

Toxicity Identification Evaluation of Sediment (Sediment TIE) in Ballona Creek Estuary

Final Report

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December 2010

Technical Report 634

EXECUTIVE SUMMARY

Previous studies have reported that sediments within Ballona Creek Estuary are contaminated and toxic to marine life. This prevalence of toxicity led to an Environmental Protection Agency 303(d) listing and the subsequent development of a total maximum daily load (TMDL) for multiple trace organics and metals. In support of the TMDL, a three-year study was conducted to determine the current extent of chemical contamination within the estuary and identify the likely causes of toxicity. Advanced chemical analysis and toxicity identification evaluation (TIE) methods were used in this study.

The results of the study indicated that chemical contamination and toxicity were widespread in the estuary. Each sampling event detected toxicity at multiple stations within the estuary. Concentrations of TMDL listed compounds often exceeded target levels, but there was a poor correlation between these concentrations and toxicity. Toxicity and chemical concentrations were highly variable in both space and time. This variability was likely due to the dynamic forces of tidal action and runoff.

TIE analyses of whole sediments and pore water found that pyrethroid pesticides were the likely primary source of toxicity within the estuary. Comparison of these pesticides' toxicity thresholds to chemical analysis results confirmed that sufficient pyrethroids were present in the estuary sediments to cause toxicity. Another current use pesticide, fipronil, was detected in estuary sediments and may also be of concern.

Spiked sediment tests were conducted to estimate the toxicity thresholds of several trace organics listed in the TMDL: DDT, DDE, and chlordane. Comparison of Ballona Creek Estuary sediment chemical concentrations to the toxicity thresholds indicated that these chemicals were not present at concentrations high enough to cause toxicity. Concentrations of DDT, DDE, and chlordane were 10 to 10000 times below toxicity thresholds either developed in this study or reported in other studies. Sediment concentrations of PAHs and PCBs were also below levels likely to cause direct sediment toxicity. Metals concentrations in field sampled sediment pore water were below California water quality standards for the protection of aquatic life.

The Effects Range Low (ERL) sediment quality guideline values used as target concentrations for the chemicals listed in the TMDL were found to be inaccurate and highly conservative. The ERLs for some metals were below background concentrations typical of estuarine environments. For the organic compounds, ERLs were several orders of magnitude below toxicity thresholds for benthic organisms.

ACKNOWLEDGEMENTS

The authors would like to thank the staff of the City of Los Angeles, Environmental Monitoring Division for their help in collecting samples, providing chemical analysis, and for toxicity testing. We would specifically like to thank Shokoufe Marashi, Gerald McGowen, Curtis Cash, and Stan Asato for assistance with planning, logistics, and oversight of this study. We would also like to thank the staff of Southern California Coastal Water Research: Diana Young and Monica Mays for their assistance in conducting toxicity testing, David Tsukada for chemical analysis, Dario Diehl for sample collection, Becky Schaffner for map production, and Karlene Miller for editorial assistance with preparation of this document.

Funding for this study was provided by the City of Los Angeles Watershed Protection Division, California Department of Transportation, the County of Los Angeles, and the cities of Culver City, Inglewood, Beverly Hills, West Hollywood, and Santa Monica.

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INTRODUCTION

Ballona Creek Estuary (BCE), like many other bays and estuaries in highly urbanized watersheds, is contaminated with a wide variety of trace metals and trace organic compounds. Historical data showing the presence of sediment toxicity and elevated contaminants were important factors in BCE being included as an impaired water body on the Environmental Protection Agency (EPA) 303(d) list and subsequent development of a TMDL. Although specific contaminants are listed in the BCE Toxics TMDL, very little reliable information is available to identify the cause of toxicity or to determine appropriate target concentrations. The current TMDL sediment targets are based on National Oceanic and Atmospheric Administration (NOAA) Effects Range-Low (ERL) sediment quality guidelines, which were not developed for use as clean up targets or to determine the cause of toxicity. In 2003, the Southern California Coastal Water Research Project (SCCWRP) conducted preliminary Toxicity Identification Evaluations (TIE) at two BCE stations; the results indicated that organic contaminants were the likely cause of the observed toxicity. The TIE results further suggested that unmonitored current use pesticides, such as pyrethroids, were a possible cause of toxicity. The 2003 studies were limited in scope and did not include chemical analyses or additional TIEs to confirm the results. These data gaps resulted in substantial uncertainty regarding whether the important contaminants have been identified in BCE. In addition the relationship between current TMDL target concentrations and BCE sediment toxicity is unknown; these targets may not correspond to sediment toxicity thresholds, thereby potentially reducing the effectiveness of the TMDL.

This special TIE study was conducted to fill the aforementioned data gaps regarding the chemical contamination and toxicity in BCE sediments. Field and laboratory research was conducted during 2007-2010 to answer the following questions:

- What are the current toxicity and chemistry conditions in the sediment within BCE?
- Are current use pesticides contaminating the sediments of the BCE?
- Which contaminants are causing sediment toxicity in BCE?
- What are the toxicity threshold concentrations for contaminants of concern in BCE?

METHODS

Study Design

Sampling activities for the special study were designed to coordinate with the semiannual monitoring program established under the TMDL and conducted by the City of Los Angeles' Environmental Monitoring Division (EMD). Both programs analyzed sediments from the same set of six stations, selected to represent a gradient of sediment characteristics throughout BCE (Figure 1). In many cases, sediment samples from the same collection event were shared between EMD and SCCWRP to provide maximum data comparability.

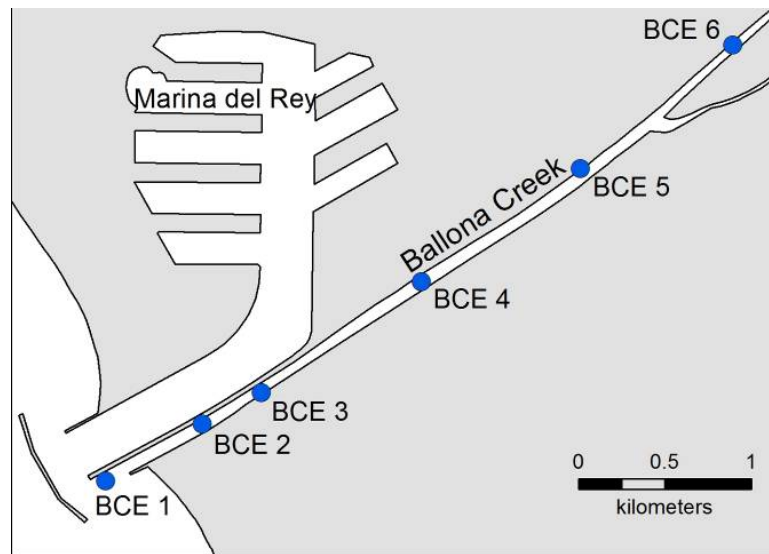


Figure 1. Study site locations in Ballona Creek Estuary.

Sampling and laboratory analyses were conducted from 2007 to 2010, and included chemical and/or toxicity analysis of samples collected from seven time periods. The analyses were organized as three overlapping phases, each designed to address specific elements of the four study questions.

- **Phase I: Patterns of chemical contamination and toxicity.** This phase used advanced chemical analysis methods to measure the concentrations of two types of current use pesticides (pyrethroids and fipronil). Several types of toxicity tests were also conducted to evaluate spatial patterns in toxicity and to select samples for TIE analyses.
- **Phase II: Cause of sediment toxicity.** Research in this phase included two types of analyses. First, samples of sediment and pore water were treated with various materials to selectively modify the toxicity of different chemical groups. These TIE treatments were based on methods established by the EPA. The second group of activities used specialized field methods to measure the concentration of contaminants in sediment pore water at multiple stations in BCE. These measurements provide a more accurate measure of the concentration of contaminants that are biologically available to sediment-dwelling organisms.

