual laboratories prepare quality assurance evaluations of each discrete set of samples analyzed and authorized by task order. These documents were submitted to the CDFG for review, then forwarded to the SWRCB for further review.

#### III. RESULTS AND DISCUSSION

Tabulated data for all chemical, benthic, and toxicological analyses are presented in Appendices C, D, E and F. The summary data presented in the following results section were used to present findings of ecological significance in the North Coast Region based on the analysis of the full data set.

# Distribution of Chemical Pollutants

# **Chemical Specific Screening Values**

Bioavailability is the key to understanding the relationship between sediment chemistry and biological impacts. However, using toxic identification evaluations (TIE's), bioaccumulation analyses, or other specialized methods to evaluate bioavailability were not possible on the large number of samples evaluated in the BPTCP studies to date. In order to assess large numbers of samples for their potential to impact biological resources, we compared sediment chemical concentrations to published guideline values derived from studies of approximately one thousand samples collected nationwide. These studies have used empirical observations of large data sets containing matching chemistry and biological data to provide guidance for evaluating the probability that measured contaminant concentrations may contribute to observed biological effects (MacDonald, 1994a,b; Long et al. 1995). While the reported guideline values were derived from sediments containing mixtures of chemicals, they were calculated individually for each chemical. Their application may be confounded in sediments where biological responses are affected by synergistic or antagonistic interactions among multiple compounds, by unmeasured or unidentified compounds, or by unconsidered physical factors. The following paragraphs provide a brief description of how these guideline values were calculated.

The National Status and Trends Program has used chemical and toxicological evidence from a number of modeling, field and laboratory studies to determine the ranges of chemical concentrations which are rarely, sometimes, or usually associated with toxicity (Long and Morgan, 1992). Evaluation of available data (Long *et al.*, 1995) has led to identification of three ranges in concentration for each chemical:

- 1) Minimal Effects Range: The range in concentration over which toxic effects are rarely observed;
- 2) Possible Effects Range: The range in concentrations over which toxic effects are occasionally observed;
- 3) Probable-Effects Range: The range in chemical concentrations over which toxic effects are frequently or always observed.

Two slightly different methods were used to determine these chemical ranges. One method developed by NOAA (Long and Morgan, 1990; Long et al., 1995) used chemical data which were associated with a toxic biological effect. These data were used to determine the lower 10th percentile of ranked data, where the chemical level was associated with an effect (Effects Range-Low, or ERL). Sediment samples in which all chemical concentrations were below the 30 ERL values were not expected to be toxic. The Effects Range-Median (ERM) reflects the 50th percentile of ranked data and represents the level above which effects are expected to occur. Effects are expected to occur occasionally when chemical concentrations fall between the ERL and ERM (Figure 4). The probability of toxicity was expected to increase with the number and degree of exceedances of the ERM values.

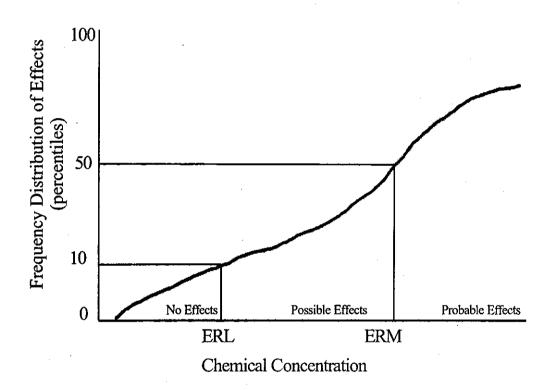


Figure 4 Conceptual Outline of the relationships between the no effects, possible effects and Probable effects ranges in chemical concentrations (from Long and MacDonald 1992).

Another method identifies ranges using chemical concentration data associated with both toxic biological effects and no observed effects (MacDonald, 1992; MacDonald, 1994a,b; MacDonald et al., 1996). The ranges are identified as TEL (Threshold Effects Level) and the PEL (Probable Effects Level). TEL values were derived by taking the geometric mean of the 50th percentile of the "no effects" data and the 15th percentile of the "effects" data. The PEL values were derived by taking the geometric mean of the 85th percentile of the "no effects" data and the 50th percentile of the "effects" data. Although different percentiles were used for these two methods, they are in close agreement, usually within a factor of 2. Values reported for both methods are shown in Table 9. Neither of these methods is advocated over the use of the other in this report.

A cautionary note should be included; the degree of confidence which MacDonald (1994a,b) and Long et al. (1995) had in their respective guidelines varied considerably among chemicals. They express low confidence in the values derived for nickel, mercury, DDTs, chlordane, dieldrin, and endrin. When more data become available regarding these chemicals and their potential effects their guidelines may be revised, probably increasing for some substances. Due to low confidence in guideline values, in the case of DDT, the guideline value used was that of Swartz et al. (1994). This value was normalized to organic carbon, to which DDT strongly binds, therefore this TOC normalized value may be more reflective of DDT bioavailability in the environment.

# **Chemicals Without Screening Values**

In order to evaluate those chemicals for which no guideline values have been calculated, individual chemical concentrations were compared to the range of chemical concentrations collected by BPTCP. This database contains approximately 120 analytes that were measured in sediments throughout California's bays and estuaries. Based upon the number of samples analyzed for a specific chemical, and the number of samples that exceeded the method detection limit, the 90<sup>th</sup> and 95<sup>th</sup> percentiles were calculated for each chemical using the range of samples above the MDL (Table 10). These percentiles then were used to compare individual chemical concentrations relative to the range of concentrations throughout the state.

Table 9. Comparisons of Sediment Quality Guideline Values Developed by the State of Florida and NOAA.

and NOAA.	State of 1	Florida (1)	NOA	A(2):
Substance	TEL	PEL	ERL	ERM
Organics (ng/g- dry weight)		• .		
Total PCBs	21.550	188.79	22.70	180.0
PAHs			•	•
Acenaphthene	6.710	88.90	16.00	500.0
Acenaphthylene	5.870	127.89	44.00	640.0
Anthracene	46.850	245.00	85.30	1100.0
Fluorene	21.170	144.35	19.00	540.0
2-methylnaphthalene	20.210	201.28	70.00	670.0
Naphthalene	34.570	390.64	160.00	2100.0
Phenanthrene	86.680	543.53	240.00	1500.0
Total LMW-PAHs	311.700	1442.00	552.00	3160.0
Benz(a)anthracene	74.830	692.53	261.00	1600.0
Benzo(a)pyrene	88.810	763.22	430.00	1600.0
Chrysene	107.710	845.98	384.00	2800.0
Dibenz(a,h)an	6.220	134.61	63.40	260.0
thracene				
Fluoranthene	112.820	1493.54	600.00	5100.0
Pyrene	152.660	1397.60	665.00	2600.0
Total HMW-PAHs	655.340	6676.14	1700.00	9600.0
Total PAHs	1684.060	16770.54	4022.00	44792.0
Pesticides				
p,p'-DDE	2.070	374.17	2.20	27.0
p,p'-DDT	1.190	4.77	n/a	n/a
Total DDT	3.890	51.70	1.58	46.1
Lindane	0.320	0.99	n/a	n/a
Chlordane	2.260	4.79	2.00	6.0
Dieldrin	0.715	4.30	n/a	8.0
Endrin	n/a	n/a	n/a	45.0
Metals (μg/g-dry weight)				
Arsenic	7.240	41.60	8.20	70.0
Antimony	n/a	n/a	2.00	25.0
Cadmium	0.676	4.21	1.20	9.6
Chromium	52.300	160.40	81.00	370.0
Copper	18.700	108.20	34.00	270.0
Lead	30.240	112.18	46.70	218.0
Mercury	0.130	0.70	0.15	0.7
Nickel	15.900	42.80	20.90	51.6
Silver	0.733	1.77	1.00	3.7
Zinc	124.000	271.00	150.00	410.0

<sup>(1)</sup> D.D. MacDonald, 1994; (2) Long et al. 1995 & Long and Morgan, 1990

Table 10. Individual Chemical Screening Values for the BPTCP.

•		#	# above	Highest	90%	95%	ERM
Chemical Name	MDL	Analyzed	MDL	Value	Threshold	Threshold	Guideline Value
Aluminum	1	603	603	165,000	83,000	101,000	n/a
Antimony	0.1	603	603	52.8	3.35	5.35	25
Arsenic	0.1	544	544	1140	21.2	26	70
Cadmium	0.002	603	603	27.9	1.76	2.67	9.6
Chromium	0.02	603	603	860	212	250	370
Copper	0.003	603	603	7,800	300	400	270
Iron	0.1	603	603	336,300	55,300	59,900	n/a
Lead	0.03	603	603	2100	120	171	218
Manganese	0.05	603	603	1190	630	682	n/a
Mercury	0.03	603	603	9.14	0.969	1.54	0.7
Nickel	0.1	550	550	167	88	109	51.6
Silver	0.002	603	603	35.7	1.58	2.22	3.7
Selenium	0.1	544	386	35.7	1.09	1.9	n/a
Γin	0.02	603	603	92.9	9.03	12	n/a
Zinc	0.05	603	603	6,000	490	630	410
Aldrin	0.5	621	22	8.2	4.7	8.2	n/a
Chloropyrifos	1	444	130	78	28	44.4	n/a
Total Chlordane	3	612	403	246	44.57	69.5	- 6
Dacthal	0.2	465	59	25.2	7.51	19	n/a
Fotal DDT	5.4	621	507	3,569	235.5	471.9	46.1, 100/OC
o',p'-Dichlorobenzophenone	3	465	46	63.3	30.6	35.2	n/a
Dieldrin	0.5	618	210	62.6	11.7	16.8	8
Endosulfan I	0.5	606	17	19.6	13.4	19.6	n/a
Endosulfan II	1	606	59	59.8	10.4	13.8	n/a
Endosulfan Sulfate	2	606	40	163	21	45.6	n/a
Endrin	2	618	15	21.8	16.4	21.8	45
Ethion	2	69	4	36.4	36.4	36.4	n/a
alpha-HCH	0.2	465	14	292	26.1	292	n/a
beta-HCH	. 1	465	6	56.8	56.8	56.8	n/a
gamma-HCH (Lindane)	0.2	618	43	8.4	2.82	8.24	0.99 (PEL)
delta-HCH	0.5	465	11	99.4	14.4	99.4	n/a
Heptachlor	0.5	621	58	15.8	4.5	7.3	n/a
Heptachlor Epoxide	0.5	618	27	17.8	2.5	3.1	n/a
Hexachlorobenzene	0.2	621	174	59.7	3.63	7.07	n/a
Methoxychlor	1.5	606	60	131	55.3	78.6	n/a n/a
Mirex	0.5	620	25	103	2.6	3.74	n/a
villex Oxadiazon	6	465	12	114	45.8	114	n/a
	0.5	465	37	30.3	10.7	12.3	n/a
Oxychlordane	50	609	10	15,700	3,200	15,700	n/a
Γοxaphene Γributyltin	0.003	555	555	6.21	0.422	0.724	n/a
-						865	180
Total PCB	9	684	628	19,901	497		500
Acenapthene	5	624	320	1,350	140	272	
2-Methylnapthalene	5	624	446	15,700	131	243	670
Benzo[a]pyrene	5	628	610	47,300	1660	2720	1600
Dibenz[a,h]anthracene	5	. 628	498	15,500	343	541	260
MW PAHs	60	624	473	92,097	2,585	4,253	3,160
HMW PAHs	60	628	606	225,740	15,727	24,473	9,600
Total PAHs	60	628	628	227,801	17,107	27,485	44,792
Total Organic Carbon	n/a	686	686	26.8	3	4.01	n/a
Grain Size	n/a	689	n/a	100	98.16	99.6	n/a
ERM Summary Quotient	n/a	546	n/a	3.94	1.01	1.3	n/a
PEL Summary Quotient	n/a	553	n/a	7.8	1.52	1.95	n/a

# **Primary Chemicals of Concern**

Figure 5 presents a summary of the chemicals and chemical groups that exceeded sediment chemistry guideline values for the 34 trace metal samples and 33 trace organic samples on which sediment chemical analysis was performed (note the number of organic analytes measured varied among stations, refer to Appendix C). Based on the available data, the North Coast Region has relatively few chemicals that exceeded ERM or PEL guideline values. This is characteristic of the relatively pristing nature of the region. Preservation of the pristing nature of this region is an objective which validates use of guidelines which are more environmentally conservative than those used in more industrialized areas of the state. Therefore, to provide a more extensive evaluation of the chemical composition of this region it was necessary to include ERL and TEL guideline exceedances. These guideline values are substantially lower than their respective ERM and PEL counterparts. It should be stressed these values were intended to represent chemical concentrations towards the lower end of the effects range, the level below which biological effects were rarely observed (Long et al. 1998). However, in the case of the North Coast Region, these lower guideline values provide a cautious estimate for chemicals of potential concern in the environment. The chemicals that most often exceeded ERM or PEL guideline values were chromium, nickel, PAHs and lindane. Although copper, mercury, and zinc, did not exceed ERM or PEL guidelines values, these chemicals often exceeded ERL or TEL guideline values and may have a potential impact on the environment.

