

**CHEMICAL AND BIOLOGICAL MEASURES
OF SEDIMENT QUALITY IN THE
CENTRAL COAST REGION**

**INTERNAL DRAFT REPORT
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EXECUTIVE SUMMARY

This report describes and evaluates chemical and biological data collected from water bodies in the Central Coast Region between August, 1992 and May, 1997. The study was conducted as part of the ongoing Bay Protection and Toxic Cleanup Program, a legislatively mandated program designed to assess the degree of chemical pollution and associated biological effects in California's bays, estuaries and harbors. The workplan for this study was synthesized by the State Water Resources Control Board. Monitoring and reporting aspects of the study were conducted by the Oil Spill Prevention and Response Division of the California Department of Fish and Game and its subcontractors.

The study objectives were:

1. Determine presence or absence of statistically significant toxicity effects in representative areas of water bodies in the Central 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.

This study involved chemical analysis of sediments, and toxicity testing of sediments and sediment pore water. Other analyses added as required included benthic community analysis, water column toxicity tests, semipermeable membrane devices for measuring water-borne organic pollutants, fish tissue analysis, and field water quality analyses. Chemical analyses and bioassays were performed using aliquots of homogenized sediment samples collected at each station. Benthic community analysis was done on a subset of stations chosen for specific evaluation of the residual effects of a lead slag heap in Monterey Harbor. Water column toxicity, semipermeable membrane device (SPMD) tests and field water quality analyses were employed in a pilot watershed study in the Tembladero drainage.

Eighty seven samples from 53 stations were collected between August, 1992 and May, 1997. Areas sampled included Morro Bay, Elkhorn Slough and its tributaries, Monterey Harbor, and coastal river and stream estuaries from Carpinteria Marsh in the south to Scott Creek in the north. These areas are collectively termed "the Central Coast Region" in the following document.

Chemical pollution was identified using comparisons to established sediment quality guidelines. Two sets of guidelines were used: the Effects Range-Low (ERL)/Effects Range-Median (ERM) guidelines developed by the National Oceanic and Atmospheric Administration (NOAA) (Long and Morgan, 1990; Long *et al.*, 1995) and the Threshold Effects Level (TEL)/Probable Effects Level (PEL) guidelines used in Florida (McDonald, 1992; McDonald, 1994a,b). Total chlordane, dieldrin, and PAHs were most often found to exceed critical ERM or PEL values and were considered the major chemicals or chemical groups of concern in the Central Coast Region. Chromium and nickel also frequently exceeded ERM or PEL values but due to their likely

geologic sources, were not considered primary chemicals of concern. DDT was also found commonly but in quantities for which confidence in the likelihood of biological effect is low.

Any station with exceedances of ERM or PEL values was considered to have elevated chemical content. Chemical summary quotients were used as indices for addressing the pollution of sediments with multiple chemicals and to compare relative levels to other stations within the program. The quotients incorporate degree of chemical pollution with number of chemicals found. This technique allows stations with many chemicals not in exceedance of guideline values to be considered alongside those with smaller numbers of chemical constituents which do exceed guideline values. Although this value may have several interpretive variables and does not necessarily imply biological significance, it is a useful comparative tool within the region and program. Stations with quotient values in the top 10% for the region were considered to have elevated chemistry. Twenty one stations had sufficiently complete chemistry datasets to calculate quotient values.

Toxicity was defined as a value significantly different from control values and less than the minimum significant difference (MSD). The MSD proved to be a useful tool to compare the typical variability of the toxicity test method to the difference between the sample and control effects. A positive toxic response was measured from 53 of the 83 samples taken in the region. Of the 53 toxic responses, 23 had concurrent chemical measurements in excess of established sediment quality guidelines (ERM or PEL).

Multiple regression analyses failed to reveal strong relationships between amphipod survival and chemical and physical factors. Since variances for this type of data are characteristically high, more replication is needed to see relationships among the many variables.

Special studies in the Monterey Harbor and Tembladero watershed were used to address specific water quality questions related to each area. The Monterey Lead study used a directed sampling approach to identify any remaining lead gradient in sediments near the site of removal of a lead slag heap. Measured lead levels did not exceed guideline values at any of the stations sampled, but were among the highest measured program-wide. Physical factors may confound the results, however. Low percent fines at all of the Monterey Harbor sites suggest that the area is dynamic and that smaller particles to which metals tend to adsorb may be suspended long enough to be transported away. While this process may benefit benthic invertebrates in the local area, the potential for bioaccumulation in filter feeders still exists. Benthic community analysis was run on the four Monterey Lead samples, but the results were inconclusive. Urchin larval development was inhibited at the closest site to the slag heap, but no toxicity tests were done at the other sites. PAHs were measured in excess of the PEL at the site closest to the slag heap also, so other sources of toxicity cannot be ruled out.

The Tembladero watershed was the focus of a pilot watershed study prompted by regular measurement of high levels of pesticides in sediment and bivalve tissue at Sandholdt Bridge in Moss Landing Harbor. The station is the mouth of the Tembladero slough which drains a largely agricultural watershed. The study tested sediment for pesticides, PAHs, and toxicity, water for toxicity and general water quality parameters (nitrate, phosphate, dissolved oxygen, pH), and

used semipermeable membrane devices to test bioaccumulation potential. Stations were selected near confluences to characterize subdrainages.

All but one station in the watershed had pesticide levels exceeding ERM guideline values. The highest chemical values in sediment were found at the furthest upstream station, as well as the strongest toxic response. Since this station is located just downstream of the city of Salinas, but drains a fairly large agricultural area identification of sources will require further upstream sampling. Samples taken from the subdrainages of the Tembladero slough also showed high levels of pesticides and strong toxic response, indicating multiple inputs of pollutants to the system.

Stations were grouped together by their completeness of information and by chemical and toxicity test results. Specific criteria for grouping were: the incidence of repeat toxicity (defined as significant toxicity in any test on separate sampling dates), and elevated chemistry (defined as any sediment chemistry measurement above guideline values, above the 90th percentile program wide, having a chemical summary quotient in the 90th percentile in the region, or a chemical level judged high enough by best professional judgement to cause biological effect). Stations with no repeat samples were grouped according to the number and degree of chemical guideline exceedances and results of toxicity tests from the single visit.

Other areas of interest included those for which more information is needed to characterize either chemical pollutants or toxic response. Sediment from Santa Maria River Estuary was toxic to amphipods and had the highest DDT value measured in the region. Confirming data are unavailable. Boat harbors in the region (Santa Cruz Yacht Basin, Monterey Harbor) tended to show exceedances of various chemicals, especially PAHs. Santa Cruz Yacht Basin, however also showed high levels of some metals, PCBs, and chlordane.

BPTCP data from the Central Coast Region present many challenges in interpretation due not only ecological differences between sites, but to the programmatic constraints placed on sampling and analysis. Completion of the dataset for sites such as Santa Maria River Estuary, Salinas River Lagoon, Santa Barbara Harbor, and sites in Morro Bay could be of great benefit. Confirming data need to be obtained from many sites to determine temporal and spatial patterns. Many river and stream mouths along the Regions coastline were not sampled at all. Sampling cleaner sites could help establish benchmarks to aid in the determination of the degree of degradation of more impacted stations. Such confirmation efforts should include other types of biological measures such as bioaccumulation and/or benthic community analysis to aid in a weight of evidence determination of the effects of pollution.

Sites of concern are present in all types of habitats. Boat harbors in Santa Cruz, Moss Landing, Monterey, and Morro Bay all had pollutant and toxic effects measured. The Tembladero drainage study is a particularly effective illustration of the need to investigate the distribution of pollutants in watersheds in the region. Significant potential for water quality improvement exists from the application of more complete sampling, analytical and management efforts.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
ASTM	American Society for Testing Materials
AVS	Acid Volatile Sulfide
BPTCP	Bay Protection and Toxic Cleanup Program
CDF	Cumulative Distribution Frequencies
CDFG	California Department of Fish and Game
CH	Chlorinated Hydrocarbon
COC	Chain of Custody
COR	Chain of Records
EDTA	Ethylenediaminetetraacetic Acid
EMAP	Environmental Monitoring and Assessment Program
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
HNO ₃	Nitric Acid
HPLC/SEC	High Performance Liquid Chromatography Size Exclusion
H ₂ 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
LOEC	Lowest Observable Effects Concentration
MDL	Method Detection Limit
MDS	Multi-Dimensional Scaling
MLML	Moss Landing Marine Laboratories
MPSL	Marine Pollution Studies Laboratory
MSD	Minimum Significant Difference
NH ₃	Ammonia
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
NS&T	National Status and Trends Program
PAH	Polynuclear Aromatic Hydrocarbons
PBO	Piperonyl Butoxide
PCB	Polychlorinated Biphenyl
PEL	Probable Effects Level
PELQ	Probable Effects Level Summary Quotient
PPE	Porous Polyethylene

LIST OF ABBREVIATIONS (continued)

PVC	Polyvinyl Chloride
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
REF	Reference
RWQCB	Regional Water Quality Control Board
SEM	Simultaneously Extracted Metals
SPARC	Scientific Planning and Review Committee
SPE	Solid Phase Extraction
SQC	Sediment Quality Criteria
STS	Sodium Thiosulfate
SWI	Sediment Water Interface
SWRCB	State Water Resources Control Board
T	Temperature
TBT	Tributyltin
TEL	Threshold Effects Level
TFE	Tefzel Teflon [®]
TIE	Toxicity Identification Evaluation
TOC	Total Organic Carbon
TOF	Trace Organics Facility
UCSC	University of California Santa Cruz
USEPA	U.S. Environmental Protection Agency
WCS	Whole Core Squeezing

UNITS

liter = 1 l

milliliter = 1 ml

microliter = 1 μ l

gram = 1 g

milligram = 1 mg

microgram = 1 μ g

nanogram = 1 ng

kilogram = 1 kg

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

1 part per million (ppm) = 1 mg/kg, 1 μ g/g

1 part per billion (ppb) = 1 μ g/kg, 1 ng/g

INTRODUCTION

BPTCP Program Description and Funding Sources

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 (RWQCB) to provide the maximum protection of existing and future beneficial uses of bay 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. The BPTCP has four major goals: (1) provide protection of present and future beneficial uses of the bays and estuarine waters of California; (2) identify and characterize toxic hot spots; (3) plan for toxic hot spot cleanup or other remedial or mitigation actions; (4) develop prevention and control strategies for toxic pollutants that will prevent creation of new toxic hot spots or the perpetuation of existing ones within the bays and estuaries of the State.

Sediment characterization approaches currently used by the Bay Protection and Toxic Cleanup Program (BPTCP) range from chemical or toxicity assessment only, to synoptic designs which 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. Funding was provided by the SWRCB.

Investigations for the Central Coast Region involved toxicity testing and chemical analysis of sediments and sediment pore water. Toxicity tests were run on all samples with few exceptions. Chemical analysis was reserved for a subset of stations, usually based on results of toxicity tests. Analyses of benthic community structure were also done on a subset of stations. A pilot watershed study was also conducted to test the utility of a watershed approach to addressing downstream pollution problems. This study employed synoptic chemistry and toxicity tests of the sediment along with water toxicity and comparative chemistry using semipermeable membrane devices (SPMDs).

Field and laboratory work was accomplished under interagency agreement with, and under the direction of, the CDFG. Sample collections were performed by staff of the San Jose State University Foundation at Moss Landing Marine Laboratories, Moss Landing, CA (MLML). Trace metal analyses were performed by CDFG personnel at the trace metal facility at Moss Landing Marine Laboratories. Synthetic organic pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) were analyzed at the University of California Santa Cruz (UCSC) trace organics analytical facility at Long Marine Laboratory in Santa Cruz, California. MLML staff also performed total organic carbon (TOC) and grain size analyses, as well as benthic community analyses. Toxicity testing was conducted by UCSC staff at the CDFG Granite Canyon toxicity testing laboratory.

Regional and project goals and objectives

The Goals and Objectives of the study were:

1. Determine presence or absence of statistically significant toxicity effects in representative areas of water bodies in the Central 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.

General description of attributes of region

The Central Coast Region includes 378 miles of coastline. It encompasses all of Santa Cruz, San Benito, Monterey, San Luis Obispo, and Santa Barbara Counties as well as the southern third of Santa Clara County, and small portions of San Mateo, Kern, and Ventura Counties. The region has urban areas such as San Luis Obispo, Morro Bay, the Monterey Peninsula and the Santa Barbara coastal plain; prime agricultural lands in the Salinas, Santa Maria, and Lompoc Valleys; and many coastal mountain ranges. The diverse topography within the long coastline gives rise to equally diverse marine habitats. These habitats are all influenced by human activities in inland, nearshore, and marine areas.

Due to the long and varied history of human activity in the Central Coast and its surrounding waters, there is a need to assess any environmentally detrimental effects associated with those activities to insure continued beneficial uses. The BPTCP was designed to investigate these effects by evaluating the biological and chemical state of California bay and estuarine sediments, including those in the Central Coast region.

Sampling areas vary widely in many respects. A conspicuous marine floral and faunal break occurs at Point Conception, providing the most noteworthy physical and biological differences between northern and southern water bodies. Further differences are evident in the types of water bodies investigated. Stations are included in sloughs, boat harbors, bays, and estuaries of every exposure regime. Physical factors such as tidal exchange, exposure to surf, and runoff vary greatly between, and to a significant but lesser degree, within these water bodies.

Climatic and population differences are distinct between areas as well. Population centers exist on the Santa Barbara coastal plain, in the San Luis Obispo and Morro Bay areas, and all around the Monterey Bay. Northern areas receive a greater amount of rainfall and runoff than do southern areas. The interaction of rainfall and runoff with urban, industrial and agricultural land uses creates a complex set of possible impacts on the bay and estuarine environments within the region. Possible marine impacts include those related to boat traffic and maintenance, oil production, agriculture, waste and storm water, and industry. Although these differences make comparison between sites difficult, it is still possible to make recommendations about specific sites based on individual analytical results.

Although few bays or estuaries in the region can be regarded as truly pristine, many areas are thought to be minimally impacted by human activities. Sites such as these were omitted from investigations in order to better direct resources toward evaluation of those areas more likely to be of concern. The focus of investigation was therefore on areas with the greatest population, industry or other potential sources of impact. A list of the selected water bodies with descriptions of the uses of each follows.

Site specific description of water bodies and stations therein

Station locations for the samples taken in the Central Coast region are shown in figures 1a-d. Sites are included in coastal lagoons, estuaries, boat harbors and bays. Nearly every type of protected and semiprotected water body is represented in the region. Study areas included Carpinteria Marsh, Santa Barbara Harbor, Goleta Slough, Cañada de la Gaviota, Santa Ynez and Santa Maria River Estuaries, San Luis Harbor, Morro Bay, Monterey Harbor, Elkhorn Slough, Moro Cojo Slough, Pajaro River Estuary, Soquel Lagoon, Santa Cruz Yacht Harbor, and Scott Creek. As a pilot watershed study, sites in the Tembladero drainage were investigated using amended and expanded BPTCP protocols.

Carpinteria Marsh stations were within the 120 acre Carpinteria Salt Marsh Reserve, managed by the University of California at Santa Barbara (UCSB). Although the marsh is protected as a research reserve, water quality may be affected by agricultural and suburban uses of the surrounding watershed. Agricultural uses include avocado orchards and commercial greenhouses. Possible sources of petroleum pollution include nearby natural oil seeps and off shore oil production from Point Conception to Ventura. The marsh is tidally influenced, except when a sand bar forms at the mouth. The bar is excavated with heavy equipment to allow year round tidal exchange. The tidal flow influences both Santa Monica and Franklin Creeks, the main inputs to the marsh.

Santa Barbara harbor is a small boat harbor, protected from exposure by a sea wall. The harbor is home port to many pleasure craft and a small fleet of commercial and fishing boats. Larger boats and boats without slips are seasonally moored outside the harbor to the southeast. Potential pollutants in any harbor of this type include antifouling paints, metals, petroleum products and solvents. Previous studies have identified copper and TBT in sediments and water at this location (Rasmussen 1995a,b).