- **Phase III: Toxicity thresholds.** The final phase of the study used sediments that were spiked with chemicals in order to determine the threshold of toxicity for four contaminants of concern. Toxicity tests were conducted on the spiked sediments to determine concentration associated with the absence of toxicity and the concentration causing mortality to 50% of the test organisms.

Sampling and Handling

Sediment samples were collected by a variety of methods, depending on the location of the station and study phase. Station BCE1 was usually sampled from the RV La Mer using a Van Veen grab. Stations BCE2, 3, and 4 were generally sampled from an inflatable boat using a petite Ponar grab. Stations BCE5 and 6 were always sampled by personnel wading into the creek and using a stainless steel shovel. For activities utilizing specialized field methods in Phase II, sediment was collected from BCE1, 2 and 3 by diver using a stainless steel trowel. In all cases, an effort was made to collect only the top 5 cm of sediment. Regardless of the collection method, sediment from multiple grabs or shovel loads were taken to provide adequate sample volume and were placed into a plastic bin and homogenized with a stainless steel spoon. Aliquots of the homogenized sediment were then transferred into various jars for toxicity and chemical analysis. Samples were placed on ice in the field for transport to the appropriate laboratory. Samples for toxicity, grain size and pore water chemistry were refrigerated at 5°C in darkness, until analyzed. All other sample types were frozen at -20°C until analysis.

Toxicity Analysis

Sediment toxicity was measured using two standardized methods: a test of whole sediment toxicity and a test of pore water toxicity (USEPA 1994). Whole sediment toxicity was measured by exposing the estuarine amphipod *Eohaustorius estuarius* to BCE surface sediment for 10-days (Figure 2). The percentage survival of the amphipods was used as the measure of toxic effects in this test. The 10-day amphipod test was also used to evaluate the effects of TIE sample treatments and to measure the toxicity of spiked sediments.



Figure 2. Amphipod (*Eohaustorius estuarius*) used in sediment toxicity tests and exposure chambers.

Sediment pore water was tested for toxicity using two methods: a modified version of the 10-day amphipod survival test described previously or a sea urchin fertilization test. The sea urchin test was conducted using the gametes of the purple sea urchin, *Strongylocentrotus purpuratus* (USEPA 1995). Sea urchin sperm were exposed for 20 minutes to samples of pore water in glass vials and then eggs were added to assess effects on fertilization (Figure 3). The percentage of eggs with a fertilization membrane was used as the measure of toxicity in this test. Pore water samples were obtained by centrifuging samples of sediment at 3,000x g, then removing the overlying layer of pore water with a pipette.

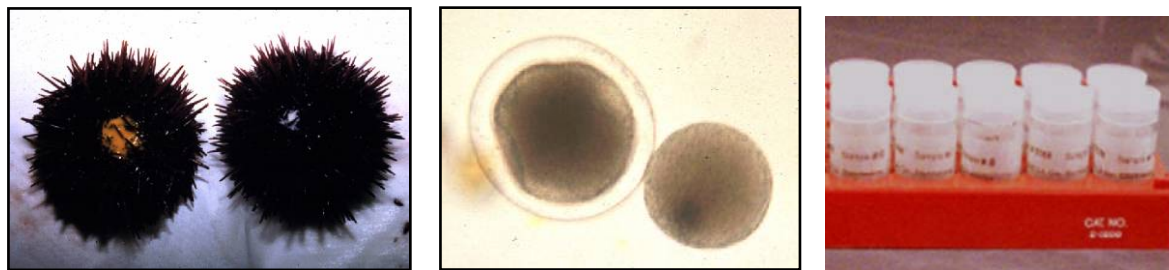


Figure 3. Purple sea urchins (*Strongylocentrotus purpuratus*) used in pore water toxicity tests of egg fertilization and exposure chambers.

Chemical Analysis

Analysis of sediment samples for TMDL target constituents (e.g., trace metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and legacy pesticides) was conducted in coordination with CL&EMD laboratories. Additional analyses were conducted by SCCWRP to measure the concentration of two groups of current use pesticides: pyrethroids and fipronil. Pyrethroids are one of the most commonly used types of pesticides throughout California. Over one thousand pesticide products, ranging from garden sprays and pellets used by homeowners, to products used by commercial exterminators and agriculture, contain pyrethroids as the active ingredient. Fipronil is widely used as a treatment to control fire ants in southern California and as an ingredient in some flea control medications for pets.

For the SCCWRP analyses, freeze dried sediments were extracted using methylene chloride in a Dionex Accelerated Solvent Extraction 300 system. The extracts were concentrated and solvent exchanged into hexane. Copper powder was then added to remove sulfur. For analysis of PAHs, PCBs, and chlorinated pesticides, the extracts were cleaned using a silica/alumina column. For analysis of pyrethroids, fipronil, and fipronil degradates, the extracts were cleaned up on a Florisil column; the extracts were then analyzed using gas chromatograph mass spectrometry (GC/MS). Pyrethroids, fipronil, PCBs, and chlorinated pesticides were analyzed using negative chemical ionization mode. PAHs were analyzed using electron impact ionization mode.

RESULTS

The results presented in the body of this report summarize all three years of data for this project. The appendices contain three progress reports which contain raw data for each year's efforts. The data tables included in the progress reports have been updated where necessary to reflect changes in some of the chemical analysis results. Where changes have occurred, they are so noted in the table caption and underlined in the table body.

What are the Current Sediment Toxicity and Chemistry Conditions in BCE?

Sediment and pore water toxicity testing of samples collected between 2007 and 2009 confirm that BCE sediments are frequently toxic and that the toxicity can be of a high magnitude. The amphipod survival test of whole sediment usually detected toxicity more frequently than did the sea urchin fertilization test of pore water (Figure 4). The magnitude of toxicity was highly variable, both between stations and between sampling events. However, every sample of sediment from BCE stations 2, 3, 5, and 6 was always toxic to amphipods. Samples of sediment from BCE stations 1 and 4 ranged from nontoxic to highly toxic (e.g., <50% survival) among surveys.

Sediment contamination above background levels was detected at most BCE stations. The concentrations of contaminants were frequently in excess of the TMDL target concentrations (Figures 5 and 6). The exception was for PAHs; concentrations of PAHs measured by SCCWRP or EMD throughout the study never exceeded the TMDL target. Total PCB concentrations were relatively low, but occasionally exceeded the TMDL target concentration.

Similar to the toxicity data, contaminant concentrations were highly variable among stations and dates. Some of the variation in contaminant concentrations was related to variations in sediment particle size and organic carbon content (Figure 7). Trace organics (e.g., dichlorodiphenyl trichloroethane (DDT) and chlordane) and trace metals (e.g., copper and zinc), preferentially bind to fine and organic rich sediments. In addition, naturally occurring trace metals are more abundant in silts and clays, the components of the fine sediment fraction, resulting in a direct correlation between metals concentrations and sediment fines that is not related to anthropogenic inputs (Figure 8). Much of the variation in contaminants, particle size and total organic carbon (TOC) within BCE is likely due to processes such as storm water runoff, tides, and the deposition of Ballona Creek suspended sediments due to mixing with seawater. Additional spatial and temporal variation in the chemistry data is unexplained, but could be related to factors such as analytical differences and small scale spatial variability in sediment concentrations.

Variation in sediment concentrations of the TMDL contaminants was poorly associated with the magnitude of toxicity. Results from the 2007 survey of sediment contamination and toxicity illustrate this poor association (Table 1). For example, multiple exceedances of TMDL targets and high toxicity were present for BCE2 and 3, but a similar level of toxicity was present at BCE4 and 6 even though these stations had no TMDL exceedances. In addition, no whole sediment toxicity was detected at BCE1 even though two of the TMDL targets were exceeded.