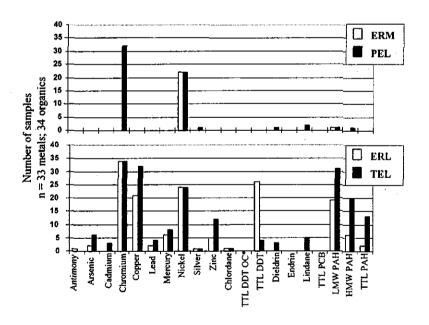


Figure 5. Samples with chemical guideline exceedances \* total DDT [n = 27] is normalized to TOC.

In addition to sediment chemical analysis, tissue samples were collected from 10 stations. Resident and transplanted mussels, oysters, crabs and polychaete worms were analyzed for a variety of chemicals, and results are shown in Appendix C, sections VI through X. To further evaluate the extent of chemical bioaccumulation within the North Coast Region, data collected by the California State Mussel Watch Program (SMWP) were reviewed. The SMWP has been evaluating bioaccumulation in mussels, fresh water clams, and oyster tissues since the mid 1970s and has 15 stations which correspond to BPTCP stations (Figures 6, 7). When applicable these SMWP stations also were assessed for chemical contamination and provided supplemental information about stations. Tissue chemical concentrations were evaluated based on recommended U.S. EPA human health risk screening values (USEPA, 1995b). These screening values are based on the general U.S. population's average consumption rate for fish and shellfish, although many North Coast residents naturally exceed those consumption rates. In addition to EPA screening values, two criteria used in SMWP reports (Rasmussen, 1995; 1996), Elevated Detection Levels (EDLs) and Maximum Tissue Residual Levels (MTRLs) were evaluated as well. SMWP EDLs were established to provide a comparative measure that ranks a given concentration of a particular substance with previous data collected by the SMWP (Rasmussen, 1996). An exceedance of the 85<sup>th</sup> or 95<sup>th</sup> percentile indicates the sample was significantly elevated above the median concentration values for the SMWP data set. MTRLs were set by the SWRCB staff for protection against consumption of fish and shellfish that contain substances at levels which could result in significant human health problems (SWRCB, 1990a; 1990b; 1991). These conservative estimates are important in protecting the sensitive seafood and shellfish industries. In general, tissue samples had organic compound concentration levels, such as pesticides, BTEX and TPH, which were below detection limits (Appendix C). Thereby indicating relatively low levels of tissue contamination in the North Coast Region. Nevertheless, tissue samples did have several trace metals detected in patterns similar to those found in sediment samples. For example both tissue and sediment samples had elevated levels of chromium and nickel at several stations and there were a few cases of relatively greater concentrations of copper and mercury in the two media types.

Chromium and nickel sediment concentrations within the North Coast exceeded PEL guideline values at a majority of stations analyzed. In fact, samples were often greater than the 90<sup>th</sup> percentile for sediment concentrations measured within the state (>212 ug/g and >88 ug/g for chromium and nickel respectively). There are many anthropogenic means by which chromium and nickel can be introduced in the environment. Both are commonly used in construction of metal alloys, protective coatings on other metals, magnetic tapes, paints, cement, wood preservatives, photochemical processing, coal gasification, petroleum refining, hydrogenation of fats and oils and municipal waste water discharges. Although these chemicals have the potential to adversely effect the environment, it is important to consider the distinction between natural and anthropogenic sources. Chromium and nickel are considered rare earth elements, and generally are found in greater concentrations due to crustal abundances (Mearnes and Young, 1977; Cornwall, 1966). Chromium is found in quantities sufficient to mine in 24 counties of California, with high grade ore deposits throughout much of northern California (Bradley *et al.* 1918). Nickel bearing rock formations also have been described throughout northern California (Cornwall, 1966; Foose, 1992).

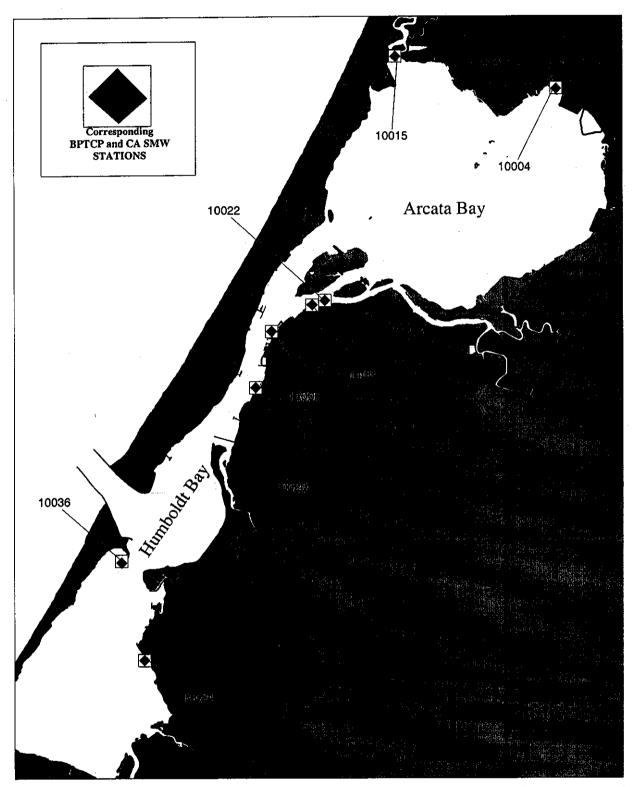


Figure 6. Bay Protection Toxic Cleanup Program stations which have corresponding State Mussel Watch stations. These stations were not sampled synoptically.

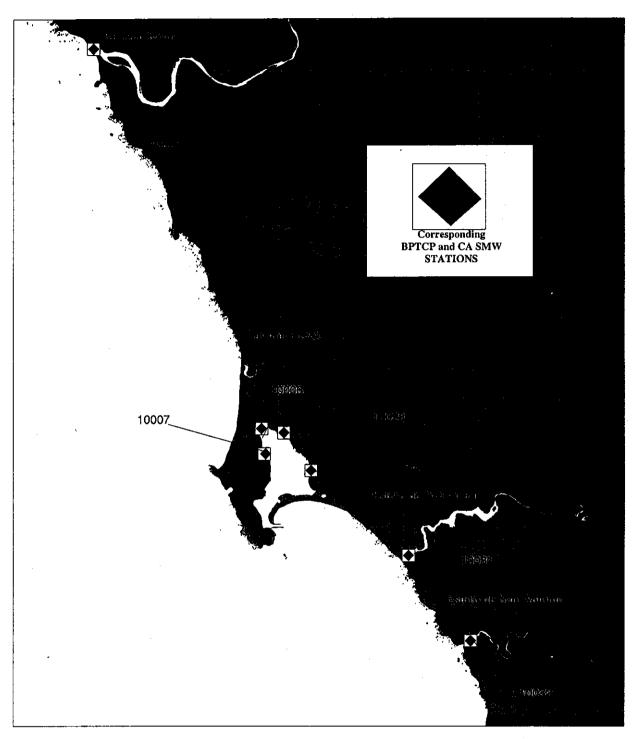


Figure 7. Bay Protection Toxic Cleanup Program stations which have corresponding State Mussel Watch stations. These stations were not sampled synoptically.

To definitively determine whether elevated metal concentrations are due to the geologic composition of an area or if they are a result of industrial activities, a more extensive chemical analysis must be performed than those completed for this study. However, a benthic surveillance survey conducted by NOAA (1994) attempted to distinguish between background metal concentrations and anthropogenic inputs at a variety of locations throughout the west coast of the United States, including Bodega Bay. The NOAA study evaluated extractable metal concentration ratios (Katz and Kaplan, 1981) and concluded Bodega Bay sediments had greater chromium concentrations due to the geological components of the area. Although nickel had a relatively greater concentration of extractable metal, it was determined not to be unusually great because of similar elevated concentrations throughout most of northern California. Thus it was concluded that these greater concentrations of nickel were probably due to the natural weathering of rock formations or possibly from river inputs. Based on the NOAA (1994) findings, it appears the North Coast Region's levels of both chromium and nickel could be caused by the geologic composition of the area rather than anthropogenic inputs. This distinction between acceptable background levels and anthropogenic inputs is further supported by the fact that several samples, which had elevated concentrations of both chromium and nickel, were non toxic during amphipod survival tests. Therefore, although found in elevated concentrations, chromium and nickel currently will not be considered pollutants of concern.

Polycyclic aromatic hydrocarbons (PAHs) were considered a chemical group of concern within the North Coast Region during this study. This is due to their frequent exceedances of lower level sediment quality guideline values and their potential for broad biological impacts. Because of their similar modes of toxic action, individual PAHs often are grouped into low and high molecular weight compounds. Individual PAHs used for the summations of low and high molecular weight PAHs and total PAHs are given in Appendix C -Section IV and X. Only station 14002, located on the northern most reach of the Eureka waterfront, exceeded both the ERM and PEL guideline values (4759.2 ng/g) for low molecular weight PAHs. Many other stations had low, high, and total PAHs concentrations greater than TEL and PEL guideline values. Figures 8, 9 depict those stations exceeding low molecular weight PAHs sediment quality guidelines. Samples with greater PAH concentrations were found primarily near the central and northern portion of the Eureka Waterfront and within the northern boat harbors of Bodega Bay where vessel traffic is more concentrated. Similar distribution patterns also were displayed by individual PAH compounds, such as 2- methylnaphthalene, fluoranthene (FLA), phenanthrene (PHN), and Pyrene (PYR), in which PEL guideline values often were exceeded. SMWP data (Rasmussen 1995) also indicated PAH levels above MTRLs for transplanted mussels at corresponding stations along the Eureka Waterfront. In addition to these stations SMWP data further indicate stations 10007, 10015, 10024,10031, and 10036, which were not analyzed for PAHs during this study, may be of concern because they exceed total PAHs MTRLs for resident mussels. PAHs are components of crude and refined petroleum products and also are products of incomplete combustion of organic materials. Exposure to PAHs may result in a wide range of carcinogenic and mutagenic effects to terrestrial and aquatic organisms (Eisler, 1987). This is of particular concern in Humboldt Bay, Bodega Bay, and the Esteros vicinity with respect to commercial shellfish production and seafood harvesting.