Goleta Slough is a tidal wetland similar in many respects to Carpinteria Slough. It is bordered by the city of Goleta and UCSB. The Santa Barbara Airport, a sanitary treatment plant, and a power generation station are all located on filled areas of the marsh. Goleta Slough is an ecological reserve, supporting study and research activities by UCSB students and researchers. It includes large areas of pickleweed (*Salicornia virginica*) marsh. The south central region of the marsh is tidally influenced, and the mouth of the slough is opened periodically to allow tidal flow when the summer berm at the beach becomes high enough to restrict water movement.

Cañada de la Gaviota is a small canyon formed by Gaviota Creek. The creek creates a small lagoon behind the beach berm. The flow from the creek seasonally breaks through the berm and flows to the ocean, flushing the lagoon with fresh water and allowing sea water in at high tide.

Although the lagoon at the mouth of the creek is within Gaviota State Park, the upland area is largely agricultural and ranch land with some oil production in the hills near the creek.

At the Santa Ynez River mouth is an estuary with seasonal flow to the ocean. The river flows through part of Vandenberg Air Force Base and the town of Lompoc on its way to the ocean. Agriculture and cattle ranching are the primary activities in the sparsely populated areas surrounding the watershed.

Santa Maria River Estuary flows adjacent to the Guadalupe Oil Field near the town of Guadalupe. The oil field has been the site of cleanup efforts by Unocal to remove diluent from the soil. The diluent, used to dilute the oil to a viscosity appropriate for pumping, has leaked from underground pipelines, and has occasionally entered the waters of the estuary. In addition to these potential sources, an intensive agriculture industry has existed for many years in the watershed of the river.

San Luis Harbor is located at the west side of San Luis Obispo Bay. Potential pollution in the area comes from aging petroleum storage tanks and pipelines above the town of Avila Beach. Leakage from these tanks and lines has created an underground plume of various petroleum products which has been shown to reach at least as far south as the ocean. Small commercial and pleasure boat moorings are immediately to the west.

Morro Bay has a long history as a fishing and commercial port. The southern end of the bay is a large salt marsh with extensive tidal mudflats. Morro Bay has potential impacts from maritime activities, runoff from rivers and streams, and storm water runoff from local population centers. In addition, PG&E operates a large electrical generation plant in the Bay.

Monterey Harbor has a long history as a fishing port and those activities continue today. Railroads historically carried supplies and products to and from the port. A lead slag heap from railroad activities was removed from the area in the late 1980s. The harbor has a number of storm drain outlets that drain into it from the city of Monterey. Other potential sources of pollution include those associated with boat maintenance and operation.

The areas around Moss Landing and Elkhorn Slough have been primarily agricultural for many years. The Salinas river flowed northward along the back of a dune system until 1946 when the Army Corps of Engineers opened the mouth of Elkhorn Slough and diverted the flow of the River to exit far south of its original breakout point. At that time, Elkhorn Slough became largely saline. Pesticides, including DDT, have been detected periodically in outplanted mussels at the Sandholdt Bridge location, the mouth of the old Salinas River channel (Rasmussen 1996). This tributary also drains sloughs from the watershed around the city of Salinas and surrounding croplands. The area around Elkhorn Slough has been used for agricultural concerns such as dairies and strawberry farms but contains other potential sources of pollution such as auto wrecking yards. Potential pollutant sources are past and present agriculture, urban runoff from the city of Salinas, and sources related to boat maintenance and operation. In addition, PG&E

operates a power plant adjacent to the harbor which is capable of using various types of fuels historically offloaded at offshore pumping stations.

The Pajaro River estuary is a seasonal lagoon that breaks through the beach berm seasonally and flows to the ocean. The river flows through the cities of Gilroy, Morgan Hill and Hollister on its way to coastal plains near the towns of Pajaro and Watsonville where heavy agriculture drains into the river. Potential sources of pollutants in the lagoon include local heavy agriculture, runoff from all of these urbanized areas and abandoned mines upstream.

Soquel lagoon is a small water body formed by the continuously flowing Soquel Creek. The creek flows through the towns of Capitola and Soquel and along a portion of The Forest of Nisene Marks State Park. A sewer outfall from the city of Soquel is located offshore of the creek mouth.

The Santa Cruz Yacht Harbor is a small boat harbor with a moderate number of commercial boats and pleasure craft. The chief potential inputs of pollutants are from operations related to these concerns. A small amount of urban runoff also enters the boat harbor during the rainy season.

North of the town of Davenport, Scott Creek creates a small lagoon at its mouth which seasonally breaks through to the ocean. The upstream area is sparsely populated with some cattle ranching, logging, and agriculture nearby.

METHODS

Introduction

The standard approach used to assess environmental impacts included sediment and interstitial water bioassays, sediment chemistry analyses and benthic community analyses. Other techniques were also used depending on the specific needs of the area under investigation. Programmatic funding limitations made it necessary to use subsets of these analyses to address potential problems in various areas. This meant that areas did not receive equal treatment with respect to the type or number of analyses performed.

Toxicity tests were generally used as a litmus test to determine whether a station warranted chemical analysis. Due to the high cost of chemical analysis, stations which produced no toxic result from standard toxicity tests usually did not receive it. This allowed a greater number of stations to be sampled with the given funding, but decreased the programs ability to determine variability in the relationship between toxicity and chemistry.

Sediment chemistry measurements were taken from 37 samples out of the total 87. Subsets of chemical analyses were done on these samples to economize, based on information already known about particular sites. The analyses ranged from a full suite of analyses including PAH, PCB, Pesticide, organometal, and trace metals, to as little as lead only, depending on the need for information at a particular station and economy.

Benthic community analysis was only done on a set of four stations in Monterey Harbor. Although the tool is considered indispensable in many regions, it was judged to have limited value in the Central Coast region due to highly variable salinity at the mostly estuarine sampling locations.

No specific modifications to the standard approach were used in Region 3 except for those necessary for special studies. These studies included the Monterey lead study and the Tembladero drainage study. The Monterey lead study was only focused on the analysis of lead contamination in and around the remediated site of a slag heap near Monterey Harbor. Because the Tembladero study made use of a watershed approach, deviations from the standard BPTCP protocols were necessary to achieve project-specific goals. Methods were added for salinity-specific applications and to accommodate analyses of water quality in freshwater environments. A summary of analyses by sample is given in Table 1.

Station Selection

Stations were selected based on results of previous studies that indicated potential anthropogenic contamination of sediments, water or tissue. Additional stations not suspected to have high levels of pollutants or significant toxicity were selected as potential reference stations for comparison purposes.

Sampling design

A directed point sampling design was required to address SWRCB's need to identify specific toxic hot spots. Stations were chosen based on previous results supplied by sources such as the State Mussel Watch Program (Rasmussen 1996). Some stations were selected for use as travel controls and reference stations for work in other regions. Since confirmation work in other regions often required replicate sampling, field replicates were also taken at the reference stations in the Central Coast Region. These reference stations were selected because they were presumed to be relatively free of pollutants and not likely to produce toxic responses in test organisms.

Areas of interest were identified and prioritized by regional and state water board staff for sampling. Station locations (latitude & longitude) were determined by agreement of the SWRCB, RWQCB, and CDFG personnel. A change in the station location during sediment collection was allowed only under the following conditions:

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

This phase of work was intended to give a broad assessment of toxicity throughout the Central Coast area using various toxicity test species and endpoints. Samples were collected between August, 1992 and May, 1997. Chemical analyses were done on selected samples for which toxicity results prompted further analysis.

A total of 87 samples were collected from 53 station locations in the Central Coast Region (Figure 1a-d). Station locations sampled more than once were always resampled at the original location using navigational equipment, photographic references, and lineups. Bioassays, grain size and total organic carbon analyses were performed on all 87 samples. Chemical analysis was done according to the need for that particular station and funds available for analysis.

Sampling methods

Introduction

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 EMAP (Weisberg *et al.* 1993), NS&T (NOAA 1991), and ASTM (1992), 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.

Table 1. Summary of Analyses

STANUM	IDORG	Tox Tests	METAL	PEST	PCB	PAH	BENTH
36007.0	1768	EE,HC	sem/avs	x	x	x	
36006.0	1767	CDSS,HA	sem/avs	x	x	x	
36005.0	1766	CDSS,HA	sem/avs	x	x	x	
36004.0	1765	CDSS,HA	sem/avs	x	x	x	
36003.0	1764	CDSS,HA	sem/avs	x	x	x	
36002.0	1763	EE,HC	sem/avs	x	x	x	
30007.0	1762	EE,HC	sem/avs	x	x	x	
30007.0	1597	EE,SPDI,MEP100		x	x	x	
30002.0	1596	EE,SPDI		x	x	x	
35006.0	1594		x (lead)				x
35005.0	1593		x (lead)				x
35004.0	1592		x (lead)				x
35003.0	1591	EE,SPDI	x (lead)	x	x	x	x
35002.0	1590			x	x	x	
35001.0	1589			x	x	x	
30001.0	1588	EE,SPDI		x	x	x	
31003.0	1379	RA,NA					
31003.0	1378	RA,NA					
31003.0	1377	RA,NA					
31002.0	1376	RA,NA					
31002.0	1375	RA,NA					
31002.0	1374	RA,NA					
31001.0	1373	RA,NA					
31001.0	1372	RA,NA					
31001.0	1371	RA,NA					
30023.0	1370	RA,NA					
30023.0	1369	RA,NA					
30023.0	1368	RA,NA					
30007.0	1367	RA,NA					
30007.0	1366	RA,NA					
30007.0	1365	RA,NA					
30004.0	1364	RA,NA					
30004.0	1363	RA,NA					
30004.0	1362	RA,NA					
30032.0	1330	RA,NA					
30029.0	1329	RA,NA					
30008.0	1328	RA,NA					
31002.0	1327	RA,NA					
30019.0	1326	RA,NA					
30028.0	1325	RA,NA					
30013.0	1324	RA,NA					
30027.0	1323	RA,NA					
31002.0	675	RA,HRP100,SPPD100					
30033.0	534	RA,HRS100					
30032.0	533	RA,MES100					
30031.0	532	RA,MES100	x	x	x	x	
30030.0	531	EE,MES100,MEP100					
30029.0	530	RA,HRS	x	x	x	x	
30028.0	528	RA,NA,MEP	x	x	x	x	
30027.0	527	RA,NA,HRS100	x	x	x	x	
30026.0	526	EE					

STANUM	IDORG	Tox Tests	METAL	PEST	PCB	PAH	BENTH
30025.0	525	RA					
30024.0	524	RA,HRS	x	x	x	x	
30023.0	523	RA,NA,HRS100	x	x	x	x	
30022.0	522	EE,MES100,MEP100					
30021.0	521	EE,MES100,MEP100					
30020.0	520	EE,MES100,MEP100	x	x	x	x	
30019.0	519	RA,NA,HRS100,SPPD100,	x	x	x	x	
30014.0	514	RA,NA,HRS100,MEP100	x	x	x	x	
30013.0	513	RA,NA,HRS100,SPPD100,	x	x	x	x	
30012.0	512	RA,NA,HRS100,SPPD100,	x	x	x	x	
30011.0	511	EE,MES100,MEP100					
30010.0	510	RA,MES100					
30009.0	509	EE,MES100,MEP100					
30008.0	508	RA					
30007.0	507	RA,NA,HRS100,SPPD100	x	x	x	x	
30006.0	506	RA,NA,HRS100,MES100,SPPD100	x	x	x	x	
30005.0	505	RA,NA,HRS100,SPPD100	x	x	x	x	
30004.0	504	RA,NA,HRS100,SPPD100	x	x	x	x	
30003.0	503	RA,HRS100					
30002.0	502	RA,NA,HRS100,SPPD100	x	x	x	x	
30001.0	501	RA,NA,HRS100,SPPD100	x	x	x	x	
31003.0	451	RA,SPPD100	x	x	x	x	
31002.0	352	RA,MES100					
31002.0	351	RA,NA					
31003.0	258	RA,SPPD100	x	x	x	x	
31002.0	254	RA,NA	x	x	x	x	
31001.0	251	RA	x	x	x	x	
30036.3	135	RA,HRP					
30036.2	134	RA,HRP					
30036.1	133	RA,HRP					
30035.3	132	RA,HRP					
30035.2	131	RA,HRP					
30035.1	130	RA,HRP					
30034.3	102	RA,HRP					
30034.2	101	RA,HRP					
30034.1	100	RA,HRP					

Plastic containers (HDPE or TFE) for trace metal analysis media (sediment, archive sediment, pore water, and subsurface water) were cleaned by: a two-day Micro[®] detergent soak, three tap-, three Type II Milli-Q[®] water rinses, air dry, three petroleum ether rinses, and air dry. water rinses, three deionized water rinses, a three-day soak in 10% HCl or HNO₃, 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, pore water, 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 HNO₃

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 0.1m² Young-modified Van Veen grab aboard a sampling vessel. Modifications include a non-contaminating Kynar coating which covered the grab's sample box and jaws. After the filled grab sampler was secured

on the boat rail, 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 fine-grained surficial sediment. Once overlying water was removed, the top 2 cm of surficial sediment was sub-sampled from the grab. Subsamples were taken using a precleaned 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. 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. Such removals were noted on the field data sheet. 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 site (e.g., <1 meter), divers sampled that site 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. Divers entered a study site from one end and sampled in one direction, so as to not disturb the sediment with feet or fins. Cores were taken to a depth of at least 15 cm. 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.

Benthic Sampling

Replicate benthic samples (n=3) were obtained at predetermined sites from separate deployments of the sampler. The coring device was 10 cm in diameter and 14 cm in height, enclosing a 0.0075 m² area. Corers were placed into sediment with minimum disruption of 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.

Fish Collection and Homogenization

Composites of five fish each were collected for tissue analysis. One composite of five white surfperch was collected at Sandholdt Bridge (30007). One composite each of topsmelt and shiner surfperch were collected at Pajaro River Estuary (30006).

Fish at the Pajaro River Estuary were collected for tissue analysis using 100 m beach seine with a mesh size of 0.5 in. The beach seine was stretched in a semicircle from the water's edge and then drawn to shore. Fish collected at the Sandholdt Bridge station were obtained from otter trawls approximately 200m in length at slow (2-3 kt) speeds. With either technique, all individuals of the target species were collected immediately by hand using clean polyethylene gloves. The fish were placed in a polyethylene bag for no more than one hour, until they could be prepared for transport to the lab. After measurement, the fish were wrapped individually in teflon sheets, placed in clean polyethylene bags, and frozen in the field on dry ice.

Before dissection, all fish were rinsed with MilliQ[®] water. Dissections and tissue sample preparations were done using non-contaminating techniques in a clean room environment. White surfperch (Sandholdt Bridge 30007) were filleted. Fillets of muscle tissue were removed in 5 to 10 g portions with teflon forceps. Equal weight fillets were taken from each fish of the sample to composite a total of 200 grams from five fish. Topsmelt and shiner surfperch (Pajaro River Estuary 30006) were homogenized whole (five each). All samples were polytroned to provide a homogeneous material for analysis. Sample splits were taken for each analysis after homogenization was completed.

Subsurface Water Collection

Subsurface water samples were collected in pre-cleaned polyethylene bottles. The bottles were rinsed three times with ambient water and drained. They were then submerged mouth down so that the entire bottle was submerged and allowed to fill. The bottles were then capped under water to avoid exposure to air and stored on ice.

For stations where a boat and grab were used to collect sediment, a bottle was loaded onto the grab in a polycarbonate container with an automatic cork puller and polyethylene cork installed in the top of the bottle. When the grab was tripped, the cork was pulled from the top of the bottle by the grab mechanism and the bottle was allowed to fill at depth.

Transport of Samples

Six-liter sample containers were packed (three to an ice chest) with enough ice to keep them cool for 48 hours. Each container was sealed in precleaned 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

Sediment Sample Processing/Distribution Methods

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 prelabeled 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, porewater 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 Pore water

The BPTCP primarily used whole core squeezing to extract 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. Pore water 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 techniques.

