SEDIMENT TOXICITY IDENTIFICATION EVALUATION FOR THE MOUTHS OF CHOLLAS AND PALETA CREEKS, SAN DIEGO

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EXECUTIVE SUMMARY

This report describes results of the final component in a three-part investigation into the potential impairment of beneficial uses at the mouths of Chollas Creek and Paleta Creek (also known as Seventh Street Channel) where they enter San Diego Bay. The investigation was prompted by the designation of the mouths of Chollas Creek and Paleta Creek as toxic hot spots by the Regional Water Quality Control Board, San Diego Region (SDRWQCB), based on chemical contamination of sediments and aquatic life impacts.

Each of the three parts of the investigation was designed to support a three-phased program to assess impacts, develop TMDLs, and conduct remediation activities at the sites. The goal of the first part of the investigation was to conduct a comprehensive weight of evidence (WOE) evaluation of the impairment of aquatic life beneficial uses as well as a screening level evaluation of wildlife and human health beneficial uses at both sites. The goal of the second part was to describe the temporal variability in sediment quality at the Chollas and Paleta Creek sites in order to identify reliable indicators of impairment. The goal of the final part of the study was to use sediment toxicity identification evaluation (TIE) procedures to ascertain the chemical constituents responsible for the toxicity observed in the previous two phases of the study. The results of the TIE investigation are described in this report, along with recommendations for further study.

The technical approach taken for this study was to apply TIE methods to samples from stations that had shown toxicity during the spatial study. Three rounds of TIE testing were performed, one on samples taken in 2001 during the spatial study, one on samples taken in 2002 during the temporal study and the final set of samples collected in 2004. In each case, initial toxicity tests were performed on the samples to verify that there was sufficient toxicity present to warrant conducting a TIE.

Concentrations of a suite of metals, PAHs, PCBs, and chlorinated pesticides were measured in the bulk surface sediment. For the 2004 samples, a larger suite of organic chemicals was measured that included organophosphorus and pyrethroid pesticides. Acute and sublethal toxic effects of bulk sediment, pore water, and contaminants fluxing across the sediment-water interface were measured using a variety of tests. The presence of acute toxicity was assessed by measuring survival of the amphipod crustacean, *Eohaustorius estuarius,* after 10 days of exposure to bulk sediment or pore water. The presence of sublethal effects and potential impacts of contaminated sediments on the water column was assessed by measuring the effects of a 3-day exposure to water from the sediment-water interface on sea urchin (*Strongylocentrotus purpuratus*) embryo development.

Sediment TIE manipulations were performed on the whole sediment from each station. Three primary treatments were applied to each sample. Cation exchange resin was added to one aliquot of sediment to bind cationic metals. To a second aliquot, coconut charcoal was added to bind organics. The final primary treatment consisted of adding clean home sediment to a third aliquot of sediment; this treatment was used to test for any dilution or aeration effect that the other treatments might be having on the sample. Two additional TIE treatments were applied to samples collected in 2004: extraction of

the sediment using a supercritical fluid process and addition of PBO to inhibit organophosphorus pesticide effects.

TIE procedures were also performed on pore water samples using methods adapted from the U.S. EPA. Four treatments were used: addition of EDTA, a chelator of metals; addition of sodium thiosulfate to neutralize oxidants and also decrease the toxicity of some metals; addition of PBO, and solid phase extraction of the sample using a C-18 column to remove nonpolar organic compounds.

The TIE process indicated that most of the toxicity to amphipods at the sites was associated with organic compounds. Treatment of the sediment with carbon particles (coconut charcoal) removed toxicity in most cases, while treatment to reduce metal exposure was usually ineffective. In addition, statistical correlations were strongest between several types of organic chemicals and toxicity. Chemical analyses also indicated that the bioavailability of divalent metal contaminants in sediment and pore water was very low.

While the specific contaminants responsible for toxicity could not be confirmed with the data available, chlordanes and PAHs appear to be the most probable contaminant groups (of those compounds measured) associated with the toxicity. Chlordane concentration was highly correlated with sediment toxicity at the Chollas site. Data from other field studies shows that sediments with chlordane concentrations higher than those measured at Chollas are almost always toxic. Calculations based on equilibrium partitioning theory indicate that PAH exposure from sediment contact is likely to result in chronic toxicity at the most contaminated sites from the Paleta study area and may contribute to the toxicity at Chollas. The PAH concentrations from the Chollas and Paleta sites are greater than most other locations in southern California.

DDTs and PCBs, while prevalent at the sites, are unlikely to be a probable cause of direct sediment toxicity. Data from other laboratory and field studies indicate that the measured concentrations of DDTs and PCBs at the study sites are several orders of magnitude lower that the levels associated with direct toxicity from sediment exposure. The significant correlations with toxicity found for these compounds are likely to be coincidental, probably the result of similar sources of loading with those contaminants causing the toxicity.

It is likely that the sediment toxicity observed at the study sites is the product of the joint effects of both measured and unmeasured contaminants. The patterns of toxicity differed between the Chollas and Paleta sites and there were inconsistent relationships between the sediment chemistry and toxicity results. These results suggest that there is no simple single cause of sediment toxicity. Some of this variability may be due to site variability; sediment grain size and TOC varied throughout the study sites and multiple sources of contaminants were present. Additional unmeasured contaminants may also be responsible for a portion of the toxicity; the standard chemical analyte list did not include potential toxicants such as organotins and pesticides in current use.

More data are needed to verify the conclusions of this study. This study was limited to using general methods to characterize the major classes of toxicants, which is the first and most cost-efficient step in the TIE process. Additional studies are recommended in order to provide more specificity to the toxicant identifications for the Chollas and Paleta study areas. These studies should include conducting spiked sediment tests with

contaminants of concern. Toxicity tests of San Diego Bay sediment spiked with chlordane or other suspected toxicants would provide a direct test of the TIE conclusions. These tests would also provide data that could be used to establish clean up thresholds or interpret assessment data from other locations.

Toxicity studies that included measurement of body burdens would also improve confidence in the results. Greater specificity in toxicant identification can be obtained through the analysis of tissue contaminant data from animals exposed to field sediments. Such data provide a more accurate measurement of the organism's exposure to contaminants and can be compared to existing residue effects data from laboratory studies to indicate the potential for toxicity from specific contaminants. These data are most useful for contaminants that are not metabolized by the organism, such as chlordane, PCBs, DDTs, and metals.

The potential for unmeasured contaminants to cause toxicity at the study sites should be addressed through the use of sediment fractionation studies. The importance of unmeasured contaminants as a cause of sediment toxicity cannot be determined using conventional chemical analysis strategies, as these methods only quantify a restricted list of target analytes. Conventional sediment TIE methods are also limited because they can only distinguish between broad categories of contaminants, which increase the chance that the true cause of toxicity may be obscured by the presence of other compounds. A promising approach is to separate a chemical extract of the sediment into multiple fractions based on polarity or other characteristics, which are then tested for toxicity. This approach is useful for verifying that a presumed toxicant is present in the toxic fraction and also for isolating previously unknown toxicants. This method is particularly useful for determining whether new or emerging contaminants are of concern at the study site.

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LIST OF ACCRONYMS

BCA	Benthic Community Analysis
BRI	Benthic Response Index
Bight'98	Southern California Bight 1998 Regional Marine Monitoring Survey
BPJ	Best Professional Judgment
BPTCP	Bay Protection and Toxic Cleanup Program
BSAF	Biota-Sediment Accumulation Factors
BTAG	Biological Technical Assistance Group
CNRSW	Commander Navy Region Southwest
CoPC	Contaminants of Potential Concern
CSM	Conceptual Site Model
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DQO	Data Quality Objectives
EPA	Environmental Protection Agency
ERL	Effects Range Low
ERM	Effects Range Median
ERMQ	Effects Range Median Quotient
GC/ECD	Gas Chromatograph/Electron Capture Detector
GC/MS	Gas Chromatograph/Mass Spectrometer
HMWPAH	High Molecular Weight PAH
HPLC	High-Pressure Liquid Chromatography
HQ	Hazard Quotient
LMWPAH	Low Molecular Weight PAH
LOE	Line of Evidence
MSD	Minimum Significant Difference
NASSCO	National Steel and Shipbuilding Company
NAVSTA	Naval Station San Diego
NPDES	National Pollutant Discharge Elimination System
PAH	Polynuclear Aromatic Hydrocarbons
PCB	Polychlorinated biphenyls
PEL	Probable Effects Level
PELQ	Probable Effects Level Quotient
PPB	Parts per billion
PPM	Parts per million
PPPAH	Priority Pollutant PAH
PPT	Parts per thousand
RSD	Relative Standard Deviation
QA/QC	Quality Assurance/Quality Control
SAP	Sampling and Analysis Plan
SCCWRP	Southern California Coastal Water Research Project
SDRWQCB	Regional Water Quality Control Board, San Diego Region
SIM	Selective Ion Monitoring
SQG	Sediment Quality Guideline
SSC-SD	SPAWAR Systems Center San Diego

SWRCB	State Water Resources Control Board
TCHLOR	total Chlordane
TDDT	total DDT
TEL	Threshold Effects Level
THS	Toxic Hot Spot
TIE	Toxicity Identification Evaluation
TMDL	Total Maximum Daily Load
TOC	total Organic Carbon
TPAH	total PAH
TPCB	total PCB
TRV	Toxicity Reference Values
TSL	Tissue Screening Level
UCL	Upper Confidence Limit
WOE	Weight of Evidence

1.0 INTRODUCTION

This report describes results of the final component in a three-part investigation into the potential impairment of beneficial uses at the mouths of Chollas Creek and Paleta Creek (also known as Seventh Street Channel) where they enter San Diego Bay (Figure 1-1). The investigation was prompted by the designation of the mouths of Chollas Creek and Paleta Creek as toxic hot spots by the Regional Water Quality Control Board, San Diego Region (SDRWQCB), based on chemical contamination of sediments and aquatic life impacts. The SDRWQCB also initiated development of a Total Maximum Daily Load (TMDL) assessment to address potential source reduction requirements at these two sites.

Each of the three parts of the investigation was designed to support a three phased program to assess impacts, develop TMDLs, and conduct remediation activities at the sites (Figure 1-2). The goal of the first part of the investigation was to conduct a comprehensive weight of evidence (WOE) evaluation of the impairment of aquatic life beneficial uses as well as a screening level evaluation of wildlife and human health beneficial uses at both sites (SCCWRP and SPAWAR 2004). The goal of the second part was to describe the temporal variability in sediment quality at the Chollas and Paleta Creek sites in order to identify reliable indicators of impairment (Brown and Bay 2005). The goal of the final part of the study was to use sediment toxicity identification evaluation (TIE) procedures to ascertain the chemical constituents responsible for the toxicity observed in the previous two phases of the study. The results of the TIE investigation are described in this report, along with recommendations for further study.

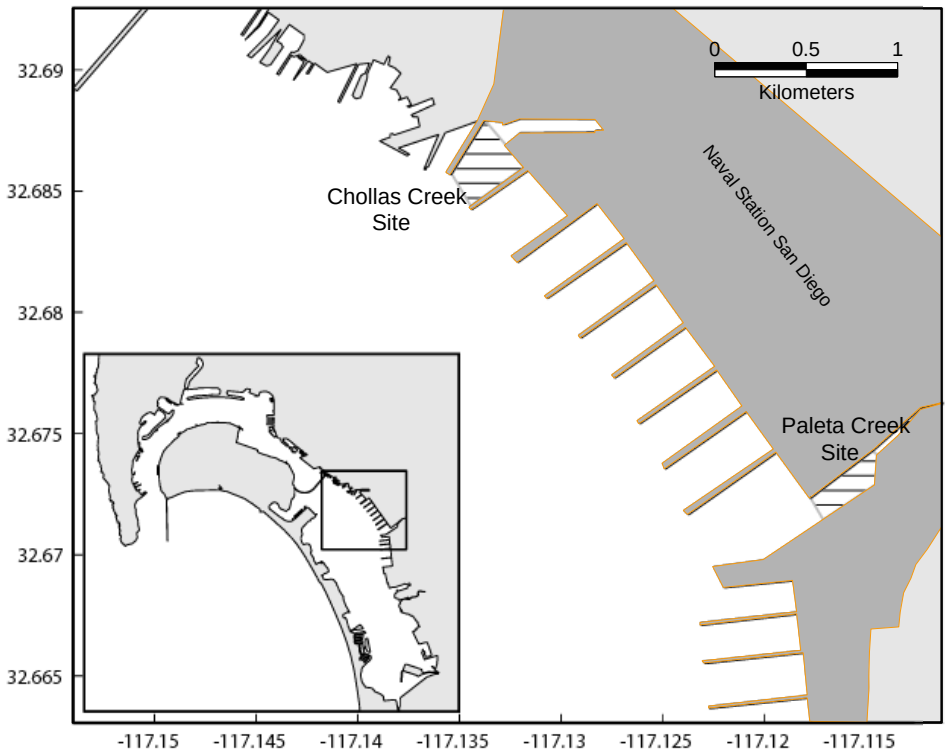

Figure 1-1. Location of Chollas Creek and Paleta Creek Toxic Hot Spot strata (crosshatch areas) designated under the Bay Protection Toxic Cleanup Program (Fairey et al. 1996).

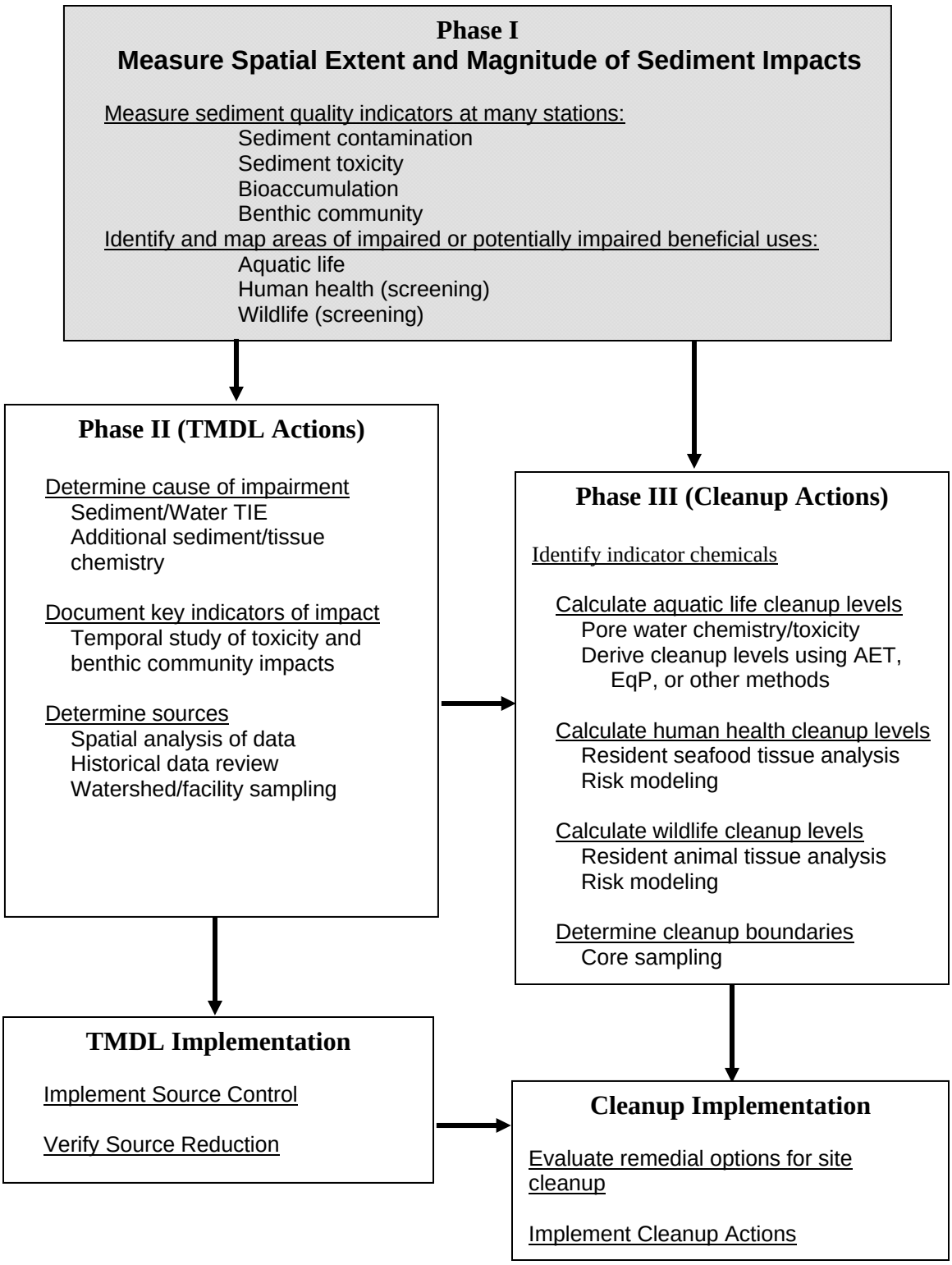

Figure 1-2. Phased sampling and analysis approach showing the relationship of the TIE investigation to potential TMDL and cleanup activities at the study sites.