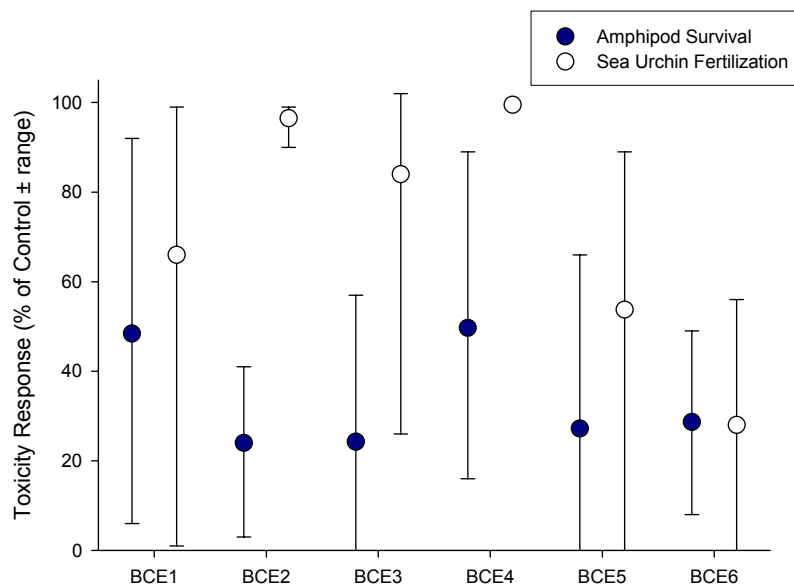


Figure 4. Mean and range of toxicity results by for all Ballona Creek Estuary samples. Results are expressed as a percentage of the control value for each experiment.

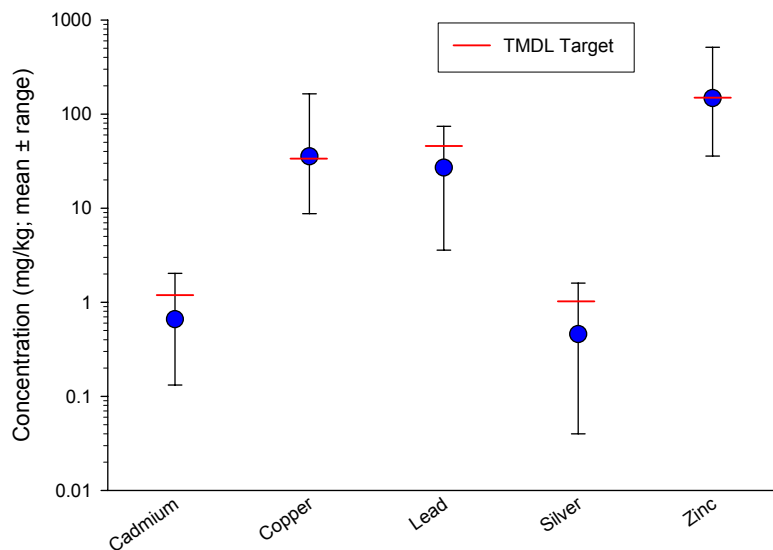


Figure 5. Mean and range of TMDL concentrations for trace metals in the Ballona Creek Estuary. Values are based on all stations and time points in the study.

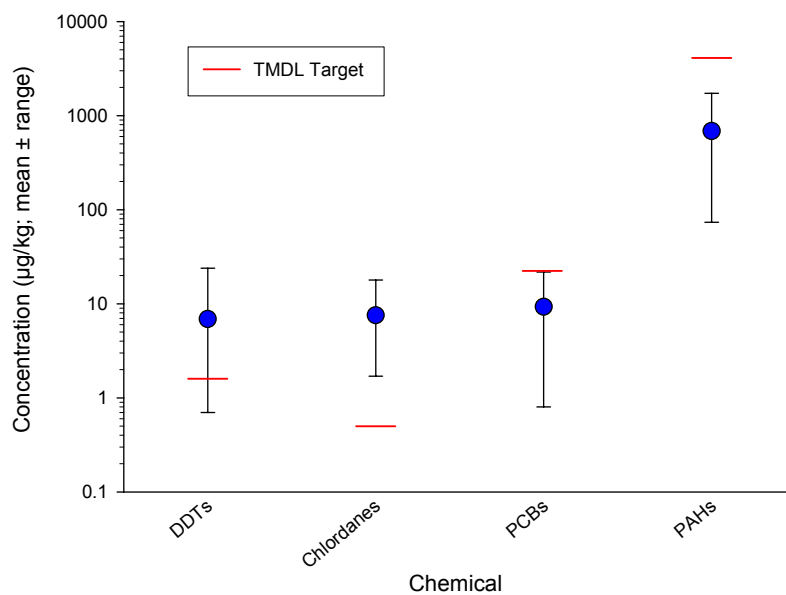


Figure 6. Mean and range of TMDL concentrations for organic compounds in the Ballona Creek Estuary. Values are based on all stations and time points in the study.

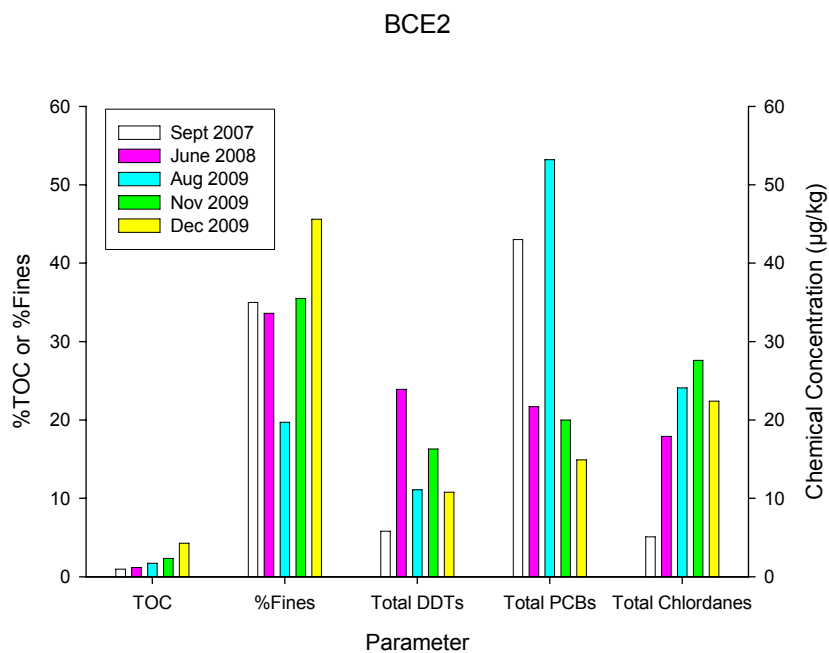


Figure 7. Concentrations of TOC, %Fines, total DDTs, total PCBs, and total chlordanes in sediments from BCE2 over the course of the study.

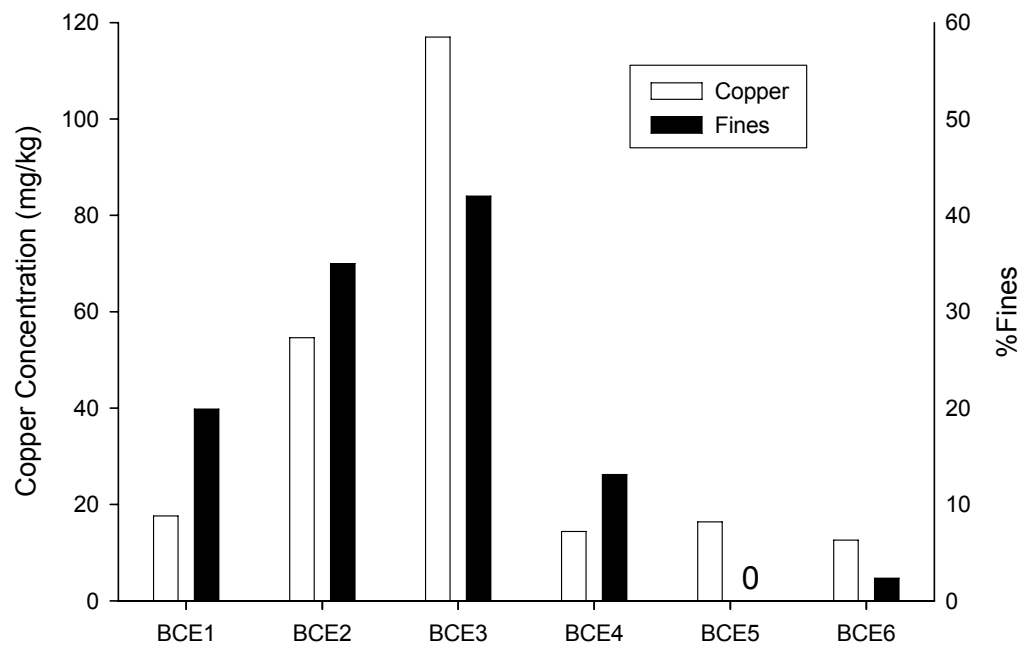


Figure 8. Relationship between sediment copper and particle size (%Fines) for Ballona Creek Estuary 2007 samples (data from City of Los Angeles, EMD analyses).