After leg 30, centrifugation was used for the extraction of pore water. All procedures for the extraction of pore water by centrifugation were performed utilizing trace metal and trace organic “clean” techniques. Operations were performed in a positive pressure “clean” room with filtered air to prevent airborne contamination and poly gloves were worn by personnel handling samples and laboratory equipment. All sample containers or sampling equipment in contact with

sediment or pore water receives a scrub and 2 day soak in Micro[®] detergent, followed by triple fresh and deionized water rinses. Equipment is then immersed in 10% HCl for 3 days, triple rinsed in MILLI-Q[®] Type II water, air dried, and triple rinsed with petroleum ether. This cleaning process is suitable for trace analysis of metals and organics.

Samples were received and stored on ice until centrifugation can commence. Pre-cleaned Teflon scoops were used to transfer sediment from sample containers to centrifuge jars. High speed one-liter polycarbonate centrifuge jars were used for extraction of pore water. Opposing jars were balanced to within +/- 0.1g and placed in centrifuge swinging buckets. Samples were spun at 2500 G for 30 minutes at 4°C in a Beckman J-6B refrigerated centrifuge.

Pore water is transferred from each centrifuge jar into final sample containers using pre-cleaned polyethylene siphons. While decanting, care is used to avoid floating debris, fauna, shell fragments or other solid material. After transfer into final sample containers, pore water is immediately refrigerated or frozen as protocols for the individual project dictate.

Date, start and finish time, G, temperature, and sample volume were recorded in the permanent lab notebook and maintained by the laboratory.

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 number and station name, 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 signed and dated 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 CDFG personnel, or its authorized designee, and were signed and accepted by both the CDFG 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 CDFG, and other information specific to the lab/analyses being performed.

Trace Metal Analysis of Sediments, Tissue, and Water

Summary of Methods

Trace Metals analyses were conducted at the CDFG Trace Metals Facility at Moss Landing, CA. Table 2 shows the trace metals analyzed and lists method detection limits for sediments, water and tissue. These methods were modifications of those described by Evans and Hanson (1993) as well as those developed by the CDFG (California Department of Fish and Game, 1990).

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. The vessel was capped and heated in a vented oven at 1300 C for four hours. Three ml Hydrofluoric acid were added to vessel, recapped and returned to oven overnight. Twenty ml of 2.5% boric acid were added to vessel and placed in oven for an additional 8 hours. Weights of vessel and solution were recorded, and solution transferred to 30 ml polyethylene bottles.

AA METHODS (Sediments and Tissues)

Samples were analyzed by furnace AA on a Perkin-Elmer Zeeman 3030 Atomic Absorption Spectrophotometer with an AS60 auto-sampler and HGA 500 graphite furnace. Samples, blanks, matrix modifiers, and standards were prepared using clean techniques inside a clean lab. MQ water and ultra-clean chemicals were used for all standard preparations. To ensure accurate results the samples were analyzed using the stabilized-temperature platform technique. Matrix modifiers were used when the components of the matrix interfere with adsorption. The matrix modifier was used for As and Pb. Calibration curves were run with three concentrations after every 10 samples. Continuing calibration check standards (CLC) were analyzed with each set of samples. The values for the elements used showed excellent results. Blanks and a standard reference material, MESS3 National Research Council Canada (sediment) and 1566a Oyster tissue NIST (tissue), were run with each set of samples.

Trace Metal Analysis of Tissues

Tissue samples were prepared for trace metal analysis by digesting with concentrated 4:1 nitric:perchloric acid in a Teflon[®] vessel. Tissue samples were first heated on hot plates for five hours. Caps were tightened and heated in a vented oven at 130°C for four hours. The liquid digestate was diluted with Type II Milli-Q[®] water to a final volume of 20.0 ml.

Tissue digestates were analyzed for trace metal analysis by graphite furnace atomic absorption spectrophotometry (GFAAS) on a Perkin-Elmer Model 3030 Zeeman or by flame atomic absorption spectrophotometry (FAAS) on a Perkin-Elmer Model 2280 for Ag, Al, As, Cu, Cd, Cr, Mn, Ni, Pb, Se, Sn, and Zn depending on concentration. Mercury was analyzed by cold vapor technique using the Perkin-Elmer Model 2280. Detection limits for trace metal analysis are shown in Table 2. Analytical methods follow the technique developed by the CDFG (California Department of Fish and Game, 1990).

Trace Metal Analysis of Water

Evaporation Methods

Two hundred fifty ml Teflon[®] beakers are removed from acid bath and rinsed thoroughly in Milli-Q[®] water (MQ). The beaker is then filled with MQ and placed on a hot plate in a laminar-flow, clean hood where it is heated on low for 20 to 30 minutes. MQ is then discarded and the beaker is rinsed with MQ again, dried on the hot plate and then cooled prior to weighing. The sample bottle is inverted to homogenize the sample. An aliquot is then weighed into the Teflon[®] beaker. This is generally 250 g unless there is a great deal of sediment evident in the sample bottle. A blank is also made, consisting of 10 ml MQ plus 1.25 ml Q-HNO₃. The beaker chosen for the blank is rotated among those available. Beakers are placed on a hot plate on low

temperature in a clean-air, laminar-flow hood. The blank is placed in the hood immediately adjacent to the hot plates. Samples are heated until dry. This generally takes 40-48 hours. Following evaporation, 1 ml of concentrated Q-HNO₃ is added to each beaker to redissolve the residue. Then 9 ml MQ are added to each beaker. This solution is rolled around the walls of the beaker to ensure dissolution of all salts. The weight is then recorded for the concentrated sample. The density for each sample is calculated following the weighing of small aliquots of sample. The weight of the concentrated sample is then converted into a volume. Concentrated samples are decanted into 30 ml low density polyethylene bottles for analysis. The Teflon[®] beakers are rinsed in MQ, scrubbed with 2N HNO₃, rinsed again in MQ, and then placed in a 6N HCl acid bath. Beakers are subsequently soaked in a Q-HNO₃ acid bath prior to reuse.

AA METHODS (WATER)

Samples were analyzed by flameless AA on a Perkin-Elmer Zeeman 5000 Atomic Absorption Spectrophotometer equipped with an HGA 500 graphite furnace. Due to high concentrations, a few samples were analyzed using flame AA on a Perkin-Elmer 603 AAS. Samples and standards were prepared in a laminar-flow clean bench inside the trace metal lab. To ensure accurate results the samples were analyzed using the stabilized-temperature platform technique. The characteristic mass for each element was computed to ensure the proper functioning of the Zeeman AA. Samples may be analyzed using a matrix modifier made up from ultra-clean chemicals. When no modifier is used, high-char temperatures allow interfering matrix components of the sample to be volatilized prior to atomization. Single spike additions to samples also allow a check for recovery when standards are linear. Finally, the SLRS-3 river water standard reference material is evapoconcentrated and analyzed with each set of samples.

Analytes and Method Detection Limits

Table 2a. Dry Weight Trace Metal Method Detection Limits*

Analytes [†]	MDL, µg/g dry Sediment	MDL, µg/g dry Tissue	MDL, µg/L Water
Silver	0.002	0.01	0.001
Aluminum	1	1	NA
Arsenic	0.1	0.25	0.1
Cadmium	0.002	0.01	0.002
Copper	0.003	0.1	0.04
Chromium	0.02	0.1	0.05
Iron	0.1	0.1	0.1
Mercury	0.03	0.03	NA
Manganese	0.05	0.05	NA
Nickel	0.1	0.1	0.1
Lead	0.03	0.1	0.01
Antimony	0.1	0.1	NA
Tin	0.02	0.02	NA
Selenium	0.1	0.1	NA
Zinc	0.05	0.05	0.02

Table 2b. Dry Weight Method Detection Limits for Tributyl Tin

Analytes [†]	Database Abbreviation	MDL, ng/g	MDL, ng/g	MDL, ng/L
		dry Sediment	dry Tissue	Water
Tributyltin	TBT	13	20	1

* All tissue MDLs are reported in dry weight units. Wet weight MDL is calculated based on percent moisture of the individual sample.

AVS/SEM Methods

Samples were prepared for Acid Volatile Sulfide (AVS) extraction by weighing a 2 gram sediment sample in a pre-weighed teflon bomb. Samples were diluted with 100 ml of oxygen-free MilliQ[®] water and bubbled with nitrogen gas for 10 minutes. AVS in the sample was converted to hydrogen sulfide gas (H₂S) by acidification with 20 ml of 6 Molar hydrochloric acid at room temperature. The H₂S was then purged from the sample with nitrogen gas and trapped in 80 ml of 0.5 Molar sodium hydroxide. The amount of sulfide that has been trapped is then determined by colorimetric methods. The Simultaneously Extracted Metals (SEM) are selected metals liberated from the sediment during the acidification procedure. SEM analysis is conducted with 20 ml of centrifuged sample supernatant taken after AVS extraction. The H₂S released by acidifying the sample is quantified using a colorimetric method:

Hydrogen sulfide is trapped in 80 ml of 0.5M NaOH. Ten ml of this solution is added to a 100 ml volumetric flask containing 70 ml of sulfide-free 0.5M NaOH, 10 ml of MDR reagent and 10 ml of DI water. The sulfide reacts with the N-N-dimethyl-p-phenylenediamine in the MDR reagent to form methylene blue. Absorbances are determined with a Milton Roy Spectronic 301 Spectrophotometer and compared to a standardized curve. Analytes and method detection limits are given in Table 3.

Table 3. AVS/SEM Analytes and Method Detection Limits

<i>Analytes[†]</i>	<i>mmol/g</i>	<i>ng/g</i>
Cadmium	0.0001	0.01
Copper	0.02	1.0
Lead	0.001	0.1
Nickel	0.002	0.1
Zinc	0.001	0.05
Sulfide	0.5	

Trace Organic Analysis of Sediments (Pesticides, PCBs, and PAHs)

Summary of Methods

Analytical sets of 12 samples were scheduled such that extraction and analysis occurred within a 40 day window. The methods employed by the UCSC trace organics facility were modifications of those described by Sloan *et al.* (1993). Tables 4a-e show the pesticides, PCBs, and PAHs currently analyzed and list method detection limits for sediments on a dry weight basis.

Analytes and Method Detection Limits

Table 4a Dry Weight Method Detection Limits of Chlorinated Pesticides

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

[†] The quantitation surrogate is PCB 103.

[‡] The quantitation surrogate is d8-p,p'-DDD

Table 4b Dry Weight Method Detection Limits of NIST PCB Congeners

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

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

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

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

[†] The quantitation surrogate is PCB 207.

[‡] The quantitation surrogate is d8-p,p'-DDD

Table 4d. Additional PCB Congeners and Their Dry Weight Method Detection Limits

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

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

Table 4e. Dry Weight Detection Limits of Polyaromatic Hydrocarbons in Tissue.

<i>Analytes</i> [†]	<i>Database Abbreviation</i>	<i>MDL, ng/g dry Sediment</i>	<i>MDL, ng/g dry Tissue</i>	<i>MDL, ng/L Water</i>
Naphthalene	NPH	5	10	30
2-Methylnaphthalene	MNP2	5	10	30
1-Methylnaphthalene	MNP1	5	10	30
Biphenyl	BPH	5	10	30
2,6-Dimethylnaphthalene	DMN	5	10	30
Acenaphthylene	ACY	5	10	30
Acenaphthene	ACE	5	10	30
2,3,5-Trimethylnaphthalene	TMN	5	10	30
Fluorene	FLU	5	10	30
Dibenzothiophene	DBT	5	10	30
Phenanthrene	PHN	5	10	30
Anthracene	ANT	5	10	30
1-Methylphenanthrene	MPH1	5	10	30
Fluoranthene	FLA	5	10	30
Pyrene	PYR	5	10	30
Benz[a]anthracene	BAA	5	10	30
Chrysene	CHR	5	10	30
Tryphenylene	TRY	5	10	30
Benzo[b]fluoranthene	BBF	5	10	30
Benzo[k]fluoranthene	BKF	5	10	30
Benzo[e]pyrene	BEP	5	10	30
Benzo[a]pyrene	BAP	5	10	30
Perylene	PER	5	10	30
Indeno[1,2,3-cd]pyrene	IND	5	15	45
Dibenz[a,h]anthracene	DBA	5	15	45
Benzo[ghi]perylene	BGP	5	15	45
Coronene	COR	5	15	45

[†] See individual QA reports for surrogate assignments.

Extraction and Analysis

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.

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 contains > 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 μ 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 μ L 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 μ L in the same manner as the CH fractions.

Trace Organic Analysis of Tissue

Tissue homogenates were analyzed for detection of PCBs, pesticides and PAHs after extraction with methylene chloride. The extract was divided into three portions: one quarter of the volume for lipid weight determination, one half for aromatic and chlorinated hydrocarbon (AH/CH) analysis and one quarter for validation of the single fraction analysis. The AH/CH fraction was analyzed by capillary gas chromatography for chlorinated hydrocarbons, utilizing an electron capture detector. The AH/CH fraction was also analyzed by gas chromatography mass spectrometry (GC/MS) for aromatic hydrocarbons.

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 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_3), 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_3). 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 commercially available ball mill for three minutes to homogenize the dried sample.

A modification of the high temperature combustion method, utilizing a Wheatstone bridge current differential was used in a commercially available instrument, (Control Equipment Co., 440 Elemental Analyzer) to determine carbon and nitrogen concentrations. The manufacturers suggested procedures were followed. The methods are comparable to the validation study of USEPA method MARPCPN I (1992). Two to three aliquots of 5-10 mg of dried prepared subsample 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 µg/mg, carbon and 0.01 µg/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 + 0.09% carbon (2.19% Average). Nitrogen was not reported on the standard data report, but was accepted at + 0.008% nitrogen (0.195% Average) from the USEPA 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 + 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 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.

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 appendix of each data report. 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 were also measured at these times. Samples of

overlying and interstitial water for hydrogen sulfide measurement were taken at the beginning and end of each toxicity test. Due to the update of standards after the program was underway, only samples after leg 29 had interstitial water samples taken. 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). Unfrozen porewater samples were stored in the dark, at 4°C. Samples from legs 4-23 were frozen, samples from legs after 31 were not. 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, mussel and urchin embryo-larval development tests were performed on water column samples collected with the modified Van Veen grab. 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 (from Whitfield 1974, 1978):

$$[\text{NH}_3] = [\text{total ammonia}] \times ((1 + \text{antilog}(\text{pK}_a^\circ - \text{pH}))^{-1}),$$

where pK_a° is the stoichiometric acidic hydrolysis constant for the test temperature and salinity. Values for pK_a° were experimentally derived by Khoo *et al.* (1977). The 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):

$$[\text{H}_2\text{S}] = [\text{S}^{2-}] \times (1 - ((1 + \text{antilog}(\text{pK}_a^\circ - \text{pH}))^{-1})),$$

where temperature and salinity dependent pK_a° 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 USEPA 1994. All *Eohaustorius estuarius* and *Rhepoxynius abronius* 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 *Eohaustorius* 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. Upon arrival at Granite Canyon, the amphipods were acclimated slowly (<2‰ per day) to 28‰ seawater (T=20°C). Once acclimated, the animals were held for an additional 48 hours prior to inoculation into 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:

$$\frac{(\text{Number of surviving amphipods}) \times 100}{(\text{Initial number of amphipods})}$$

***Neanthes arenaceodentata* Polychaete Survival and Growth Test**

The *Neanthes* test followed procedures described in PSEP (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:

$$\text{Percent worm survival} = \frac{(\text{Number of surviving worms})}{(\text{Initial number of worms})} \times 100$$

$$\text{Mean weight per worm} = \frac{(\text{Total weight} - \text{foil weight})}{(\text{Number of surviving worms})} \times 100$$

***Strongylocentrotus purpuratus* Sea Urchin Embryo-Larval Development Test**

The sea urchin (*Strongylocentrotus purpuratus*) larval development test was conducted on marine porewater samples. Details of the test protocol are given in USEPA 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). Samples were tested at full concentration or three dilutions: 100, 50 and 25% pore water, each having three or five replicates. Porewater samples 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 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 USEPA 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:

$$\frac{\text{Number of normally developed larvae counted}}{\text{Total number of larvae counted}} \times 100$$

***Strongylocentrotus purpuratus* Sea Urchin Embryo-Larval Development Test using the Sediment-Water Interface Exposure System**

The purple sea urchin (*Strongylocentrotus purpuratus*) embryo/larval development test at the sediment-water interface was conducted on intact core marine 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 USEPA 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- μ m 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 \pm 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 USEPA 1995a. Percent normal development was calculated as:

$$\frac{\text{Number of normally developed larvae counted}}{\text{Total number of larvae counted}} \times 100$$

***Strongylocentrotus purpuratus* Sea Urchin Fertilization Test**

The sea urchin (*Strongylocentrotus 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:

$$\frac{\text{Number of fertilized eggs}}{\text{Number of eggs observed}} \times 100$$

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

The bay mussel (*Mytilus* spp.) embryo-larval development test was conducted on marine porewater and subsurface water samples. Details of the test protocol are given in USEPA 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 the 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 USEPA 1995a. Percent normal live larvae was calculated as:

$$\frac{\text{Number of normal larvae}}{\text{Initial embryo density}} \times 100$$

***Haliotis rufescens* Abalone Embryo-Larval Development Test**

The red abalone (*Haliotis rufescens*) embryo-larval development test was conducted on porewater and subsurface water samples. Details of the test protocol are given in USEPA 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 USEPA 1995a. Percent normal development was calculated as:

$$\frac{\text{Number of normally developed larvae counted}}{\text{Total number of larvae counted}} \times 100$$

***Holmesimysis costata* Mysid Survival Test**

Aquatic toxicity of marine subsurface water samples was assessed using the mysid (*Holmesimysis costata*) acute survival test. This 96-hour method was adapted from USEPA 1995a. A brief description of the method follows.