2.0 TECHNICAL APPROACH

The technical approach taken for this study was to apply TIE methods to samples from stations that had shown toxicity during the spatial study. Three rounds of TIE testing were performed, one on samples taken in 2001 during the spatial study, one on samples taken in 2002 during the temporal study and the final set of samples collected in 2004. In each case, initial toxicity tests were performed on the samples to verify that there was sufficient toxicity present to warrant conducting a TIE.

Concentrations of a suite of metals, PAHs, PCBs, and chlorinated pesticides were measured in the bulk surface (0 to 2.5 cm) sediment. These sediment chemical contamination measurements were used to document the magnitude of sediment contamination in each sample. For the 2004 samples, a larger suite of organic chemicals was measured that included organophosphorus and pyrethroid pesticides.

Acute and sublethal toxic effects of bulk sediment, pore water, and contaminants fluxing across the sediment-water interface were measured using a variety of tests. Acute toxicity was assessed by measuring survival of the amphipod crustacean, *Eohaustorius estuarius,* after 10 days of exposure to bulk sediment or pore water. The presence of sublethal effects and potential impacts of contaminated sediments on the water column was assessed by measuring the effects of a 3-day exposure to water from the sediment-water interface on sea urchin (*Strongylocentrotus purpuratus*) embryo development.

TIE treatments that are well established for use with aqueous marine samples were used on the porewater or sediment-water interface samples (U.S. EPA 1996). Modifications of published methods for reducing the toxicity of metals and organics in whole sediment were also used (Lebo et al. 1999, Burgess et al. 2000, Ho et al. 2000). For the final sampling, in addition to established methods, some more novel approaches to toxicity removal were applied to both porewater and whole sediment samples.

3.0 METHODS

3.1 SITES

Samples were collected at three different times during the course of the project: July 2001, October 2002, and April 2004. The samples tested in July 2001 were part of the larger sampling effort for the Phase I spatial study. Stations C01 and C14 which were found to be toxic to amphipods during that part of the study were further tested using toxicity identification techniques on both the sediment and pore water using the amphipods. Station CP2433 was also tested as a reference location (Figure 3-1).

The samples tested in October 2002 were part of the temporal study. Based on results from the initial toxicity testing of these samples, stations C10 and P17 were chosen for TIE testing using the sediment-water interface method on developing sea urchin embryos. Stations C14, P11 and P17 were selected for whole sediment TIE testing using amphipods (Figure 3-1).

Based on the consistency with which toxicity was observed during the spatial and temporal sampling programs six stations were selected for testing in April 2004. Stations CP2433, C10, C13, C14, P11 and P17 were screened for initial whole sediment toxicity testing using amphipods. Following the initial testing, stations CP2433, C13 and P11 were chosen for TIE testing on both the whole sediment and pore water using amphipods (Figure 3-1).

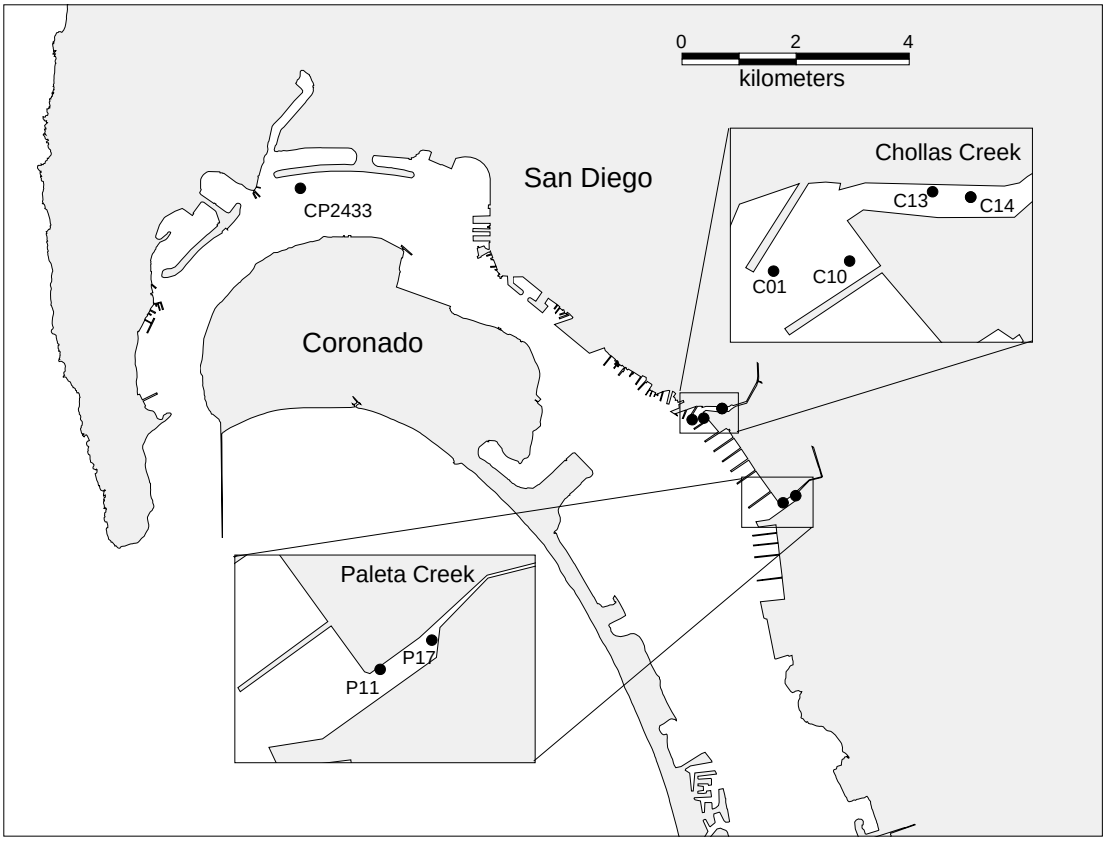

Figure 3-1. All sites tested for sediment TIEs in July 2001, October 2002 and April 2004.

3.2 BULK SEDIMENT

Sampling and Preparation

Sediment samples were collected using a modified Van Veen grab. Sediment from multiple grabs at each station was composited and homogenized by placing it in a large plastic bowl and manually stirring with a plastic spoon. Large shells, rocks, or other large debris were manually excluded from the samples. Subsamples for sediment chemistry and whole sediment toxicity were taken from the homogenized composite sample. The samples for chemistry were frozen at –20 °C until analyzed. Samples for sediment toxicity and grain size were stored at 5 °C until analyzed.

For the October 2002 sampling, an Ocean Instruments Inc. multicorer was used to collect sediment cores at all sites for use in the sediment-water interface toxicity test. This corer was used because its design produces intact cores with little or no disturbance to the very top surface layer of sediment. The multicorer takes four simultaneous cores up to 30 cm in length. The cores are taken approximately at the corners of a square pattern that is about 25 cm on a side. The corer was set to collect cores with a nominal length of ~20 cm so that about 10 cm of overlying water would still be present. Though most cores collected were about 20 cm, core lengths varied from 6 to 29 cm. Once the multicorer was recovered, the four cores were removed, their outsides rinsed with site water and the ends sealed with plastic endcaps. The end caps were secured with vinyl tape. The cores were placed into coolers with specially built holders to maintain them in an upright position and kept cool until arrival at the toxicology laboratory for analysis.

Toxicity Testing

The amphipod survival test was used to evaluate the toxicity of bulk sediment. The amphipods, *Eohaustorius estuarius*, were collected from Yaquina Bay near Newport, Oregon. The animals were held in the laboratory on their native sediment for up to a week before testing began. Except for the initial samples from July 2001, the sediments were press sieved through a 2 mm stainless steel screen to remove macroinvertebrates and debris. The whole sediment tests were conducted in 250 ml glass beakers containing approximately 40 mL of sediment and 160 mL of water. Ten amphipods were added to each beaker and were exposed for 10 days. The overlying water had a salinity of 20 g/kg, the beakers were gently aerated and the exposures were conducted at 15 °C with a photoperiod of 16 h light and 8 h dark. The beakers were monitored daily for visible changes to the sediment or death of the animals. At the end of the exposure period, the sediment from the beakers was passed through a 0.5 mm sieve to recover the animals. The number of surviving animals was recorded. Samples of amphipod home sediment were tested as negative controls. Water quality parameters (temperature, pH, dissolved oxygen, ammonia, and salinity) were measured on the pore water and overlying water of surrogate beakers at both the beginning and end of the exposure period.

The preparation of the sediment-water interface (SWI) test samples was conducted according to the procedures described by Anderson et al. (1996). The toxicity of the SWI samples was tested using the purple sea urchin development test (U. S. Environmental Protection Agency 1995). This test measures the ability of the sea urchin embryos to develop normally from a fertilized egg in test media. The purple sea urchins

(*Strongylocentrotus purpuratus*) used in the tests were collected from the intertidal zone in northern Santa Monica Bay.

To test a SWI sample, the overlying water in each of the four core tube replicates was first replaced with clean seawater. Aeration was then applied to the core tubes. Four replicate cores were used for each sediment type. After equilibration for 24 h, a polycarbonate cylinder with a fine mesh screen bottom (screen tube) was placed on the sediment inside the core tube. Two controls were included in the test: a screen tube blank (screen tube placed in a beaker of seawater) and a core tube blank (core containing only seawater). Four replicates of each control were tested. Fertilized sea urchin eggs were then added to the screen tube and given 72 hr to develop at 15°C. After the exposure period, the screen tubes were removed from the core tube and the outside rinsed to remove any adhering sediment. The embryos were then rinsed into glass shell vials and preserved in formalin. Each sample was examined using a microscope to determine the percentage of normally developed embryos. Water quality parameters (temperature, pH, dissolved oxygen, ammonia, and salinity) were measured on the overlying water at both the beginning and end of the exposure period.

Sediment TIE manipulations were performed on the whole sediment from each station for both samplings using methods based on recent research (Lebo et al. 1999, Burgess et al. 2000). While the objective of the sediment TIEs is to remove toxicity, as in the aqueous samples, alternate methods must be used because of the sediment matrix. Five different manipulations were performed on each sample. To one aliquot of sediment, cation exchange resin (ResinTech SIR-300) was added at a concentration of 20% by weight to bind cationic metals. To a second aliquot, coconut charcoal was added at a concentration of 15% by weight to bind organics. After addition of the modifying agent for each treatment, the sample was stirred vigorously with a glass rod for 1 minute. The third treatment consisted of adding clean home sediment to a third aliquot at a concentration of 20% by weight. This treatment was used to test for any dilution or aeration effect that the other treatments might be having on the sample. With the exception of the dilution treatment, these methods were used on sediment samples from all three sampling events. For the July 2001 samples, the dilution test was not performed; instead an aliquot of sediment was vigorously stirred with a glass rod in the same manner as the other treatments. This stirring procedure was termed the aeration treatment.

A novel treatment based on Supercritical Fluid Extraction (SFE) was used on the whole sediment samples from the April 2004 collection. This method has previously been used for the extraction of sediment for organic chemical analysis. The process involves the extraction of the sample with carbon dioxide at very high pressure causing the gas to act as a liquid and leaving behind no solvent residue as in conventional organic extracts. Supercritical carbon dioxide (unmodified) will remove n-alkanes and other nonpolar compounds. Supercritical carbon dioxide with a methanol modifier will additionally increase the removal of high molecular weight compounds from the sediment (Librando et al. 2004). The sediments to be extracted by SFE must first be freeze-dried. An aliquot of freeze-dried sediment was tested for toxicity to determine if freeze-drying alone had an effect. Sediment samples from all three April stations were extracted with the methanol modifier. Due to time constraints, only the sample from C13 was extracted by unmodified SFE. For all the samples the extracts were collected into hexane and stored at 4°C. Prior to toxicity testing, the sediments were re-hydrated with DI water, placed in beakers with overlying seawater and allowed to equilibrate overnight before

addition of the animals. The samples were then tested for toxicity using the amphipod survival method described above.

The SFE extractor consisted of a 10-mL stainless steel extraction cartridge, layered from the bottom with a glass fiber filter, 4 mm of granular copper (20–30 mesh), 1.5 cm glass wool, and a final glass fiber filter on top of the glass wool to separate the sample from the copper. The extraction was performed using an SFX-220 Supercritical Fluid Extraction System (ISCO, Lincoln, NE) with heated restrictors. Samples were subject to a 10-min static extraction, followed by a 30-mL dynamic extraction, at 50 °C and 450 atm, with the restrictors at 80 °C (Librando et al. 2004). The modified samples were spiked just prior to extraction with 300 μL of optimal grade methanol.

Another treatment that was only used for the April 2004 samples was the addition of piperonyl butoxide (PBO) to the overlying water of the whole sediment exposure. PBO inhibits the enzymes within the amphipods that activate organophosphorus pesticides, thus rendering them nontoxic. The PBO was added to the overlying water to achieve a concentration of 500 µg/L.

For the October 2002 event, TIEs were performed on samples from the sediment-water interface. The TIE manipulations were conducted on overlying water that was removed from the core tubes after the initial sea urchin development test was terminated. Overlying water from all the replicates within each station was composited to provide sufficient volume for testing. The overlying water was then tested in a similar manner to the pore water as described below.

3.3 PORE WATER

Sampling and Preparation

Pore water was obtained from the homogenized whole sediment sample by centrifuging an aliquot at 3000 X g for 30 minutes. Pore water was extracted the day before toxicity testing and was stored at 5 °C.

Toxicity Testing

The amphipod survival test was used to evaluate the toxicity of pore water. The pore water tests were conducted in glass vials containing 10 mL of sample at a temperature of 15 °C. The experiment was conducted under 24 h dark conditions. Five amphipods were added to each vial for an exposure period of 10 days. Three to five replicates were tested for each sample. At the end of the exposure period, the number of amphipods surviving in each vial was counted. Notes on survival were also made after 4 and 7 days of exposure. The samples were tested at the ambient salinity (approximately 30 g/kg); laboratory water at both 20 and 33 g/kg salinity were tested as negative controls.

Phase I TIE procedures were performed on the pore water samples using methods adapted from the U.S. EPA (1996). The purpose of the Phase I TIE is to characterize the general category of the toxicants (e.g., whether they resemble metals or organics). Ethylenediaminetetraacetic acid (EDTA), a chelator of metals, was added to produce a concentration of 60 mg/L in the test samples. Sodium thiosulfate (STS), a treatment that reduces oxidants such as chlorine and also decreases the toxicity of some metals, was added to a final concentration of 50 mg/L to separate portions of each sample. PBO

was added to a total concentration of 500 µg/L to another aliquot of sample. The final treatment consisted of passing an aliquot of pore water through a Varian Mega Bond Elut C-18 solid phase extraction column in order to remove nonpolar organic compounds.

These treatments were given at least one hour to interact with the sample before the animals were added. After treatment, the pore water samples were tested for toxicity using the amphipod survival test. The effectiveness of the TIE treatments was determined by comparing the test results to the initial toxicity results (usually conducted several days before TIE testing to verify the presence of toxicity) and baseline toxicity results (untreated sample tested concurrently with the TIE treatments). A sample of laboratory seawater was subjected to each of the TIE treatments as a blank to assure that the manipulations were not themselves causing toxicity.

3.4 CHEMISTRY

Since the samples for this project were collected over three years in conjunction with different project segments, three different laboratories or groups of laboratories performed the analytical chemistry. The methods used by each laboratory differed and are presented below.

July 2001

Sediment samples were analyzed for grain size by Battelle's Sequim, WA laboratory. Samples were analyzed for grain size according to the methods of Plumb (1981). Sand and gravel are measured by weight after sieve analysis. The fine fraction is stirred and aliquots taken to determine the percent silt (0.0625 mm to 0.0039 mm) and clay (<0.005 mm) using hydrometers as described in ASTM D-422.