Table 1. Ballona Creek Estuary sediment chemistry and toxicity results for 2007. Trace metals concentrations are reported in mg/kg and organic chemical concentrations are reported in µg/kg. Concentrations exceeding the TMDL target are enclosed in boxes.

Parameter	Target	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Amphipod %Survival		89	3	0	16	18	8
Cadmium	1.2	0.5	1.6	1.8	0.5	0.4	0.3
Copper	34	18	55	117	14	16	13
Lead	46.7	30.3	52.1	66.7	11.3	15.2	4.9
Silver	1.0	0.6	1.4	1.6	0.2	0.3	<0.02
Zinc	150	89	228	430	103	107	58
DDTs	1.6	5.3	5.8	5.3	1.1	1.2	<0.7
Chlordanes	0.5	5.1	5.1	6	<0.18	<0.18	<0.18
PCBs	22.7	<3	43	39	<3	82	<3
PAHs	4022	<150	<150	<150	<150	<150	<150

Are Current Use Pesticides Contaminating the Sediments of the Estuary?

Chemical analyses by SCCWRP detected high levels of pyrethroid pesticides in BCE sediment from every collection event. The mean total pyrethroid concentration for all stations and sampling periods was 79 $\mu\text{g/kg}$; concentrations ranged from 2 to 494 $\mu\text{g/kg}$. Pyrethroid concentration was found to vary greatly among the BCE stations and sampling events, showing probable associations with sediment fines and storm water runoff.

Multiple types of pyrethroid compounds were present, suggesting that there are multiple sources of these pesticides in the Ballona Creek watershed. In general, permethrin and bifenthrin were present in the highest concentrations (Figure 9). Commercial usage statistics for 2008 (the most recent year available, http://www.cdpr.ca.gov/docs/pur/pur08rep/chemcnty/losang08_ai.pdf), indicate that permethrin is by far the most commonly applied pyrethroid in Los Angeles County. The usage information corresponds fairly well with the concentrations that were observed in the sediments, with permethrin having both the highest usage and concentration. Other pyrethroids having very low usage also had low concentrations. Commercial usage of bifenthrin, cyfluthrin and cypermethrin did not match as well with concentration.

Within the Ballona Creek watershed, all commercial usage of pyrethroids is likely for structural and landscape maintenance applications, since there are no areas classified as having an agriculture land use within the watershed. However, the actual amount of pyrethroid use within the watershed is unknown. Commercial application data specific for the Ballona Creek watershed are not available. In addition, accurate information on homeowner use of pyrethroids contained in over the counter pesticide products (e.g., sprays and pellets purchased from home improvement stores) is not available. Residential use of pyrethroids may be a large contributor to the pesticide load carried by Ballona Creek. This undocumented usage may account for some of the differences between the commercial usage and BCE sediment concentration data.

Sediment toxicity thresholds are available for several pyrethroid compounds, which allow estimation of their potential to cause sediment toxicity. Pyrethroid toxicity was estimated by calculating the toxic units (TUs) of four pyrethroid compounds for which there is a threshold value for *E. estuarius* and three others for which there are thresholds for the freshwater amphipod *Hyaella azteca* (Table 2). Toxic units were calculated by dividing the sediment organic carbon normalized concentration by the organic carbon normalized LC50 (sediment concentration causing 50% amphipod mortality). Organic carbon normalization consisted of dividing the dry weight concentration of each compound by the TOC content of the sediment. A toxic unit value of one or greater indicates that the chemical is present in sufficient quantity to likely cause substantial toxicity to that species. The TUs for individual pyrethroids frequently exceeded 1.0 for at least one compound at each station, and the sum of pyrethroid TUs was much greater (Table 3). These results indicate that most BCE samples contained a sufficient amount of pyrethroids to potentially cause the observed toxicity to amphipods. Variations in sediment characteristics and the sensitivity of individual organisms can influence the toxic effects of a given concentration of pyrethroids, so predictions of toxicity based on LC50 values may not have absolute accuracy in predicting the magnitude of toxicity.

The relative composition of sediment pyrethroids based on concentration differs from that based on toxic potency (Figure 10). While permethrin had by far the highest relative concentration among the pyrethroids, the relatively high LC50 for this compound indicates it is the least toxic of the pyrethroids detected in BCE (Table 2). Consequently, permethrin's contribution to

potential toxicity at BCE is relatively small, ranking sixth out of the seven pyrethroids for which there are LC50 values (Figure 10). Conversely, cyfluthrin ranks third in mean concentration, but due to its high toxicity (low LC50) it accounts for nearly half of the total toxic units.

Another type of current use pesticide, fipronil, was also detected in some BCE sediment samples (Figure 11). The concentration of fipronil and its three principal environmental metabolites was more than ten-fold lower than pyrethroids at the same stations. As with the other chemical constituents, fipronil concentrations were variable, both spatially and temporally. Commercial use of fipronil in Los Angeles County for 2008 was 4,115 kg for structural and landscape application. Relatively little is known about the toxicity of fipronil to marine organisms. Fipronil was found to be acutely toxic to the estuarine copepod *Amphiascus tenuiremis* at 6.8 $\mu\text{g/L}$ and had reproductive effects at 0.22 $\mu\text{g/L}$ (Chandler et al. 2004). In preliminary testing at SCCWRP with *E. estuarius*, we found a nominal EC50 of about 3 $\mu\text{g/L}$ for water and a NOEC of ≤ 10 $\mu\text{g/kg}$ in sediment. A freshwater midge larvae, *Chironomus tentans (dilatatus)* has been found to be very sensitive to fipronil with an EC50 of 0.9 $\mu\text{g/kg}$ (Maul et al. 2008). The majority of the fipronil compounds that were detected in BCE sediments were the degradation products (Figure 11). The degradate compounds have been found to be as toxic or more so than the parent chemical. These values indicate that there is a potential for fipronil to be of concern in the estuary.

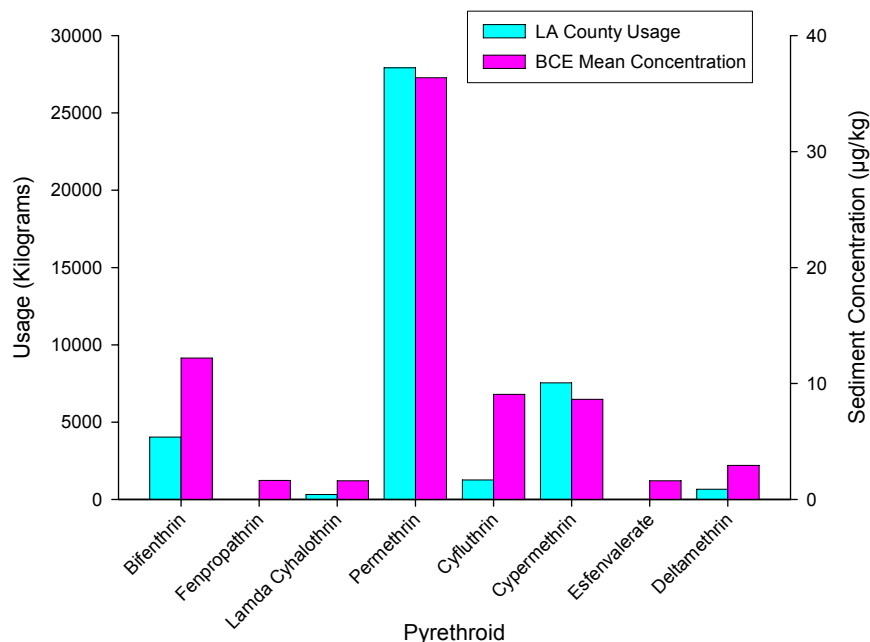


Figure 9. Los Angeles County usage data and mean pyrethroid concentration in the Ballona Creek Estuary. Concentrations represent mean for all stations and time points during the study.