The mysid shrimp, *Holmesimysis costata*, commonly inhabits the surface canopy of the giant kelp *Macrocystis pyrifera*. Mysids were collected approximately 7 days prior to test initiation. Females carrying embryos in the eye-development stage were placed in brood compartments within holding tanks. Juvenile mysids released over a twenty-four hour period were isolated and transferred to a separate tank. Three to four day-old juveniles were randomly distributed to test containers containing 200-mL of sample. Each container received five mysids.

Test containers were checked daily and the number of living mysids was recorded. Immobile mysids not responding to stimulus were considered dead. Mysids were fed 20 freshly hatched *Artemia* nauplii per mysid twice daily. Test solutions were 50% renewed at 48 hours. The laboratory negative control consisted of Granite Canyon seawater filtered to one micron. A positive control reference test was conducted concurrently with the test using a dilution series of zinc sulfate as the reference toxicant.

***Ceriodaphnia dubia* Water Flea Acute Survival Test**

Aquatic toxicity of freshwater samples was assessed using the Cladoceran water flea (*Ceriodaphnia dubia*) acute survival test. Details of the test protocol are given in the MPSL Standard Operating Procedure for *Ceriodaphnia dubia* which follows USEPA freshwater acute methods (USEPA 1993a).

Ceriodaphnia neonates (<24-h) were obtained from in house cultures or from Toxscan Laboratories (Watsonville, CA). Neonates were isolated from cultures or obtained from Toxscan on Day 0 of the test. All dilution water was prepared according to USEPA (1993a). Porewater

test containers were 50-mL glass beakers containing 15-mL of test solution. Each test container was inoculated with 5 or 8 neonates depending on availability. The laboratory negative control consisted of USEPA dilution water. After an exposure period of 96 hours neonates were counted. A positive control reference test was conducted concurrently with the test using a dilution series of copper chloride as the reference toxicant.

***Ceriodaphnia dubia* Water Flea Acute Survival Test using Sediment-Water Interface Exposure System**

The toxicity of solid-phase freshwater sediments was assessed using the water flea (*Ceriodaphnia dubia*) acute survival test at the sediment-water interface. Details of the test protocol are given in the MPSL Standard Operating Procedure for *Ceriodaphnia dubia* which follows USEPA freshwater acute methods (USEPA 1993a).

Ceriodaphnia neonates (<24 h) were obtained from in house cultures or from Toxscan Laboratories (Watsonville, CA). Neonates were isolated from cultures or obtained from Toxscan on Day 0 of the test. All dilution water was prepared according to USEPA (1993a). Sediment-water interface test containers consisted of a polycarbonate tube with a 25- μ m screened bottom placed so that the screen was within 1-cm of the surface of an intact sediment core (Anderson *et al.* 1996). Dilution water was poured into the screen tube at the surface of each core and allowed to equilibrate for 24 hours before the start of the test. Each test container was inoculated with 5 or 8 neonates depending on availability. The laboratory negative control consisted of Yaquina Bay amphipod home sediment from Northwestern Aquatic Sciences. After an exposure period of 96 hours, screens were removed from the intact cores, and neonates were counted. A positive control reference test was conducted concurrently with the test using a dilution series of copper chloride as the reference toxicant.

***Hyalella azteca* Amphipod Survival Test for Freshwater Sediments**

These amphipod tests followed ASTM (1993) procedures for *Hyalella azteca*. All *Hyalella* were obtained from Northwestern Aquatic Sciences (NWAS) in Yaquina Bay, Oregon. Animals were separated into groups of approximately 1000 and placed in polyethylene cubitainers containing NWAS laboratory water, then shipped via overnight courier. Upon arrival at Granite Canyon, the amphipods were acclimated to Granite Canyon well water (T=25°C). Once acclimated, the animals were held for an additional 48-h prior to addition to the test containers.

Test containers were one-liter glass jars containing 2-cm of sediment and filled to the 700-mL line with Granite Canyon well water. Test sediment and overlying water were allowed to equilibrate for 24 hours, then 20 amphipods were placed in each beaker along with well water to fill each test container to the one-liter line. Test chambers were gently aerated and continuously illuminated.

Five replicates of each sample were tested for 10 days. In addition, a negative sediment control consisting of 5 replicates of Yaquina Bay home sediment was included with each set of samples tested. Test containers were fed a slurry of crushed alfalfa pellets three times per week (ASTM 1993). After 10 days, samples 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. In these tests, amphipod mortality was recorded in three replicates of four cadmium concentrations after a 96-hour water-only exposure. A dilution water control consisting of Granite Canyon well water was included in each test.

$$\frac{(\text{Number of surviving amphipods}) \times 100}{(\text{Initial number of amphipods})}$$

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.
- 9: not analyzed

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

Ammonia and sulfides are potential confounding factors for toxicity tests. These chemicals can be anthropogenic in origin but many natural sources exist as well. If threshold values are exceeded, inference on toxic effect as a result of pollutant content cannot be made. Table 5 lists the threshold ammonia and sulfide values for the test species used in the region.

Statistical Determination of Toxicity

Samples were defined as toxic if the following two 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 the difference between sample and control by the variance among replicates. A “separate variance” t-test was used 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

Table 5. Unionized Ammonia and H2S effects Thresholds for BPTC Toxicity Test Protocols

Species	Unionized Ammonia (mg/L)	Limit Definition	Reference
<i>Eohaustorius</i> (EE)	0.8	Application Limit	USEPA 1994
<i>Haliotis</i> (HR)	0.05	NOEC	MPSL*
<i>Mytilus</i> (ME)	0.15	LOEC	Tang <i>et al.</i> 1997
<i>Neanthes</i> (NA)	1.25	LOEC	Dillon 1993
<i>Rhepoxynius</i> (RA)	0.4	Application Limit	USEPA 1994
Urchin Development (SPD)	0.07	NOEC	Bay <i>et al.</i> 1993
Urchin Fertilization (SPF)	>1.4	NOEC	Bay <i>et al.</i> 1993
Species	Hydrogen Sulfide (mg/L)	Limit Definition	Reference
<i>Eohaustorius</i> (EE)	0.114	LOEC	Knezovich <i>et al.</i> 1996
<i>Mytilus</i> (ME)	0.0053	LOEC	Knezovich <i>et al.</i> 1996
<i>Rhepoxynius</i> (RA)	0.087	LOEC	Knezovich <i>et al.</i> 1996
Urchin Development (SPD)	0.0076	LOEC	Knezovich <i>et al.</i> 1996
Urchin Fertilization (SPF)	0.007-0.014	NOEC	Bay <i>et al.</i> 1993

*Unpublished data

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 Schlekot, 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 6. Samples with toxicity test results lower than the values given, as a percentage of control response, would be considered toxic if the result was also significantly different from the control in the individual t-test.

Table 6. Ninetieth percentile MSD values used to define sample toxicity

Species	Name	MSD	% of Control	N	Reference
Cd	Cerio. surv.	20	80		Thursby <i>et al</i> 1997
Cd SWI	Cerio. SWI	20	80		Thursby <i>et al.</i> 1997
Ee	Eohaustorius	25	75	385	MPSL*
Ha	Hyaella	20	80		Thursby <i>et al.</i> 1997
Hr	Abalone (5 reps)	10	90	131	MPSL*
Hr	Abalone (3 reps)	36	64	336	MPSL*
Hr	Abalone (all reps)	32	68	467	MPSL*
Me	Mytilus	20	80	223	MPSL*
Na Sv	Neanthes surv.	36	64	335	MPSL*
Na Wt	Neanthes wt.	56	44	335	MPSL*
Ra	Rhepoxynius	23	77	720	MPSL*
Sp Dev	Urchin dev. (5 reps)	22	78	309	MPSL*
Sp Dev	Urchin dev. (3 reps)	45	55	630	MPSL*
Sp Dev	Urchin dev.(all)	40	60	939	MPSL*
Sp Fert	Urchin fert.	12	88	79	MPSL*
SP SWI	Urchin SWI	41	59	109	MPSL*

*Unpublished data

Statistical Analyses

Relationships between toxicity and chemistry 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). Covarying 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 arcsine transformations when appropriate (Zar, 1984).

Chemical Specific Screening Values

Investigations of sediment chemistry and assignment of pollutant levels thought to have biological effects are incomplete without consideration of bioavailability. Tools to directly test biological effect, however (TIE, bioaccumulation analyses, etc.) could not be applied broadly in the BPTCP due to the expense of these types of analyses. Such studies are often best reserved for directed investigations of cause and effect after a screening effort has identified potential pollution problems. In order to evaluate larger numbers of samples for their potential for biological impact, sediment chemical concentrations were compared to published guideline values that compare pollutant concentration to concurrent biological effect. There have been several recent studies associating pollutant concentrations with biological responses (Long and Morgan, 1990; MacDonald, 1992; Long *et al.* 1998). These studies provide guidance for evaluating the degree to which sediment chemical pollutants levels are responsible for effects observed in a toxicity test. Reported values are based on individual chemical pollutants in sediments. Therefore, their application may be confounded when dealing with biological effects

which could be attributed to a synergistic effect of low levels of multiple chemicals, unrecognized chemicals, or physical parameters in the sediment which were not measured.

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 of concentrations over which toxic effects are rarely observed;
- 2) Possible Effects Range: The range of concentrations over which toxic effects are occasionally observed;
- 3) Probable-Effects Range: The range of 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 25 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. The probability of toxicity was expected to increase with the number and degree of exceedances of the ERM values.

Another method identifies three 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 7. Neither of these methods is advocated over the use of the other in this report. Instead, both are used in the following analysis to create a weight of evidence which should help explain toxicity observed from some sediments.

As a cautionary note; the degree of confidence which MacDonald (1994) and Long *et al.* (1995) had in their respective guidelines varied considerably among the different chemicals. High confidence is expressed in the ERM and PEL values derived for copper, zinc, total PCBs and PAHs. Relatively low confidence is expressed for the values for nickel, chromium, and DDTs.

Table 7. Comparison of sediment screening levels developed by NOAA and the state of Florida

SUBSTANCE	State of Florida (1)		NOAA (2,3)	
	TEL	PEL	ERL	ERM
<u>Organics (ng/g- dry weight)</u>				
Total PCBs	21.550	188.79	22.70	180.0
<u>PAHs</u>				
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)anthracene	6.220	134.61	63.40	260.0
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
<u>Pesticides</u>				
p,p'-DDE	2.070	374.17	2.20	27.0
p,p'-DDT	1.190	4.77		
Total DDT	3.890	51.70	1.58	46.1
Lindane	0.320	0.99		
Chlordane	2.260	4.79	2.00	6.0
Dieldrin	0.715	4.30		8.0
Endrin				45.0
<u>Metals (mg/kg- dry weight)</u>				
Arsenic	7.240	41.60	8.20	70.0
Antimony			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

(1) MacDonald, 1994 (2) Long *et al.*, 1995

(3) Long and Morgan, 1990

DDT and its metabolites must be considered carefully due to this lack of confidence in guideline values. Other authors (Swartz *et al.*, 1994, Chapman 1996) have expressed more confidence in total DDT values normalized to organic carbon content in the sediments. It is suggested that when the OC normalized DDT value is high enough, there is sufficient free DDT (unbound to organic carbon) to be available to aquatic organisms. Swartz (1994) reports decreased abundance of amphipods for total DDT values of about 100 µg DDT/g OC from field samples. This normalized value has been used to calculate the total DDT quotient value (TTLDDTQE) in this report. The quotient value is expressed as: $(TTL_DDT/TOC)/100$, where TTL_DDT is the sum of the six DDT metabolites, TOC is the total organic carbon content of the sample, and 100 reflects the DDT/OC value reported by Swartz to be associated with biological effect.

Chemical Comparisons

Comparisons of the data to effects-based numerical guidelines were made to assess how sediment pollution in the Central Coast Region compares to sediment pollution on a national scale. These comparisons were made using summary ERM-quotients (ERMQ) and PEL-quotients (PELQ). Summary quotients were calculated by dividing chemical concentrations for pollutants in Table 7 by their respective ERM or PEL value, summing, and then dividing by the total number of chemicals used in the summation. 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 summation. This 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.

This technique is useful for characterizing sediments in heavily urbanized and industrialized areas where chemical constituents can be numerous. In less heavily populated areas or where adjacent watersheds have fewer types of uses such as in agricultural areas, pollutants tend to be less varied. In this case, the quotient values may have limited utility because they tend to exclude stations where only a few chemical constituents are high and most others are well below the ERM or PEL value. The quotient value is therefore a useful comparative tool, but does not necessarily infer direct biological relevance.

For the purposes of chemical comparison within the Central Coast Region, stations were singled out if they met any of the following criteria:

1. An ERMQ equal to or greater than the top 90th percentile for the Region.
2. Exceedance of ERM or PEL value.
3. An individual chemical level within the top 10% program wide for that chemical.
4. Any chemical concentration likely to cause biological effect by best professional judgement.

Quality Assurance/Quality Control

Summaries of quality assurance and quality control procedures are described under separate cover in the BPTCP Quality Assurance Project Plan (QAPP). This document describes procedures within the program which ensure data quality and integrity. Quality assurance procedures follow those of the NOAA Status & Trends (NS&T) program to ensure comparability

Chlordane

Chlordane is a multipurpose insecticide that has been used extensively in home and agricultural applications for the control of termites and other insects. Although use of this compound ended in the mid-70s, its persistence in sediments of the region is apparent. Total chlordane is the summation of major constituents of technical grade chlordane and its metabolites (Appendix C Section IV). Chlordane is still present in the soils and sediments of many areas. Presumably it is washed from soils during rain events and travels down stormdrains, streams, and rivers to be deposited in nearshore areas. In areas with little or only seasonal flushing by the ocean, chlordane and other pollutants can accumulate in the sediment. Areas prone to such deposition include bays, harbors, estuaries and coastal lagoons.