Sediment samples were analyzed for metals at Battelle's Sequim, WA laboratory. Samples were digested using a strong acid (total metals) digestion technique (NOAA 1998). All metals, except mercury, selenium, and silver, were analyzed by either inductively coupled plasma mass spectrometry (ICPMS) following EPA method 200.8 or inductively coupled plasma atomic emission spectroscopy (ICPAES) method 200.7. Silver was analyzed by graphite furnace atomic absorption (GFAA) method 200.9. Mercury was analyzed by cold vapor atomic absorption (CVAA) following modified EPA Method 245.5. Selenium was analyzed by hydride atomic absorption (HAA).

All organic chemical analysis of sediment samples was performed at Arthur D. Little Inc.'s (ADL) Cambridge, MA laboratory. Sediment samples were extracted for semivolatile organic compounds per ADL's standard operating procedure ADL-2819. The extraction procedure allowed for the simultaneous extraction of PAHs, PCBs, and chlorinated pesticides. The method uses sonication, an orbital shaker, and centrifugation. The sample extracts were analyzed for PAHs per ADL's standard operating procedure ADL-2827. ADL's PAH analysis method is a modified version of EPA's SW-846 Method 8270. The gas chromatograph/mass spectrometer (GC/MS) was operated in selective ion monitoring (SIM) mode to obtain the desired sensitivity. The extracts were analyzed for PCB congeners per ADL's SOP ADL-2818. This method was used to simultaneously measure chlorinated pesticides. ADL's PCB congener analysis method is a modified version of EPA's SW-846 Method 8081. The extracts were analyzed for chlorinated pesticides simultaneously with PCB per ADL's SOP ADL-2818.

October 2002

All physical and chemical sediment parameters from the October 2002 sampling event were analyzed by Columbia Analytical (Kelso, WA). Samples were analyzed for grain size according to the methods of Plumb (1981). Sand and gravel are measured by weight after sieve analysis. The fine fraction is stirred and aliquots taken to determine the percent silt (0.0625 mm to 0.0039 mm) and clay (<0.005 mm) using hydrometers as described in ASTM D-422.

Samples were digested using a strong acid (total metals) digestion technique (NOAA 1998). All metals, except Hg and Ag were analyzed using either ICPMS following EPA method 200.8 or ICPAES Method 200.7. Mercury was analyzed by CVAA following modified EPA method 245.5. Silver was analyzed by GFAA method 200.9. Selenium was analyzed by HAA.

Sediments were extracted for PAHs using EPA method 3541: Automated Soxhlet Extraction. The sample extracts were analyzed for PAHs using a modified version of EPA's SW-846 Method 8270. The gas chromatograph/mass spectrometer (GC/MS) was operated in selected ion monitoring (SIM) mode to obtain the desired sensitivity. Samples were extracted for PCBs with EPA method 3540C: soxhlet extraction, and analyzed using a modified version of EPA's SW-846 Method 8082. Samples were extracted for chlorinated pesticides with EPA method 3540C: soxhlet extraction, and analyzed using a modified version of EPA's SW-846 Method 8081A.

April 2004

Sediment grain size measurements were made by ABC Laboratories (Ventura, CA) using a Horiba laser particle size analyzer. All metal and organic analysis on the sediment and water samples was performed by CRG Marine Laboratories (Torrance, CA).

Trace metals were digested from the sediments using EPA method 6020: strong acid digestion using microwave. The samples were analyzed by ICPMS. Trace metals were extracted from the pore water by using EPA method 1640: APDC and FePD chelation. The extracts were analyzed by means of EPA method 200.8 on ICPMS.

Acid-Volatile Sulfides/Simultaneously Extracted Metals (AVS/SEM) were measured on the sediment samples. In this procedure the sediment is acidified and the volatiles produced are captured and analyzed colorimetrically for sulfides. The acid extract is analyzed directly by ICPMS for metals.

Samples were extracted for PAHs, PCBs and chlorinated pesticides by EPA Method 3540C soxhlet extraction, and the extracts were analyzed by EPA's SW-846 Method 8270.

Laboratory blanks were processed and analyzed with each batch of samples. All samples for organic analysis were spiked with recovery surrogates.

4.0 RESULTS

4.1 JULY 2001 SAMPLES

Toxicity

Review of the spatial survey toxicity results led to three stations being chosen for TIE analysis, a reference station (CP2433) and two stations from the Chollas Creek study site (C01 and C14). The results of the baseline testing concurrent with the TIE testing found that only station C14 exhibited toxicity in either the pore water or whole sediment (Figure 4-1). There was no survival of the amphipods in the baseline whole sediment exposure to sediment from C14, and a mean survival of 25% in the pore water.

The results of the whole sediment TIE procedure found that only the addition of coconut charcoal reduced the toxicity of sediment from C14 (Figure 4-2). The addition of the carbon source was very effective, with survival increasing from 0% in the untreated sediment to 100% in the treated sample. This indicates that organic chemicals are the likely cause of toxicity in this sediment sample.

The results of the TIE treatments to the pore water indicated that both the addition of EDTA and extraction with the C-18 column removed nearly all of the toxicity (Figure 4-3). This result indicates that a mixture of metals and organics caused the toxicity. However, previous studies have found that the C-18 column is capable of binding metals to cause a reduction in the toxicity of a sample. Thus, the role of organics as a cause of the porewater toxicity in this sample is uncertain.

Sediment Chemistry

Analysis of sediment characteristics found that the two Chollas stations had similar grain size, but that C14 had much higher total organic carbon (TOC) (Table 4-1). Station CP2433 had considerably coarser grained sediment and much lower TOC than the other two stations.

The metals concentrations of the two Chollas stations were a factor two or more greater than CP2433 for most contaminants of interest (Table 4-2). The concentrations of contaminants were compared to the effects range medium values (ERM) above which adverse effects on the benthic environment are likely to occur (Long et al. 1995). However, the ERM was not exceeded for any of the metals at any of the stations.

The concentrations of organic constituents at the two Chollas stations were about an order of magnitude higher than at the reference station (Tables 4-3 to 4-5). The ERM for total DDTs (46.1 µg/Kg) was exceeded by more than a factor of two at Station C14. The ERM for total PCBs (180 µg/Kg) was exceeded at both Chollas stations. Every PAH in the measured suite was detected at both the Chollas stations, but the ERM for total PAHs (44,792 µg/Kg) was not exceeded at either station.

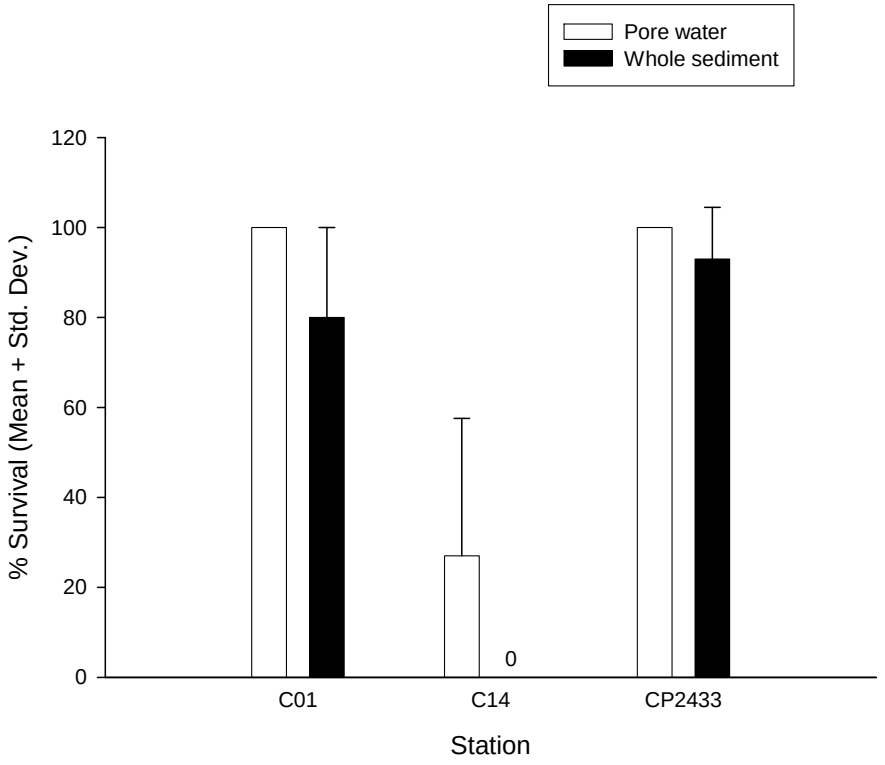

Figure 4-1. Results of baseline *Eohaustorius* 10 day exposures to pore water and whole sediment samples from San Diego Bay in July 2001.

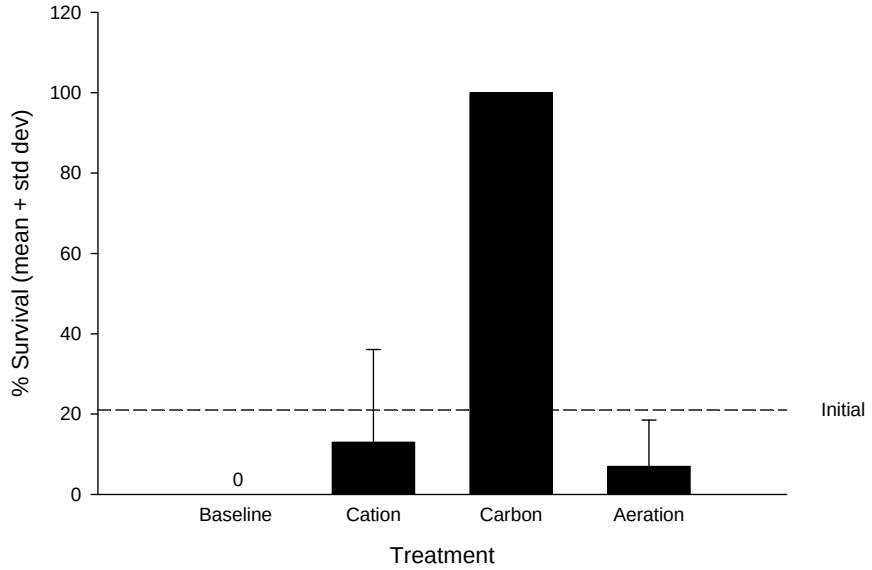

Figure 4-2. Results of whole sediment TIE treatments from station C14 using *Eohaustorius* 10 day exposures in July 2001.

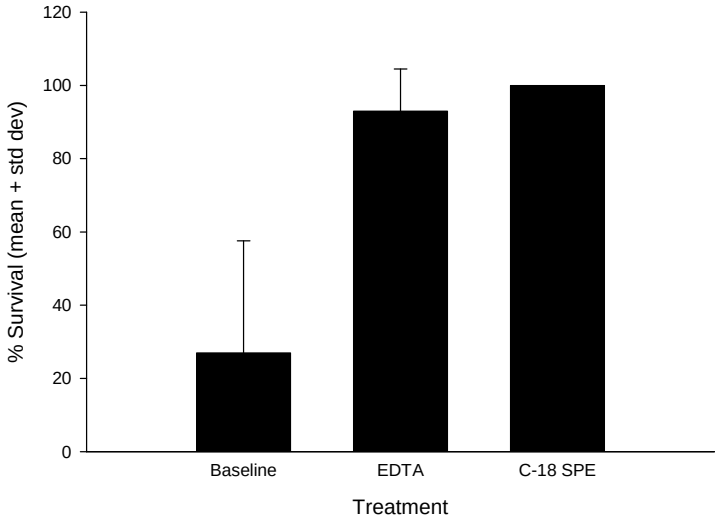

Figure 4-3. Results of pore water TIE treatments from station C14 using *Eohaustorius* 10 day exposures in July 2001.

Table 4-1. General sediment characteristics of TIE samples from San Diego Bay collected in July 2001.

Parameter (%)	CP2433	C01	C14
Gravel	NA[1]	0	0
Sand	NA	35	20
Silt	NA	32	40
Clay	NA	33	40
Fines	38	65	80
TOC	0.5	1.8	6.1

1 = Not analyzed.
2 = sum of silt and clay fractions.

Table 4-2. Sediment metals concentrations of San Diego Bay TIE samples collected in July 2001. All concentrations are expressed as mg/kg dry weight.

Constituent	ERM	CP2433	C01	C14
Aluminum		73900	73800	71700
Antimony		0.561	2.81	2.66
Arsenic	70	5.55	11.8	9.41
Barium		527.5	483	477
Beryllium		1.12	1.28	1.17
Cadmium	9.6	0.288	0.428	1.37
Chromium	370	42.15	56	51.6
Copper	270	43.3	139	94.9
Iron		29950	41000	41900
Lead	218	23.25	77.3	103
Mercury	0.71	0.2505	0.419	0.235
Nickel	51.6	11.15	17.5	22.8
Selenium		0.18	0.346	0.45
Silver	3.7	0.3845	0.703	0.461
Zinc	410	114.5	235	347

Table 4-3. Sediment pesticide concentrations of San Diego Bay TIE samples collected in July 2001. All concentrations are expressed as µg/kg dry weight.

Constituent	ERM	CP2433	C01	C14
gamma-Chlordane		0.39[j]	17	65
alpha-Chlordane		0.18[j]	12	54
2,4'-DDE		0.29[u]	0.2[u]	4
4,4'-DDE	27	1.1	15	51
2,4'-DDD		0.22[j]	2.5	9.8
4,4'-DDD		0.34[j]	5.5	25
2,4'-DDT		0.18[j]	2.5	13
4,4'-DDT		0.11[j]	3.2	20
total DDTs*	46.1	1.95	28.71	122.8

U = Non-detected, the value is the MDL.
J = The value was estimated because it is below the reporting limit but above the detection limit.
* = All non-detects were given the value 0 to calculate the total DDTs.

Table 4-4. Sediment PCB concentrations of San Diego Bay TIE samples collected in July 2001. All concentrations are expressed as µg/kg dry weight.

Constituent	CP2433	C01	C14
PCB18	0.51	0.65	0.1[u]
PCB28	0.5	1.4	3.5
PCB37	0.58	3.3	8.2
PCB44	0.41	4.7	14
PCB49	0.38	2.9	6
PCB52	0.52	3.2	5.6
PCB66	0.68	2.9	5.4
PCB70	0.64	3.8	5.8
PCB74	0.41	2.8	9.7
PCB81	0.4	2.1	4
PCB77	0.64	6.0	4.9
PCB87	0.31	3.0	2.6
PCB99	0.91	5.1	6.6
PCB101	1.4	11	9.6
PCB105	0.72	5.1	5.4
PCB110	0.83	11	10
PCB114	0.16	4.1	17
PCB118	1.5	11	8.3
PCB119	0.072[j]	1.2	3.9
PCB123	0.83	2.7	3.0
PCB126	0.12[u]	0.079[u]	0.1[u]
PCB128	0.37	3.2	2.4
PCB138	2.6	18	9.6
PCB149	1.2	4.4	6.9
PCB151	0.59	4.0	6.3
PCB153	3.0	20	10
PCB156	0.26	3.1	0.1[u]
PCB157	0.054[j]	0.86	0.37
PCB158	0.64	6.0	13
PCB167	0.35	3.1	1.2
PCB168	0.12[u]	0.079[u]	0.1[u]
PCB169	0.12[u]	0.079[u]	0.1[u]
PCB170	0.77	5.5	2.2
PCB177	0.58	4.4	9.3
PCB180	1.2	9.9	4.5
PCB183	0.42	3.4	2.2
PCB187	1.1	6.6	3.3
PCB189	0.054[j]	0.31	0.1[u]
PCB194	0.35	3.2	1.3
PCB201	0.61	3.6	4.0
PCB206	0.21	2.0	1.5
total PCBs*	26.76	189.49	211.57

U = Non-detected, the value is the MDL.
J = The value was estimated because it is below the reporting limit but above the detection limit.
* = All non-detects were given the value 0 to calculate the total PCBs.

Table 4-5. Sediment PAH concentrations of San Diego Bay TIE samples collected in July 2001. All concentrations are expressed in µg/kg dry weight.