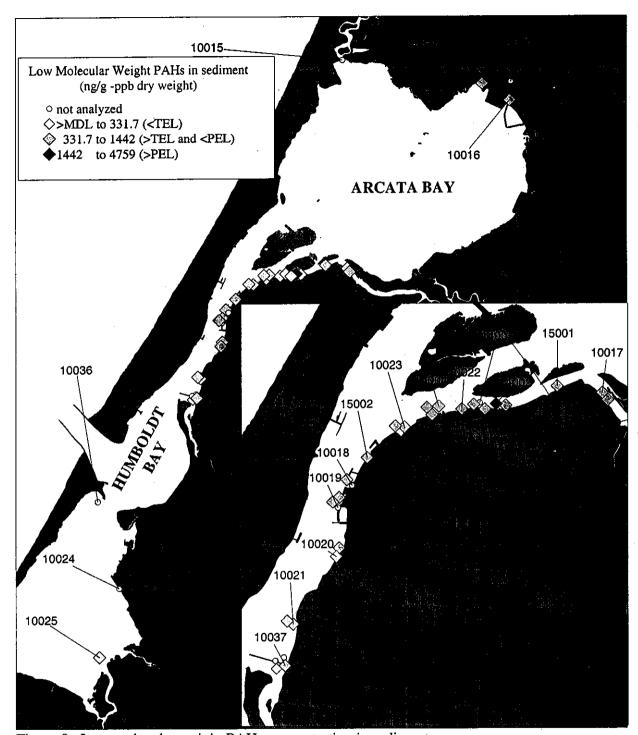


Figure 8. Low molecular weight PAHs concentration in sediments.

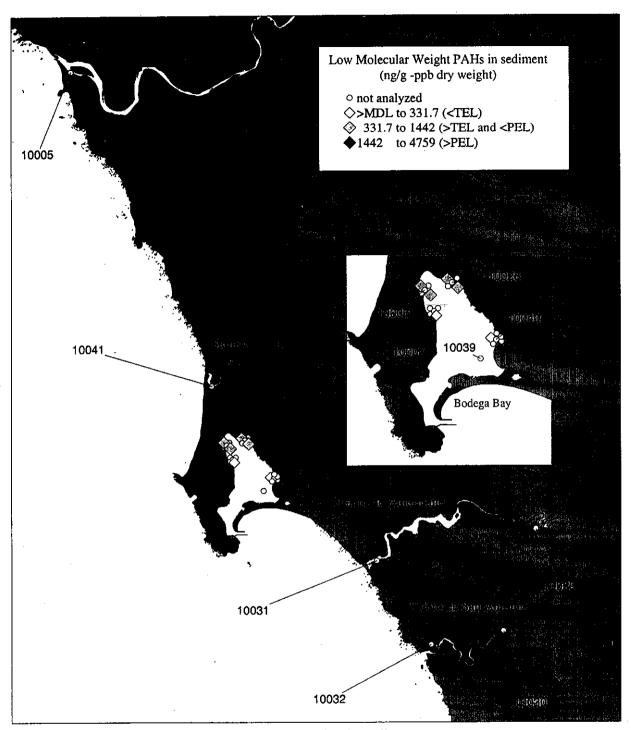


Figure 9. Low molecular weight PAHs concentration in sediments.

Lindane is considered a potential chemical of concern because it exceeded the PEL guideline value of 0.99 ng/g at two stations along the central portion of the Eureka waterfront (Figures 10, 11). There were three additional stations that had TEL exceedances (>0.320 ng/g). These TEL exceedances were located in the northern section of the Eureka waterfront and the southern most station in Arcata Bay. Tissue data were not analyzed for lindane during this study; nevertheless, recent SMWP data (Rasmussen, 1995) indicate one 85<sup>th</sup> percentile EDL exceedance at station 10031. Sediment organic chemistry was not analyzed at this station therefore, lindane sediment concentrations can not be evaluated. Lindane is used primarily as an insecticide on hardwood logs and lumber, seeds, fruits, vegetables, hardwood forests, existing structures, and livestock and pets (for external parasite control). Since 1985, many uses of lindane have been banned or restricted because it is classified as a "probable/ possible" human carcinogen (Howard, 1991).

Although copper never exceeded ERM or PEL guideline values, it is considered a potential chemical of concern, for the region, due to multiple ERL and TEL exceedances. Copper concentrations were above ERL (>34.0 ug/g) or TEL (>18.7 ug/g) values throughout the Eureka waterfront and in Arcata Bay (Figures 12, 13). The two boat harbors in the northern portion of Bodega Bay also were found to exceed ERL and TEL values. Tissue samples from resident mussel collected along the Eureka waterfront, at stations 14002 and 14001, exceeded SMWP 95<sup>th</sup> percentile EDLs. Furthermore, SMWP stations corresponding to BPTCP stations 10005, 10006, 10028, 10031, 10040 also were found to exceed the 85<sup>th</sup> and 95<sup>th</sup> percentile copper EDLs of 1.55 ug/g and 2.01 ug/g respectively. Copper is a broad spectrum biocide which may be associated with acute and chronic toxicity, reduction in growth, and a wide variety of sublethal effects (Spear and Pierce, 1979). Copper often is found to occur in excess concentrations at those stations associated with urbanization, shipyard operations and repair activities (NOAA, 1994). Several boat harbor exist along the Eureka waterfront and copper also is known to enter the environment through the dissolution of antifouling paints in boat harbors.

Zinc was another trace metal that never exceeded ERM or PEL guideline values, but did have several exceedances of ERL levels (>150 ug/g) or TEL levels (>124 ug/g). As with copper, greater concentration of zinc were found in the northern portion of the Eureka waterfront, the northeast corner of Arcata Bay and in the northern portion of Bodega Bay (Figures 12, 13). BPTCP resident mussel tissue samples collected in the northern end of the Eureka Waterfront (stations 14001, 14002, and 15001) exceeded SMWP 85<sup>th</sup> percentile EDLs as did the SMWP data located in the southeastern portion of Bodega Bay. Zinc can be introduced into the environment by the pulp and paper industry and often is associated with industrial activities (Dexter et al.1985) and harbors due to sacrificial zinc anodes on boats.

Mercury was not found to exceed ERM or PEL guideline values but could be of concern due to several ERL and TEL sediment guideline value exceedances. ERL exceedances (> 0.15 ng/g) and TEL exceedances (> 0.130 ng/g) of mercury were found at seven stations, primarily along the Eureka waterfront and the eastern portion of Arcata Bay (Figures 12, 13). Mercury concentrations also exceeded ERL and TEL guideline values at the two northern most boat harbors in Bodega Bay (stations 10006 and 10028). Tissue data indicated mercury concentrations above Mussel Watch's 85<sup>th</sup> percentile EDL for resident mussel tissue at station 14002, located on the Eureka waterfront. Recent SMWP data (SWRCB, unpublished) also indicate elevated mercury levels at stations which were not analyzed for tissue chemistry during this study

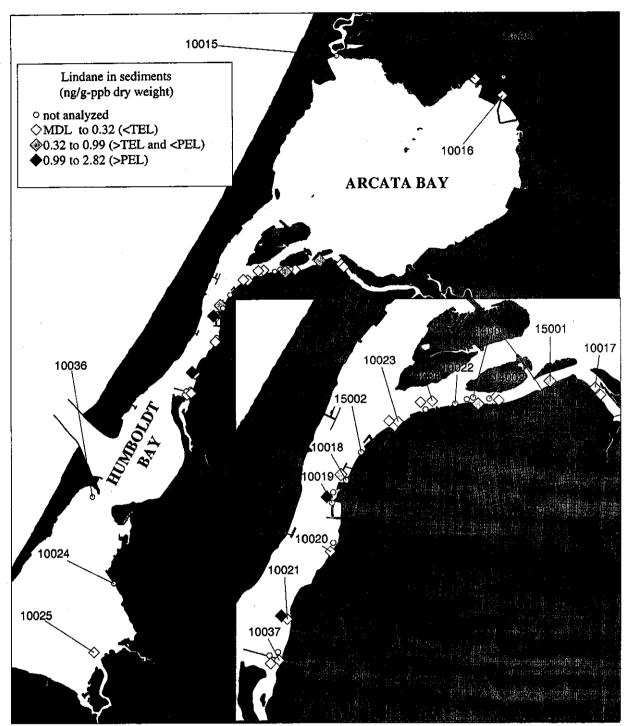


Figure 10. Lindane concentrations in sediments.

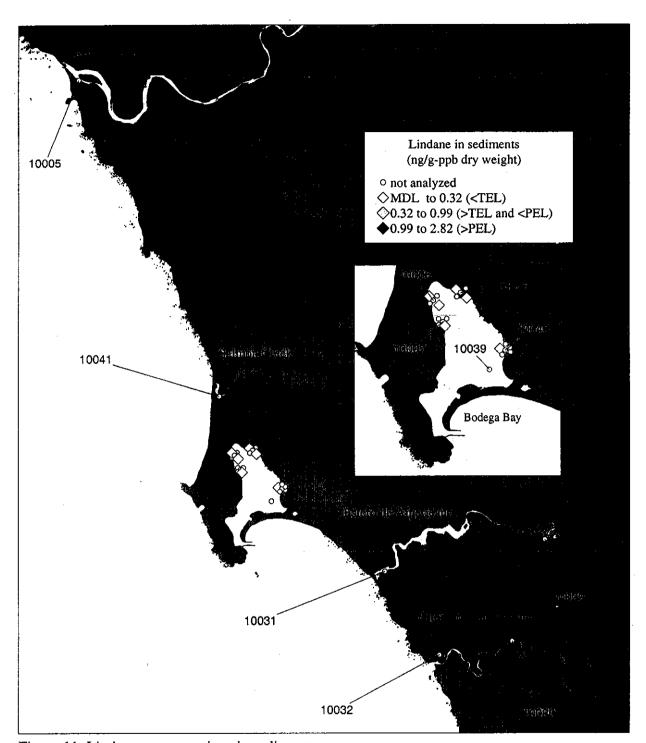


Figure 11. Lindane concentrations in sediments.

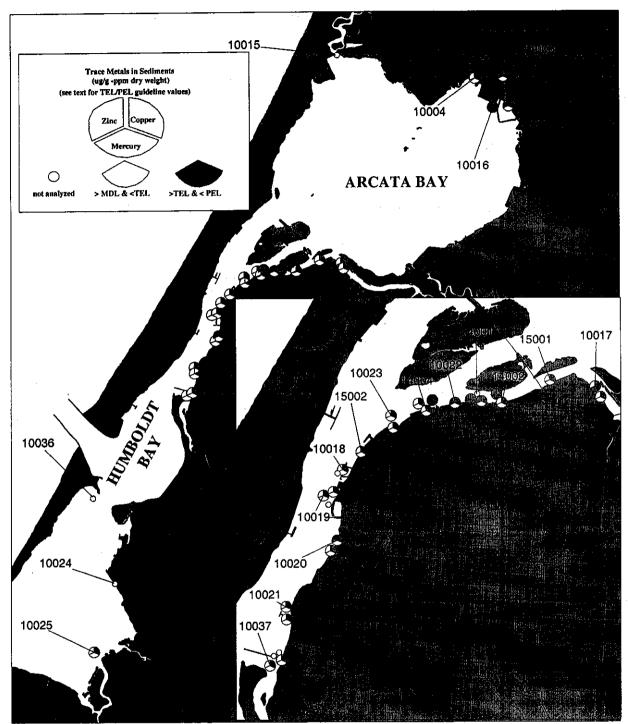


Figure 12. Copper, mercury and zinc concentrations in sediments.