Table 2. Pyrethroid toxicity thresholds (median lethal concentration) for *Hyalella azteca* and *Eohaustorius estuarius*.

Pyrethroid	<i>H. azteca</i>	<i>E. estuarius</i>
	LC50 (µg/g OC)	LC50 (µg/g OC)
Bifenthrin	0.52 ¹	1.03 ²
Lamda-Cyhalothrin	0.45 ¹	NA
Permethrin	10.83 ¹	17.9 ²
Cyfluthrin	1.08 ¹	0.33 ³
Cypermethrin	0.38 ¹	1.41 ²
Esfenvalerate	1.54 ¹	NA
Deltamethrin	0.79 ¹	NA

NA=Not available

¹Amweg et al. 2005, ²Anderson et al. 2008, ³This study

Table 3. Mean and range of pyrethroid toxic units for all samples analyzed during the study.

	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6	All Stations
Bifenthrin ¹	1.4	1.0	2.9	0.8	0.6	0.9	1.3
Lamda-Cyhalothrin ²	0.3	0.4	0.9	0.2	0.1	0.4	0.4
Permethrin ¹	0.3	0.2	0.5	0.1	0.1	0.2	0.2
Cyfluthrin ¹	1.7	3.9	7.0	1.0	0.4	1.4	2.8
Cypermethrin ¹	0.6	0.7	1.5	0.2	0.1	0.4	0.7
Esfenvalerate ²	0.02	0.2	0.3	0.02	0.01	0.01	0.1
Deltamethrin ²	0.3	0.4	0.7	0.1	0.1	0.4	0.3
Total Pyrethroids	4.7	6.8	13.8	2.5	1.4	3.7	
	(0.9-12.8)	(1.0-26.4)	(2.1-34.7)	(1.1-4.6)	(0.4-2.4)	(3.4-4.0)	

¹TU calculation based on *Eohaustorius estuarius* EC50.

²TU calculation based on *Hyalella azteca* EC50

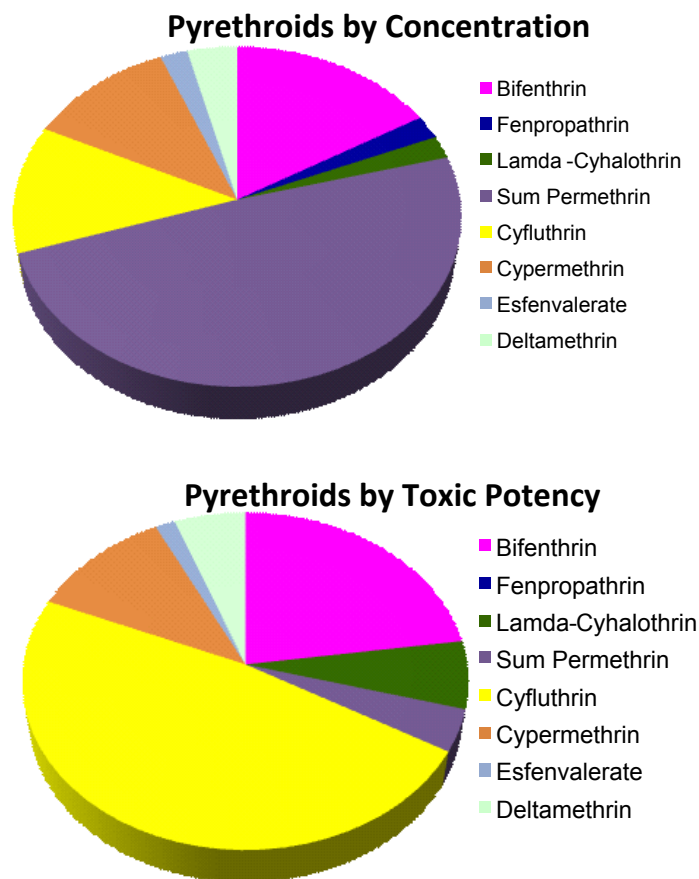


Figure 10. Relative composition of pyrethroids in Ballona Creek Estuary based on concentration (top) and toxic potency (bottom).

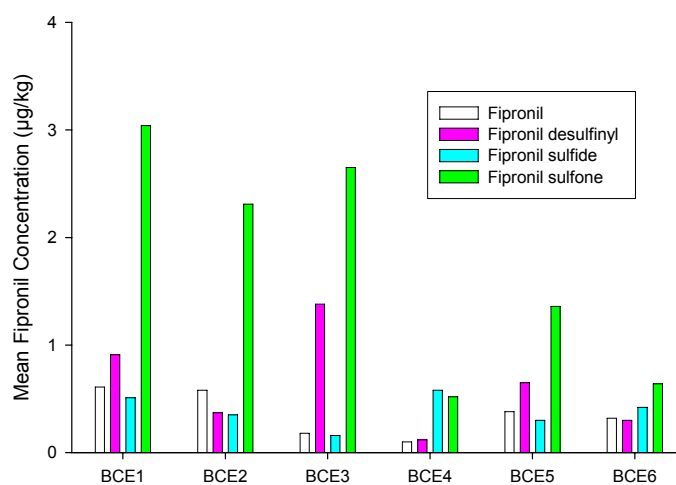


Figure 11. Average concentration of fipronil and degradates in the Ballona Creek Estuary for all samples analyzed during the study.

Which Contaminants are Causing Sediment Toxicity in BCE?

Toxicity identification evaluations

Samples of BCE sediment and pore water collected from 2007 to 2009 were investigated using Toxicity Identification Evaluation (TIE) methods recommended by the EPA (USEPA 1996, 2007). A TIE consists of several chemical or physical modifications of a toxic sample (Figure 12). Each treatment is designed to affect the toxicity of a particular type of contaminant (e.g., trace metals or organics). By comparing the post-treatment sample toxicity with that of an unmodified sample (baseline toxicity), it is possible to identify whether certain types of contaminants are contributing to the sample's toxicity. A variety of TIE treatments were applied in this study, depending on whether a sediment or pore water sample was analyzed. Three types of treatments were usually applied to the whole sediments or pore water; these treatments enabled sediment toxicity to be classified as likely due to trace metals, trace organics, or pyrethroid pesticides (Table 4).

Variations in sediment toxicity limited the information obtained from some TIE analyses, as a relatively high level of toxicity is needed to interpret the results. However, every whole sediment TIE conducted with toxic samples yielded a similar overall pattern of results (Figure 13): addition of carbon reduced toxicity (indicating toxic levels of organics), binding of trace metals had little effect, and addition of piperonyl butoxide (PBO) increased toxicity (indicating pyrethroid toxicity). The addition of PBO increased the toxicity of every sample investigated using TIE, indicating that pyrethroids were contributing to the toxicity of the sediment (Table 5).

Amphipod TIEs conducted using pore water produced results similar to the whole sediment, with solid phase extraction of organic compounds reducing toxicity and addition of PBO increasing toxicity (Figure 14, Table 6). This pattern confirmed the likely role of pyrethroids as a cause of toxicity within the estuary.

Limited success was achieved in determining the cause of pore water toxicity to sea urchin gametes. Several TIE experiments were conducted, but most results were inconclusive due to unpredictable changes in sample toxicity during sample storage. However, the addition of ethylenediaminetetraacetic acid (EDTA) was found to reduce toxicity in some samples. While no final conclusions can be made regarding the principal cause of toxicity, these partial TIE results suggest that trace metals may be contributing to the toxicity detected using the sea urchin fertilization test.