Constituent	ERM	CP2433	C01	C14
Naphthalene	2100	3.1	10	35
C1 Naphthalene		3.1	6.5	30
C2 Naphthalene		6.0	9.9	71
C3 Naphthalene		6.1	15	120
C4 Naphthalene		4.7	19	130
Acenaphthylene	640	6.0	45	34
Acenaphthene	500	1.5[j]	9.2	93
Biphenyl		0.72[j]	3	16
Fluorene	540	3.1	15	120
C1 Fluorene		0.53[u]	9.3	60
C2 Fluorene		0.53[u]	15	130
C3 Fluorene		7.5	55	280
Anthracene	1100	18	130	300
Phenanthrene	1500	21	110	600
C1 Phenanthrene/anthracene		18	81	370
C2 Phenanthrene/anthracene		16	81	530
C3 Phenanthrene/anthracene		10	77	510
C4 Phenanthrene/anthracene		26	180	560
Dibenzothiophene		1.4[j]	8.6	59
C1 Dibenzothiophene		2.2[j]	12	87
C2 Dibenzothiophene		5.1	30	230
C3 Dibenzothiophene		5.1	50	350
Fluoranthene	5100	78	360	1800
Pyrene	2600	89	520	1500
C1 Fluoranthene/pyrene		66	390	720
C2 Fluoranthene/pyrene		34	240	520
C3 Fluoranthene/pyrene		16	160	400
Benzo[a]anthracene	1600	58	260	520
Chrysene	2800	86	440	840
C1 Chrysene		32	210	510
C2 Chrysene		19	190	550
C3 Chrysene		15	180	570
C4 Chrysene		9.1	120	400
Benzo[b]fluoranthene		140	930	850
Benzo[k]fluoranthene		51	290	210
Benzo[e]pyrene		72	480	510
Benzo[a]pyrene	1600	90	510	450
Perylene		24	150	190
Indeno[1,2,3,-c,d]pyrene		62	350	340
Dibenzo[a,h]anthracene	260	14	94	84
Benzo[g,h,i]perylene		59	360	480
total PAHs*	44792	1166	7105	15433

U = Non-detected, the value is the MDL.
J = The value was estimated because it is below the reporting limit but above the detection limit.
* = All non-detects were given the value 0 to calculate the total PAHs.

4.2 OCTOBER 2002 SAMPLES

Toxicity

Results from the initial whole sediment toxicity tests showed no effects at stations CP2433 and P11, a small reduction in survival at station C10, but more substantial toxicity at C14 and P17 (Figure 4-4). Based on these results, whole sediment TIE treatments were performed on samples from C14 and P17, with P11 used as a reference point for the treatments. The TIE procedure found that the addition of carbon had a substantial effect on reducing toxicity at C14 and also increased survival at P11 and P17 (Figure 4-5), suggesting that nonpolar organics were present in toxic amounts. Some increase in survival was also produced by the cation exchange resin treatment for all three stations. However, survival in the dilution treatment was also increased by a similar amount, indicating that the beneficial effect of the cation resin treatment was likely caused by physical modification of the sediment (e.g., dilution and mixing) associated with resin addition.

The initial sediment-water interface test with the sea urchin embryo development endpoint identified toxicity only at C10 and P17 (Figure 4-6). Both stations had high variability between replicates. TIE treatments were performed on the water overlying the sediment in the core tubes from both stations. However, the baseline testing performed concurrently with the TIEs found there to be no toxicity present and the experiment was therefore inconclusive (Figure 4-7).

Sediment chemistry

Grain size analysis of the sediments indicated that CP2433 and P11 were similar and were less than 50% fines. The remaining stations all had finer grain sediment with C14 being greater that 90% fines (Table 4-6). Total organic carbon (TOC) measurements were not made on any of the samples from this collection.

Stations C14 and P17 had the highest concentrations of most of the metallic contaminants, followed by C10, then P11 and CP2433 (Table 4-7). The ERM for zinc (410 mg/Kg) was exceeded at both C14 and P17. The laboratory that performed the analyses for chlordanes and DDTs was unable to achieve detection limits that were as low as those for the July 2001 samples. Therefore, all the values fell below either the detection limit or reporting limit (Table 4-8). The PCB values for CP2433 were similar to those found in July 2001. Station C14 PCB concentrations were about 25% lower than those reported in July 2001, but again this may be due to the difference in detection limits. Station P17 had the highest concentration of total PCBs (Table 4-9). While detection limits for PAHs were again higher than for the 2001 samples, most of the analytes were detected at the Chollas and Paleta stations. The PAH concentrations for CP2433 and C14 were similar to those reported in July 2001. Station P17 had the highest PAH concentration followed by C14 and P11. CP2433 had a PAH concentration an order of magnitude or more lower than the other stations (Table 4-10).

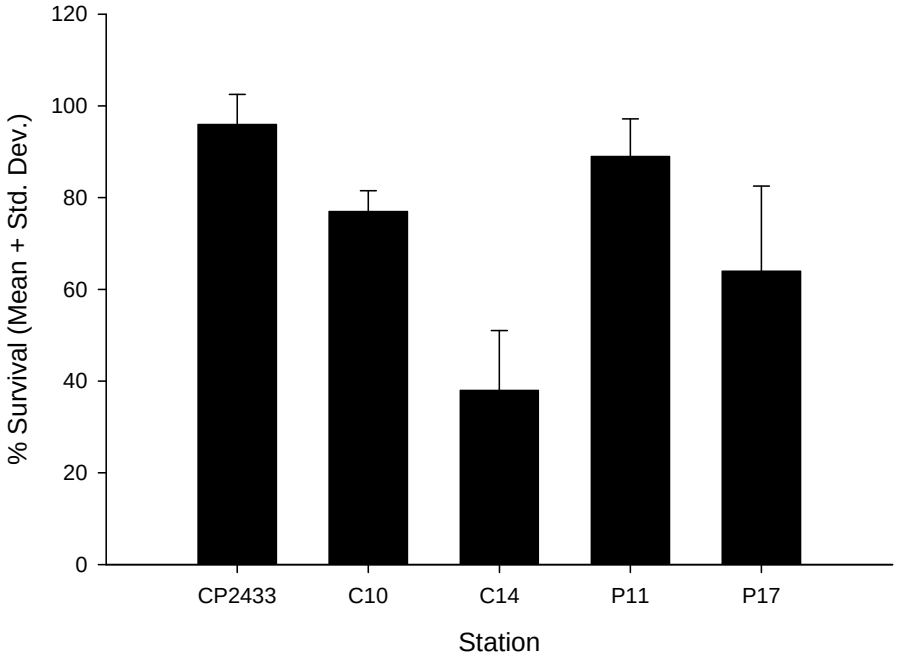

Figure 4-4. Results of initial 10 day *Eohaustorius* exposure to whole sediments from San Diego Bay stations collected in October 2002.

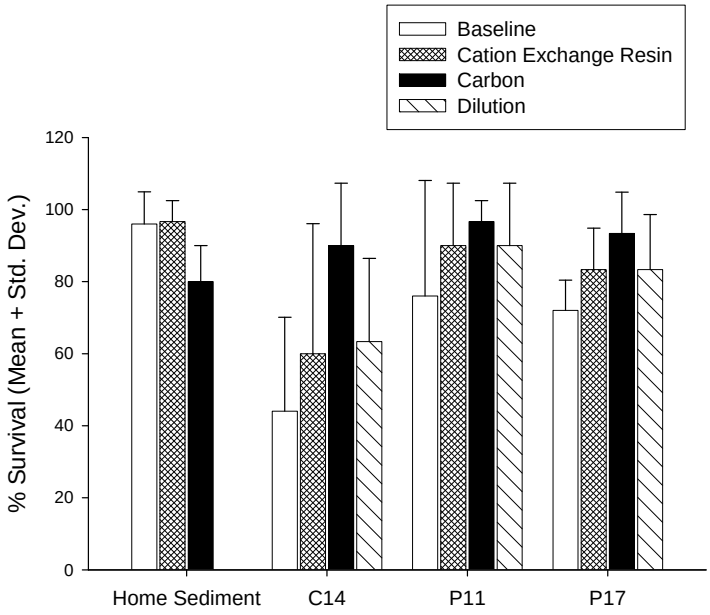

Figure 4-5. Results of whole sediment TIE on San Diego Bay stations collected in October 2002 using the 10 day *Eohaustorius* test.

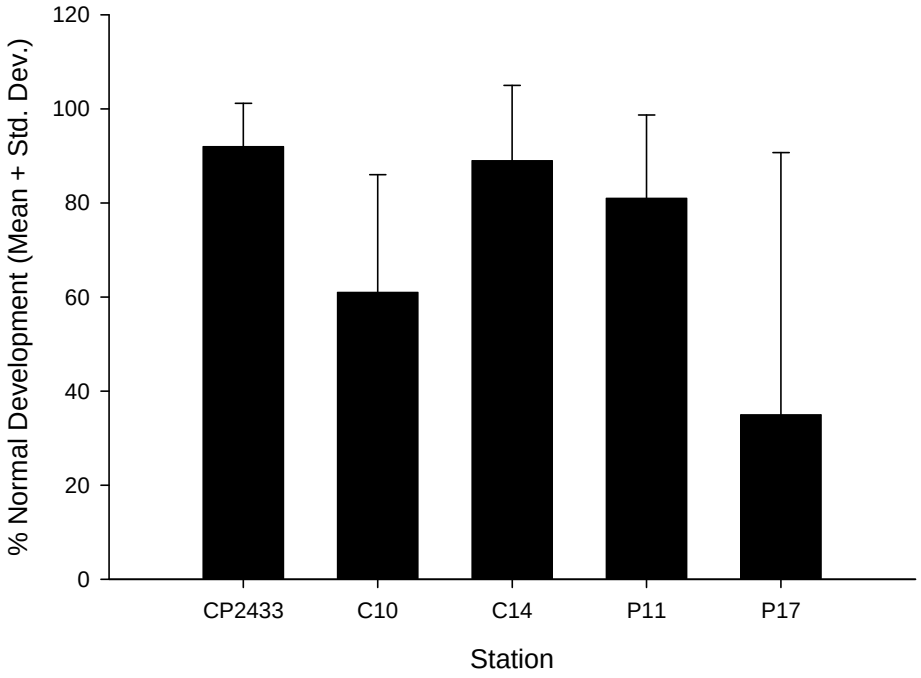

Figure 4-6. Results of initial sediment-water interface exposure to developing sea urchin embryos from San Diego Bay stations collected in October 2002.

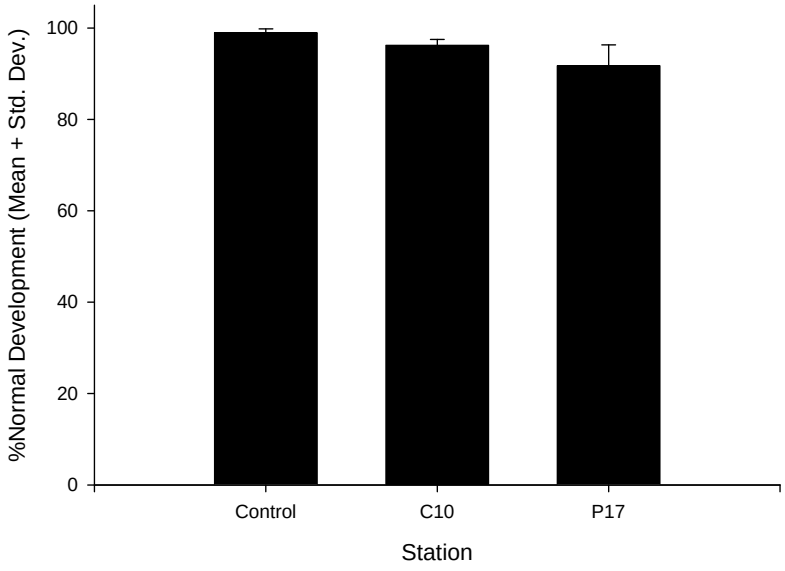

Figure 4-7. Results of baseline sea urchin embryo development test on overlying water from sediment-water interface tests of San Diego Bay stations in October 2002.

Table 4-6. General sediment characteristics of TIE samples from San Diego Bay collected in October 2002.

Parameter (%)	CP2433	C10	C14	P11	P17
Gravel	0	1	0	0	0
Sand	55	34	9	53	22
Silt	11	28	21	18	24
Clay	34	38	70	26	54
Fines	45	67	91	44	78
TOC	NA	NA	NA	NA	NA

NA = not analyzed

Table 4-7. Sediment metals concentrations of San Diego Bay TIE samples collected in October 2002. All concentrations are expressed in mg/kg dry weight.

Constituent	CP2433	C10	C14	P11	P17
Aluminum	13500	22300	27800	19600	25500
Antimony	5.5	8.6	5.5	6.1	7.6
Arsenic	4.5	8.0	9.1	5.6	8.2
Barium	62.3	93.9	151	92.5	126
Cadmium	0.5	0.9	1.9	1.1	1.9
Chromium	28.6	49.5	40.7	42.5	55.3
Copper	47.8	163	119	134	228
Iron	18100	28300	32500	25500	32100
Lead	20.3	84	107	65	136
Manganese	151	184	206	178	219
Mercury	0.22	0.49	0.16	0.48	0.54
Nickel	8.8	16.5	19.7	12.3	20.7
Selenium	0.6	0.6	0.8	1	1.1
Silver	1.9	2.0	1.1	1.2	1.6
Tin	7.1	15.4	15.8	19.5	6.9
Zinc	114	245	543	246	497

Table 4-8. Sediment pesticide concentrations of San Diego Bay TIE samples collected in October 2002. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C10	C14	P11	P17
gamma-Chlordane	2.6^{u}	6.0^{u}	31^{j}	7.2^{j}	16^{j}
alpha-Chlordane	1.9^{u}	4.4^{u}	34^{j}	4.0^{u}	10^{j}
2,4'-DDE	0.85^{u}	2.0^{u}	24^{j}	1.8^{u}	28^{j}
4,4'-DDE	4.3^{u}	10^{u}	27^{j}	5.9^{j}	24^{j}
2,4'-DDD	0.56^{u}	16^{j}	55^{u}	19^{j}	21^{j}
4,4'-DDD	2.7^{u}	6.2^{u}	8.3^{u}	5.6^{u}	7.2^{u}
2,4'-DDT	2.6^{u}	41^{u}	55^{u}	5.4^{u}	27^{u}
4,4'-DDT	3.0^{u}	6.9^{u}	55^{u}	6.3^{u}	8.0^{u}
total DDTs*	0	16	51	24.9	73

U = Non-detected, the value is the MDL.

J = The value was estimated because it is below the reporting limit but above the detection limit.