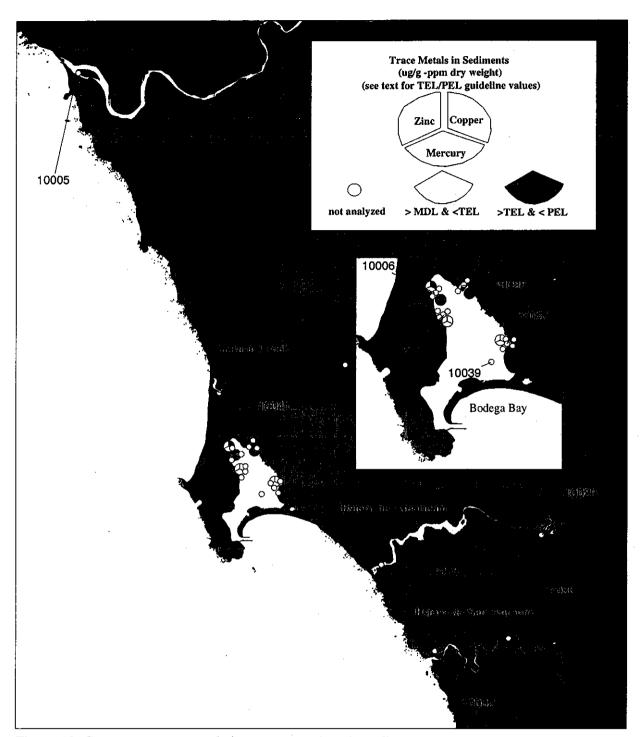


Figure 13. Copper, mercury, and zinc concentrations in sediments.

(stations 10006, 10007, and 10028). Mercury, particularly methylmercury, is highly toxic to aquatic biota. Although there is variability in sensitivity of different organisms to the substance, bioaccumulation of mercury in aquatic species has significant implications with respect to human health (U.S. EPA, 1995b).

# **ERM, PEL Summary Quotients**

In this report, comparisons of the data to effects-based numerical guidelines (ERM and PEL) were made to assess how sediment pollution in the North Coast Region compares to sediment pollution on a state and national scale. Additionally, these guidelines were used to identify stations of concern for sediment quality management within the North Coast Region.

Comparisons were made in this report using chemical summary quotients (ERMQ & PELQ) as described previously by Fairey et al. (1998). Summary quotients are summations of chemical concentrations for chemicals listed in Table 9, divided by their respective ERM or PEL value, and then divided by total number of chemicals used. In samples where levels of measured chemicals were below the analytical method detection limit (MDL), a value of one-half the MDL was used for summations. Summary quotients are being employed to evaluate BPTCP data throughout the state. However, due to differences in the data set for Region 1 the calculation of the summary quotient has been modified slightly relative to other BPTCP summary quotient calculations. A more detailed description of methods and analytes used for summations and averaging are given in Appendix C- Section VI.

The use of summary quotients was a simple approach for addressing overall chemical pollution where there were multiple pollutants at a station, and was in addition to the standard chemical by chemical approach discussed earlier. This approach considered not only the presence of guideline exceedances, but the number and degree of multiple exceedances. Based upon analyses of the national NS&T and EMAP database, the incidence of toxicity has been shown to increase with increasing summary ERM and PEL quotients (Long et al. 1998). Synergistic effects are possible, but not implied by the quotient summations, therefore, this method should be recognized only as a categorization scheme meant to better focus management efforts on interpretation of ambient sediment chemistry data.

Long et al. (in press) examined the use of sediment quality guidelines and the probability of toxicity being associated with summary quotient ranges. This extensive national study developed four sediment categories to help prioritize areas of concern, based on the probability of toxicity being associated with summary quotient and ERM/PEL guideline exceedances. Medium-high and highest priority sites had ERM quotients >0.51 or PEL quotients >1.51 because the probability of associated amphipod toxicity was greater than 46%. Sites with sediments having ERM quotients <0.5 or PEL quotients <1.5 were generally assigned to lower categories (medium-low or low priority) because the probability of associated toxicity was less than 30%. Sediment chemistry samples in the current study ranged from 0.095-0.243 for the ERM quotients and 0.187-0.528 for PEL quotients. Therefore, in a national comparison, North Coast stations could be considered low to medium-low priority sites because all samples fall below the ERMQ and PELQ thresholds of 0.5 and 1.5, respectively.

Summary quotients also were used in the current study to evaluate relative chemical concentrations at stations within California and the North Coast Region. Twenty-five sediment samples received the extensive chemical analyses from which summary quotients were derived. The upper 90<sup>th</sup> percentiles, for sediment summary quotient ranges, for the North Coast Region, were ERMO> 0.201 and PELQ >0.422 (Figure 14). These values are used later in the report to help identify stations that exceeded regional chemistry screening levels. Although these values cannot be considered threshold levels with proven ecological significance, they can be used for comparative purposes to indicate the worst 10% of the samples in the region, with respect to concentrations of chemical mixtures. This approach has been used previously in the BPTCP in the San Diego Bay Region. The San Diego Region's upper 90<sup>th</sup> percentiles for summary quotients were ERMO> 0.85 and PELO> 1.29 (Fairey et al. 1998) (Table 10). Calculated summary quotient values allow for comparisons to be made between state regions. In this case, they indicate that the North Coast Region has relatively low pollutant levels relative to the highly urbanized and industrialized harbor environments of southern California. In fact, North Coast summary quotient values are less than a third of San Diego's values. Based on a state-wide comparison, the North Coast Region's summary quotients again are considerably less than California's 90<sup>th</sup> percentile summary quotient values (ERMQ>1.01 and PELQ>1.52). However, these low values are to be expected because California's north coast is not as heavily populated or industrialized as much of California. Although it is apparent that the North Coast Region's quotient values are lower than in other areas of the state they should not be used to infer that chemical pollution does not exist at discrete locations within the region. An in depth evaluation of individual pollutants must be made concurrently with this indicator of multiple chemical contaminants when station specific evaluations are made.

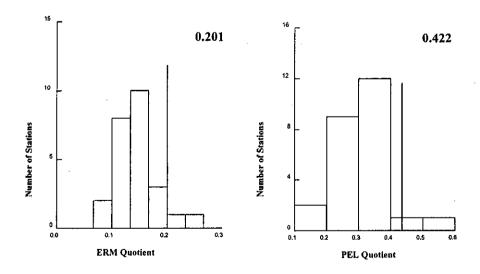


Figure 14. Frequency histogram of ERM and PEL Summary Quotient Exceedances. Vertical lines indicate 90<sup>th</sup> percentiles for 25 samples.

Distribution of Toxicity

The results of all toxicity tests conducted as part of this study are presented in Appendix E. These tables show means and standard deviations for each toxicity test response (e.g. percent survival of amphipods; percent normal development of larval sea urchins) for replicates of each sample tested. Associated ammonia and hydrogen sulfide concentrations also are presented in Appendix E. All samples were screened against water quality thresholds shown in Table 11. A sample was classified as toxic if the test response was significantly different from controls as indicated by a t-test and was lower than a threshold percentage of the control value calculated using the 90<sup>th</sup> percentile MSD for the particular toxicity test protocol (see methods section).

Table 11. Unionized NH<sub>4</sub> and H<sub>2</sub>S Effects Thresholds for BPTCP Toxicity Test Protocols.

Species	Unionized NH <sub>4</sub> (mg/L)	Limit Definition	Reference
Eohaustorius	0.8	Application Limit	USEPA 1994
Haliotis	0.05	NOEC	MPSL
Mytilus	0.15	LOEC	Tang <i>et al</i> . 1997
Neanthes	1.25	LOEC	Dillon et al 1993
Rhepoxynius	0.4	Application Limit	USEPA 1994
Strongylocentrotus Devel.	0.07	NOEC	Bay et al. 1993
Strongylocentrotus Fert.	>0.4	NOEC	Bay et al. 1993
Species	H <sub>2</sub> S (mg/L)	Limit Definition	Reference
Eohaustorius	0.114	LOEC	Knezovich et al. 1996
Mytilus	0.0053	LOEC	Knezovich et al. 1996
Rhepoxynius	0.087	LOEC	Knezovich et al. 1996
Strongylocentrotus Devel.	0.0076	LOEC	Knezovich et al. 1996
Strongylocentrotus Fert	0.007-0.014	NOEC	Bay et al. 1993

Twenty-nine of the 31 stations sampled were tested for toxicity using solid phase amphipod survival tests. Several stations were tested more than once, bringing the total amphipod test count to 57. Of those samples, 23% were found to be toxic to either *Eohaustorius* or *Rhepoxynius*, with amphipod survival ranging from 38-99%. Twenty-five percent (5 out of 20) *Eohaustorius* samples were toxic. Twenty-two percent (8 out of 37) samples tested using *Rhepoxynius* were toxic. Stations shown to be toxic were scattered along the northern section of the Eureka waterfront, at the northern most station in Arcata Bay, and at the three boating marinas in Bodega Bay (Figures 15, 16).

Samples that were toxic to amphipods, and had synoptic chemical analysis performed on them, all had at least one ERM or PEL exceedance and at least 3 ERL or TEL exceedances. Three samples, taken from stations 10019, 10028, and 14001, had ERMQ or PELQ exceeding the 90th percentile levels (ERMQ> 0.201 and PELQ >0.422). Two samples (stations 10028 and 14001) out of three were found to have amphipod toxicity corresponding to chemical concentrations exceeding regional chemistry screening levels. These corresponding chemistry and toxicity results are greater than those predicted in the Long et al. (in press) study, discussed previously. Long et al. found stations with a mean ERM quotient value of 0.11 to 0.5 were toxic in amphipod survival tests only 30% of the time, while stations with a mean PEL quotient value of 0.11 to 1.5 were toxic only 25% of the time.

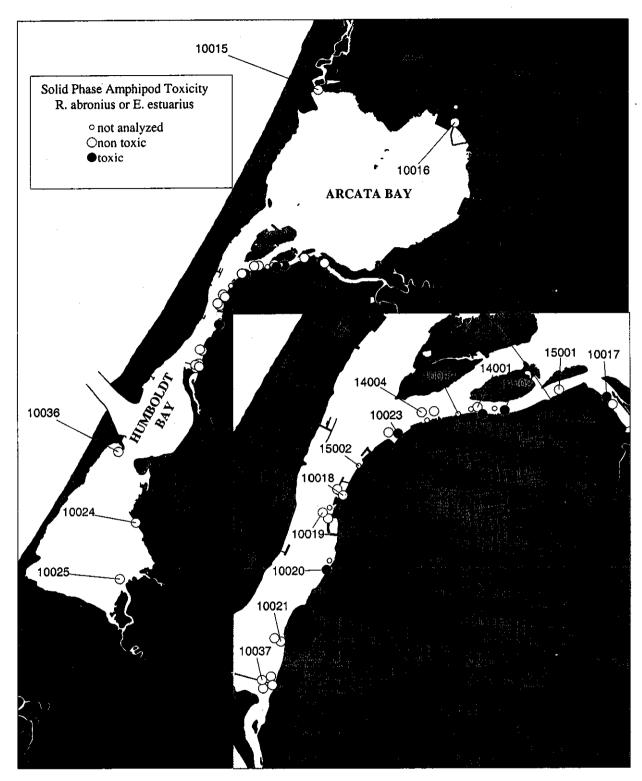


Figure 15. Humboldt and Arcata Bays toxicity. Samples were toxic if significantly different from controls using a t-test and less than control based MSD values (see text for toxicity definition).

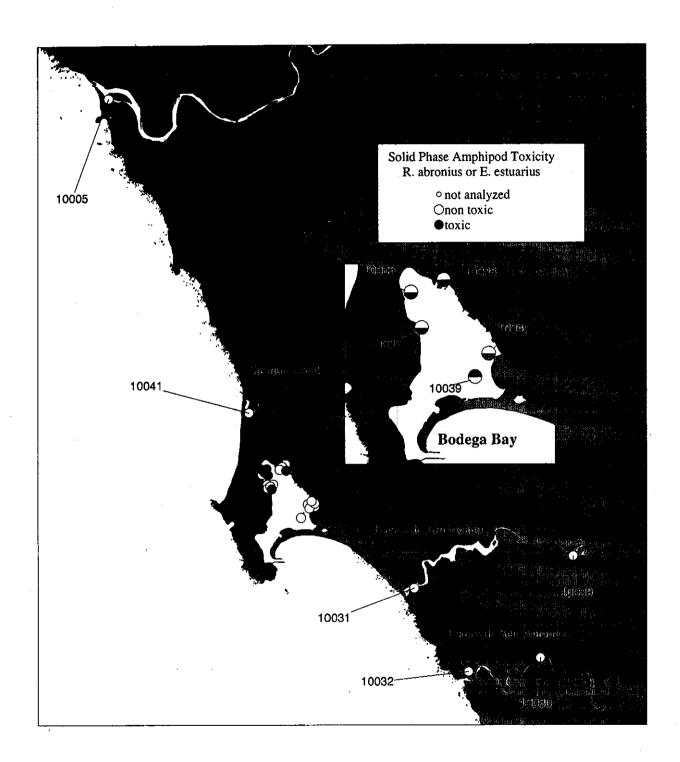


Figure 16. Humboldt and Arcata Bays toxicity. Samples were toxic if significantly different from controls using a t-test and less than control based MSD values (see text for toxicity definition).