Total chlordane was found at levels exceeding the ERM in two locations in Santa Cruz Harbor (35001 & 35002), and on two separate sampling occasions at the Sandholdt Bridge station (30007). Four stations in the Tembladero watershed study also exceeded guideline values for chlordane including the Sandholdt Bridge station. The highest value in the region was measured at Santa Cruz Yacht Basin-A9 (35002) which exceeded the ERM of 6.0 ppb by over four times. Eight of the 34 stations analyzed for chlordane exceeded the PEL (4.79ppb) and seven exceeded the ERM. Distribution of chlordane in sediment samples throughout the region is shown in figure 3a-c.

Dieldrin

Dieldrin is also common in sediments in the region. Its use was banned in 1984 except for subsurface termite control and other limited uses, but it persists in soils and sediments from earlier applications. Six of the seven stations sampled in the Tembladero watershed study were within the top ten percent of stations sampled program-wide for this chemical. Sediment in the Santa Maria River Estuary (30020) also had a dieldrin concentration above the ERM value. Figure 4 shows the distribution of elevated dieldrin levels in sediment samples in the Central Coast region.

This pattern of distribution for dieldrin is consistent with its agricultural applications, but for some locations urban sources may exist as well. One of the highest values measured in the region was from the Upper Tembladero-Salinas City (36004) station, a drainage close to a large urban area. Since the Tembladero Slough flows through the city of Salinas on its way to this station, and the watershed above the city is largely agricultural, it is impossible to identify individual source types with the current information.

PAHs

Polycyclic (polynuclear) aromatic hydrocarbons (PAHs) are base/neutral organic compounds with a fused ring structure of two or more benzene rings. They are components of crude and refined petroleum products and are also products of incomplete combustion of organic materials. Exposure to PAHs may result in a wide range of carcinogenic, teratogenic and mutagenic effects to terrestrial and aquatic organisms (Eisler, 1987). Due to their similar modes of toxic action, individual PAHs are often grouped into low and high molecular weight compounds for concise reporting purposes. Individual PAHs used for the summations of low and high molecular weight PAHs in this report are given in Appendix C -Section X. Concentrations of high molecular

weight PAHs exceed the PEL (>6676.14 ng/g) or ERM (>9600 ng/g) at the Monterey boatyard 35003 (ERM), the Monterey Yacht Club 30002 (ERM), Upper Tembladero-Salinas City 36004 (PEL) and Santa Cruz Yacht Basin 30001 (ERM). A summary of the number of exceedances and their locations is shown in figure 5.

The distribution of PAHs in the region is consistent with their presence in petroleum products and as a combustion product. Harbors and populated urban areas are common places to find this type of chemical pollutant. In the Central Coast region, both Santa Cruz and Monterey Harbors exhibited various exceedances of guidelines for these chemicals. In Morro Bay, however, two stations (Morro Bay 30024, and Morro Bay Mid Bay 30029) did not exceed guideline values for PAHs. The remaining stations in Morro Bay (Fuel Dock 30033, and Morro Bay-South Bay 30025), and in Santa Barbara Harbor (30003) received no chemical analyses.

Other Chemicals

DDT and its metabolites were found in most sediments of the region. The historical widespread use of DDT is well known. The pesticide is present in soils and sediments of most areas as a result of this ubiquitous use. The presence of these chemicals in marine environments has long been known in areas such as Moss Landing Harbor, where sediment containing DDT is deposited by seasonal runoff (Rasmussen 1996). Sediment values measured at Santa Maria River Estuary (30020) and Upper Tembladero/Salinas City (96004) were among the highest five percent program-wide. Of the thirty four stations that received pesticide analysis, eleven exceeded the ERM and fourteen exceeded the PEL for total DDT or at least one of its metabolites.

Various authors have expressed low confidence in the ERM and PEL values for DDT. (Mac Donald 1994, Long *et al.* 1995). Values normalized to organic carbon content have produced more consistent relationships between toxicity and pollutant content. Chapman. (1996) Swartz *et al.* (1994) have expressed confidence in OC normalized thresholds of between 100 and 200 mg DDT/kg OC dry weight. Although many stations in the region exceeded previously established ERM or PEL values, only Santa Maria River Estuary (30020) exceeded the OC-normalized value adopted in this study, 100mg DDT/kg OC. The relevance of DDT cannot be dismissed, however, especially in light of studies in which DDT has been shown to be bioavailable (Stephenson *et al.* 1995,). Indeed, regression analysis results in this study suggest that given appropriate replication, clear relationships between DDT and toxicity might be revealed.

Nickel and chromium are found throughout the region, but their presence is often thought to be geologic in origin (NOAA 1994, Mearnes and Young, 1977, Cornwall 1966). The high likelihood of natural sources coupled with a low confidence in the ERM and PEL values for these chemicals (Long *et al.*, 1998) give them lower weight compared to other unquestionably anthropogenic chemicals. Thirteen of 21 samples analyzed for nickel and chromium in the Central Coast Region exceeded the PEL for one or both. This is the largest number of exceedances in the region for any chemical class, and the largest proportion of exceedances per number of analyses.

Copper, mercury, zinc, lindane and PCBs were also found at levels exceeding guideline values at several stations in the region but may be only a localized concern.

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. Copper was found locally in excess of the ERM and PEL at Santa Cruz Yacht Basin (30001) and greater than the PEL only at Monterey Yacht Club (30002). Considering the historical use of copper based anti-fouling paint, this distribution pattern is not surprising.

Zinc is commonly used in marine applications for corrosion control and is common in sediments in many boat harbors statewide. Zinc levels greater than the PEL were measured in sediment from Monterey Yacht Club (30002). No ERM exceedences were measured in the region.

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. ERM and PEL exceedences of mercury were found at Santa Cruz Yacht Basin (30001).

PCBs are base/neutral compounds, formed by direct chlorination of biphenyl. There are 209 numerically designated individual compounds, called congeners (*i.e.*, PCB #101), based on the possible chlorine substitution patterns. Mixtures of various PCB congeners have been manufactured in the U.S. since 1929 (Phillips, 1987) and are used commercially under the trade name Aroclor. Each PCB mixture has a number designation (*i.e.*, Aroclor 1254) with the last two numbers indicating the percentage of chlorine in the mixture. PCB mixtures were used extensively in the U.S. prior to 1979 for industrial applications which required fluids with thermal stability, fire and oxidation resistance and solubility in organic compounds (Hodges, 1977). PCBs have proven to be extremely persistent in the environment and have demonstrated a variety of adverse carcinogenic and non-carcinogenic effects (USEPA, 1993c). These substances have a high potential to accumulate in the tissues of aquatic organisms and can represent significant hazards to consumers of aquatic species (Moore and Walker, 1991). Total PCB (the sum of 18 congeners, Appendix C - Section IX) was used as the comparative value and is the only value for which a PEL and ERM are presently available. PCB levels exceeded the ERM at Santa Cruz Yacht Basin (30001).

Many chemicals were analyzed for which no guideline values have been developed. These chemicals include various metals, tributyltin (TBT), and some pesticides. To compare the regional dataset with that of the entire state, those stations showing a chemical value in the ninetieth percentile program wide for these chemicals were considered to have elevated chemistry. None of these chemicals were found commonly throughout the region, however, so they will be discussed as they relate to individual stations.

Fish Tissue Chemistry

Screening values for pollutants in fish tissue were taken from USEPA guidance documents (USEPA 1995b). No fish tissue chemical concentrations were in exceedance of these guidance values. Among the chemicals that were found at detectable levels were: total DDT, chlordane, dieldrin, toxaphene, and total PCBs. Since fish were combined into a single composite sample for each species, there is no replication within species. Therefore data from these analyses are simply reported in appendix C, sections VIII-X

Chemical Summary Quotients

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 the association of toxicity with summary quotient and ERM/PEL guideline exceedances. Medium-high and highest priority stations had ERM quotients >0.51 or PEL quotients >1.51 . The probability of associated amphipod toxicity in this range was 46%. Stations with ERM quotients <0.5 or PEL quotients <1.5 were assigned to lower categories because the probability was less than 30%.

It should be noted here that quotient values in the Central Coast region were calculated differently than in Long *et al.* As discussed previously, DDT values were normalized to organic carbon content and scaled to values reported by Swartz *et al.* (1994). Additionally, sums of high and low molecular weight PAHs were used in this study rather than individual PAH values used by Long *et al.* These differences will affect the quotient, sometimes producing a dramatically lower value than the technique Long *et al.* employed. Because so many high DDT values were encountered in samples in the Central Coast Region, use of the values for broader scale comparisons may be particularly inappropriate. Detailed descriptions of the methods used to calculate the ERMQ and PELQ are offered in Appendix C section VII.

Twenty-one samples had sufficiently complete chemical analyses from which to calculate ERM and PEL summary quotients. The mean quotient values for these stations were 0.179 (ERM) and 0.308 (PEL). The highest ERM and PEL quotient values were seen at Santa Cruz Yacht Basin (0.447 and 0.735 respectively), Monterey Yacht Club (0.421 and 0.720), and Santa Maria River Estuary (0.367 and 0.491). The ninetieth percentile ERMQ and PELQ for the Central Coast region were 0.402 and 0.662 respectively.

These values are lower than those calculated for many more urbanized areas such as San Diego Bay or Los Angeles Harbor (Fairey *et al.*, 1996, Anderson *et al.* 1997). By comparison, the program-wide 90th percentile ERMQ and PELQ were 1.11 and 1.52. It should be noted, however, that these numbers do not reflect a random distribution of sites. Sampling has been understandably focused on more populated areas such as San Diego bay and Los Angeles Harbor. In addition, sediment samples with many low level concentrations of pollutants tend to produce higher ERMQ values than stations with only a few high concentrations. Therefore, values listed above are not necessarily good benchmarks for all regions in the State.

Summary quotients proved useful in areas such as San Diego Bay where sediments often showed complex mixtures of chemicals (Fairey *et al.* 1996). In less heavily populated areas such as the Central Coast Region, however, pollutants tend to be fewer in number. In these areas, individual chemicals may be present at high concentrations, but the summary quotient value can still be relatively low if other measured chemicals are in low concentrations. The higher values reported in other areas of the state often reflect more complex mixtures of pollutants. The values are useful, however when comparing the overall degree of pollution within the Region. Summary quotients provide a means of comparison independent of pollutant type.

Table 8 lists the chemical summary quotients for the 21 stations in the Central Coast Region for which data were complete enough to calculate the values. Those stations with many guideline exceedances usually produce the highest summary quotient values, although some stations such as Santa Maria River Estuary produce relatively high values with only a few chemical guideline exceedances.

Table 8. Chemical Summary Quotient Values

STANUM	STATION	ERMQ	PELQ
30001.0	Santa Cruz Yacht Basin	0.447	0.735
30002.0	Monterey Yacht Club	0.421	0.720
30020.0	Santa Maria River Estuary	0.367	0.491
30014.0	Monterey Stormdrain No. 3	0.281	0.454
30007.0	Sandholdt Bridge	0.240	0.385
30023.0	Bennett Sl./Estuary	0.209	0.355
30024.0	Morro Bay	0.208	0.448
30012.0	Monterey Boatyard	0.175	0.275
30029.0	Morro Bay-Mid Bay	0.165	0.365
30006.0	Pajaro River Estuary	0.149	0.267
30004.0	M.L. Yacht Harbor	0.137	0.245
30019.0	Moro Cojo Slough	0.130	0.233
30028.0	Elkhorn Sl. Portrero Ref.	0.122	0.218
30031.0	Carpinteria Marsh-2	0.108	0.168
31001.0	Egret Landing- Ref	0.102	0.181
30013.0	Monterey Stormdrain No.2	0.099	0.170
30005.0	M.L. South Harbor	0.094	0.169
31002.0	Highway 1 Bridge- Ref	0.089	0.185
31003.0	Andrews Pond- Ref	0.088	0.166
31003.0	Andrew's Pond Ref.	0.087	0.147
30027.0	Monterey Bay Ref. South	0.046	0.084

Toxicity Results

Amphipod survival (*Rhepoxynius abronius* or *Eohaustorius estuarius*) was significantly reduced in various areas throughout the region (Figures 6a-c). Of 82 samples on which toxicity tests were run, 52 produced at least one positive toxic result. Thirteen different toxicity test protocols were used in various combinations during the course of the study, each with unique sensitivities to pollutants and physical factors. A summary of toxicity results is given in Table 10.

Bedded sediment tests with amphipods were the most widely used in the region and provide the most comprehensive data set for comparisons of toxicity among stations. Other tests (urchin and abalone development, urchin fertilization, *Neanthes* weight gain and survival, sediment/water interface tests, etc) were employed as necessary. Abalone development was consistently inhibited in 100% and 50% porewater concentrations, even in samples from sites presumed to be clean (e.g., Monterey Bay Reference 30034). This suggests that the test may be sensitive to unmeasured factors.

Four samples had exceedances of cutoff values for ammonia. Two of these samples IDORG 507, from Sandholdt Bridge 30007 on 12/21/92 and 1374, from Highway One Bridge 31002 on 6/15/94 showed no toxic result. Sample IDORG 1597, from the Sandholdt Bridge 30007 on 5/9/96 had an ammonia value greater than the test threshold level for urchin development and showed a toxic result in both the urchin development SWI test and a bedded sediment *Eohaustorius* test for which no thresholds were exceeded. Sample IDORG 1368, field replicate number one from Bennet Slough 30023.1 on 6/16/94, exceeded the ammonia value for the *Rhepoxynius abronius* bedded sediment test and showed a toxic result. The two other field replicates at this site also produced toxic results but had ammonia values within acceptable ranges. There were no exceedances of hydrogen sulfide thresholds.

Exceedance of ammonia cutoff values should not disqualify toxicity results from consideration, however. These levels are designed to provide additional information on the confidence in results from individual samples and tests.

Urchin fertilization toxicity tests on pore water were not included in comparisons due to methodological discrepancies. When tests were performed on frozen samples and controls, controls failed, making comparison impossible. Because all pore water samples for fertilization tests were stored frozen in Teflon bottles, we have no assurance the data from any of these fertilization tests are truly indicative of sample toxicity. Any toxicity observed in the fertilization tests may have been wholly or partially due to storage effects. Changes in accepted methodology regarding extraction and storage were adopted but the urchin fertilization protocol was not used again in the region. For these reasons, there is little confidence expressed in results from this test. The data are reported in appendix E section V.

Controls for the storage effects of frozen pore water samples in Teflon bottles were included in later tests. These additional controls, which were not required by the original QAPP, indicated that toxicity may be associated with frozen sample storage in Teflon bottles. Because all pore water samples for fertilization tests were stored frozen in Teflon bottles, we have no assurance the data from any of these fertilization tests is truly indicative of sample toxicity. Any toxicity observed in the fertilization tests may be wholly or partially due to storage effects. For this reason, the urchin fertilization test was replaced with the sea urchin larval development test, unless those samples had already been tested with the development test which has been unaffected by storage artifacts, as indicated by response in frozen storage bottle controls. While sea urchin fertilization data are reported in appendix E section V, they were not used in any further data analysis for this report. The use of fertilization data, for determination of toxicity, was therefore not considered prudent considering the possibility of false positive results related to sample storage.

Except as discussed above, all samples were within acceptable ranges of control criteria for most assessment and reporting purposes. No major exceedances of control criteria requirements occurred.

Statistical relationships

Pearson correlation was used to screen for co-varying chemicals which were withdrawn from analysis. The remaining variables (all log (x+1) transformed) iron, cadmium, copper, total DDT,

total chlordane, and low molecular weight PAH, were used as independent variables along with grain size (arcsine transformed) and TOC (arcsine transformed) in a multiple regression. The results of the ANOVA for the multiple regression revealed no significant relationship between amphipod survival and the independent variables ($p=0.105$, Table 10). Total DDT was negatively correlated with amphipod survival (std. coefficient = -0.657), however the relationship was not significant ($p=0.061$). Normalizing total DDT to TOC did not improve this relationship. Tabachnick and Fidell, (1996) recommend an N of five per variable as a rule of thumb. The available dataset had only 21 stations available for the eight variables. Larger sample sizes might have produced significant relationships, especially in the case of DDT.

Because of large variances and relatively small sample sizes, regression analysis of chemical content versus toxic response showed no significant relationships. A region-wide evaluation of toxicity as a function of priority pollutant concentrations was therefore impossible with the current data set.