* = All non-detects were given the value 0 to calculate the total DDTs

Table 4-9. Sediment PCB concentrations of San Diego Bay TIE samples collected in October 2002. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C10	C14	P11	P17
PCB18	0.092[u]	1.1j	0.39[j]	0.93	0.93[j]
PCB28	0.13[u]	0.94[j]	1.4	2.1	2.4
PCB37	0.094[u]	0.11[u]	0.15[u]	0.93	0.13[u]
PCB44	0.17[j]	1.7	3.2	2.2	3.9
PCB49	0.19[u]	2.9	2.5	4.1	3.9
PCB52	0.38[j]	3.9	3.8	4.8	5.7
PCB66	0.31[j]	2.3	2.3	3.5	4.7
PCB70	0.87[u]	2.3	2.3	3.7	5.2
PCB74	0.13[u]	0.15[u]	3.1[u]	1.7	2.6
PCB81	0.75[u]	0.17[u]	4.9[u]	3.8	0.19[u]
PCB77	0.87[u]	1.1[u]	1.4[u]	0.93	1.2[u]
PCB87	0.29[j]	3.3	5.5[u]	4.6	13
PCB99	0.55[u]	4.7	2.6	4.9	5.5
PCB90/101	0.14[u]	8.5	0.81[u]	8.7	12
PCB105	0.073[u]	0.086[u]	0.12[u]	5.5	0.10[u]
PCB110	0.87[u]	8.8	1.4[u]	9.7	15
PCB114	0.87[u]	1.1[u]	1.4[u]	0.93	1.2[u]
PCB118	0.79[j]	8.2	4.6	7.5	11
PCB119	0.87[j]	0.19[u]	0.26[u]	0.93	0.22[u]
PCB123	0.87[j]	1.1[u]	1.4[u]	1.9	2.0[u]
PCB126	0.87[j]	1.1	0.17[u]	0.93	0.15[u]
PCB128	0.87[j]	3.0	1.4[u]	2.4	5.5
PCB138	0.98	13	12	9.7	16
PCB149	0.87[j]	7.7	4.1	9.9	13
PCB151	0.87[j]	2.8	0.37[u]	2.9	5.1
PCB153	1.2	12	6.1	12	17
PCB156	0.87[j]	2.2	1.4[u]	1.8	4.9
PCB157	0.87[j]	1.1[u]	1.4[u]	0.93	1.2[u]
PCB158	0.87[j]	0.2[u]	0.26[u]	1.5	1.9[u]
PCB167	0.87[j]	1.1[u]	1.5[u]	1.1	2.5[u]
PCB168	0.87[j]	1.1[u]	1.5[u]	0.93	1.2[u]
PCB169	0.87[j]	3.8[u]	3.5[u]	0.93	6.4[u]
PCB170	0.33[j]	3.4	1.8	3.5	6.0
PCB177	0.073[u]	2.0	0.12[u]	2.1	3.5
PCB180	0.58[j]	6.6	3.6	7.7	13
PCB183	0.17[j]	1.6	1.1[j]	1.6	3.1
PCB187	0.45[j]	4.7	2.0	5.9	7.6
PCB189	0.34[u]	0.40[u]	2.6[u]	0.93	0.46[u]
PCB194	0.085[u]	2.8	1.4[u]	3.3	2.2[u]
PCB201	0.87[u]	1.1[u]	1.4[u]	0.93	2.8
PCB206	0.23[u]	1.4	0.79[j]	4.5	0.32[u]
total PCBs*	16.06	112.94	54.58	148.8	183.33

U = Non-detected, the value is the MDL.
J = The value was estimated because it is below the reporting limit but above the detection limit.
* = All non-detects were given the value 0 to calculate the total PCBs

Table 4-10. Sediment PAH concentrations of San Diego Bay TIE samples collected in October 2002. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C10	C14	P11	P17
Naphthalene	1.7[j]	6.9[j]	20	11	14
2-Methylnaphthalene	0.99[j]	3.8[j]	18	6.3[j]	11[j]
1-Methylnaphthalene	0.55[j]	1.8[j]	8.8[j]	2.6[j]	4.8[j]
C2 Naphthalene	8.7[u]	11[u]	61	14	27
C3 Naphthalene	8.7[u]	11[u]	120	14	72
C4 Naphthalene	8.7[u]	15	120	110	120
Acenaphthylene	3.0[j]	35	47	69	60
Acenaphthene	0.96[j]	4.9[j]	46	13	15
Biphenyl	0.65[j]	2.5[j]	10[j]	3[j]	5.3[j]
Fluorene	1.7[j]	9.9[j]	81	23	25
C1 Fluorene	8.7[u]	11[u]	63	29	12[u]
C2 Fluorene	8.7[u]	16	160	59	99
C3 Fluorene	8.7[u]	11[u]	280	320	630
Anthracene	8.7[u]	110	340	160	230
Phenanthrene	16	88	370	120	190
C1 Phenanthrene/anthracene	13	100	320	140	270
C2 Phenanthrene/anthracene	13	95	430	260	340
C3 Phenanthrene/anthracene	9.2	84	500	400	810
C4 Phenanthrene/anthracene	8.7[u]	11[u]	310	350	790
Dibenzothiophene	0.91[j]	6.1[j]	53	10	20
C1 Dibenzothiophene	8.7[u]	11[u]	91	9.3[u]	12[u]
C2 Dibenzothiophene	8.7[u]	11[u]	230	110	12[u]
C3 Dibenzothiophene	8.7[u]	11[u]	320	270	620
Fluoranthene	59	270	2000	910	1200
Pyrene	59	440	1800	1600	1700
C1 Fluoranthene/pyrene	44	570	1100	1500	1600
Dibenzofuran	1.0[j]	4.7[j]	39	11	15
Benzo[a]anthracene	40	320	720	490	750
Chrysene	63	690	1100	920	1300
C1 Chrysene	36	550	720	900	1100
C2 Chrysene	33	470	720	700	1000
C3 Chrysene	12	190	450	240	440
C4 Chrysene	8.7[u]	92	290	120	250
Benzo[b]fluoranthene	66	950	960	1400	1900
Benzo[k]fluoranthene	47	690	590	890	1200
Benzo[e]pyrene	47	630	680	830	1200
Benzo[a]pyrene	63	890	750	1200	1500
Perylene	15	190	200	260	360
Indeno[1,2,3,-c,d]pyrene	54	530	540	580	870
Dibenzo[a,h]anthracene	10	110	110	140	200
Benzo[g,h,i]perylene	49	420	630	410	690
total PAHs*	759.6	8586	17398	15594.7	21628

U = Non-detected, the value is the MDL.
J = The value was estimated because it is below the reporting limit but above the detection limit.
* = All non-detects were given the value 0 to calculate the total PAHs

4.3 APRIL 2004 SAMPLES

Toxicity

Initial testing on the whole sediment from the April 2004 sampling found that stations C13, C14 and P11 had less than 40% survival for the 10 day amphipod exposure. Stations C10 and P17 had slight reductions in survival compared to the reference station (Figure 4-8). Given that one of the objectives for this sampling period was to perform a TIE from each of the creek areas, stations C13 and P11 were chosen to do both whole sediment and porewater TIEs, even though C14 had a lower survival rate than P11. Sediment and pore water from station CP2433 was also tested as a reference.

The baseline test results for the porewater and whole sediment TIEs showed agreement in the degree of toxicity for two of the stations. Survival for CP2433 was greater than 80% for both the porewater and whole sediment exposures, and there was no survival of the amphipods in either the sediment or pore water for C13 (Figure 4-9). However for station P11, the survival in whole sediment was less than 30%, while the survival in the pore water was greater than 90%.

The whole sediment TIE for station CP2433 showed that all of the treatments had survival very similar to the baseline (Figure 4-10). This is an indication that the treatments themselves were not causing toxicity. The addition of PBO to the overlying water in the whole sediment tests did not reduce toxicity for stations C13 and C14, suggesting that organophosphorus pesticides were not contributing to the observed effects (Figures 4-11 and 4-12).

Two TIE treatments of C13 sediment increased survival over the baseline value. Addition of coconut carbon increased survival to nearly 100% and the SFE extraction with addition of the methanol modifier increased survival to about 30%, but with high variability between replicates (Figure 4-11). Since the sediment had to be freeze-dried before the SFE extraction, a sample of the freeze-dried, but otherwise unmanipulated sediment was tested to determine if the sample preparation affected the toxicity. Other than a slight increase in toxicity in the P11 sample, freeze-drying had no effect on the toxicity of the sediment samples. Both the charcoal and SFE treatments are expected to reduce the amount of organic chemicals that are bioavailable. Since the unmodified SFE (no methanol added) did not reduce toxicity, the indication is that the organic chemicals causing toxicity are likely to be found in the higher molecular weight fraction. The SFE treatment with no methanol removes non-polar, lower molecular weight organic compounds. When the methanol is added to the SFE extraction, more polar and higher molecular weight compounds are removed.

Both the carbon and cation treatments slightly reduced the toxicity of P11 sediment (Figure 4-12). The dilution treatment also had a similar effect, indicating that the improvements observed for the carbon and cation treatments were likely just artifacts of sediment preparation. Extraction by SFE with methanol modifier had the most profound effect, increasing survival to greater than 80% (Figure 4-12). These results were similar to those obtained for C13 and indicate that high molecular weight organics may be a primary cause of toxicity.

Station C13 was the only sample that had any toxicity in the baseline porewater tests (Figure 4-9). Of the four TIE treatments applied to C13, only the C-18 column extraction had a small increase in survival after 10 days of exposure (Figure 4-13). Examination of survival during the test showed that the C18 treatment produced a greater reduction in

toxicity during the first four days of the exposure period (Figure 4-14). As time progressed, all of the C13 treatments converged toward zero survival. These results indicate that organic chemicals played a role in the porewater toxicity at station C13, but that the C18 treatment was only partially effective. The partial effectiveness may have been caused by several factors: a high concentration of the toxicant that exceeded the capacity of the C18 column, poor efficiency of the C18 column to remove the toxicant, or the presence of other types of toxicants that are not removed by the C18 treatment. The high mortality rate for C13 may be due in part to the very high ammonia values that were associated with the pore water from this station. The total ammonia value for the baseline C13 sample started at 22 mg/L and increased to 26 mg/L by the end. While the initial and final ammonia concentration for P11 was 5.5 and 7.2 mg/L, and CP2433 was 6.8 and 13.7 mg/L, respectively.

The daily survival counts for stations CP2433 and P11 and the laboratory blanks showed little change over the course of the exposure for most of the TIE treatments (Figures 4-15 to 4-17). An exception was the PBO treatment, which reduced survival in all of the samples, including the blanks. These results indicate that the PBO treatment may have caused some toxicity to the amphipods, which complicates the interpretation of the data.

Sediment chemistry

The physical parameters for the stations were similar to what had been measured previously, except that the grain size at P11 was somewhat finer than was observed in the October 2002 sample (Tables 4-6 and 4-11). The relatively high TOC concentration at C13 is consistent with the high ammonia values measured in pore water from this station.

A larger suite of chlorinated organic compounds was analyzed for this sampling and lower detection limits were achieved. Total DDT concentrations were below the ERM value at all stations (Table 4-12). Of the remaining chlorinated pesticides, only the two chlordanes and nonachlor were detected.

Station P11 exhibited the highest concentrations of most of the metals with the ERM exceeded for zinc (Table 4-13). No ERM exceedances were found for Station C13 and Station CP2433 had the lowest values for most constituents. The analysis of acid volatile sulfides and simultaneously extracted metals (AVS/SEM) showed that on a molar basis, the AVS exceeded the SEM at all three stations (Table 4-14). Samples having a greater AVS concentration than SEM are considered to not have bioavailable concentrations of metals.

PCBs were only detected at P11 (Table 4-15) and the concentration there was considerably lower than found in previous samples from this station. While measurable concentrations of PAHs were found at all three stations, again these levels were much lower than observed in previous samples (Table 4-16). No organophosphorus or pyrethroid pesticides were detected at the stations (Table 4-17).

Dissolved metals were measured on the pore water from all three stations. The patterns of concentrations in the pore water usually differed from those observed in the whole sediment (Table 4-18). For example, there was nearly an order of magnitude difference in the lead concentration between stations CP2433 and P11 for the whole sediment (Table 4-13), yet the concentration in the pore water was very similar for all three stations. The relative concentrations of copper among the stations also differed between the sediment and porewater samples. Also, while the zinc concentrations in the whole

sediment samples were fairly high, the pore water concentrations were low and below the level where toxicity would be expected. The recommended National water quality criterion maximum concentration for copper (4.8 µg/L) was exceeded at all three stations. The criterion for lead (210 µg/L) and mercury (1.8 µg/L) was exceeded at CP2433 and P11.

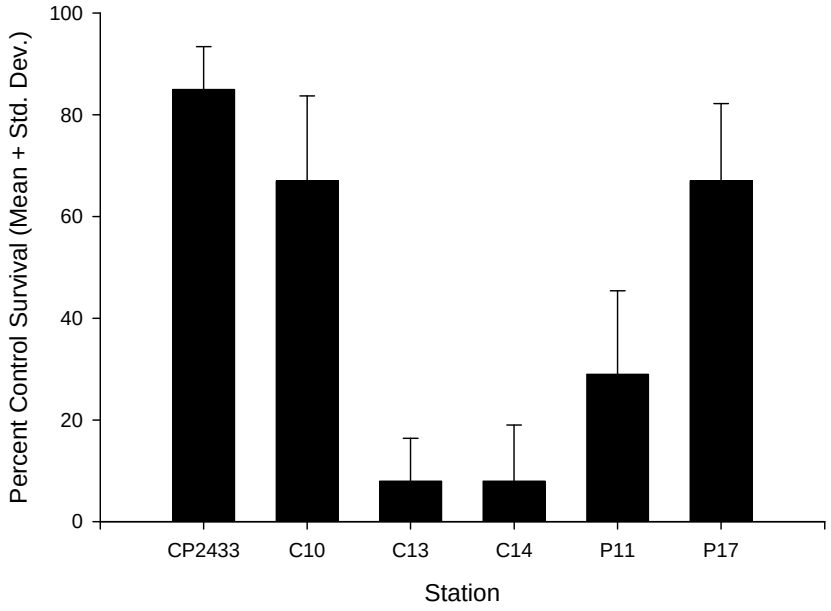

Figure 4-8. Results of initial 10 day *Eohaustorius* exposure to whole sediment from San Diego Bay stations collected in April 2004.

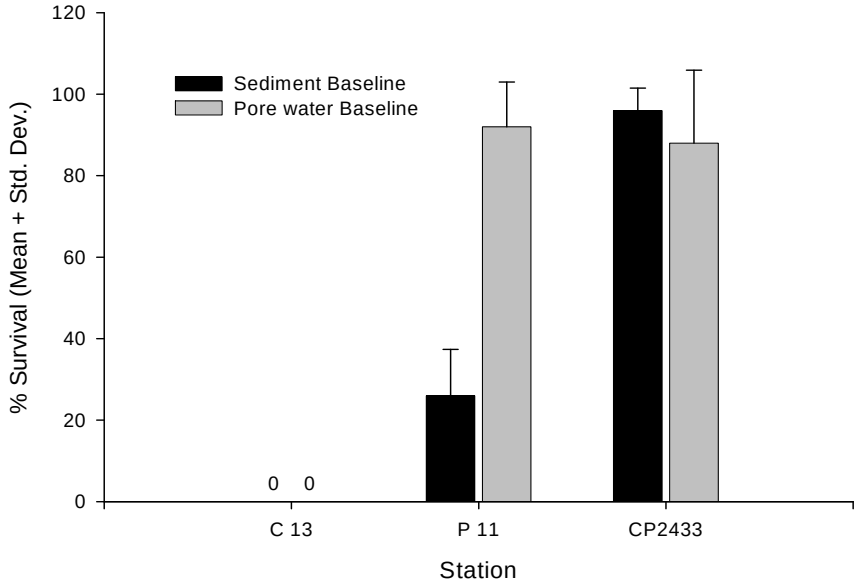

Figure 4-9. Results of baseline 10 day *Eohaustorius* exposure to whole sediment and pore water concurrent with TIEs from San Diego Bay stations in April 2004.

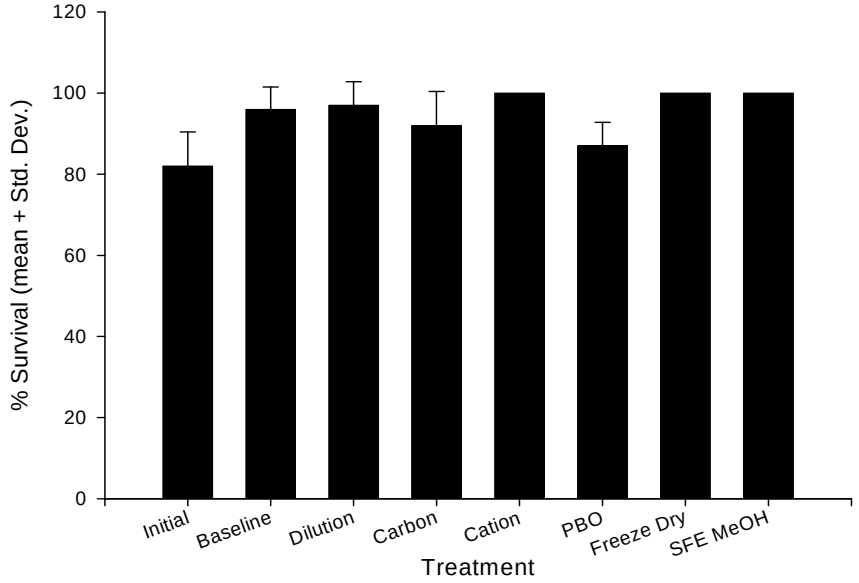

Figure 4-10. Results of whole sediment TIE treatments on station CP2433 using 10 day *Eohaustorius* exposure in April 2004.