In addition to amphipod toxicity testing, several supplemental toxicity tests were performed on selected stations within the North Coast Region. Nineteen subsurface water samples were tested with the red abalone (Haliotis rufescens) embryo-larval development test. None of these nineteen samples were found to be toxic. Twelve porewater samples, taken from the bioassay control station (station 10037), were tested using the sea urchin (Strongylocentrotus purpuratus) larval development test, and again none were found to be toxic at any three porewater concentrations. Thirty-one porewater samples had sea urchin fertilization tests performed, of these six were toxic. Although Carr and Chapman (1995) indicates no negative effects due to porewater sample freezing, frozen seawater controls used in this study were often found to inhibit sea urchin fertilization, presumably an artifact of freezing seawater in teflon bottles. Because all porewater samples were frozen prior to testing, sea urchin porewater fertilization test results were not used in station analysis. Four samples had sea urchin embryo-larval development test performed using the sediment-water interface exposure system (Figure 17). One of these four was found to be toxic; this sample also had amphipod toxicity. Seven samples had Mytilus spp. embryo-larval development test conducted in porewater and subsurface water (Figure 17). None of the subsurface water samples were found to be toxic; though, six out of seven porewater samples were shown to be toxic. Toxicity in several of these stations should be viewed with caution due to greater levels of unionized ammonia during the bioassays (unionized NH<sub>3</sub>>0.15) (Tang et al. 1997). Stations located near Estero de Amercano, in south Bodega Bay, and in Salmon Creek Estuary (10032, 10040, and 10041), had acceptable unionized NH<sub>3</sub> levels and were found to be toxic. However, stations 10039 and 10029 greatly exceeded the unionized ammonia water criteria, and station 10030 was slightly greater than the criteria (unionized NH<sub>3</sub>=0.20). Thirty-seven samples were tested with the polychaete, Neanthes arenaceodentata, survival and growth protocol, none were found to be toxic.

#### **OA/OC** Evaluation

Toxicity test data produced for this report were evaluated for acceptability using the Quality Assurance guidelines described in the BPTCP Quality Assurance Project Plan (Stephenson et al. 1994). With the exception of station 10037, there were no deviations from quality assurance criteria other than minor deviations of control criteria that were unlikely to affect sample assessment. IDORG numbers 900, 901, 902, 912, 913, and 914, all from station10037, had toxicity in brine controls. However, these IDORGs from station 10037 were not samples on which station evaluations were made. Instead they were primarily used for assessing test acceptability when examining subsequent samples from a southern California study. As stated previously, no sea urchin porewater fertilization tests were used in station analysis due to failures in frozen control tests.

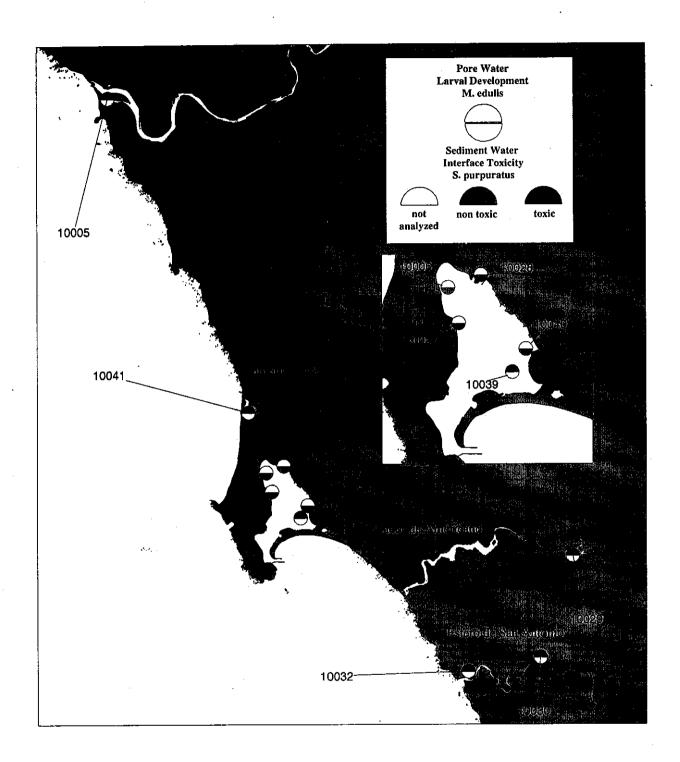


Figure 17. Humboldt and Arcata Bays toxicity. Samples were toxic if significantly different from controls using a t-test and less than control based MSD values (see text for toxicity definition).

# Statistical Relationships Analysis

Multivariate statistics were used to assess relationships among variables. Screening for covarying chemicals using Pearson correlation matrices, allowed the following variables to be used as independent variables in a multiple regression: aluminum ( $\log (x+1)$  transformed), antimony, chromium, copper, iron ( $\log(x+1)$ ), lead ( $\log(x+1)$ ), manganese, mercury ( $\log(x+1)$ , tin ( $\log(1+x)$ ), total PAH ( $\log(1+x)$ ), total DDT ( $\log(x+1)$ ), fine grain size (arcsin transformed) and TOC (arcsin transformed).

Nickel, selenium, and arsenic were not included because there were less than 25 samples analyzed for each element. The results of the ANOVA for the multiple regression showed no significant relationship between amphipod survival and any of the independent variables (p=0.469, Table 12). Amphipod survival had a negative correlation with copper concentration (std. coefficient = -0.799), however, the relationship was not significant (p=0.157). Normalizing total DDT to TOC did not improve this relationship. Statistically significant relationships between chemicals and bioassay results can be difficult to test when a small number of stations are sampled and there are many variables measured.

Table 12. Multiple regression of relationship between amphipod survival (dependent variable) and chemicals and physical variables (independent variables).

Dep. Var: Amphipod survival N:25 Multiple R: 0.745 Squared Multiple R: 0.556 Adjusted squared Multiple R: 0.030 Standard error of estimate: 8.426

Adjusted squared Multiple R: 0.030 Standard error of estimate: 8.426						
•		std.	std.			
Effect	Coefficient	Error	Coefficient	Tolerance	t	p (2 tail)
constant	23.8	178.2	0.0		0.134	0.896
aluminum	-6.85	7.96	-0.284	0.370	-0.860	0.408
antimony	6.55	6.40	0.331	0.386	1.024	0.328
chromium	0.058	0.084	0.285	0.237	0.690	0.504
copper 🐃	-0.445	0.293	-0.799	0.146	-1.519	0:157
iron	8.80	17.1	0.303	0.117	0.515	0.617
lead	-1.42	3.90	-0.098	0.563	-0.365	0.722
manganese	-0.024	0.065	-0.195	0.147	-0.371	0.717
mercury	4.31	52.1	0.036	0.219	0.083	0.936
tin	3.48	10.4	0.142	0.223	0.333	0.746
total PAH	-3.00	4.15	-0.326	0.199	-0.723	0.485
total DDT	23.5	19.6	0.437	0.303	1.20	0.256
total organic carbon	2.35	1.84	0.510	0.255	1.28	0.227
fines	-0.005	0.335	-0.009	0.112	-0.015	0.988

Analysis of Variance

Source	Sum-of-Squares	df	Mean-square	F-ratio	р
Regression	976.326	13	75.102	1.058	0.469
Residual	781.039	11	71.004		

# Distribution of Benthic Community Degradation

# **Data Analysis and Interpretation**

The results of all benthic community analyses conducted as part of this study are presented in tables in Appendix F. These tables show the species, taxa, number of individuals per core, and summary statistics for each of the 14 stations sampled.

A benthic community's structure can be highly dynamic; however, it is important to assess benthic communities as an independent measure of the overall quality of a station. As stated previously, the high and low ranges of the Relative Benthic Index (RBI) vary based on the extreme values within each data set. The RBI does, however, indicate the relative "health" of each of the stations in a given data set compared to the other stations in the same data set. The RBI used in this study is a refined version of the indices used in southern California (Anderson et al. 1997) and San Diego (Fairey et al. 1996). The San Diego study had 75 samples from which to derive their data and used reference stations to generate classifications of degraded, transitional, and undegraded. The southern California study contained 43 samples and was a modified version of the San Diego study. The benthic index used in this study also is modified from the San Diego study. It combines the use of benthic community data with the presence or absence of positive and negative indicator species in order to provide a measure of the relative degree of degradation within the benthic fauna. This version of the index does not require the presence of an uncontaminated reference station and does not refer to data beyond that collected during this study. Because of small sample size (n=14) and the fact the index is based only on samples collected in the North Coast Region, it should be interpreted with some degree of caution.

A summary of data collected from the benthic sampling in the North Coast Region is provided in Table 13. Stations with greater numbers of negative indicator species, such as polychaetes and oligochaetes, in association with low species diversity generally denote an area of disturbance. In contrast, stations with a greater number of positive indicator species, such as gammarid amphipods or ostracods, and higher species diversity indicate a relatively undisturbed area with a mature benthic community.

The Relative Benthic Index for the North Coast Region ranged between 0.4 and 0.9. No stations had a RBI of 0.3 or less, thus none were classified as having degraded benthic communities. Nine stations were classified as having transitional benthic communities because their RBI value ranged between 0.4 and 0.6 (Table 13). These stations were scattered throughout the study area, particularly in Bodega Bay. The three highest RBI stations (RBI=0.8-0.9) were located on the central portion of the Eureka Waterfront. The RBI should not be used to indicate causality because a low RBI value could be the result of chemical toxicity, anthropogenic disturbance, such as dredging or natural disturbances, such as freshwater runoff, temperature stratification, or storm impacts. Due to the relatively low pollution levels and greater levels of precipitation runoff within this region, specific patterns or relationship between sediment chemistry and Relative Benthic Index values should not be expected (Fairey et al., 1997).

Table 13. Benthic community analysis for 14 stations in the north coast region. Sample means are from three replicate cores.