Table 9. Multiple regression; Amphipod survival on chemical and physical variables.

Dep. Var: Amphipod survival N:21 Multiple R: 0.771 Squared Multiple R: 0.595 Adjusted squared Multiple R: 0.324 Standard error of estimate: 14.086							
Effect	Coefficient	Std Error	Std Coefficient	Tolerance	t	p (2 Tail)	
CONSTANT	34.6	114.12	0.0		0.303	0.767	
finest	-0.36	0.39	-0.383	0.199	-0.93	0.37	
total organic carbon	-2.96	1.55	-0.434	0.652	-1.907	0.081	
iron	6.00	12.17	0.189	0.231	0.493	0.631	
cadmium	8.70	20.49	0.114	0.473	0.425	0.679	
copper	2.11	7.70	0.123	0.168	0.274	0.789	
total chlordane	3.29	11.11	0.065	0.693	0.296	0.772	
total DDT	-8.73	4.22	-0.657	0.335	-2.067	0.061	
LMW PAHs	0.98	5.33	0.084	0.163	0.184	0.857	

Analysis of Variance

Source	Sum-of-Squares	df	Mean-square	F-ratio	p
Regression	3493.69	8	436.7	2.201	0.105
Residual	2381.12	12	198.42		

Although some relationships are negative as might be expected (e.g., total DDT std. coefficient = -0.657), the relationship is not significant. ($p = 0.061$). This value is nearly significant, however, suggesting that greater replication might reveal statistically significant relationships.

SPECIAL STUDIES

Monterey Lead Study

Introduction

A large slag heap in Monterey Harbor, left from operations of the Southern Pacific Railroad in the area, was the presumed source of elevated lead levels found in shellfish in Monterey Harbor (Rasmussen 1996). The slag heap was removed in the late 1980s, but no comprehensive study of the residual effects on the sediments was done after cleanup. To assess the extent of any possible remaining contamination, a gradient study was designed using BPTCP collection and analysis protocols to identify elevated lead levels and associated bioeffects in the sediments near the slag heap and in other parts of the harbor.

Methods

Four stations were arranged with increasing distance at 0, 70, 120, and 280 meters from the historical location of the slag heap to represent a potential gradient of remaining lead contamination. Standard BPTCP protocols were used for the collection and chemical analysis of the sediments but lead was the only metal analyzed. At the closest station to the slag pile site, a full organic scan was performed on the sediments. A standard bedded sediment toxicity test (*E. abronius*) and a sediment/water interface test using sea urchin development were used to assess toxicity. Benthic community structure was also characterized at all four stations.

Results and Discussion

Lead levels showed a clear gradient outward from the site of the slag heap (90.1, 70.4, 32.6, 29.2 µg/g with increasing distance). All the values measured were below the ERM and PEL guideline values, however. Toxicity and synoptic chemistry were only tested at the station with the highest lead concentration (35003). Amphipod survival was not inhibited in the bulk phase toxicity test for this station, but urchin development was inhibited in a sediment/water interface test. Other chemicals exceeded guideline values at this station, so it is impossible to attribute the toxicity results to lead alone. Guidelines exceeded at this station included PEL values for high and low molecular weight PAHs. No ERM values were exceeded.

Benthic community analysis revealed no clear patterns of degradation of benthos between the stations. Polychaetes were the most commonly found organism in the sediments of all four stations, followed by crustaceans. *Capitella capitata* is thought to be negative indicator species, commonly found in disturbed or polluted locations (Grassle and Grassle 1974, 1976, Oliver *et al.* 1977, Mc Call 1977, Pearson and Rosenberg 1978, Lenihan and Oliver 1995, Okey 1997). These polychaetes were found at all four stations along with positive indicator species commonly found in undisturbed areas such as *Tellina sp.* (Oliver *et al.* 1980), *Ampelisca sp.* (Mills 1967, Oliver *et al.* 1983, 1984, Oliver and Slattery 1985) and *Macoma sp.*, (Reid and Reid 1969, Oliver *et al.* 1977)

Lead was not present in surficial sediments at levels thought to be acutely toxic, but levels are higher in the Monterey Harbor area than in any other location measured in the Central Coast region. Sediments in this area relatively coarse-grained (17% fines). This often suggests that the area is dynamic and that fine grained sediments are frequently resuspended and transported

away. Sediments of this type are far less frequently toxic in bedded sediment tests than fine-grained depositional sediments. For this reason, other tests such as bivalve bioaccumulation may be more appropriate measures of biological effect related to lead and other pollutants at this site.

Tembladero Drainage Pilot Watershed Study

Introduction

Water and sediment quality of the Tembladero Slough are thought to be degraded by agricultural and urban runoff. The areas adjacent to the slough are some of the most heavily used agricultural lands in California. While pollutant levels in sediment near the Sandholdt Bridge station in Moss Landing Harbor have presented problems for dredge spoil disposal, no comprehensive data exist for pollutant levels in the watershed itself. Without a complete analysis of upstream sediments and water, a full understanding of the influence of this watershed on downstream areas is difficult. This study was designed to characterize the pollutant loading and toxicity of various sub-drainages of the watershed which may contribute to the pollution levels and toxicity effects seen in the lower watershed and Moss Landing Harbor.

Toxicity and bioaccumulation potential of the individual sub-drainages of this watershed were assessed using a combination of freshwater and marine sediment and water column toxicity tests as well as lipid filled semipermeable membrane devices (SPMD's). Additional intents of this study were to demonstrate the utility of a watershed approach to pollutant monitoring and to supply useful information to ongoing projects designed to prevent or minimize pollutant inputs to the system.

Methods

Unlike most systems under study in the BPTCP, the Tembladero drainage contains environments from fresh water to marine. Water column and sediment toxicity tests were selected so that comparisons could be made between environments of each type. Standard amphipod toxicity tests were run on bedded homogenized sediment samples using *Hyalella azteca* or *Eohaustorius estuarius*, depending on the salinity of the overlying water. Similarly, water column toxicity was tested using *Ceriodaphnia dubia* or *Holmsemysis costata*, depending on sample salinity. All toxicity tests were performed according to protocols described previously in this document. The suite of chemical analyses was chosen to focus on the organic compounds that were likely to be the major pollutants in the system, although AVS/SEM was also done on major metal pollutants.

Seven sampling stations were selected to characterize the Tembladero watershed (Figure 1d). These stations included areas with heavy agricultural and/or urban runoff, and downstream areas which integrate the inputs. The stations were located at major divisions of the watershed to characterize sub-drainages and facilitate identification of pollutant sources.

A watershed-wide water quality characterization including measurements of oxygen, conductivity, pH, temperature, turbidity (total suspended solids), hardness, and nitrates was used to classify inputs and potential degradation of the watershed. Since nitrate and pesticide levels often covary, this measurement helps screen areas of concern to direct further sampling. Turbidity was also measured to identify areas of erosion which may contribute to loads of

pollutant laden sediments. Sediment samples were collected using standard BPTCP protocols to measure chemistry and toxicity of depositional sediments.

One large sediment sample (30-40l) was collected at the Sandholdt Bridge station for TIE analysis. This analysis links chemistry measurement to toxic effect and better documents the impact of pollutants on the watershed and Bay. A large (5 l) water sample was taken from the Upper Tembladero-Salinas City (36004) station for water TIE. The use of a TIE analysis will help coordinate efforts between this study and the State Water Resources Control Board Marine Bio-Assay study by providing a test bed for TIE protocols and supplying useful causal information related to pollutant levels in the watershed.

In addition to standard collections of sediment and subsurface water, field water quality measurements were taken for dissolved oxygen, pH, and turbidity. Nitrate analysis was done on subsurface water samples. Lipid filled semipermeable membrane devices (SPMD's) were deployed at the same stations to measure organic pollutant loading in the water. A summary of analyses by station is included in Table 1. Field water quality measurements are given in Table 13.

Sediment samples were handled as per the BPTCP protocols and delivered to the BPTCP analysis facilities (Granite Canyon Toxicology Lab, and Long Marine Lab Trace Organics Lab). Based on results of previous Mussel Watch program data, trace metals are not thought to be as high a concern as pesticides and other organic substances in the watershed, and were not analyzed. Semipermeable membrane devices were submerged at sampling stations for one month and extracted by AST laboratories. Analysis of the extract was done at Long Marine Lab Trace Organics Lab.

TIE Methods

Porewater was extracted from sediment using a Beckman J6B refrigerated centrifuge as described in the methods section. Samples were extracted no more than 48 hours before the TIE procedures were begun. Subsurface water was handled in a similar fashion, except that no centrifugation was necessary.

Toxicity Identification Evaluations (TIEs) with *Eohaustorius* (Station 30007)

Phase I TIEs are designed to characterize samples by isolating broad classes of compounds to determine their relationship to observed toxicity. Phase I TIE procedures include adjustment of sample pH, chelation of cationic compounds (e.g. many trace metals), neutralization of oxidants (such as chlorine), aeration to remove volatiles, inactivation of metabolically activated toxicants, solid-phase extraction (SPE) of non-polar organic compounds on C-18 columns, and subsequent elution of extracted compounds. Each sample fraction in which classes of compounds have been removed, inactivated, or isolated, is then tested for toxicity. All TIE procedures followed methods developed by USEPA (1996). Tests were done with *Eohaustorius estuarius* held in home sediment until applied to treatment solutions. Treatment solutions (sample fractions) were divided into 15 replicate 20-mL scintillation vials (15-mL of solution), with one amphipod placed in each vial. Each sample was tested at three dilutions. The sample underwent TIE treatment prior to being diluted with one micron-filtered Granite Canyon seawater (adjusted to

the appropriate salinity) that had also undergone TIE treatment. Testing sample dilutions provides information on the degree of sample toxicity. TIE treatments are described as follows:

Baseline – Sample was tested with no treatment but dilution within the range where effects were seen in the initial toxicity test

EDTA Chelation - Addition of EDTA binds cationic trace metals, such as copper, cadmium, mercury, zinc, lead, nickel, and, to a lesser extent, silver and manganese, resulting in relatively non-toxic metal complexes (Hockett and Mount 1996). EDTA was added to the sample for a final concentration of 100-mg/L. The sample was allowed to interact with EDTA for three hours before the pH was adjusted with sodium hydroxide. The pH was checked prior to distributing sample into test containers.

Sodium Thiosulfate Addition - Addition of sodium thiosulfate (STS) reduces oxidants, such as chlorine, ozone, chlorine dioxide, mono- and di-chloroamines, bromine, iodide, manganous ions, and certain electrophilic organic chemicals (USEPA 1991). It also binds some trace metals, such as copper, cadmium, mercury, silver, and to a lesser extent, zinc, lead, and nickel (Hockett and Mount, 1996). STS was added to the sample for a final concentration of 100-mg/L. The sample was allowed to interact for one hour.

Aeration - Sample was aerated for one hour to remove volatile compounds.

Filtration - Sample was filtered through a 0.45- μ m glass fiber filter to remove toxicants associated with particulate material.

Solid Phase Extraction (SPE) - Solid-phase extraction through a C-18 SPE column was used to remove a range of non-polar organic compounds from sample solutions. SPE columns later were eluted with 100% methanol to allow toxicity testing of compounds retained on the column. The sample was pumped through silicone tubing that had been cleaned by running 25-mL of distilled water followed by 25-mL of methanol through each tubing apparatus (but not through the column). The column was prepared by pumping 30-mL of methanol through it, followed by 50-mL of distilled water. Next, laboratory dilution water was pumped through the column; the first 20-mL was discarded, and the remaining volume was kept as the column control solution. Finally, 350-mL of sample was run through the column; the first 20-mL was discarded, and the remaining volume collected as SPE treated sample. The column was kept wet until all sample had been passed through. The column was then run dry and air-dried with a syringe. With the stopcock tightly shut, 2-mL of 100% methanol was added to the column. The stopcock then was opened, and air was pumped into the column at 2-mL/min until the column was dry. Eluate was collected in a small vial. The 2-mL aliquot of eluate then was delivered into 350-mL of laboratory dilution water. Assuming that all non-polar organic constants from the sample were retained on the column (no breakthrough), and assuming that all of these compounds were then completely removed from the column in the methanol eluate, the eluate treatment (2-mL in 350-mL) would contain the same concentration of these constituents as did the original sample. An eluate control consisting of 2-mL of methanol added to 350-mL of laboratory dilution water was tested with each C-18 eluate treatment.

After passing the sample through the C18 column, EDTA was added to the sample to mitigate possible toxicity in the event that both metals and organics were responsible for observed toxicity.

Piperonyl Butoxide (PBO) Tests - A number of organophosphate pesticides (phosphorothioate compounds such as diazinon, chlorpyrifos, malathion, parathion, methyl parathion and fenthion) require metabolic activation by exposed organisms before they become toxic. These activation reactions consist of oxidative metabolism by the cytochrome P-450 group of enzymes (USEPA, 1993b). This activation can be blocked by compounds, such as piperonyl butoxide (PBO), thereby reducing or eliminating toxicity due to this class of compounds.

In this study, PBO was added to test samples to determine whether metabolically activated pesticides were responsible for observed toxicity. Two point five-mL of 50-mg/L PBO stock solution was added to 250-mL of each sample (resulting in a concentration of 0.5-mg/L PBO). PBO controls were made by adding 20-mL PBO to 180-mL of laboratory dilution water.

Graduated pH - Adjusting sample pH can affect the toxicity of hydrolyzable, ionic, acidic, or basic compounds. Sample pH was adjusted and maintained at pH 7, 8 and 9 by the addition of hydrochloric acid and sodium hydroxide.

Toxicity Identification Evaluations (TIEs) with *Ceriodaphnia* (station 36004) EDTA, STS, PBO, aeration, and C18 column techniques for TIEs with *Ceriodaphnia* were identical to those with *Eohaustorius* except that five *Ceriodaphnia* neonates were placed in each sample vial and were tested at full strength and two dilutions. Filtration and pH adjustment steps were not done. Other TIE treatments are described as follows:

pH Adjustment - Adjusting sample pH can aid in the identification of hydrolyzable, ionic, acidic, or basic compounds. Sample pH was adjusted to pH 3 by addition of HCl, then held at that pH for 6 hours before returning the sample to initial pH by addition of sodium hydroxide. An additional treatment adjusted the sample to pH 11 by addition of sodium hydroxide, then held at that pH for 6 hours before returning the sample to initial pH by addition of HCl. Toxicity tests were conducted after the treatment solutions had been restored to initial pH.

Cation Column - Solid-phase extraction through a Cation SPE column was used to remove divalent cations from sample solutions. The SPE columns were later eluted with hydrochloric acid to allow toxicity testing of compounds retained on the column. Sample was pumped through silicone tubing that had been cleaned by running pumping 10 ml 1 M HCl then 25 ml distilled water (but not through the column). The column was prepared by adjusting water flow to 2.5 ml/min. and passing 2 ml of MEOH through column followed by 6 ml distilled water. Make sure to leave a small amount of liquid in the column after each step. Next, laboratory dilution water was pumped through the column; the first 20-mL was discarded, and the remaining volume was kept as the column control solution. Finally, 350 ml of sample was run through the column; the first 20 ml was discarded, and the remaining volume collected as SPE treated sample. Column was kept wet until all sample had been passed through.

The column was then run dry and air-dried with a syringe. Six ml 1 M HCl was pumped through column using a flow rate of 0.5 ml/min until the column was dry. Column eluate was collected in a small vial, and delivered into 350 ml of laboratory dilution water. Assuming that all divalent cation constituents from the sample were retained on the column (no breakthrough), and assuming that all of these compounds were then completely removed from the column in the acid eluate, the eluate treatment (6 ml in 350 ml) would contain the same concentration of these constituents as did the original sample.