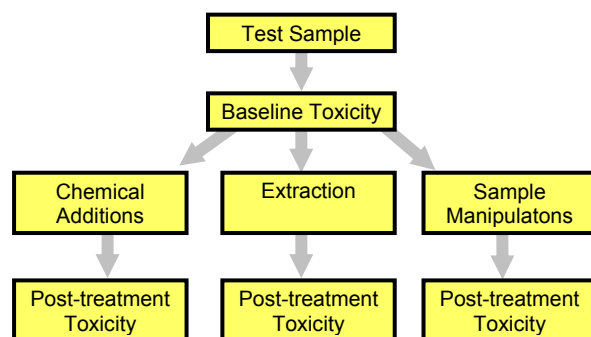


Figure 12. Schematic of TIE approach.

Table 4. Primary treatments used for whole sediment and pore water TIEs.

Treatment	Matrix	Purpose
Coconut carbon addition	Sediment	Binds organic contaminants
Cation exchange resin addition	Sediment	Binds of trace metals
Piperonyl butoxide (PBO) addition	Sediment/ Pore water	Inhibits pesticide metabolism. Reduces toxicity of organophosphorus pesticides; increases toxicity of pyrethroid pesticides
C18 Extraction	Pore water	Removes non-polar organic compounds
EDTA	Pore water	Chelates cationic metals

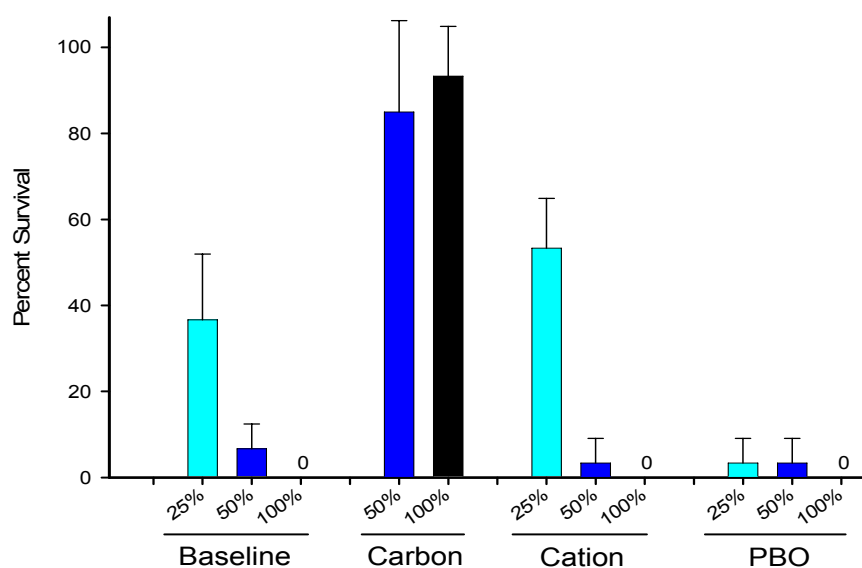


Figure 13. Whole sediment TIE results for 2007 BCE2 sediment sample. Ballona Creek Estuary sediment was diluted with control sediment to produce test concentrations of 50% and 25%. Increased toxicity in the 25% concentration following PBO addition is indicative of pyrethroid pesticide toxicity.

Table 5. Summary of whole sediment TIE results using *Eohaustorius estuarius*. Inconclusive results were obtained for some treatments due to the presence of low toxicity (high survival) in the baseline sample.

	2007		2008		2009
Treatment	BCE2	BCE4	BCE2	BCE5	BCE3
Piperonyl Butoxide	Reduced Survival	Reduced Survival	Reduced Survival	Reduced Survival	Reduced Survival
Cation Exchange Resin	Slightly Increased Survival	Slightly Increased Survival	Inconclusive	Inconclusive	Slightly Increased Survival
Coconut Carbon	Increased Survival	Not Tested	Inconclusive	Inconclusive	Increased Survival
Baseline Survival (%)	37	73	86	98	32

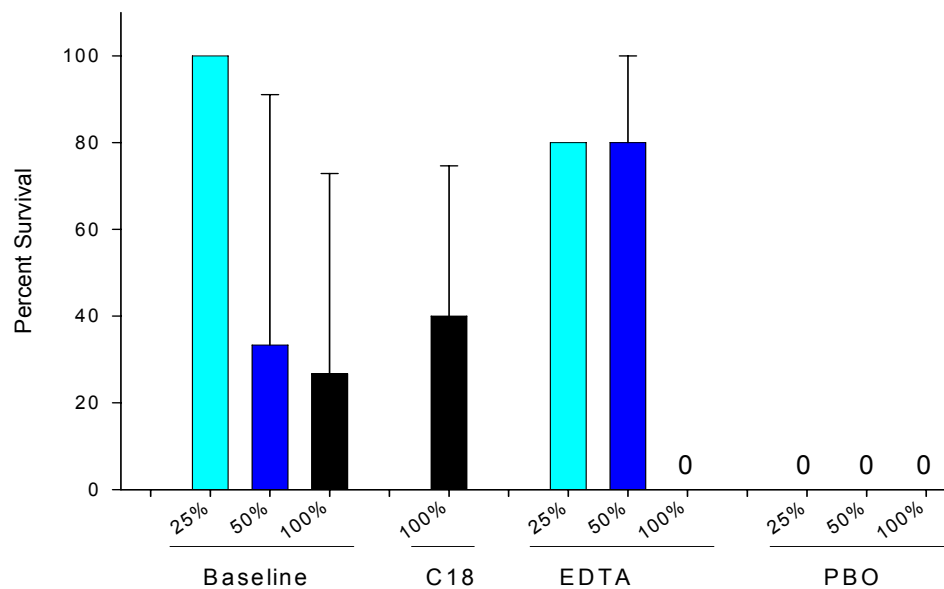


Figure 14. Pore water TIE results for 2007 BCE2 sediment sample. Increased toxicity following PBO addition is indicative of pyrethroid pesticide toxicity.

Table 6. Summary of pore water TIE results using *Eohaustorius estuarius*. Inconclusive results were obtained for the PBO for BC5 in 2008 due to the presence of high toxicity (low survival) in the baseline sample.

	2007		2008	
Treatment	BCE2	BCE4	BCE2	BCE5
Piperonyl Butoxide	Reduced Survival	Reduced Survival	Reduced Survival	Inconclusive
EDTA	Increased Survival	No Effect	No Effect	No Effect
C18 SPE	Slightly Increased Survival	Slightly Increased Survival	Increased Survival	Increased Survival
Baseline Survival (%)	30	81	61	0

Measurement of bioavailable contaminants

Most contaminants present in sediments are tightly bound to the particles and are not biologically available (i.e., do not enter or contribute to the chemical dose of the organism). However, contaminants dissolved in the sediment pore water have much higher biological availability and their concentration provides a more accurate measure of the chemical exposure to sediment dwelling organisms. It is difficult to measure pore water contaminant concentrations in sediment samples collected from the environment; only a small volume of sample is usually available, which limits the sensitivity of the analysis, and changes in contaminant concentrations can be caused by the extraction (e.g., by centrifugation) and storage of the sample, resulting in inaccurate data. To minimize these complications, this study used in situ passive sampling devices to collect pore water contaminants from BCE sediments.

Two types of passive samplers were used (Figure 15). Peepers, consisting of a plastic vial capped with a 0.45 µm pore size membrane were used to collect samples for trace metal analysis. Solid phase microextraction fibers (SPME), in a protective casing of metal mesh and glass fiber filter paper, were used to extract trace organics from the pore water. Divers placed both types of samplers within the sediment surface layer at four BCE stations. After one month of exposure, the passive samplers were retrieved and the contents analyzed for TMDL target contaminants and current use pesticides. Amphipod toxicity tests were also conducted on sediment samples from the study sites at the time of sampler deployment and retrieval. All samples were highly toxic, with survival ranging from 5 to 37% after 10 days of sediment exposure.