							Total Taxa Ind	lividuals					
Station Number	Station Name	IDORG	Leg		Salinity (ppt)	Gammarid mean SE	Other Crustaceans mean SE	Total Crustacean mean SE	Mollusc mean SE	Polychaete mean SE	Öligochaete mean SE	Total Individuals mean SE	Benthic Indices
14004.0	DAVENPORT MARINE	1578	42	3	26	2.7 0.3	21.0 11.3	23.7 11.6	7.7 1.2	96.0 22.8	132.3 102.3	279.0 129.0	0.8
10023.0	H. BAY EUREKA STORM 23	1579	42	2	22	6.7 6.2	46.3 41.9	53.0 48.1	23.7 16.3	153.7 35.7	373.3 342.0	615.3 315.9	0.9
10016.0	ARCATA BAY-JOLLY GIANT SL.	1580	42	0	15	363.0 39.2	0.7 0.3	363.7 39.6	0.7 0.7	286.0 4.0	74.7 69.2	725.0 35.4	0.5
10017.0	ARCATA BAY-EUREKA SL.	1581	42	3	22	3.0 0.6	14.3 3.3	17.3 2.7	1.3 0.9	136.0 51.8	1.3 0.7	156.7 53.3	0.5
10021.0	H. BAY-CHEVRON TERMINAL	1582	42	3	30	0.0 0.0	14.7 3.9	14.7 3.9	13.0 5.5	138.0 25.4	1713.0 1706.0	1882.7 1683.3	0.4
10019.0	H. BAY-COAL/OIL/GAS PLANT	1583	42	1	29	45.0 43.0	20.7 7.2	65.7 50.2	18.3 3.8	354.3 63.9	1750.0 1736.0	2215.0 1768.0	0.9
10018.0	H. BAY-UNION OIL PLANT	1584	42	1	28	6.7 2.9	92.7 22.9	99.3 24.0	26.0 5.5	234.7 92.1	97.3 77.8	466.3 10.3	0.6
15001.0	H. BAY- HALBERSON SHORELINE	1585	42	2	27	14.3 8.4	40.7 19.0	55.0 26.9	4.7 1.8	291.7 72.3	0.0 0.0	356.3 98.5	0.5
14002.0	EUREKA WATERFRONT- J STREET	1586	42	4	28	1.7 0.7	37.7 13.0	39.3 12.3	12.7 6.4	257.0 31.5	35.0 35.0	350.0 11.0	0.7
14001.0	<b>EUREKA WATERFRONT- H STREET</b>	1587	42	2	26	3.7 2.0	25.0 21.5	28.7 23.2	10.0 3.8	291.0 28.2	29.7 17.9	363.3 42.2	0.6
10006.0	BODEGA BAY MASON'S MARINA	1682	47	5	32	4.3 0.9	7.0 3.1	11.3 3.2	7.0 4.0	119.3 18.3	40.0 36.5	182.0 51.6	0.7
10007.0	BODEGA-SPUD POINT MARINA	1683	47	. 3	32	109.7 16.5	4.3 0.3	114.0 16.8	14.7 2.2	228.7 39.0	7.7 5.4	373.7 34.4	0.6
10028.0	PORTO BODEGA MARINA	1684	47	4	28	0.3 0.3	26.3 3.8	26.7 3.8	5.3 0.3	200.3 19.0	33.7 21.5	267.7 17.9	0.6
10040.0	UNCONTAMINATED SITE-33D	1685	47	0.1	31	0.7 0.3	7.7 0.9	8.3 0.9	20.7 3.8	23.7 0.9	13.3 12.3	66.0 9.0	0.4
							Number of	Species					
							Other	Total			Total		
				Depth	Salinity	Gammarid	Crustaceans	Crustacean	Mollusc	Polychaete	Species	Benthic	
Station Number	Station Name	IDORG	Leg	•	(ppt)	mean SE	mean SE	mean SE	mean SE	mean SE	mean SE	Indices	
14004.0	DAVENPORT MARINE	1578	42	3	26	2.3 0.3	2.7 0.9	5.0 1.0	2.7 0.3	12.0 0.6	23.0 0.6	0.8	
10023.0	H. BAY EUREKA STORM 23	1579	42	2	22	1.3 0.9	2.0 1.2	3.3 2.0	3.7 1.9	18.0 2.1	27.7 6.1	0.9	
10016.0	ARCATA BAY-JOLLY GIANT SL.	1580	42	0	15	2.0 0.0	0.7 0.3	2.7 0.3	0.7 0.7	6.7 0.3	11.0 1.2	0.5	
10017.0	ARCATA BAY-EUREKA SL.	1581	42	3	22	1.7 0.3	1.3 0.3	3.0 0.6	1.0 0.6	8.7 0.9	14.0 0.0	0.5	
10021.0	H. BAY-CHEVRON TERMINAL	1582	42	3	30	0.0 0.0	3.7 0.9	3.7 0.9	2.3 0.9	13.3 0.9	22.0 2.1	0.4	
10019.0	H. BAY-COAL/OIL/GAS PLANT	1583	42	1	29	2.3 1.3	2.0 0.6	4.3 1.9	4.7 0.7	17.0 2.6	29.0 3.8	0.9	
10018.0	H. BAY-UNION OIL PLANT	1584	42	1	28	1.7 0.3	2.0 0.0	3.7 0.3	4.3 0.9	16.7 3.2	28.7 2.3	0.6	
15001.0	H. BAY- HALBERSON SHORELINE	1585	42	2	27	1.7 0.9	2.0 0.0	3.7 0.9	1.3 0.3	11.7 1.3	18.3 2.2	0.5	
14002.0	EUREKA WATERFRONT- J STREET	1586	42	4	28	1.7 0.7	4.7 0.3	6.3 0.9	3.0 1.5	13.0 0.0	24.3 1.2	0.7	
14001.0	EUREKA WATERFRONT- H STREET	1587	42	2	26	1.3 0.7	2.7 0.7	4.0 1.2	3.0 1.0	13.3 1.5	23.0 2.6	0.6	
10006.0	BODEGA BAY MASON'S MARINA	1682	47	5	32	2.3 0.9	3.0 0.0	5.3 0.9	1.7 0.7	15.7 2.2	25.0 1.5	0.7	
10007.0	BODEGA-SPUD POINT MARINA	1683	47	3	32	3.3 0.9	2.0 0.0	5.3 0.9	1.0 0.0	12.0 0.6	21.0 1.7	0.6	
10028.0	PORTO BODEGA MARINA	1684	47	4	28	0.3 0.3	3.3 0.7	3.7 0.3	2.7 0.3	14.3 1.5	22.7 2.0	0.6	
10040.0	UNCONTAMINATED SITE-33D	1685	47	0.1	31	0.7 0.3	2.0 0.0	2.7 0.3	1.0 0.0	6.3 1.2	11.0 1.2	0.4	

## Station Specific Sediment Quality Assessments

In order to assist the RWQCB in identifying potential stations of concern for the region, overall sediment quality was assessed. Station specific sediment quality assessments were based upon a weight of evidence approach using toxicity test results, sediment quality guideline exceedances, tissue bioaccumulation, and benthic community analysis. This approach is consistent with generally accepted methods of sediment quality assessment, such as the commonly used "sediment quality triad" approach described by Chapman et al. (1987). However, due to budgetary constraints, not all stations received evaluations of each triad leg.

Because these samples were collected over a four year period, a station's specific analytical results varied over time and were dependant upon the particular sampling event. A summary of each stations individual sampling results is shown in Table 14. This table reflects how some stations toxicity test results or chemical analysis may have changed over the course of this study and provides specific sample results.

For the purpose of identifying stations of concern, these temporal data were pooled and measured effects were summarized by station (Table 15). These evaluations are based on all toxicity, chemistry, and benthic community information collected by the BPTCP on a per station basis. "Repeated toxicity" is defined as a station that has been classified as toxic (significantly different from controls and less than MSD based thresholds) on at least two separate sampling dates, based on all available bioassays, but excluded sea urchin fertilization tests. As mentioned previously sea urchin fertilization tests were not included due to potential artifacts from sample freezing. Also individual toxicity test results were not included in this station evaluation if a water quality parameter, such as unionized ammonia, may have influenced test result interpretations. The "single toxicity" field refers to a station that has shown toxicity at one time during the study regardless of the number of times the station was visited. An exceedance of regional chemistry screening levels was defined as meeting any of the following criteria:a station's sample exceeded regional sediment guideline quotient values (ERMQ > 0.201 or PELQ > 0.422); had 5 or more ERM or PEL exceedances; or if an individual chemical concentration was greater than the 90th percentile of the BPTCP data set calculated for the state (Table 10). As explained in the discussion on sediment chemistry results, the ERMO and PELO values were derived based upon the 90<sup>th</sup> percentile of chemistry samples collected within this regional study and are relatively low based on national and state comparisons. Despite their relatively low value they are necessary to evaluate regional pollution. Because of the low number of ERM and PEL exceedances, ERL and TEL exceedances also are summarized to provide further insight into the station's chemical composition. However, as mentioned earlier, they should be interpreted with caution because these guidelines represent the level below which biological effects are not expected to occur. Station evaluation of bioaccumulation data was based solely on BPTCP tissue samples and data were interpreted using EPA and SMWP screening values as explained previously. When tissue screening value exceedances occurred the chemical of concern was noted, as well as, the screening value used for comparison. Tissue data collected at corresponding stations from the SMWP were not included in Table 15 because they were not specifically a part of this study's sampling design. However, due to the similar manner in which SWMP and BPTCP tissue samples were collected and analyzed, SWMP data provided valuable supplemental information about a station's chemical composition thus, it was included in station descriptions. The benthic field

Table 14. Sample summary of toxicity, sediment chemistry exceedances, benthic indices results. Only those bioassay protocols which showed toxicity are listed. Complete results are listed in the amendices (shaded survival indicates samples which were toxic; n/a indicates no chemical analyses)

10004.0		-	•	į,											
	Station	IDORG	Date		TOC	sarvival	survival	Inter Tox.	porewater	Exceedances	ERMQ	PELQ	Exc.	Exc.	Indices
	ARCATA BAY-MCDANIEL SL.	304	11/30/92	0.06	0.58	38	-			Cr, Ni	0.112	0.226	\$	\$	•
	RUSSIAN RIVER MOUTH SMW 280.0	305	2/25/93	48.0	0.99	•	92		NT (0.009)	n/a	D/a	п⁄а	17,8	n/a	•
10006.0	BODEGA BAY-MASON'S MARINA	306	2725193	98.0	2.00	38				Ni, ACE, FLA, PHN, PYR	0.175	0.335	00	0	•
0.90001	BODEGA BAY-MASONS MARINA REPI	1350	6/14/94	7.96	3.4	.5	,		i	n/a	n/a	n/a	Ľ/3	<b>8</b> /2	٠
0.90001	BODEGA BAY-MASON'S MARINA REP2	1351	6/14/94	94.1	3.50	52			i	n/a	11/8	n/a	u/a	<u>1</u> /a	•
10006.0	BODEGA BAY-MASON'S MARINA REP3	1352	6/14/94	98.5	3.58	75			,	n/a	n/a	₽/u	n/a	2	
0.9000	BODEGA BAY MASON'S MARINA	1682	12/6/96	98.9	3.34	٠	57	¥		ž	0.165	0.312	9	Φ	0.7
0.0007.0	BODEGA BAY-SPUD POINT MARINA	307	2/25/93	27.0	8.	80				n/a	n/a	17/3	<u> </u>	5/2	
	RODEGA-SPUD POINT MARINA REPL	1353	6/13/94	861	0.43	<b>.</b> %				n/a	1/2	10/3	D/9		٠
10007.0	BODEGA-SPUD POINT MARINA REP2	1354	6/13/94	2	0.48	35				1/9	17/8	n/a	n/a		•
	BODEGA-SPUD POINT MARINA REP3	1355	6/13/94	15.2	0.35	16			,	n/a	n/a	n/a	n/a	n/a	•
10007.0	BODEGA-SPUD POINT MARINA	1683	12/5/96	16.7	9.64	•	. <b>2</b> 6	<b>-</b>	ě	ర	0.095	0.187	m	7	9.0
10015.0	ARCATA BAY-MAD RIVER SL.	315	11/30/92	0.09	0.65	≅ .			·	n/a	n/a	ī/a	Z/2	л/a	•
10016.0	ARCATA BAY-JOLLY GIANT SL	316	11/30/92	61.0	0.75	78				S, S	0.153	0.301		20	
10016.0	ARCATA BAY-JOLLY GIANT SL.	1580	4/18/96	79.5	2.68		80			ž,	0.188	0.362	•	10	0.5
10017.0	ARCATA BAY-EUREKA SI.	317	11/29/92	88.0	0.77					ž	0.121	0.242		ø	•
	ARCATA BAY-EURÉKA SL.	1581	4/11/96		1.47		11		•	C, N	0.151		4	4	0.5
10018.0	H. BAY-LINION OIL PLANT	85	11/29/92	74.0	0.76	94	•		•		10/3	n/a	n/a	10/8	
	H. BAY-UNION OIL PLANT	1584	4/17/96				8	٠		Q, Ni	0.164	0.360	4	9	9.0
00100	H BAY, COAT MIT GAS PLANT	319	11/79/97	72.0	9 65	68					n/a	n/a	6/0	E/E	
	TA BANGO TO TO THE TANK	443	2/15/05		}	;	-			C. N. MNP2	1/2	8/2			•
	H. BAY-COALOIL/GAS PLANT	1583	4/17/96	72.1	1.73		. \$			Cr, Ni, lindane	0.143	0		vo	0.0
10020.0	H. BAY-OLD PAC. LUMBER SITE	320	11/29/92	83.0		0.70	•			Ċ, Ŋ	0.111	0.225	m	•	•
	H. BAY- OLD PAC. LUMBER SITE	144 44	2/15/95				٠			Cr, Ni, MNP2	υ⁄a	D/a	•	7	-
10021.0	H. BAY-CHEVRON TERMINAL	321	11/29/92	50.0	0.56	76	,			Cr, Ni	0.114	0.237		*	•
10021.0	H, BAY-CHEVRON TERMINAL	1582	4/11/96	76.9	F.18		98			Cr, Ni, lindane	0.122	0.312	7	4	4.0
10022.0	HUMBOLDT BAY EUREKA SM.22	1448	2/15/95	•			٠			Cr, Ni, MNP2	n/a	n/a	4	₹0	•
10023.0	H. BAY EUREKA STORM 23	323	11/29/92	67.0	1.00	74				G, N	0.137	0.274		9	٠
10023.0	H. BAY EUREKA STORM 23	1579	4/11/96	36.1	1.82		92		•	G, N	0.129		m	ν.	6.0
10024.0	H. BAY FIELDS LANDING	324	11/29/92	75.0	09.0	%	•	•	•	n/a	n/a	n/a	n/a	n/a	•
0025.0	10025.0 H. BAY HOOKTON SL.	325	11/29/92	94.0	0.54	8			. •	Ģ, Ņ	0.107	0.107 0.220	ε.	9	•