Semipermeable Membrane Devices (SPMDs)

Two lipid-filled SPMDs were deployed at each location where sediment and water samples were taken for the Tembladero Watershed Study. The devices were handled with clean polyethylene gloves and attached to submerged steel rods immediately after opening their shipping container. Exposure to air was minimized so that no device was out of its shipping/storage container for more than 30 seconds. After one month of submergence, they were retrieved in a similar manner and replaced into their original shipping/storage containers for return to the manufacturer for extraction. Extraction of the lipid medium was done at Environmental Sampling Technologies in St. Joseph, MO. Extraction methods followed those of Huckins *et al.* (1990) and Lebo *et al.* (1992). Extracts were sent to the trace organics analysis facility at UCSC's Long Marine Lab for analysis.

Hydrology

Hydrologic data were collected using a Global Water Level Logger model WL14. The sensor was placed at the mouth of the Tembladero and allowed to collect data for the entire duration of the SPMD deployment. Sightings were taken with a surveyors transit along the lower length of the Tembladero slough from the mouth to the gaging station at the Pajaro Dunes Colony to determine flow rates in the watershed.

Dissolved Oxygen Measurement

Dissolved Oxygen was measured in the field using a modified Winkler's titration. A LaMotte[®] dissolved oxygen check kit was used to determine oxygen concentrations. All reagents were standard solutions purchased directly from the manufacturer and were newer than the printed expiration date.

Fixing the sample:

A 60 ml glass water sampling bottle was rinsed three times with sample water and then filled under water. All air was then purged from the bottle before capping. Eight drops of manganous sulfate solution and eight drops of potassium iodide azide were added to the sample water. The bottle was then re-capped and inverted several times to mix the solutions. After allowing the resultant precipitate to settle below the shoulder of the bottle, 1.0 g of sulfamic acid powder was added with a 1.0 g measuring spoon filled level full. The sample was capped again and gently shaken until the reagent and precipitate had dissolved. The resultant solution was yellow to orange-brown depending on oxygen content.

Titration:

The 20 ml glass titration tube was filled to the 20 ml line with fixed sample water and capped with the special titrating cap. The direct reading titrator was filled with sodium thiosulfate (0.25N) and inserted into the cap. While shaking gently, the titrator plunger is depressed until enough sodium thiosulfate has been delivered to turn the solution to a faint yellow. At this point, eight drops of starch indicator solution was added to the solution, turning it blue. Titrating was continued until the blue color just disappeared. The point that the plunger reached on the direct reading titrator was then recorded. The scale has precision of +/- 0.2 ppm.

Nitrate Analysis of Water

Frozen water samples were thawed in warm water, returned to a dark box and run within 2 hours of defrosting. Samples were run on an RFA-300 (Alpkem-automatic analyzer) configured for NO₃-NO₂ and PO₄ analysis.

NO₃-NO₂ method consists of a cadmium column reduction of NO₃⁺ to NO₂⁺ and a colorimetric measurement of the NO₂⁺+NED dye produced. PO₄ method consists of the colorimetric measurement of a PO₄⁺ -molybdate/hydrazine dye. Standards were made up from 24 hr dried (60°) reagent grade KNO₃ and KH₂PO₄, weighed to 1/1000th of a gram and diluted volumetrically. Standards were diluted to working ranges to bracketed samples and be in range of method (high standard for NO₃=45µM, PO₄=7.5µM). Initial comparison is run with old and new standards to check for accuracy.

Samples were run in batches of less than 20, bracketed with hi/low standards at the beginning and end of runs. Replicates were run at various times and sometimes various dilutions to check method, dilution accuracy, variability and sensitivity of the system. Replicates were run at least 15% of the time. Six Replicates of one sample were run to calculate standard variation. Spike recovery was run on one sample to test efficiency of the system. Spike recovery for NO₃-NO₂ was 98%. Recovery for PO₄ was 99%.

Results and Discussion

Toxicity

Sediments were toxic to amphipods throughout the watershed and subsurface water was toxic to *Ceriodaphnia sp.* in the upper reaches of the drainage (Figure 6c). Only Alisal Slough (36006) showed no toxic response from sediment or water. Salinas City (36004) was the only station to demonstrate both sediment and water toxicity. This pattern suggests that pollutants may be suspended in the water column upstream during high flow events, but settle out into the sediments or are diluted by tidal flushing downstream. Alternative explanations for this result are possible differences in sensitivity between test organisms used in fresh and salt water, and the possible differences in bioavailability of pollutants between fresh and salt water environments.

Phase I TIE Results & Discussion

Toxicity identification evaluations (TIE) were done at two stations for the Tembladero study. *Eohaustorius* ten day survival tests were done on marine pore water extracted from sediment collected at Sandholdt Bridge (30007). *Ceriodaphnia* 96 hour survival tests were done on subsurface fresh water collected from the Upper Tembladero - Salinas City (36004) station. Results from the TIE treatments are given in Tables 7a & b.

Sandholdt Bridge: Initial toxicity tests on dilutions of pore water from the station demonstrated a measurable dose response over the dilution range. TIE treatments were therefore run at control concentration (Granite Canyon water only), 10%, 32% and 75% porewater concentrations. The baseline TIE test demonstrated similar results to initial tests, but control survival was slightly reduced. This is probably attributable to variability in the test. Ethylenediaminetetraacetic acid (EDTA) stock solution additions to the test concentrations did not mitigate baseline toxicity. This treatment indicates that toxicity in the sample is not likely due to metals. Sodium thiosulfate (STS) stock solution additions likewise did not mitigate toxicity and in fact increased toxicity for all concentrations. It is unclear why the STS treatment increased toxicity so it is also unclear whether targeted oxidants such as chlorine or bromine played a significant role. Aeration mitigated toxicity at the greatest porewater concentration possibly indicating that volatile toxicants (e.g., H₂S, volatile hydrocarbons) play a role as toxic agents. A filtration manipulation did not mitigate toxicity so it is unlikely that particles or particle bound toxicants are responsible for the observed toxicity. Graduated pH shift manipulations had little effect, indicating that toxicity was not caused by pH dependent toxicants (e.g., H₂S, NH₃). The C₁₈ column extraction manipulation, which is used to determine if toxic components include non-ionic organics, did not significantly mitigate toxicity, however addition of C₁₈ column eluate indicated the eluate was toxic. This implicates some type of non-ionic organics in the eluate. The fact that there was no reduction of toxicity when sample was originally passed through the C₁₈ column, leads to the suspicion there was breakthrough with the column, but a second column in-line gave no evidence that breakthrough of non-ionic organics was occurring. Toxicity tests of sequential aliquots of post-column pore water did not show increasing toxicity, which would be expected if column breakthrough was occurring. It is more likely that the C₁₈ column retained only a portion of the multiple toxicants present in the sample. The C₁₈ column/EDTA manipulation, which is used to determine if toxicity is influenced by both non-ionic and cationic components, did not significantly mitigate toxicity, so a non-polar organic/metal combined effect appears unlikely. To test for metabolically activated toxicants, such as organophosphates, piperonyl butoxide (PBO) is added to the sample. Toxicity was not mitigated by this manipulation, so it is unlikely this class of compounds caused toxicity.

In review, the only manipulation which mitigated toxicity was aeration, but H₂S concentrations in the sample are not above tolerance limits (Knezovich *et al.*, 1995) It seems likely that toxicity in the Sandholdt Bridge sample is caused by a combination of non-polar organics and some other type of volatile organic. Metal toxicity seems unlikely but cannot be discounted, because SEM/AVS values (Table 11) in this sample are elevated and mandate caution before ruling out at least some metal toxicity. Elevated levels of organochlorine pesticides in both water and sediment samples from the station likely contribute to observed toxicity.

Upper Tembladero- Salinas City: Initial toxicity tests on dilutions of surface water from the station demonstrated limited dose response over the dilution range. Only undiluted surface water reduced *Ceriodaphnia* survival. TIE treatments were therefore run at control concentration (USEPA), 50% concentration and 100% concentration. Baseline TIE test demonstrated similar results as initial tests, however, control concentrations were slightly reduced. This is probably attributable to variability in the test. EDTA stock solution additions to the test concentrations did not mitigate baseline toxicity. This treatment indicates that toxicity at the station likely is not due

to metals. Sodium thiosulfate stock solution additions likewise did not mitigate toxicity indicating that toxicity was not likely due to oxidants such as chlorine or bromine. Aeration did not reduce toxicity, indicating that volatile toxicants (e.g., H₂S, volatile hydrocarbons) were probably not the toxic agent. Graduated pH shift manipulations had little effect indicating that toxicity was not caused by pH dependent toxicants (i.e., H₂S, NH₃, cationic and anionic toxicants, acidic, basic and hydrolyzable compounds, and polar organic compounds). The C₁₈ solid-phase extraction column manipulation, which is used to determine if toxic components are non-ionic organics (e.g., organochlorine pesticides), did significantly mitigate toxicity, however addition of C₁₈ column eluate did not cause toxicity as expected. Likewise the cation exchange manipulation, which is used to determine if toxic components are cationic (e.g., divalent metals), did significantly mitigate toxicity, however addition of cation exchange column eluate did not cause toxicity as expected. The fact that both columns mitigated toxicity, but the column eluate did not cause toxicity indicates that the causative agent is probably associated with particles and columns physically filtered out the toxicant. A filtration manipulation was not performed so this suspicion could not be confirmed. It is therefore unclear at this stage whether a particle bound toxicant is responsible for the observed toxicity or whether the particles themselves physically interfere with *Ceriodaphnia* survival. Future investigations at this station should focus on particle effects and particle associated organic toxicants.

Sediment Chemistry

Highest levels of pesticides in sediment were found in the upper areas of the watershed (figure 3c, 4). The Salinas City station showed levels of dieldrin that exceeded the ERM value by six fold. Dieldrin, PPDDE and total chlordane were the major pollutants found in sediments in the drainage. Sediments at the Central Tembladero station (36003) showed no ERM exceedances, but grain sizes were uncharacteristically large, suggesting that the sediments there were not depositional.

The Upper Tembladero/Salinas City station (36004) had the highest values in the watershed for nearly all measured pesticides and PAHs. Dieldrin concentrations generally decreased in sediments toward the Sandholdt Bridge station which showed the lowest sediment values measured in the watershed except for the Central Tembladero station (36003). If the sediments at the Central Tembladero station are not depositional, however, the comparisons from the station may be invalid.

SEM-AVS values are sometimes predictive of toxicity when above one and often predictive above five (Berry *et al.*, 1996). The highest measured AVS-SEM value was at the Central Tembladero station (36003). The value of 9.05 is among the highest program-wide, but the high value from the site was driven by a very low AVS number and not a high metal (SEM) concentration. Other stations in the watershed showing values greater than one were: Sandholdt Bridge 30007 (3.7), and Alisal Slough 36006 (5.4). Even though Alisal Slough had a high SEM/AVS result, sediment from the station was not toxic in any test. Although the primary chemicals of concern in the Tembladero watershed are thought to be organics, metals cannot be discounted in light of the SEM/AVS measurements. Of the metals measured (Cd, Cu, Ni, Pb, and Zn) zinc and nickel were the most abundant (Table 11)

Table 11. SEM/AVS

Station Number	Station Name	AVS	SEM Sum	SEM/AVS
30007	Sandholdt Bridge	0.557	2.060	3.700
36002	Tembladero Mouth	2.310	1.960	0.851
36003	Central Tembladero	0.044	0.398	9.050
36004	Upper Tembladero-Salinas City	4.460	4.050	0.909
36005	Espinosa Slough	4.160	1.620	0.389
36006	Alisal Slough	0.342	1.850	5.420
36007	Old Salinas River Channel	10.500	1.670	0.159

Table 12a. Sediment TIE for *Eohaustorius* (Station 30007)

	Porewater Dilution					
	0%	6.25%	12.5%	25%	50%	100%
Initial	0.93	0.73	0.67	0.33	0.13	0.20

Treatment	Porewater Dilution			
	0%	10%	32%	75%
Baseline	0.80	0.87	0.27	0.20
EDTA	1.00	0.67	0.33	0.20
STS	0.93	0.13	0.00	0.00
Aeration	0.93	0.73	0.33	0.47
Filter	0.73	0.13	0.00	0.00
Column	0.73	0.33	0.13	0.07
Eluate	0.60	0.73	0.27	0.00
Column/EDTA	0.53	0.53	0.00	0.07
PBO	0.80	0.07	0.00	0.00
pH7	0.80	0.40	0.20	0.00
pH8	0.93	0.53	0.13	0.07
pH9	0.80	0.47	0.13	0.07

Table 12b. Water TIE for *Ceriodaphnia* (Station 36004)

	Subsurface Water Dilution					
	0%	6.25%	12.5%	25%	50%	100%
Initial Survival	1.00	1.00	1.00	1.00	1.00	0.0

Treatment	Subsurface Water Dilution		
	0%	50%	100%
Baseline	0.80	0.96	0.0
EDTA	0.20	0.92	0.0
STS	0.96	0.92	0.0
Aeration	0.96	0.96	0.0
C18 Column	0.80	0.96	0.96
Eluate	0.96	1.00	0.92
pH 3 shift	1.00	0.84	0.04
pH 11 shift	1.00	0.72	0.00
PBO	0.0	0.24	0.12
Cation Column	0.92	1.00	0.80
Cation Eluate	1.00	0.96	0.96

Nitrate Analysis and Field Water Quality Measurements

Nitrate concentrations and turbidity often covary with pollutant loads. Nitrates in particular have been shown to correlate well with pesticide runoff from agricultural fields. Table 13 summarizes the field water quality and nitrate measurements from the Tembladero drainage. Nitrates were highest at the Central Tembladero and Upper Tembladero stations. This corresponds to high pollutant levels at the Upper Tembladero station, but does not track well with levels at the Central Tembladero. Since sediments collected at the Central Tembladero station were likely not depositional, however, the station may not fit the correlative pattern well.

Table 13. Nitrate, Phosphate, and Field Water Quality Measurements

Station Number	Station Name	Nitrate (μM)	PO ₄ (μM)	Turbidity (NTU)	O ₂ (mg/l)	pH
30007.0	Sandholdt Bridge	117.0	2.9	48	7.2	7.89
36007.0	Old Salinas River Channel	780.0	3.0	107	9.8	8.54
36002.0	Tembladero Mouth	84.5	8.3	83	11.0	8.44
36005.0	Espinosa Slough	203.0	12.7	96	10.0	8.90
36006.0	Alisal Slough	610.0	18.5	244	8.4	8.40
36003.0	Central Tembladero	1745.0	15.8	69	11.3	8.57
36004.0	Upper Tembladero-Salinas City	1250.0	27.6	21	12.5	8.51

SPMD Chemistry

It should be noted that although an attempt was made to deploy the SPMDs in hydrologically similar areas, factors such as flow rate and fouling may have acted to introduce variability between stations. Additionally, some of the devices developed small perforations, making extensive cleanup of the extract necessary and further complicating analysis. The primary value of the results from the devices is therefore only to determine comparative presence or absence of measured pollutants. Comparison of large scale differences in concentration may be appropriate, but because pollutant concentrations in water could not be calculated, the measurements should not be used to infer any exceedance of water quality standards.

Highest levels of pesticides in SPMDs were measured in the Alisal Slough, the Salinas City station, and the Old Salinas River station (figure 7). In general, pesticide concentrations were higher in the upper areas of the watershed and in some tributaries than in the more seaward stations. DDT or its metabolites were detected in SPMD extracts from all stations. Highest values were measured at the Alisal Slough station (36006). This pattern is consistent with the assumption that pollutants are either settling out or being diluted farther down the watershed. These results also parallel toxicity results where the furthest upstream station showed toxicity in water and sediment and the furthest downstream produced toxic results from only sediment.

The high values of DDT and dieldrin measured at the Alisal Slough (36006) do not correspond to either sediment values or toxicity results. This may be due to the unique shape of the Alisal Slough at the sampling location. In comparison to most other stations, the Alisal Slough is much narrower at this location. This suggests that flow past the SPMDs might have been significantly faster than at other deployment locations, possibly affecting rates of uptake.