Metals results

In situ pore water trace metal concentrations were very low, relative to toxicity thresholds (Figure 16). All metal concentrations were 1 µg/L or less and far below water quality objectives used for marine waters (California Toxics Rule). Zinc measurements from the peeper samples were not available due to suspected contamination of the samplers. As an alternative, metal concentrations in pore water obtained by centrifugation of the sediments in the laboratory were

measured. These concentrations were generally higher than the peeper samples and below California Toxics Rule criteria (including zinc).

Trace organics results

Analysis of SPME samples detected very low concentrations of all of the TMDL trace organics, pyrethroids, and fipronil in BCE sediment pore water (Figure 17). Concentrations of PCBs, chlordanes, DDTs, and pyrethroids were always less than 1 ng/L, which was 10 to 10,000 times lower than the concentrations expected to be toxic to water column or sediment organisms. Pore water PAH concentrations were higher (up to 56 ng/L), but still at least 1,000 times lower than toxicity threshold concentrations. Fipronil concentrations were also low (up to 2 ng/L) and at least 2 times lower than toxicity thresholds reported in the literature.

The very low trace organic contaminant concentrations measured in BCE pore water chemistry were unexpected, considering that both whole sediment and laboratory-extracted pore water from the stations were toxic to amphipods and sea urchins. TIEs conducted on similar sediment samples suggest that pyrethroids were the likely cause of toxicity, yet pore water pyrethroid concentrations were far below toxic concentrations in all samples. The low pore water concentrations may be due to the strong binding of these compounds to the sediment. Incomplete information regarding toxicity thresholds and the pathways of chemical exposure to *E. estuarius* and lack of a repeat experiment to confirm these results limit our ability to interpret these results. Hypotheses to explain these results include the possibility that *E. estuarius* is exposed to higher concentrations of these compounds through the ingestion of contaminated sediment, or that handling of the sediments during laboratory toxicity tests may increase pore water contaminant concentrations above those actually present in BCE.

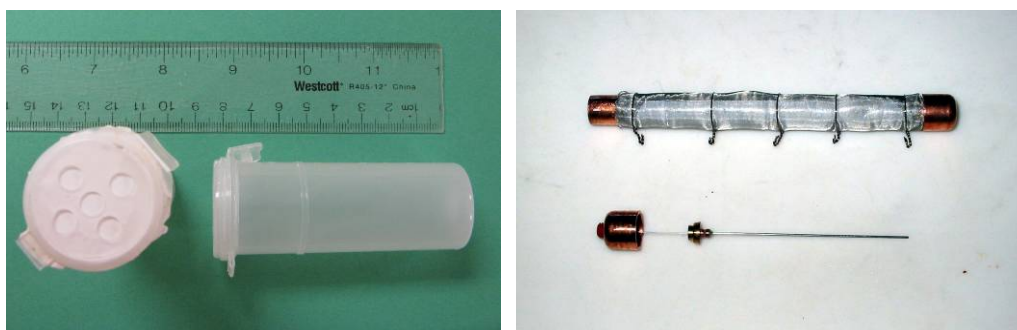


Figure 15. Passive samplers used for measurement of pore water concentrations of trace metals (left) and trace organics (right).

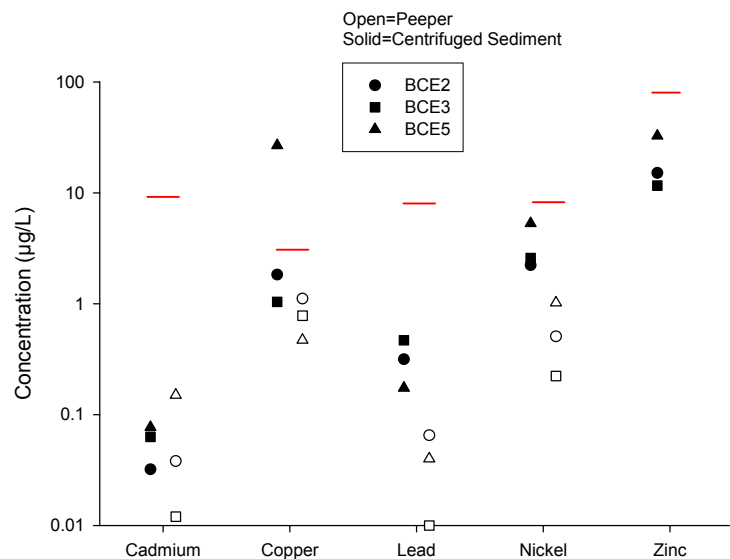


Figure 16. Concentration of trace metals in pore water obtained from in situ sediment peepers (open symbols) or by centrifugation in the laboratory (closed symbols). Horizontal lines indicate California Toxics Rule objectives for marine waters.

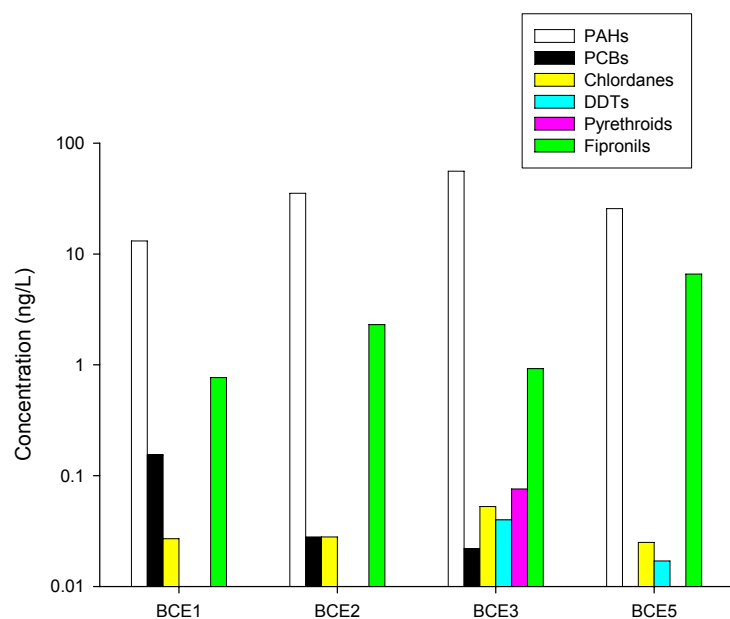


Figure 17. In situ concentration of organic contaminants in Ballona Creek Estuary sediment pore water obtained using SPME samplers. Each bar represents the sum of individual target analyte concentrations within each contaminant class.

What are the Toxicity Threshold Concentrations for Contaminants of Concern in BCE?

To determine more accurate toxicity thresholds for DDT, DDE, chlordane and cyfluthrin, it is necessary to conduct sediment spiking experiments. Sediment spiking tests are similar to the spiked water exposures used to develop water quality objectives and are the most reliable way to describe the concentration vs. response relationship for a specific chemical. However, sediment spiking experiments can be confounded by several factors, including geochemical differences between sediment types, the presence of other contaminants in the reference (spiking) sediment, and differences in chemical partitioning. These potential confounding factors were considered in the design of the spiking studies and steps were taken in this study to minimize their influence.

The reference sediment used for spiking was collected from Santa Monica Bay, offshore of the mouth of Ballona Creek (Figure 18). This site was chosen both for its proximity to Ballona Creek and its similarity in sediment geochemical parameters. The sediment had similar grain size and TOC characteristics to BCE sediment (0.63% and 30% fines, respectively).

Contaminant concentrations and toxicity were low or not detected in the reference sediment. Although the low sediment concentrations of DDTs and PCBs in the reference sediment were similar to those found in BCE, they were well below levels likely to cause toxicity (Table 7). These DDT and PCB concentrations reflect ambient background contamination levels of sediments within the Southern California Bight due to historical contaminant discharges.