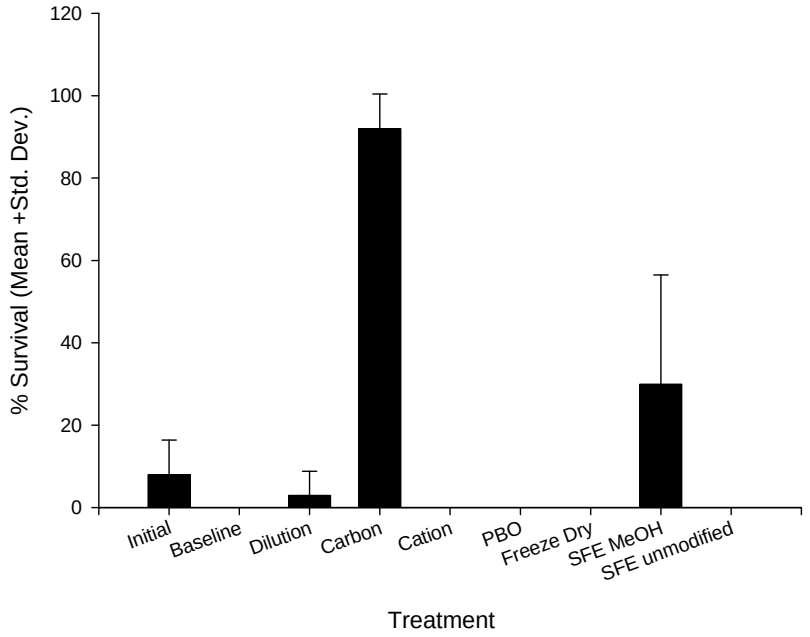

Figure 4-11. Results of whole sediment TIE treatments on station C13 using 10 day *Eohaustorius* exposure in April 2004.

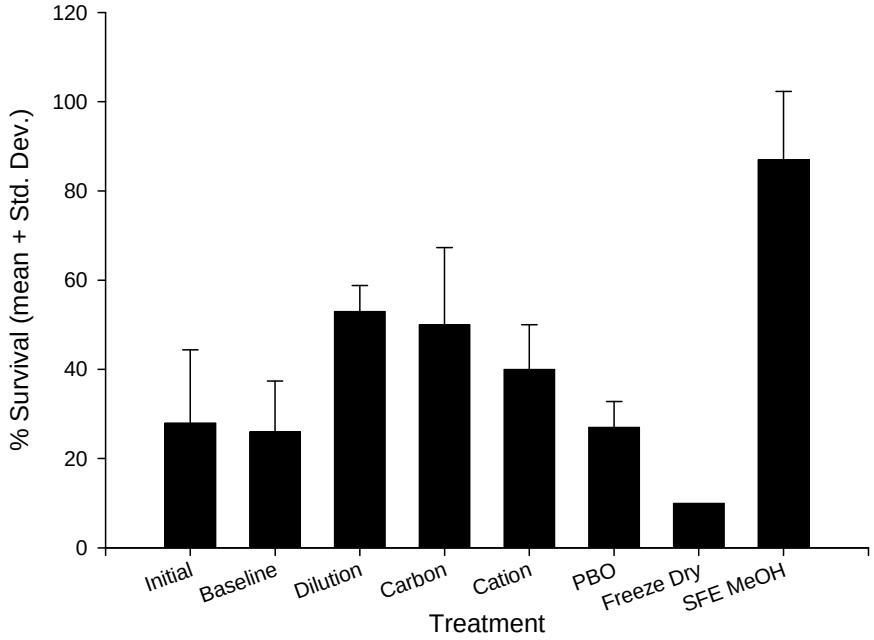

Figure 4-12. Results of whole sediment TIE treatments on station P11 using 10 day *Eohaustorius* exposure in April 2004.

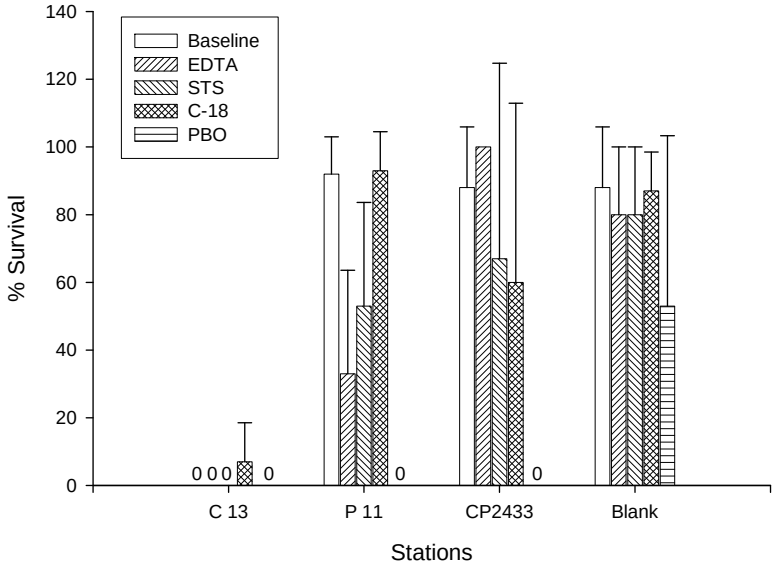

Figure 4-13. Results of pore water TIE treatments on San Diego Bay stations using 10-day *Eohaustorius* exposure in April 2004.

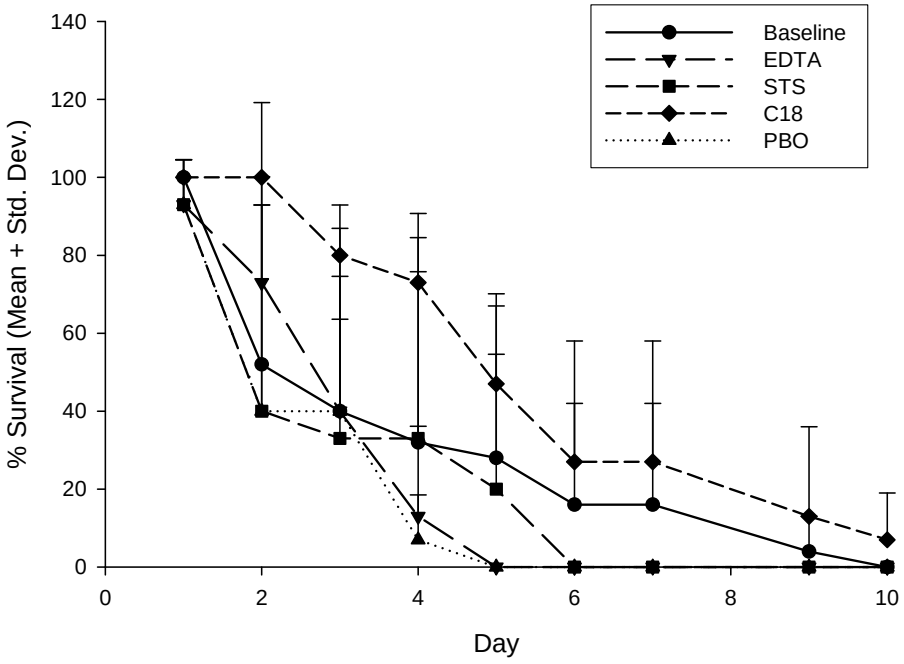

Figure 4-14. Survival of amphipods in the pore water TIE treatments over time for station C13 in April 2004.

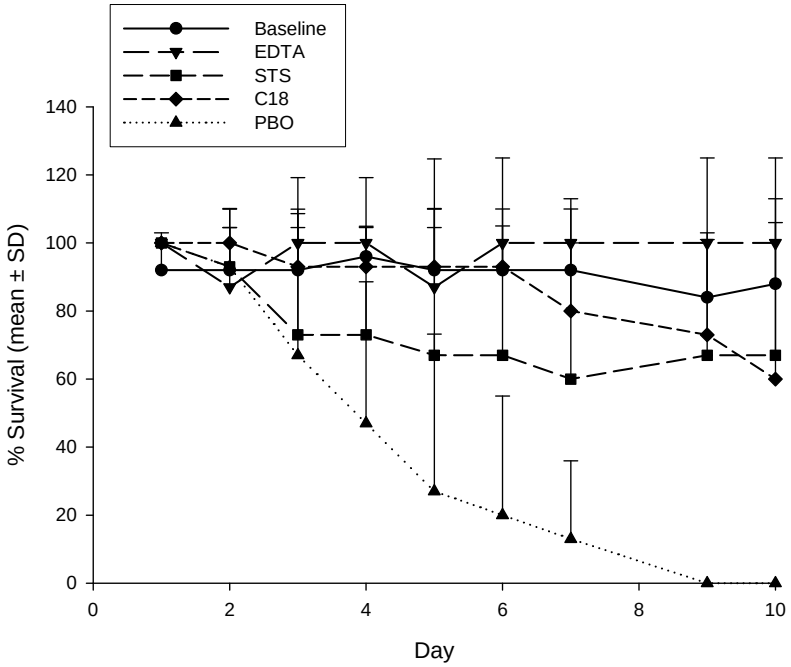

Figure 4-15. Survival of amphipods in the pore water TIE treatments over time for station CP2433 in April 2004.

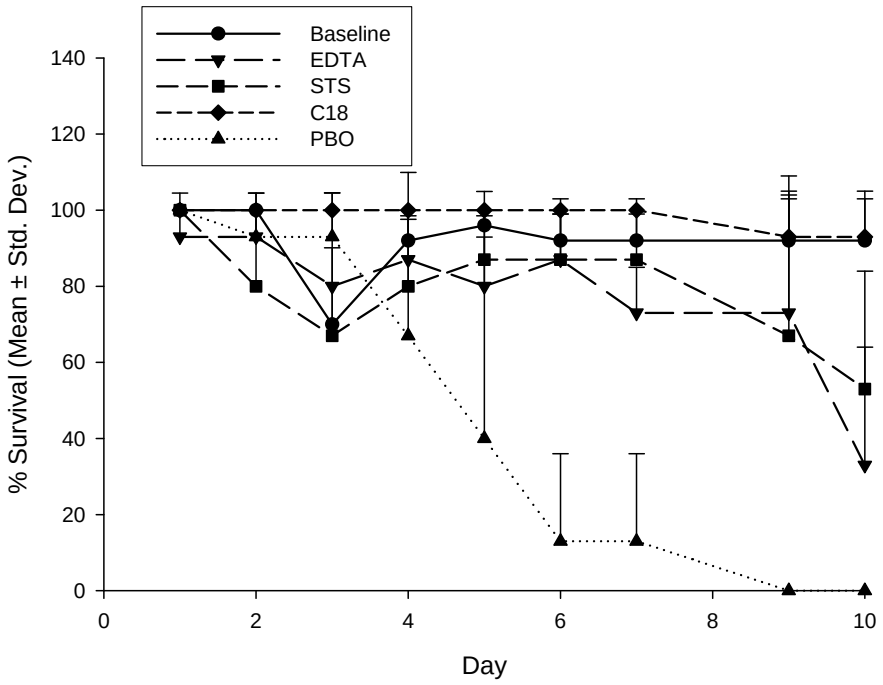

Figure 4-16. Survival of amphipods in the pore water TIE treatments over time for station P11 in April 2004.

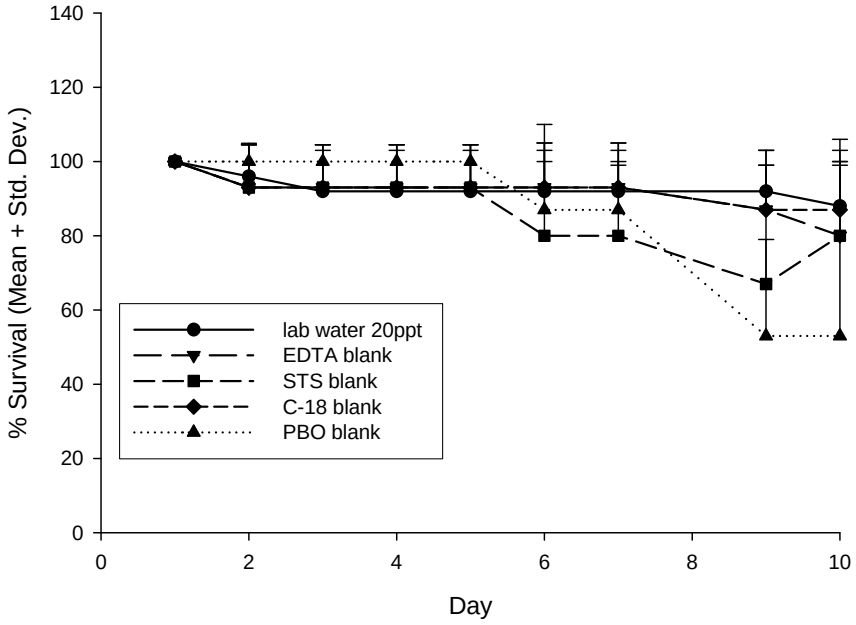

Figure 4-17. Survival of amphipods in the pore water TIE treatments over time for the water only control and blank samples in April 2004.

Table 4-11. General sediment characteristics of TIE samples from San Diego Bay collected in April 2004.

Parameter (%)	CP2433	C13	P11
Gravel	0	0	0
Sand	57	51	27
Silt	36	44	59
Clay	7	5	13
Fines	43	49	62
TOC	0.60	3.99	1.77

Table 4-12. Sediment pesticide concentrations of TIE samples from San Diego Bay collected in April 2004. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C13	P11
2,4'-DDD	1[u]	1[u]	1[u]
2,4'-DDE	1[u]	4.7	3.6
2,4'-DDT	1[u]	1[u]	1[u]
4,4'-DDD	1[u]	1.4	1[u]
4,4'-DDE	1[u]	5.2	6.3
4,4'-DDT	1[u]	1[u]	1[u]
total DDTs*	0	11.3	9.9
Aldrin	1[u]	1[u]	1[u]
BHC-alpha	1[u]	1[u]	1[u]
BHC-beta	1[u]	1[u]	1[u]
BHC-delta	1[u]	1[u]	1[u]
BHC-gamma	1[u]	1[u]	1[u]
Chlordane-alpha	1[u]	5.2	2
Chlordane-gamma	1[u]	6.0	2.8
DCPA (Dacthal)	1[u]	1[u]	1[u]
Dieldrin	1[u]	1[u]	1[u]
Endosulfan Sulfate	1[u]	1[u]	1[u]
Endosulfan-I	1[u]	1[u]	1[u]
Endosulfan-II	1[u]	1[u]	1[u]
Endrin	1[u]	1[u]	1[u]
Endrin Aldehyde	1[u]	1[u]	1[u]
Heptachlor	1[u]	1[u]	1[u]
Heptachlor Epoxide	1[u]	1[u]	1[u]
Methoxychlor	1[u]	1[u]	1[u]
Mirex	1[u]	1[u]	1[u]
Toxaphene	10[u]	10[u]	10[u]
trans-Nonachlor	1[u]	2.1	1.8

u = Non-detected, the value is the MDL.

* = All non-detects were given the value 0 to calculate the total DDTs

Table 4-13. Sediment metals concentrations of TIE samples from San Diego Bay collected in April 2004. All concentrations are expressed in mg/kg dry weight.

Constituent	CP2433	C13	P11
Aluminum	20100	26800	37700
Antimony	0.24	1.49	3.57
Arsenic	5.37	7.72	9.13
Barium	88	125	128
Beryllium	0.4	0.64	0.79
Cadmium	0.38	1.1	4.18
Chromium	48.7	42.7	98.2
Cobalt	7.53	9.87	12.5
Copper	54	73.7	189
Iron	23000	30200	39500
Lead	23.1	79	175
Manganese	190	223	278
Mercury	0.18	0.08	0.5
Molybdenum	0.66	2.92	3.6
Nickel	10.3	17.9	23.6
Selenium	0.68	1.03	0.84
Silver	0.59	0.66	2.01
Strontium	46.8	62.1	47.3
Thallium	0.33	0.35	0.56
Tin	3.4	5.38	11.9
Titanium	1628	1470	1900
Vanadium	58.4	83.6	99.4
Zinc	127	347	435

Table 4-14. Sediment AVS and SEM concentrations of TIE samples from San Diego Bay collected in April 2004.