Table 14 Sample summary of toxicity, sediment chemistry exceedances, benthic indices results. Only those bioassay protocols which showed (cont). toxicity are listed. Complete results are listed in the appendices (shaded survival indicates samples which were toxic; pla indicates no

			į			Total Section 1									
10028.0	POPTO BODECA MARRIA	330	200,200,0			TALLES OF	RALAMAN.	Inter. Tox	Parewater	Exceedances	EBRO	ı	E.	ä	Indices
10000	AMENIA PORTOR PRINCIPAL	350	2007	20.0	2	8	•		•	ž,	0.166	0.305	9	10	•
0.020	PORTO BODEUA MARINA REPT	1336	64/94 4/94	<b>\$</b>	<u>-</u>	<del>~</del>			,	1./a	1/3	n/a	Š	<b>2</b> /4	·
0.0700	POR IO BODELIA MARINA REP2	1357	6/14/94	56.7	33	22				n/a	n/a	10/2	10/2	2/2	•
10028.0	PORTO BODEGA MARINA REP3	1358	6/14/94	47.6	1.24	82				10/3	n/a	173	7,	6/6	
10028.0	PORTO BODEGA MARINA	1684	12/6/96	79.4	2.30		. 73	Þ		Cr, Ni, diedrin	0.214	0		=	9.0
10029.0	ESTERO AMERICANO-VALLEY FORD	329	2/25/93	50.0	0.95	•	<b>8</b> 8	٠.	T(0.634)	n/a	(D/a	n/a	1/4	1/3	•
10030.0	ESTERO DE SAN ANTONIO-VALLEY F	330	2/25/93	35.0	1.90		66		T(0.208)	11/2	n/a	D/a	, 2	Š.	•
0.15001	MOUTH OF ESTERO AMERICANO	331	2/26/93	10.0	0.23	33				7	4	4	÷	-	
10031.0	MOUTH OF ESTERO AMERICANO	1322	5/16/94	12.7	0.64	<b>2</b>				10/a	17/a	14 a	Z Z	5 Z	• •
10032.0	MOUTH OF ESTERO DE SAN ANTONIO	332	2/26/93	23.0	. 8.		56		T(0.068)	π⁄a	17/3	n/a	,7a	e/a	•
10036.0	SOUTHPORT CHANNEL-33B	336	11/30/92	83.0	0.81	8	•			n⁄a	n/a	Ş	n/a	Z/a	
10037.0	H. BAY-MOUTH OF ELK RIVER	337	11/30/92	53.0	2.20	8				ž	601.0	7.00			
	MEGAMUD-HUMBOLDT(ELK)-REP 1	800	6/22/93			8		٠.		Z Z	) }	\$ %	n n	۰ -	•
	MEGAMUD-HUMBOLDT(ELK)-REP 2	<u>8</u>	6/22/93			68				n/a	r/a	, <u>1</u>	, j	- <sup>1</sup> / <sub>2</sub>	
10037.0	MEGAMUD-HUMBOLDT(ELK)-REP 3	<b>%</b>	6/22/93			95				IV'a	D'a	, 2	1/a	а/u	•
10039.0	UNCONTAMINATED SITE-33C	339	2/25/93	41.0	0.83		96		T(0.705)	n/a	17/3	,5 8	11/a	n/a	•
	UNCONTAMINATED SITE-33D	340	2/26/93	43.0	0.25	\$			T(0.079)	11/3	73	17,9	0/a	E/a	•
10040.0	UNCONTAMINATED SITE-33D	1321	5/16/94	37.4	0.47	16		•		n/a	n/a	п/а	<b>1</b> √a	7/2	•
	UNCONTAMINATED SITE-33D REPL	1359	6/13/94	26.5	0.27	93			•	n/a	n/a	P,	1/2	n/a	•
	UNCONTAMINATED STIE-33D REP?	1361	6/13/94	28.6	0.27	<b>3</b> . 5				n/a	n/a	e/u	B/B	D/a	٠
	UNCONTAMINATED SITE-33D REFS	1585	12/6/96	25.0	92.0	76	. 6	. <u>Ļ</u>		10/2	n/a	, a	n/a	Z'a	
		•	i i		•		ŝ	Ē		ć.	0.099	861.0	4	r <b>r</b> 3	4.
10041.0	SALMON CREEK-34L	34	2/25/93	51.0	1.80		96		T(0.046)	n⁄a	n/a	, <u>F</u>	n/a	D/a	•
		322	11/29/92	95.0	0.84	8		٠		n/a	E/1	10/3	10/3	n/a	•
14001.0	EUREKA WATERFRONT H STREET EUREKA WATERFRONT- H STREET	1450	2/15/95	26	. 1.57		\$ <b>85</b>	•		Cr, Ni, MNP2	11/2	E/3		6	}
14002 0	GUREKA WATEREDANTI (STORET	1463	30/31/6						•	90 100		9776	•	•	Š
	EUREKA WATERPRONT. I STREET	1586	4/17/96	. 8.	1.36		. 70			O. N. ACE, FLA. FLU, MNP2, PHN, PYR, PAIS CP., Ni	0.148	n/a 0.312	0 4	» «	
14003.0	ARCATA BAY-JOLLY GIANT NORTH	1438	2/14/95							CR, Ni	n/a	73	· •	, 4	
	DAVENPORT MARINE	338	11/30/92	77.0	0.81	8		•		ź	0.187	0 323	٢	ď	
	DAVENPORT MARINE	1446	2/15/95							Cr. N. MNP2	) (c) (c)			۸ <	•
14004.0	DAVENPORT MARINE	1578	4/17/96	86.9	1.49		88			N. S	0.136	0.275	4	t m	. 6.8
15001.0	H. BAY- HALBERSON SHORELINE	1585	4/17/96	84.2	1.48		. 83			Ğ, Z.	0.136	0.326	4	4	0.5
15002.0	H. BAY- WASHINGTON STREET	1440	2/15/95							Cr. N. MAND	4	1	•	•	

Table 15. Station summary of chemistry, toxicity and benthic community results (\*\* not used in station evaluations due to water quality exceedances, SV= screening values, see text for complete descriptions).

	quanty exceedances, 5 v	- screening value		text for complete descriptions		<u> </u>		·
Station	_		ERL/TEI		Repeat	~	n 41.1	C *:
Number	Station	Sediment Chemistry	Exceed.	Tissue Chemistry	Tox	Tox	Benthics	Comments
10028.0 10006.0 14001.0 14002.0	Stations which exceeded PORTO BODEGG MARINA BODEGA BAY-MASON'S MARINA EUREKA WATERFRONT- H STREET EUREKA WATERFRONT J STREET	d regional chemistry sero ERMQ=0.214 5 PEL exceedances ERMQ=0.243, PELQ=0.528 10 PEL exceedances	11 9	>EPA SV for PCBs & MW value for CU >EPA SV for PAHs & MW value for CU	non-degr X X	aded be X X	enthic commi Transitional Undegraded Undegraded Undegraded	AG in top 95% for the state  LMW PAHs in top 95% for the state
10019.0	Stations which exceeded H. BAY-COAL/OIL/GAS PLANT	d regional chemistry scre PELQ= 0.482	eening lev 6	els, non toxic, non-degraded benthic com	nunities	1 1 1 y	Undegraded	Lindane in top 90% of the state
10007.0 10017.0 10023.0 10040.0	Stations with no region BODEGA-SPUD POINT MARINA ARCATA BAY-EUREKA SL. H. BAY EUREKA STORM 23 UNCONTAMINATED SITE-33D	al chemistry screening le	evel exceed 3 6 6 4	lances, single toxicity, non-degraded bent	hic comm	nunities X X X X X	Transitional Transitional Undegraded Transitional	Toxic once in both amphipod and SDI tests
10016.0 10018.0 10021.0 14004.0 15001.0	Stations with no region ARCATA BAY-JOLLY GIANT SL. H. BAY-UNION OIL PLANT H. BAY-CHEVRON TERMINAL DAVENPORT MARINE H. BAY- HALBERSON SHORELINE	al chemistry screening k	10 6 5 9	dances, non toxic, non-degraded benthic c	ommuni	ties	Transitional Transitional Transitional Undegraded Transitional	
10004.0 10020.0 10032.0	Stations with no region ARCATA BAY-MCDANIEL SL. H. BAY-OLD PAC. LUMBER SITE MOUTH OF ESTERO DE SAN ANTONK		evel exceed 5 7	dances, toxicty measured one or more tim	es, benth	ic comi X X X X	munity not ar	toxic R. abronius test; but 90% Fines
14003.0	Stations which exceeded ARCATA BAY- JOLLY GIANT NORTH	d regional chemistry scre	ening leve	els, toxicity not analyzed, benthic commun > EPA SV for PCBs	nity nôt s	inalyze	d 🧪 🏋	
10025.0 10037.0	Stations with no region: H. BAY HOOKTON SL. H. BAY-MOUTH OF ELK RIVER	al chemistry screening le	vel exceed 6 4	lances, non toxic, benthic community not	analyzed			The second secon
10022.0 15002.0	Stations with no region: HUMBOLDT BAY EUREKA SM 22 H. BAY- WASHINGTON STREET	al chemistry screening le	vel exceed 5 4	lances; toxicty not analyzed; benthle comi	nunity n	of analy	/zed	
10029.0 10030.0 10039.0 10041.0	Stations with no chemi ESTERO AMERICANO-VALLEY FORD ESTERO DE SAN ANTONIO-VALLEY I UNCONTAMINATED SITE-33C SALMON CREEK-34L	1	easured o	ne or more times, benthic community not	analyze	x** x x x** x		toxic M. edulis test; but exceeded NH3 by 4.2X toxic M. edulis test; but exceeded NH3 by 4.7X
10005.0 10015.0 10024.0 10031.0 10036.0	Stations with no chemic RUSSIAN RIVER MOUTH SMW 280.0 ARCATA BAY-MAD RIVER SL. H. BAY FIELDS LANDING MOUTH OF ESTERO AMERICANO SOUTHPORT CHANNEL-33B	stry analyzed, non toxic	benthic c	ommunity not analyzed				

noted the classification of a station as degraded, transitional, or undegraded based on the station's RBI value as described previously. The comment field was used to provide additional information about a station, such as extremely elevated chemical concentrations or toxicity test concerns. Based on this data evaluation the following stations were of particular interest:

Station 10028, Porto Bodega Marina, is a small boat marina located in the northeastern corner of Bodega Bay. It is one of the older marinas in Bodega Bay and has been in operation since the 1960's. Sediment from this station was toxic to amphipods in two of five sampling events. However, the station was not toxic using a sediment water interface sea urchin development test. This discrepancy in toxicity test results probably is caused by the varying chemical sensitivities within test organisms. Porto Bodega Marina also exceeded regional chemical screening levels (ERMQ=0.241) during the latest sampling event in December of 1996. Both times this station was analyzed for chemistry it had ERL or TEL guideline exceedances for low and high molecular weight PAHs, as well as, total PAHs. These PAH levels probably reflect vessel traffic and refueling operations within the harbor. Copper, mercury, and zinc also exceeded ERL or TEL guidelines both times sediment chemistry was analyzed. This station also had one of the highest aluminum sediment chemistry concentrations in the state (108,000 ug/g). Although BPTCP tissue samples were not collected at this station, corresponding SMWP data (SWRCB, unpublished data) have indicated 95<sup>th</sup> percentile EDL exceedances for copper and mercury and 85<sup>th</sup> percentile EDL exceedances for aluminum. These metal concentration levels could be due to historic boat maintenance, leeching of antifoulant paints and the relatively calm waters within the marina. The benthic community was classified as transitional (RBI=0.6) having very few gammarid amphipods or total crustaceans. For these reasons, Porto Bodega Marina is considered a station of concern for the region.