Conclusions

Clear patterns in the distribution of pollutants, primarily pesticides, were evident in the watershed. In general, pesticide concentrations in SPMD extracts decreased from upstream to downstream stations. The pattern for the most abundant pesticide, DDT, is less clear but follows the same general trend. Toxicity results were consistent with the pattern of sediment pollutants. Although SPMD chemistry cannot be compared quantitatively, the ordinal arrangement of stations is consistent with the idea that pollutants are still suspended in the water column farther up the watershed. This is also supported by the water column toxicity results where *Ceriodaphnia* survival was reduced at the Upper Tembladero station.

This study was successful in demonstrating the utility of a watershed approach to monitoring downstream impacts. However, further sampling would be needed in the Tembladero watershed both to confirm the results of the present study and to follow pollutant gradients up the watershed. Since the uppermost station (Upper Tembladero-Salinas City 36004) had the highest levels of pollutants and strongest toxic responses, it is likely that it is closer to pollutant sources than the downstream stations. In addition, techniques for deployment of the SPMDs will require modification to prevent damage to the devices in a flowing water environment. This may require

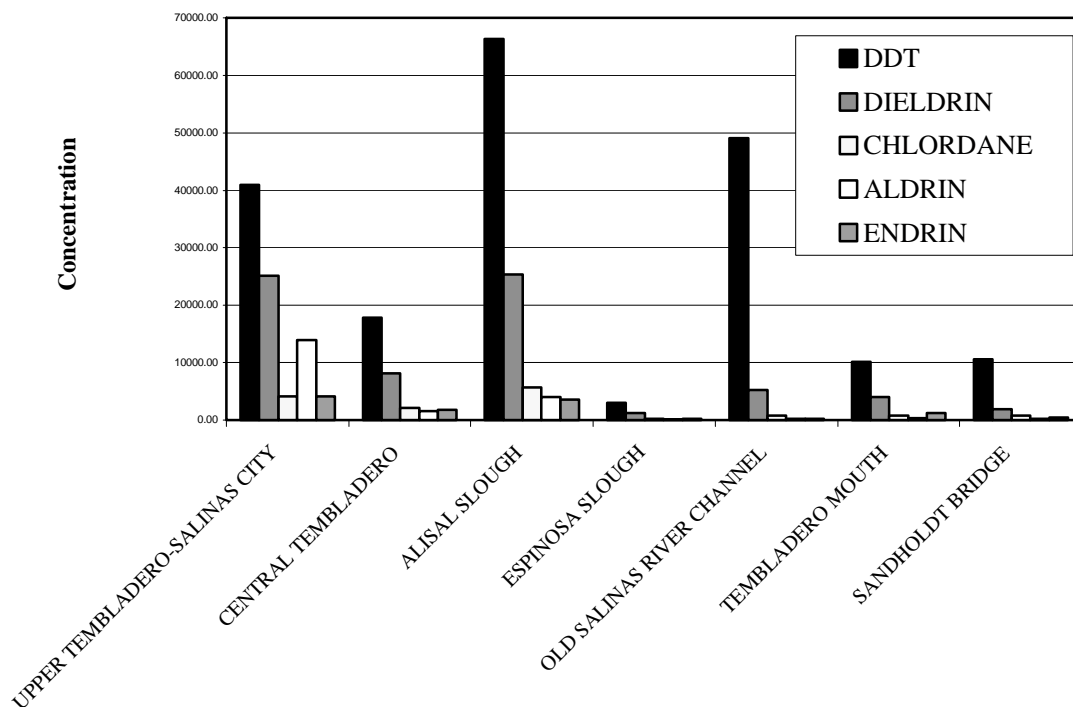


Figure 7. Pesticides in SPMD Extracts

the design of housings or protective supports that present minimal resistance to water flow such as those designed by Lebo *et al.* (1992).

The tributaries to the Tembladero should not be discounted however. Locally high levels of pollutants in adjacent drainages such as the Alisal Slough may be the result of mixing with the Tembladero or additional inputs along the subdrainages. It is likely that since the drainages flow through such similar agricultural areas, similar chemicals would be encountered in each. Clearly, sites with chronic pollution problems like the site at Sandholdt Bridge (30007) cannot be addressed in isolation. There may be many upstream contributors, and each must be addressed before water and sediment quality at downstream stations can be improved.

STATION GROUPING

For purposes of comparison between stations within the region, it is useful to group stations by the amount and type of information obtained from each. These groupings show the general results of all toxicity, chemistry, and benthic community analyses and are in addition to the program-wide categorization designed to aid identification of candidate toxic hot spots. Furthermore, this grouping does not presume a prioritization of stations, but is designed as an ordering of available information to assist Regional Water Quality Control Board staff in

planning either further study or insertion of stations into a cleanup plan incorporating all available sources of information. A synopsis of the stations in each group is given in Table 14.

In previous BPTCP reports, the highest priority for further investigation was given to stations with repeat toxicity, elevated chemistry, and degraded benthic community structure (Fairey *et al.* 1996). In the Central Coast Region, benthic community analysis was only done at four stations for the Monterey lead study. This was too few stations to effectively create a benthic community index for the region. The data were evaluated for general trends in species composition and abundance, but no such trends could be identified. Therefore, grouping within the region excludes the benthic community component.

Stations were grouped by the amount and type of data available for each. Stations with repeat toxicity (positive toxicity result from sediment or water on two or more separate occasions) and at least one exceedance of an ERM or PEL value were placed in group 1. Five stations fell into this group, four of which had three field replicate toxicity tests on at least one visit.

The second group is comprised of those stations which had exceedances of ERM or PEL guideline values and toxicity from only one visit. This group contains the largest number of stations. These stations have a wide range of chemical exceedances and may be subdivided based on which chemicals show ERM or PEL exceedances. All stations in the Tembladero watershed study fall into this group except Alisal Slough (no toxicity) and Sandholdt Bridge (multiple toxicity).

The third group contains only one station (Santa Cruz Yacht Basin 30001). This station was visited twice but exhibited a toxic response only once. ERM and PEL exceedances were both measured at this station.

The fourth group is comprised of those stations with no toxicity from single visits but with exceedances of the ERM/PEL values. Three stations are included in this group, Morro Bay-Mid Bay (30029), Morro Bay (30024), and Alisal Slough (36006).

The fifth group contains eleven stations and is made up of those with positive toxic responses from single visits but which are missing chemical analysis. This group contains stations from all around the region and may present a large subsection for further study.

The sixth and final group is comprised of two stations, Santa Cruz Yacht Basin-A9 (35002) and Santa Cruz Yacht Basin-A3 (35001). These stations exhibited chemical values in excess of the ERM/PEL but had no toxicity analysis.

DISCUSSION OF SELECTED STATIONS AND RECOMMENDATIONS

Stations analyzed in the Central Coast Region vary greatly in their completeness of information. Nearly every group contains stations which could benefit from additional types or amounts of analysis. Furthermore, scrutiny should be applied to each station in accordance with the types of chemical exceedances found. This discussion will focus on those stations of particular interest due to their degree and type of chemical or toxicity results.

Sandholdt Bridge and Tembladero Watershed

The Sandholdt Bridge station has a long history of various measures of pollution including tissue data from the California State Mussel Watch Program, showing exceedances of chlordane, DDT, dieldrin, and PCBs (Rasmussen *et al.*, 1995). The upstream environment shows similar types of pollution. The station sampled furthest upstream in the system (Upper Tembladero-Salinas City, 36004) had comparatively high levels of chlordane and dieldrin in sediments, two of the most commonly found pollutants in sediments at the Sandholdt Bridge site. Sediment from all stations in the watershed but the Central Tembladero station exceeded the ERM for dieldrin. Similarly, all stations but the Old Salinas River Channel and the Central Tembladero exceeded the PEL for total chlordane. Since use of these chemicals was widespread, sources may be located in many areas. Clearly, the SPMD information shows that these chemicals are present in the water at all stations.

Further investigations in the watershed should incorporate stations upstream of the Upper Tembladero-Salinas City station. Pesticides (dieldrin, chlordane and DDT) are the most common pollutants found in the watershed and at the Sandholdt Bridge station, so it is appropriate to focus analyses on these chemicals.

Monterey Yacht Club (30002)

Sediment quality guideline exceedances at the Monterey Yacht Club station include copper, zinc, and both high and low molecular weight PAHs. Copper and zinc are common metals found in sediments of small boat harbors due to their marine applications. PAHs are often found near fuel docks and maintenance yards. Since the Harbor is immediately adjacent to an urbanized area, other potential sources include but are not limited to stormdrain flow and street runoff. Confidence in ERM and PEL values for copper, zinc and PAHs is high. These pollutants were in exceedance of guideline values at this station. Toxicity was demonstrated twice at this station, but neither visit produced toxic results for amphipods.

Monterey Boatyard Lead-1 (35003)

This station showed significant toxicity to urchin larvae on its single visit. Sandy sediments such as those found in Monterey Harbor suggest a dynamic environment in which fine-grained sediment is regularly transported away. Significant toxicity and PEL exceedances in spite of this condition are noteworthy because toxicants are often associated with small particles. Mussel Watch bioaccumulation data from the area have shown elevated levels of lead for many years (Rasmussen 1995, 1996), even after the removal of the slag pile, suggesting that pollutants are still being suspended and made available to biofiltering organisms. Levels of PAHs in exceedance of PEL guidelines were also found at this station. This may be a characteristic of the entire harbor. Finer scale spatial sampling may be helpful in identifying sources or areas of higher concentration of these pollutants. Benthos at this station did not show evidence of degradation. Both positive and negative indicator species were present at this and all stations, and diversity was higher at this station than at the other sampling stations in the study.

Santa Cruz Yacht Harbor (30001)

Although toxicity in Santa Cruz Yacht Harbor was only demonstrated on one occasion, the presence of copper, mercury and PCBs is of concern. Nearby stations in the harbor have shown chemical pollution with chlordane and PAHs. Toxicity was not tested at these nearby stations (35001 and 35002), however. The relative magnitude of overall pollution is also of concern. Santa Cruz Yacht Harbor (30001) had the highest ERM and PEL quotient values measured in the region (0.447 and 0.735 respectively).

AVS/SEM results (Appendix C section III) showed that metals may be available to organisms in the sediments in Santa Cruz Yacht Harbor, but at comparatively low levels. Copper and zinc were found in relatively high concentrations at other stations in Santa Cruz Harbor, but AVS/SEM analysis was not done at these stations.

Of the 34 stations in the Central Coast Region for which PCB analysis was done, only Santa Cruz Yacht Basin exceeded the ERM and PEL

Santa Maria River Estuary (30020)

The Santa Maria River Estuary is of considerable interest because it drains a large agricultural watershed and is adjacent to the Guadalupe Oil Field, the site of large-scale cleanup efforts to remove compounds related to petroleum production from the soils. The region's highest DDT value and the only one in the region exceeding the OC normalized threshold was measured at this station. Nickel and dieldrin were also in exceedance of guideline values at this station. Pollutant concentrations were sufficiently high to produce the third highest ERMQ and PELQ in the region. Toxic response by *Eohaustorius* was strong, with a mean percent survival of only two percent. This station was only visited once, however, and no comparative data from sources such as the California Mussel watch are available.

Bennet Slough Estuary (30023)

This station demonstrated significant toxicity to amphipods on two visits, one of which tested three field replicates. Chemical exceedances at this station included nickel (ERM and PEL), chromium (PEL) and dieldrin (PEL). This station does not exhibit overall high chemistry (ERMQ 0.209), although, but has been toxic to amphipods on repeat visits. Careful application of TIE may be useful at stations such as this to pinpoint classes of toxic agents responsible for the observed toxic effects.

Additional Stations of Interest

Stations showing a significant toxic response but missing concurrent chemistry data include Santa Barbara Harbor (30003), Goleta Slough (30009), Morro Bay Fuel Dock (30033), Morro Bay South Bay (30025), and Salinas River Lagoon (30011). Further toxicity and concurrent chemical information from these stations would be meaningful. Some of these stations may require watershed approaches similar to that used in the Tembladero study to fully characterize pollutant sources and extents, especially those stations located at river mouths or near stream input.

REGIONAL CONSIDERATIONS AND CONCLUSIONS

The Central Coast Region is unique in that it contains a variety of environments that express a wide range of physical and chemical properties. Broad generalizations about such a diverse area are problematic and often inappropriate. Prioritization is often necessary in spite of these difficulties, however, and so must be done with great mindfulness of the individual environments under consideration. Many stations in the Central Coast Region demonstrated significant toxic response and concurrent chemistry values in excess of guidelines. These stations should be given highest priority when considering further investigations. Exclusion of those stations for which less information exists, however would be ill-advised. Many of the stations listed above have the potential to be important conduits through which pollution might enter the marine environment. The Salinas River, for example, drains one of the largest watersheds in the State and has significant potential to carry agricultural pollutants. This watershed has long been one of the most intensively farmed areas in the country, and as such, may be a significant non-point source of agricultural chemicals. This cannot be known, however, without adequate chemical and toxicological analyses both downstream and within the watershed.

Stations in the Central Coast Region that received chemical analysis showed lower pollutant content than more heavily populated and industrialized areas such as San Diego Bay and Los Angeles Harbor (Fairey *et al.*, 1996, Anderson *et al.* 1997). These results should not be discounted, however. The physical environment in the Central Coast Region is very different from that in other regions in that many stations are in highly dynamic outer coast river mouth locations or have significant water exchange with the open coast. This is demonstrated by the low percent fines in areas such as Monterey Harbor and Morro Bay. In all, 36 samples had lower than 50% fines. Notable exceptions to this trend were the Santa Maria River Estuary and Salinas River Lagoon.

As a result of the wide ranging needs for different types of data in the Central Coast region, the dataset for the region is less contiguous than in most other regions of the state. It is therefore prudent to incorporate data from other sources such as the State Mussel Watch program to augment sediment and water quality data obtained from the BPTCP. Because many stations were selected based on previous findings from other programs, the comparison for many locations should be straightforward. Caution should be used, however because temporal factors can produce results that may be difficult to interpret when data are not collected concurrently.

Since many areas in the Central Coast Region are hydrologically dynamic, conditions can be expected to vary greatly within them. It may therefore be appropriate to look to other measures of biological effects such as bioaccumulation to augment information gained from sediment analyses for a more comprehensive assessment of pollutants within the region. Effective employment of these techniques would use concurrent sampling methods so that all measures would be directly comparable on a temporal and spatial scale.

STUDY LIMITATIONS

Sampling in dynamic areas such as those in the Central Coast Region presents spatial and temporal problems not encountered in areas with more constant environmental factors. Many of

the sites in the Central Coast Region are located at or near the mouths of rivers or streams. These sites experience significant seasonal runoff and sediment transport. As a result of these processes, a particular sampling event becomes a snapshot of a much larger dynamic process. This snapshot may not be able to adequately characterize a site, especially if that site experiences appreciable seasonal change.

This study relied on initial toxicity results to provide information to prompt chemistry analysis. Budgetary constraints made it impossible to perform a full suite of chemical analyses on all samples and “best professional judgement” was used to determine the subset of stations on which analyses were to be run. Furthermore, stations that did receive chemical analysis did not always receive the full suite of analyses performed on samples in other parts of the State. This left smaller datasets on which to calculate ERM and PEL summary quotient values. The identification of trends within the region was therefore more difficult compared to other regions in the State.

Caution should be used when extrapolating the ecological meaning of data collected from studies such as this. Although measures of toxicity and chemical concentration are used extensively in this study and others like it, they can only be used as indicators of possible adverse effects to indigenous communities. In some environments, benthic community assessments can be used to demonstrate actual effects on resident biological communities, but these do not demonstrate causality. In combination with tools such as TIE however, these measures provide a strong weight of evidence for the conditions found at a particular sampling location. However, it is recommended that these lines of evidence be supported with an ecological risk assessment during subsequent investigations of stations of concern.

Except in the Tembladero Watershed and the Monterey lead studies, no attempt was made in this study to characterize areal extent of pollution in water bodies in the Central Coast Region. Although in some areas an estimate of areal extent may be obtained by measuring the size of the water body and location of replicate samples within it, this factor was not directly investigated.

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