Constituent	CP2433 (μmoles/g)	CP2433 (mg/kg)	C13 (μmoles/g)	C13 (mg/kg)	P11 (μmoles/g)	P11 (mg/kg)
SEM						
Cadmium	0.00160	0.18	0.00712	0.80	0.0139	1.56
Copper	0.393	25	0.00283	0.18	0.00283	0.18
Lead	0.104	21.5	0.240	49.7	0.403	83.5
Nickel	0.0213	1.25	0.0872	5.12	0.0463	2.72
Zinc	1.20	78.6	4.64	303	6.10	399
total SEM	1.72	127	4.98	359	6.57	487
AVS	7.33	235	52.1	1670	10.6	341

Table 4-15. Sediment PCB concentrations of TIE samples from San Diego Bay collected in April 2004. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C13	P11
PCB018	1[u]	1[u]	1[u]
PCB028	1[u]	1[u]	1[u]
PCB031	1[u]	1[u]	1[u]
PCB033	1[u]	1[u]	1[u]
PCB037	1[u]	1[u]	1[u]
PCB044	1[u]	1[u]	1[u]
PCB049	1[u]	1[u]	1[u]
PCB052	1[u]	1[u]	1[u]
PCB066	1[u]	1[u]	1[u]
PCB070	1[u]	1[u]	1[u]
PCB074	1[u]	1[u]	3.2
PCB077	1[u]	1[u]	1[u]
PCB081	1[u]	1[u]	1[u]
PCB087	1[u]	1[u]	1[u]
PCB095	1[u]	1[u]	3.1
PCB097	1[u]	1[u]	1[u]
PCB099	1[u]	1[u]	1.6
PCB101	1[u]	1[u]	4.7
PCB105	1[u]	1[u]	1[u]
PCB110	1[u]	1[u]	3
PCB114	1[u]	1[u]	1[u]
PCB118	1[u]	1[u]	1[u]
PCB119	1[u]	1[u]	1[u]
PCB123	1[u]	1[u]	1[u]
PCB126	1[u]	1[u]	1[u]
PCB128+167	1[u]	1[u]	1[u]
PCB138	1[u]	1[u]	1[u]
PCB141	1[u]	1[u]	1[u]
PCB149	1[u]	1[u]	3.7
PCB151	1[u]	1[u]	1[u]
PCB153	1[u]	1[u]	4.3
PCB156	1[u]	1[u]	1[u]
PCB157	1[u]	1[u]	1[u]
PCB158	1[u]	1[u]	1[u]
PCB168+132	1[u]	1[u]	1[u]
PCB169	1[u]	1[u]	1[u]
PCB170	1[u]	1[u]	1[u]
PCB177	1[u]	1[u]	1[u]
PCB180	1[u]	1[u]	3.4
PCB183	1[u]	1[u]	1.2
PCB187	1[u]	1[u]	1.8
PCB189	1[u]	1[u]	1[u]
PCB194	1[u]	1[u]	1[u]
PCB200	1[u]	1[u]	1[u]
PCB201	1[u]	1[u]	1[u]
PCB206	1[u]	1[u]	1[u]
total PCBs*	0	0	20

u = Non-detected, the value is the MDL.

* = All non-detects were given the value 0 to calculate the total PCBs

Table 4-16. Sediment PAH concentrations of TIE samples from San Diego Bay collected in April 2004. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C13	P11
1-Methylnaphthalene	1[u]	3	1.6
1-Methylphenanthrene	0.9	14.4	5.3
2,3,5-Trimethylnaphthalene	1[u]	7.6	8.7
2,6-Dimethylnaphthalene	0.5	7.7	5.6
2-Methylnaphthalene	1[u]	5.1	2.3
Acenaphthene	0.7	50.9	7.7
Acenaphthylene	2	12.1	14.9
Anthracene	3.4	42.9	53.1
Benz[a]anthracene	9.2	124	123
Benzo[a]pyrene	20.8	156	347
Benzo[b]fluoranthene	16.4	161	338
Benzo[e]pyrene	14.4	131	281
Benzo[g,h,i]perylene	16.3	121	175
Benzo[k]fluoranthene	19	158	333
Biphenyl	1[u]	3.2	0.3
Chrysene	19.6	226	211
Dibenz[a,h]anthracene	3.6	21.5	46.7
Fluoranthene	13.6	403	186
Fluorene	1[u]	15.2	2
Indeno[1,2,3-c,d]pyrene	15.6	92	179
Naphthalene	1[u]	12.4	1.4
Perylene	4.9	57.5	94.2
Phenanthrene	1[u]	88.5	24.4
Pyrene	15	336	582
total PAHs	183	2250	3023

u = Non-detected, the value is the MDL.

* = All non-detects were given the value 0 to calculate the total PAHs

Table 4-17. Sediment organophosphorus and pyrethroid pesticide concentrations of TIE samples from San Diego Bay collected in April 2004. All concentrations are expressed in µg/kg dry weight.

Constituent	CP2433	C13	P11
OP Pesticides			
Bolstar (Sulprofos)	10[u]	10[u]	10[u]
Chlorpyrifos	5[u]	5[u]	5[u]
Demeton	10[u]	10[u]	10[u]
Diazinon	5[u]	5[u]	5[u]
Dichlorvos	10[u]	10[u]	10[u]
Dimethoate	5[u]	5[u]	5[u]
Disulfoton	10[u]	10[u]	10[u]
Ethoprop (Ethoprofos)	10[u]	10[u]	10[u]
Fenchlorphos (Ronnel)	10[u]	10[u]	10[u]
Fensulfothion	10[u]	10[u]	10[u]
Fenthion	10[u]	10[u]	10[u]
Malathion	1[u]	1[u]	1[u]
Merphos	10[u]	10[u]	10[u]
Methyl Parathion	10[u]	10[u]	10[u]
Mevinphos (Phosdrin)	10[u]	10[u]	10[u]
Phorate	10[u]	10[u]	10[u]
Tetrachlorvinphos (Stirofos)	10[u]	10[u]	10[u]
Tokuthion (Prothiofos)	10[u]	10[u]	10[u]
Trichloronate	10[u]	10[u]	10[u]
Pyrethroids			
Allethrin	10[u]	10[u]	10[u]
Bifenthrin	10[u]	10[u]	10[u]
Cyfluthrin	10[u]	10[u]	10[u]
Cypermethrin	10[u]	10[u]	10[u]
Danitol (Fenpropathrin)	10[u]	10[u]	10[u]
Deltamethrin	10[u]	10[u]	10[u]
L-Cyhalothrin	10[u]	10[u]	10[u]
Permethrin	10[u]	10[u]	10[u]
Prallethrin	10[u]	10[u]	10[u]

u = Non-detected, the value is the MDL.
* = All non-detects were given the value 0 to calculate the total PAHs

Table 4-18. Porewater dissolved metals concentrations of TIE samples from San Diego Bay collected in April 2004. All concentrations are expressed in μg/L.

Constituent	CP2433	C13	P11
Aluminum	0.01[u]	1.03	1.87
Antimony	0.095	0.048	1.1
Arsenic	6.05	39.7	3.41
Barium	0.005[u]	0.005[u]	0.005[u]
Beryllium	0.021	0.033	0.234
Cadmium	0.51	1.52	0.86
Chromium	0.11	0.781	0.082
Cobalt	0.659	0.273	0.637
Copper	22.8	14.6	35.6
Iron	0.005[u]	0.274	0.186
Lead	219	206	217
Manganese	0.005[u]	0.005[u]	0.005[u]
Mercury	12.9	0.206	31.7
Molybdenum	1.02	2.21	1.56
Nickel	0.01[u]	0.01[u]	0.01[u]
Selenium	0.005[u]	0.005[u]	0.005[u]
Silver	0.005[u]	0.005[u]	0.005[u]
Strontium	0.031	0.019	0.005[u]
Thallium	0.457	8.3	1.19
Tin	1.01	5.18	5.15
Titanium	5.87	5.21	5.63
Vanadium	0.01[u]	1.03	1.87
Zinc	0.095	0.048	1.1

u = Non-detected, the value is the MDL.

5.0 DISCUSSION

Toxicity identification evaluations were performed on whole sediments, and/or pore water from six stations within San Diego Bay over a four-year period. A combination of established and novel methods was used in the effort to identify chemicals that were responsible for the observed toxicity at these stations. The toxicity results, when used in combination with the chemical analysis results in a weight of evidence approach, suggest several probable causes of toxicity in the areas near the mouths of Chollas and Paleta Creeks.

Chollas Creek

Toxicity was consistently observed in the whole sediment samples from the Chollas Creek site, especially at stations C13 and C14. These stations had relatively high concentrations of both metal and organic constituents. The TIE treatments on these samples always found that the addition of coconut charcoal greatly improved survival, indicating that organic chemicals were responsible for toxicity (Table 5-1). Additional evidence supporting the identification of organic compounds was the increased survival noted after extraction by methanol modified SFE. Small improvements in survival that were noted with the cation exchange resin were always coupled with similar improvements from the dilution treatment, indicating that metals were not a likely source of toxicity in the whole sediment samples. The lack of any effect with the PBO treatment indicates that organophosphorus pesticides were unlikely to be causing toxicity at station C13 in April 2004.

The sediment chemistry data also support the conclusion that metals are unlikely to be responsible for the observed sediment toxicity to amphipods. The concentration of acid volatile sulfide in C13 sediment was 10 times greater than the amount needed to bind potentially bioavailable divalent metals. The concentrations of dissolved metals in pore water from this station were also below levels expected to be toxic to amphipods. Thus, it is unlikely that metals were a significant contributor to the toxicity at this station. However, the pore water TIE on the C14 sample from July 2001 did show some indication that toxicity was associated with metals (Table 5-2). The process of obtaining the pore water may be the cause of this discrepancy. The physical act of separating the pore water from the sediment may concentrate metals in the pore water that were not available to the animals in the sediment.

It is unclear from the porewater TIE results for C14 whether solely metals or a combination of metals and organics caused the toxicity. Both the EDTA treatment and C-18 extraction were equally effective in reducing the toxicity of the porewater sample. This may indicate that both metal and organic contaminants were causing the porewater toxicity. Alternatively, the toxicity may be only due to metals, since it is known that the C-18 column is effective at binding cationic metals (Schiff et al. 2003). Further work involving extraction of the C-18 columns with organic solvents and acids would be necessary to separate the effects from binding of organic and metal contaminants.

Organic chemicals such as chlordanes, DDTs, PCBs and PAHs were found at the Chollas Creek sites in sufficient quantity to be of concern. This conclusion is based on comparison of the sediment chemistry data for C14 to plots showing the distribution of concentrations in other southern California embayments. The concentration of total chlordanes and total PAHs at C14 in July 2001 was greater than the concentration present in 95% of other locations from southern California with toxic sediments (Figure 5-1). DDT and PCB concentrations at C14 were also relatively high; these

concentrations were greater than 60-80% of the toxic samples from other southern California locations.

Limitations in the data available make it difficult to determine the specific contribution of DDTs, PCBs, PAHs, and chlordane to sediment toxicity at the Chollas Creek site. Sediment effect thresholds that relate to causality are not available for all of these chemicals, so only inferences that are based on sediment quality guidelines and statistical analysis can be made. The SQGQ1 sediment quality guideline value was calculated for the samples (Table 5-3) and the results indicated that the contaminant concentrations present were likely to be associated with toxicity. The calculation is based on a suite of chemicals and their toxicity thresholds which includes cadmium, copper, lead, silver, zinc, total chlordane, dieldrin, selected PCBs and selected PAHs (Fairey et al. 2001). The SQGQ1 values for all of the Chollas samples were greater than the value (0.5) where toxicity would be expected in 60% or more instances (Fairey et al. 2001). The July 2001 SQGQ1 value for station C14 is in the range (>2.3) where greater than a 90% expectation of toxicity occurs.

Most sediment quality guidelines are based on empirical relationships, and exceedances of specific chemical values may not relate to causality. For example, while the ERM for total DDTs was exceeded in the July 2001 sample from C14, it is unlikely that DDTs were a significant cause of toxicity at this station. When the concentration at C14 is expressed on an organic carbon basis (2.0 µg/g OC) the concentration is three orders of magnitude below the LC50 (2,500 µg/g OC) for total DDTs estimated by the analysis of spiked sediment and field data (Swartz et al. 1994). This would tend to indicate that DDTs are unlikely to be a significant source of toxicity in the Chollas Creek area samples.

The concentrations of PCBs at the Chollas stations are also below levels likely to cause direct toxicity to amphipods. Studies of PCB mixtures using another species of amphipod have found LC50 values ranging from 10800 to 25600 µg/kg (Swartz et al. 1988, Murdoch et al. 1997). In addition, the long-term exposure of adult sea urchins to southern California sediment contaminated with PCBs did not affect survival, growth, or development of embryos at sediment concentrations up to 10,000 µg/kg (Zeng et al. 2003). Sediment PCB concentrations were <500 µg/kg at all stations sampled within the Chollas study area.

The potential for sediment PAHs to cause toxicity was investigated using equilibrium partitioning sediment benchmarks for chronic toxicity to calculate the sediment toxic units due to PAHs (U. S. Environmental Protection Agency 2003). The calculated toxic units for the Chollas stations were elevated above the reference station (0.30 to 0.78) but below the value of 1.0 expected to correspond with incidence of chronic toxicity to aquatic organisms. These results do not confirm PAHs as the dominant source of sediment toxicity, but indicate PAHs may be contributing to the toxicity as part of a mixture of compounds.

Statistical analyses of the chemistry and toxicity data from the 2001 spatial study at the Chollas study site are consistent with the results of the TIE analyses. Sediment toxicity was significantly correlated with several classes of organics (e.g., chlordanes, PCBs, and DDTs), but not metals (Table 5-4). The correlation between toxicity and PAHs was relatively high but not statistically significant. Plots of the 2001 data show a trend for reduced survival at HMWPAH concentrations up 12,000 µg/kg, but no toxicity at a higher concentration of 36,000 µg/kg (Figure 5-2). The lack of toxicity at the highest

concentration may have been caused by differences in sediment composition affecting PAH bioavailability or variation in PAH concentrations among the chemistry and toxicity sediment samples, and may have confounded the correlation analysis.

The plots of the 2001 data also show a relatively consistent pattern of increased toxicity for total chlordane and total DDTs (Figure 5-2). The PCB plot for the Chollas stations also shows a consistent trend of toxicity, but additional data from the Paleta site indicates a lack of toxicity at some of the highest PCB concentrations measured. As mentioned previously, the concentrations of DDTs and PCBs present at the Chollas site are well below the levels associated with consistent toxicity in other southern California waterbodies. Of the contaminants measured, chlordanes and PAHs appear to have the strongest association with the observed sediment toxicity.

Paleta Creek

Toxicity to amphipods was often observed in the whole sediment samples from stations P11 and P17 near Paleta Creek during the spatial and temporal studies. As with the Chollas Creek samples, addition of coconut charcoal was the most effective treatment for reducing toxicity (Table 5-1), indicating an organic source of toxicity. Of note is the April 2004 sample from P11 where the carbon addition was somewhat less effective, but the methanol modified SFE treatment was very effective at reducing toxicity. This may indicate a difference in the polarity or molecular weight of the substances the two treatments are binding or extracting. The small decreases in toxicity observed with the cation exchange resin were coupled with similar effectiveness of the dilution treatment, indicating that metals were not a source of toxicity to the whole sediment samples at Paleta Creek. Organophosphorus pesticides were also not identified as likely sources of toxicity in the P11 sample from April 2004.

The results of the acid volatile sulfides and porewater metals analyses support the conclusion that divalent metals are not likely to be responsible for the observed toxicity at Paleta Creek station P11. These analyses indicated that there was an excess of sulfides present and the chemistry data confirms that low concentrations of divalent metals were present in the pore water. One notable feature in the porewater metals data was that the concentration of dissolved tin was elevated relative to the control at both P11 and C13 (5 µg/L vs 1 µg/L). No distinction between organotin and inorganic tin was made in this analysis and so the significance of this finding cannot be determined. Additional studies may be warranted to determine whether toxic concentrations of organotin are present in the Paleta or Chollas study areas.

The pattern of toxicity differed considerably between the Chollas and Paleta Creek sites. At neither time point did the Paleta stations exhibit as strong of a toxic signal as did Chollas station C14. Also, while the whole sediment from Paleta showed toxicity, there was no toxicity in the pore water (Table 5-3). Yet the concentrations of contaminants at the Paleta stations were similar to those for the Chollas stations. This indicates that the contaminants causing toxicity at the Paleta stations were more strongly bound to the sediments or that other unmeasured contaminants are primarily responsible for the toxicity.

The October 2002 and April 2004 samples from Paleta Creek had concentrations of DDTs, PCBs and PAHs that were similar to the Chollas Creek stations tested at the same time and also high relative to other southern California locations (Figure 5-1). As was the case for the Chollas stations, the PCB and organic carbon normalized DDT concentrations were far below what would be expected to cause toxicity to the

amphipods. This would tend to indicate that PCBs and DDTs are unlikely to be a significant source of toxicity in the Paleta Creek samples.