Another boat harbor of interest is station 10006, Bodega Bay- Mason's Marina. This station is located in the north west corner of Bodega Bay and, like Porto Bodega marina, has been in operation since the 1960's. The harbor has the capacity to hold 120 boats, however, generally operates at around 60% of capacity. Mason's Marina was tested for toxicity using both Rhepoxynius and Eohaustorius amphipod survival tests. It was classified as toxic in four out of five tests. Yet, the station was not toxic using a sediment water interface sea urchin development test. This station had 5 PEL sediment quality guideline exceedances including individual PAHs. such as acenaphathene and fluoranthene. It also exceeded several ERL and or TEL guideline exceedances for low and high molecular weight PAHs, total PAHs, copper, mercury, and zinc. Tissue samples were not collected at this station; however, Mussel Watch data indicate both copper and mercury exceeded 85th percentile EDL levels and aluminum exceeded the 95th percentile EDL level. As with Porto Bodega Marina, PAH levels may be due to vessel traffic and refueling operations. Metal concentration levels could be attributed to historical boat maintenance, leeching of antifoulant paints and the relatively calm waters within the marina. The benthic community was classified as undegraded (RBI=0.7), because it had one of the highest total number of species, including gammarid amphipods and crustaceans, yet still had relatively low numbers of individuals. Because of Mason Marina's repeated toxicity results and sediment quality guideline exceedances it is considered a station of concern for the region.

Station 14001, Eureka Waterfront- H Street is located near G & R Metals, a division of Levin Metals Corporation, however, the company has not been in operation since 1980 (RWQCB,

1997). Only one amphipod survival toxicity test was performed on this station and it was toxic to Eohaustorius. The station not only exceeded 90<sup>th</sup> percentile ERMQ and PELQ values, but had the greatest quotients in the region (ERMQ=0.243 and PELQ=0.528). Also there were ERL and TEL exceedances for copper, lindane, mercury, zinc, total PCB and PAHs. This sample also had a silver concentration of 3.57 ug/g, which was in the top 95<sup>th</sup> percentile for the state. Tissue samples were found to exceed EPA screening values in resident mussel tissue for PCBs and aluminum, copper and manganese levels exceeded SMWP 95<sup>th</sup> percentile EDLs. Contaminant levels may be due to the historical use of the location as a scrap metal facility. The benthic community had a RBI value of 0.6. The H street station benthic community was considered transitional because it had a great number of negative indicators species (polychaetes), however, it also had several different taxa species represented. Due to summary quotients which exceeded regional chemistry screening levels and multiple ERL and TEL sediment quality guidelines exceedances, toxic amphipod response, and bioaccumulation of PCBs and copper in tissues, it is considered a station of concern for the North Coast Region.

Station 14002, Eureka Waterfront- J Street, is located near a site called Adorni; this site has been previously identified as being polluted with petroleum (RWQCB, 1990). In 1989 the Adorni site was found to have extensive soil pollution with the groundwater being affected. J Street was tested for toxicity once, using *Eohaustorius*, and was toxic. The station had 10 PEL sediment quality guideline exceedances, primarily being individual PAHs such as acenaphthene, fluoranthene, 2-methylnaphalene, phenanthrene, and pyrene. Sediment samples had a low molecular weight PAH concentration of 4759.2 ng/g, which is in the top 95<sup>th</sup> percentile for the state. These PAH exceedances may be due to its proximity to the Adorni site. There also were copper, mercury, and zinc TEL and or ERL guideline exceedances. These metal concentration levels could be due to nearby storm drain runoff. Resident mussel tissue samples collected at the station found copper and mercury to exceed Mussel Watch 85<sup>th</sup> percentiles EDLs. The station's benthic community was classified as undegraded (RBI=0.7). It had one of the greatest numbers of crustacean species and many molluse species as well. Due to the historic background of this location and its toxicity, chemistry and bioaccumulation results, J-Street is another station of concern for the North Coast Region.

Station 10019, Humboldt Bay Coal, Gas, and Oil Plant, is located near an old coal gas plant which was in operation around the turn of the century (RWQCB, 1990). Street construction activities in the early 1990's located an underground concrete tank containing heavy hydrocarbons and PG&E has been asked to completely investigate and clean up this polluted location (RWQCB, 1990). Station 10019 was found to be non toxic both times it was tested using amphipod bioassays. However, it did exceed the regions' 90<sup>th</sup> percentile's PELQ value (PELQ=0.482). There were multiple ERL and TEL sediment guideline exceedances for individual PAH compounds, as well as low, high, and total PAHs exceedances. Copper also was shown to exceed ERL and TEL guideline values. Lindane concentrations were greater than the 90<sup>th</sup> percentile for the state (>2.82 ng/g). These chemical levels may be due to historic hydrocarbon pollution and, in the case of lindane, the station's proximity to stormdrain runoff. Because it does not show evidence of a degraded benthic community (RBI=0.9) and the lack of tissue data collected, station 10019 should be investigated further to determine if it should be a station of concern for the region.

## Limitations

As mentioned in the methods section, the two step sampling design of this study relied on an initial "screening phase" to give a broad assessment of toxicity in the North Coast Region. A full suite of analyses, including toxicity testing, chemical analysis and benthic community analysis, was performed only on selected stations (45% of the screened stations). Five of the 31 stations surveyed had toxic results from either amphipod survival tests or from *Mytilus* porewater tests yet did not receive full chemical analyses or benthic ecology due to limited funds. Therefore, statistical analysis, comparisons to chemical specific screening values, identification of undegraded and degraded habitats and summary analysis could not be performed on all stations sampled. This lack of data for stations 10005,10031, 10032, and 10041, is particularly troublesome because SMWP data indicate these areas have elevated levels of organics accumulating in mussel tissues. Unfortunately, none of these stations were analyzed for organic chemistry. Future monitoring work should stress a watershed type approach to pollution prevention and include stations, such as these, which may receive periodic influxes of pesticides or other contaminants.

It is recognized that any conclusions based on interpretation of these data should be considered preliminary because of the limited nature of the data set. As with any study of this scope, it is difficult to identify all variables that may be associated with biological responses at a particular location. For example, our characterization of organic chemical pollution is constrained by the limited number of contaminants measured. Samples often contained unidentified organic compounds which were not further characterized due to the limited scope of the study; these compounds could have contributed to the toxicity of the samples. In addition, no measures of interstitial water chemical concentrations were conducted for substances other than ammonia and hydrogen sulfide. Therefore, our ability to characterize bioactivity of the bulk-phase chemicals is confined to those stations that could be normalized to TOC. In addition, no measures of acid volatile sulfides and associated metals (AVS-SEM) were made, which limits our ability to predict bioavailability and toxicity of metals. Also conclusions regarding benthic community degradation were limited by the lack of in situ water quality parameters.

## IV. CONCLUSIONS

Sediment quality guideline values were used for comparison with chemical concentrations found within the North Coast Region. Chromium, nickel, PAHs, and lindane were found most often to exceed ERM or PEL guideline values. Due to relatively low chemical concentrations within the region, ERL and TEL guideline values also were used to provide a more relevant comparison to the chemical composition of the North Coast Region. Copper, mercury, and zinc were found most often to exceed ERL and TEL guideline values. Although ERL and TEL values are considerably lower than ERM and PEL guidelines, multiple exceedances of ERL and TEL guidelines may indicate possible impacts on the relatively pristine environment of the North Coast Region.

The upper 90<sup>th</sup> percentiles, for sediment quotient ranges, for the North Coast Region were ERMQ>0.201 and PELQ>0.422. These values are significantly lower than other summary quotient values calculated for the state (i.e., San Diego 90<sup>th</sup> percentile ERMQ>0.85 and PELQ>1.29). Nevertheless, this is to be expected because the North Coast is not as heavily populated or industrialized as much of California. It should be noted that lower summary quotient values should not be used to infer that chemical pollution does not exist at discrete stations within the region. It should be noted that in contrast to the mitigation approach employed in more urban/industrial coastal regions, prevention and prohibition are the primary approaches employed in the protection of the relatively unpolluted coastal resources of California's North Coast. Therefore, any anthropogenic pollution is of great concern.

Tissue samples were collected from 10 stations and were analyzed for a variety of chemicals. Samples included both resident and transplanted mussels, oysters, crabs and polychaete worms. When applicable, relevant SMWP data were reviewed for chemical contamination and provided supplemental information about stations. In general, measured tissue concentrations of organic contaminants, such as pesticides, BTEX and TPH, were below detection limits, indicating relatively low levels of tissue contamination in the North Coast Region. However, some trace metals were detected in patterns similar to those found in sediments. Metals that were detected in both sediments and tissues included chromium, nickel, copper, and mercury.

Toxicity within the region was examined using a variety of bioassays. Twenty-nine of 31 stations sampled were tested using solid phase amphipod survival tests. Of these stations, 9 were toxic at least once using either *Eohaustorius* or *Rhepoxynius*; amphipod survival ranged from 38-99%. Stations shown to be toxic were scattered along the northern section of the Eureka waterfront, at the northern most station in Arcata Bay, and at the three marinas in Bodega Bay. All samples that were toxic, and had synoptic chemical analysis performed on them, had at least one ERM or PEL exceedance and at least 3 ERL or TEL exceedances. However, multiple regression analysis of data from throughout the region showed no significant relationships between amphipod toxicity and chemical concentrations.

Benthic community structure within the North Coast Region was analyzed using a Relative Benthic Index. The low and high ranges of the index indicate the relative "health" of a station compared to other stations within the data set and was used to classify stations as degraded, transitional and undegraded. The RBI for the North Coast ranged between 0.4 and 0.9 and none were classified as degraded. Nine stations were classified as having transitional benthic communities. These stations were scattered throughout the study area, particularly in Bodega Bay. The three undegraded stations were located on the central portion of the Eureka Waterfront. Due to the relatively low pollution levels in this region, and the small benthic community sample, size specific patterns or relationship between sediment chemistry and RBI values were not found.

Five stations, Porto Bodega Marina, Mason's Marina, H Street, J Street, and Humboldt Bay Coal, Gas and Oil Plant were distinguished as stations of concern or interest for the region. These stations exhibited greater level impacts of toxicity, greater chemical concentrations, or biological impacts compared to the remaining 31 stations analyzed in the region, and correspond with issues of regional concern.

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