The sediment quality guideline values for the Paleta Creek TIE stations provide additional evidence that the observed toxicity is associated with sediment contamination. The SQGQ1 values for two of the three samples were >0.5, a level associated with a >60% probability of toxicity (Table 5-3). The PAH equilibrium partitioning toxic units for the Paleta TIE stations were 1.0-1.6, indicating that exposure to sediment PAHs was likely to exceed the chronic toxicity threshold for aquatic life. Thus, PAHs cannot be ruled out as potential contributors to sediment toxicity at the Paleta site.

Statistical analysis of the 2001 spatial data was of limited use in identifying the likely cause of sediment toxicity at Paleta. No significant correlations were detected between amphipod survival and the concentrations of organic contaminants (Table 5-4). Significant correlations were not expected to be present since the 2001 Paleta data set contained only one sample that was toxic to amphipods.

Other organic chemicals that were unmeasured during the TIE process, such as agricultural and residential pesticides, may be causing toxicity at the Chollas and Paleta sites. Organophosphous and pyrethroid pesticides were measured on the April 2004 samples, but these analyses may not have been of sufficient sensitivity to detect toxic concentrations of these compounds. Chlorpyrifos has been found to have an effect on benthic copepods at concentrations as low as 11 µg/kg (Chandler and Green 2001), which would be on the edge of the detection limits obtained for the April 2004 samples . These pesticides have been shown to be an emerging problem in other watersheds in California (Bailey et al. 2000). The use of PBO for discerning toxicity of organophosphorus pesticides in water is well established (Bailey et al. 1996), but not for sediments. The PBO treatment was only applied to the April 2004 samples and problems with blank toxicity for the pore water samples made the results difficult to interpret. Additional testing with PBO is recommended. A new process for reducing the toxicity of pyrethroid pesticides in water samples may also be useful (Phillips et al. 2004), but the effectiveness of this method for sediments is unknown.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The TIE process applied to the sediment samples was able to identify several candidate chemical groups that had the greatest association with sediment toxicity at the Chollas and Paleta sites. While the specific contaminants responsible for toxicity could not be confirmed with the data available, the following conclusions are evident from the results:

- **Most of the toxicity to amphipods is associated with organic compounds**

  Treatment of the sediment with carbon particles (coconut charcoal) removed toxicity in most cases, while treatment to reduce metal exposure was usually ineffective. In addition, statistical correlations were strongest between several types of organic chemicals and toxicity. Chemical analyses also indicated that the bioavailability of divalent metal contaminants in sediment and pore water was very low.

- **Chlordane is a probable cause of sediment toxicity at the Chollas site**

  Chlordane concentration was highly correlated with sediment toxicity. The concentration of chlordane at station C14, near the mouth of Chollas Creek

was higher than most other locations in southern California. Data from other field studies shows that sediments with chlordane concentrations higher than those measured at C14 are almost always toxic.

- **PAHs are a probable cause of sediment toxicity at the Chollas and Paleta sites**

  Calculations based on equilibrium partitioning theory indicate that PAH exposure from sediment contact is likely to result in chronic toxicity at the most contaminated sites from the Paleta study area. PAH concentrations from the Chollas site are lower and below the toxicity threshold, but these concentrations are still greater than most other locations in southern California.

- **PCBs and DDTs are unlikely to be a probable cause of direct sediment toxicity at the Chollas and Paleta sites**

  Data from other laboratory and field studies indicates that the measured concentrations of DDTs and PCBs at the study sites are several orders of magnitude lower that the levels associated with direct toxicity from sediment exposure. The significant correlations with toxicity found for these compounds are likely to be coincidental, probably the result of similar sources of loading with those contaminants causing the toxicity.

- **Sediment toxicity may be due to a varying mixture of measured and unmeasured contaminants**

  Patterns of toxicity differed between the Chollas and Paleta sites and there were inconsistent relationships between the sediment chemistry and toxicity results. These results suggest that there is no simple single cause of sediment toxicity. Some of this variability may be due to site variability; sediment grain size and TOC varied throughout the study sites and multiple sources of contaminants were present. Additional unmeasured contaminants may also be responsible for a portion of the toxicity; the standard chemical analyte list did not include potential toxicants such as organotins and pesticides in current use.

More data are needed to verify the conclusions stated above. This study was limited to using general methods to characterize the major classes of toxicants, which is the first and most cost-efficient step in the TIE process. The following additional types of information are recommended in order to provide more specificity to the toxicant identifications for the Chollas and Paleta study areas:

- **Spiked sediment testing**

  Toxicity tests of San Diego Bay sediment spiked with chlordane or other suspected toxicants would provide a direct test of the TIE conclusions. These tests would also provide data that could be used to establish clean up thresholds or interpret assessment data from other locations.

- **Analysis of body burdens**

  A major limitation in toxicant identification is the inability of standard sediment chemical analysis methods to accurately estimate the actual contaminant exposure of amphipods exposed to field sediments. Greater specificity in toxicant identification can be obtained through the analysis of tissue contaminant data from animals exposed to field sediments. These data provide a more accurate measurement of the organism's exposure to

contaminants and can be compared to existing residue effects data from laboratory studies to indicate the potential for toxicity from specific contaminants. These data are most useful for contaminants that are not metabolized by the organism, such as chlordane, PCBs, DDTs, and metals.

- **Sediment fractionation**

  The importance of unmeasured contaminants as a cause of sediment toxicity cannot be determined using conventional chemical analysis strategies, as these methods only quantify a restricted list of target analytes. Conventional sediment TIE methods are also limited because they can only distinguish between broad categories of contaminants, which increase the chance that the true cause of toxicity may be obscured by the presence of other compounds. A promising approach is to separate a chemical extract of the sediment into multiple fractions based on polarity or other characteristics. Each fraction is then tested for toxicity and those that are found to be toxic are analyzed to determine which compounds are present. This approach is useful for verifying that a presumed toxicant is present in the toxic fraction and also for isolating previously unknown toxicants. This method is particularly useful for determining whether new or emerging contaminants are of concern at the study site.

Table 5-1. Summary of the effectives of whole sediment TIE treatments on samples from San Diego Bay using a 10-day amphipod exposure test.

Station	Date	Carbon (organics)	Cation Exchange (metals)	PBO (pesticides)	SFE unmodified (non polar organics)	SFE Modified (broader organic spectrum)
C14	July 2001	+	+0	NT	NT	NT
C14	Oct. 2002	+	0	NT	NT	NT
P11	Oct. 2002	+	0	NT	NT	NT
P17	Oct. 2002	+	0	NT	NT	NT
C13	April 2004	+	0	0	0	+0
P11	April 2004	+0	0	0	NT	+

+ = Treatment effective (complete or nearly complete removal of toxicity)
+0 = Treatment slightly effective (partial reduction of toxicity)
? = Effectiveness could not be determined (no toxicity in baseline sample)
0 = Treatment ineffective (no reduction in toxicity from baseline result)
NT = Not tested

Table 5-2. Summary of the effectiveness of pore water TIE treatments on samples from San Diego Bay using a 10-day amphipod exposure test.

Station	Date	EDTA (metals)	STS (oxidants/metals)	C-18 (organics/metals)	PBO
C01	July 2001	?	NT	?	NT
C14	July 2001	+	NT	+	NT
C13	April 2004	0	0	+0	0
P11	April 2004	?	?	?	?

+ = Treatment effective (complete or nearly complete removal of toxicity)
+0 = Treatment slightly effective (partial reduction of toxicity)
? = Effectiveness could not be determined (no toxicity in baseline sample)
0 = Treatment ineffective (no reduction in toxicity from baseline result)
NT = Not tested

Table 5-3. Sediment quality guideline values for San Diego Bay TIE stations.

Station	Date	PAH Equilibrium Partitioning Benchmark ($\Sigma ESBTUFCV_{,TOT}$)	SQGQ1
2433	July 2001	0.250	0.158
2433	October 2002	0.164[b]	0.247[b]
2433	April 2004	0.056[1]	0.162
C01	July 2001	0.426	1.051
C10	October 2002	0.620[b]	0.531[b]
C13	April 2004	0.776[a]	0.499
C14	July 2001	0.305	2.944
C14	October 2002	0.336[b]	1.905[b]
P11	October 2002	1.59[b]	0.365[b]
P11	April 2004	0.961[a]	0.733
P17	October 2002	1.22[b]	1.305[b]

[a]Calculation is based on only 23 PAHs, so total was adjusted using 50th percentile adjustment factor (1.64).
[b]TOC concentrations were not measured. Guideline value was calculated using TOC concentration from July 2001 sample.

Table 5-4. Spearman nonparametric correlation between toxicity and chemistry results from the 2001 spatial study. Metals data were normalized to percent fines. Data for the reference stations were included in the correlation analysis.

	Chollas	Paleta
Fines	-0.621	0.045
TOC	-0.762	-0.072
Ag (fn)	0.402	-0.075
As (fn)	0.354	-0.053
Cd (fn)	0.280	-0.510
Cr (fn)	0.548	-0.040
Cu (fn)	0.190	0.143
Hg (fn)	0.338	-0.090
Ni (fn)	0.442	0.012
Pb (fn)	0.230	-0.275
Zn (fn)	0.244	-0.152
LMWPAH	-0.431	0.073
HMWPAH	-0.443	-0.146
TPCB	-0.563	-0.031
TCHLOR	-0.535	-0.131
TDDT	-0.590	-0.142

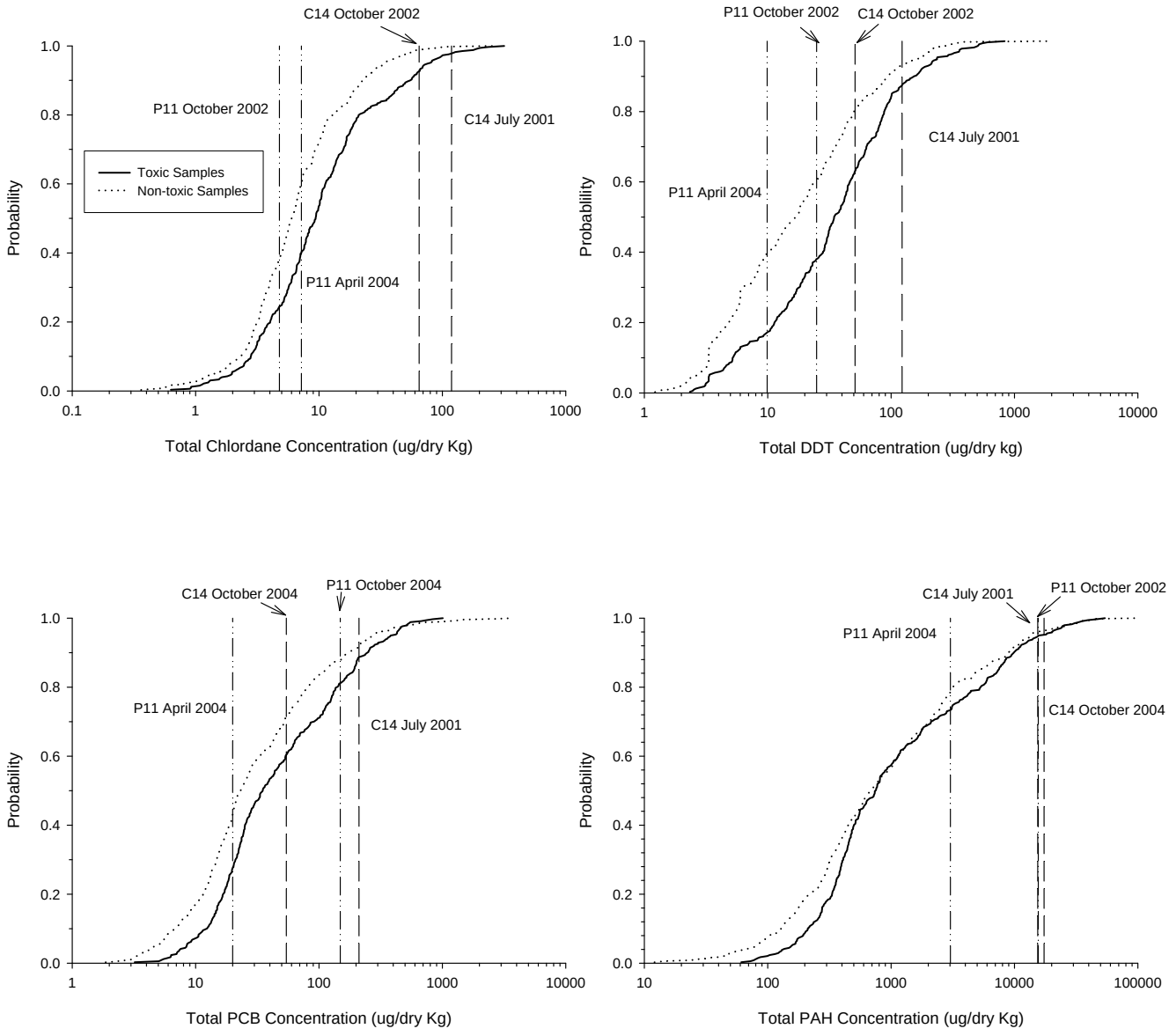

Figure 5-1. Cumulative distribution plots of toxic and non-toxic samples with the concentrations of four organic contaminants from a database of southern California samples.

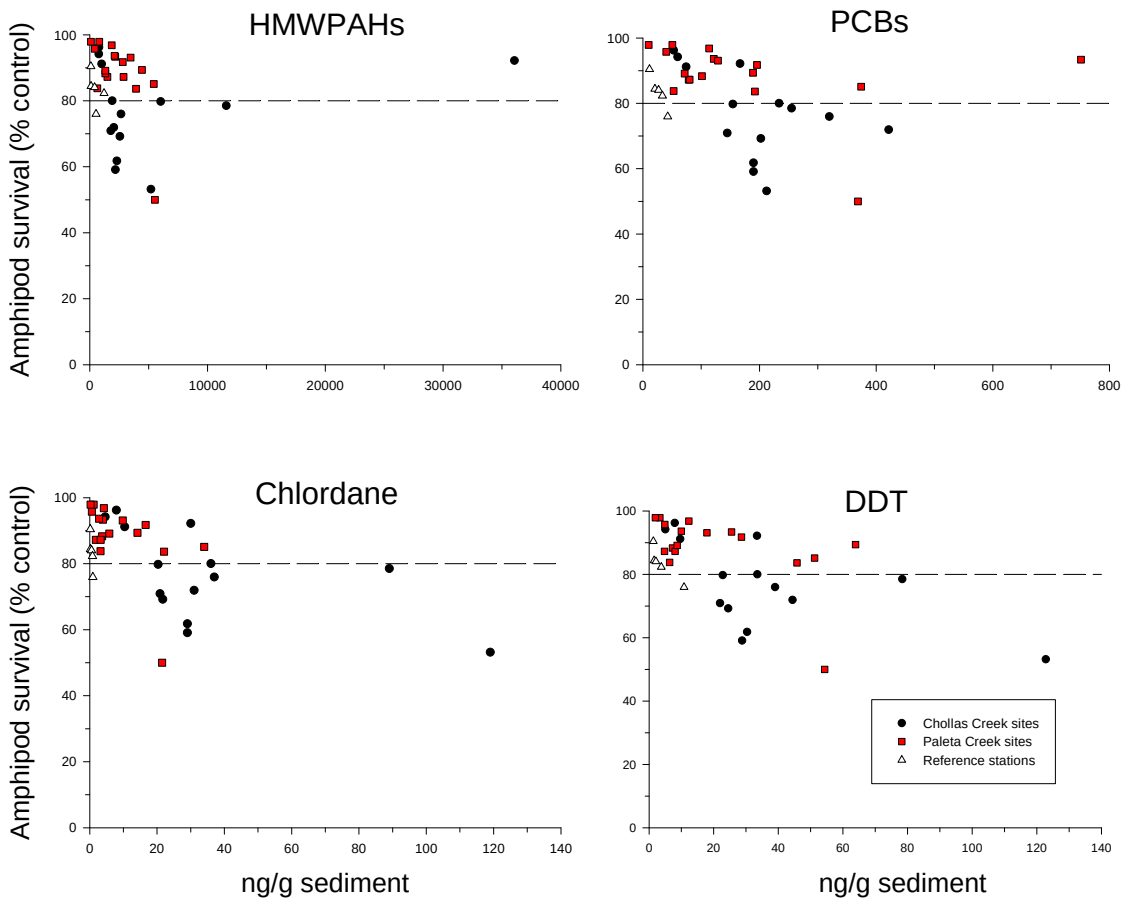

Figure 5-2. Relationship between amphipod toxicity test response and concentration of sediment contaminants for the 2001 spatial study. Data are expressed as µg/kg.

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