Variations in chemical partitioning between experiments was controlled through the use of standardized spiking procedures. Separate batches of sediment were spiked with 4,4' DDT, 4,4' DDE, alpha chlordane, and cyfluthrin dissolved in solvent. Several concentrations of each chemical were prepared, spanning the expected range of toxicity. The sediment samples were periodically mixed and allowed to equilibrate for approximately 28 days before toxicity testing with *E. estuarius*. In previous studies at SCCWRP, it was found that this duration was adequate to approximate equilibrium in contaminant partitioning between the sediment and pore water. Sediment contaminant concentrations were verified by chemical analysis.

No toxicity was observed for DDE and chlordane in spite of very high maximum spiking concentrations: 19,300 and 13,400 ug/kg respectively (Figure 19). These concentrations are several orders of magnitude greater than what has been observed in BCE sediments. For DDT and cyfluthrin, toxicity was observed in the spiked sediment in a dose dependant manner. Cyfluthrin was by far the most toxic of the four chemicals tested, with toxicity observed at concentrations more than 500 times lower than DDT and more than 10,000 times lower than the highest concentrations tested for DDE and chlordane (Table 8).

The dose response data were used to calculate two toxicity thresholds: the No Observed Effect Concentration (NOEC), which is the highest concentration not producing toxicity, and the median lethal concentration (LC50), which is the concentration expected to kill 50% of the test organisms (Table 8). The calculated LC50 for DDT was 645 µg/kg, which was similar to the value of 554 µg/kg established by another researcher using the same test organism (Weston 1996). The calculated LC50 for cyfluthrin was three times lower than the value determined for the freshwater amphipod *Hyalella azteca* (Table 2). The lack of toxicity in sediments spiked with DDE and chlordane prevented the calculation of a precise estimate of the NOEC and LC50

for these compounds. However, a lower bound estimate of the NOEC and LC50 was determined for DDE and chlordane (Table 8) that can be used to interpret BCE sediment chemistry data.

The NOEC toxicity thresholds established in this study for DDE, DDT, and chlordane are much higher than the concentrations found in BCE sediments. The estimated NOECs for DDE and chlordane are approximately 1,000 times higher than the concentrations measured in BCE sediments (Figure 20). The DDT toxicity threshold (NOEC) of 645 $\mu\text{g/kg}$ is approximately 50 times greater than the highest DDT concentrations measured in BCE. However, BCE sediment concentrations of cyfluthrin were often above the NOEC of 1 $\mu\text{g/kg}$ and the LC50 of 2.07 $\mu\text{g/kg}$ that were calculated in this study (Figure 20).

The LC50 values for DDT and cyfluthrin reported in other studies are similar to those developed in the current study (Tables 2 and 9). Published values for toxicity thresholds can be quite variable, often ranging an order of magnitude or more for the same chemical. This variability is due to many factors, including differences in sensitivity between species, different test methods between studies (e.g. duration of exposure and spiking method), and characteristics of the sediment used for spiking (e.g. sediment grain size and TOC content). Some of this variation can be reduced through standardization of spiking methods and normalization of threshold concentrations to organic carbon. However, such normalization is not possible for many of the previous studies due to a lack of information on test methods and sediment characteristics. The toxicity thresholds estimated for DDE, DDT, chlordane, and cyfluthrin in this study are considered to be most relevant for assessing BCE sediment quality because these values were normalized to organic carbon, used sediments similar to those in BCE, and were based on toxicity to the same type of organism used to establish the TMDL.

Review of other toxicity thresholds obtained from the scientific literature supports the conclusion that none of the TMDL target organic compounds (i.e. DDTs, PCBs, chlordane, and PAHs) are likely to be a significant cause of sediment toxicity in BCE. While the data are variable, even the lowest reported LC50 values for DDD, DDT, PCBs, and PAHs are 10 to 10000 times higher than the concentrations found in the estuary (Table 9). The similarity of the toxicity thresholds established in this study to those found in the literature indicates that our results are reliable.

Caution is warranted in making comparisons of the PCB and PAH thresholds to BCE. Such comparisons have greater uncertainty because PCBs and PAHs are mixtures of many individual compounds, each with potentially different toxicities, and the composition of the mixtures tested in other studies is likely different from that present in BCE. Similar uncertainty is also present in the use of most sediment quality guidelines for PCBs and PAHs (e.g., ERLs and ERM_s). Greater confidence in PCB and PAH threshold estimates could be gained by conducting spiking exposures similar to what was done for the pesticides.

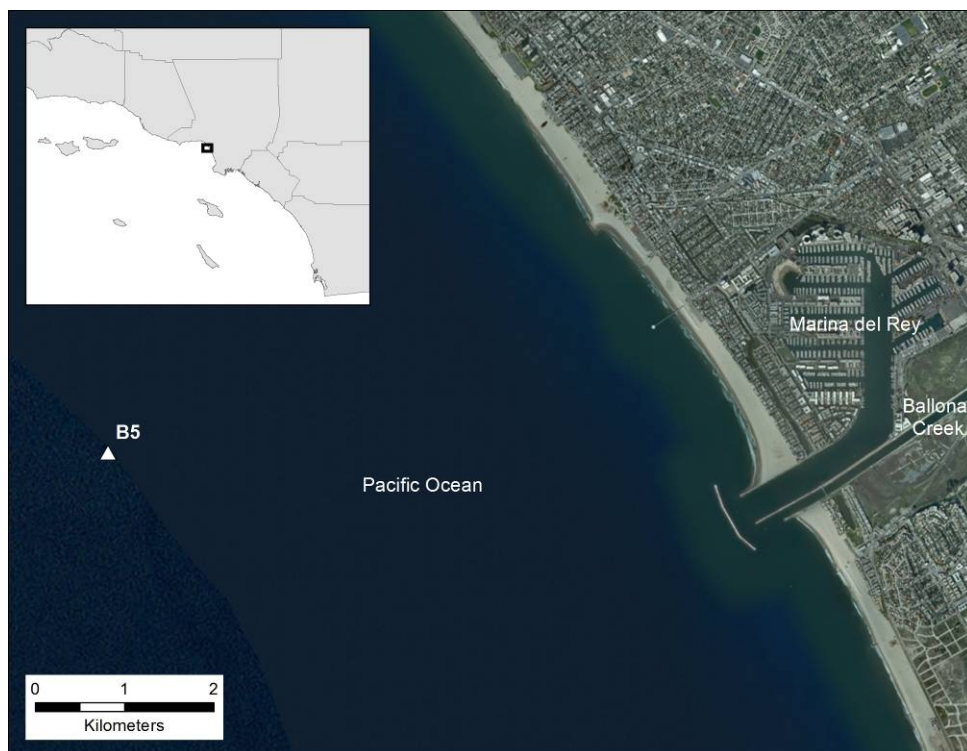


Figure 18. Location of source sediment (station B5) used for spiking experiments.

Table 7. Physical and chemical characteristics of source sediment used for spiking experiments.

Parameter (units)	Value
Survival (%)	83
Fines (%)	30
TOC (%)	0.6
Total PAHs (µg/kg)	NA
Total DDTs (µg/kg)	47
Total PCBs (µg/kg)	15
Total Pyrethroids (µg/kg)	ND
Fipronil (µg/kg)	ND
Total Chlordanes (µg/kg)	0.3

NA = Not analyzed

ND= Not detected

Table 8. Summary of toxicity thresholds obtained from spiked sediment tests. Results are expressed both on a dry weight basis and normalized to sediment organic carbon.

Chemical	NOEC¹		LC50²	
	µg/kg	µg/g OC	µg/kg	µg/g OC
4,4'-DDE	≥19300	≥3050	>19300	>3050
4,4'-DDT	645	102	1680	266
Alpha-chlordane	≥13400	≥2120	>13400	>2120
Cyfluthrin	0.95	0.15	2.07	0.33

¹NOEC = No observed effect concentration. The highest concentration not significantly different from the control response.

²LC50 = The 50% lethal concentration. The concentration that would be expected to cause 50% mortality of the test organisms.

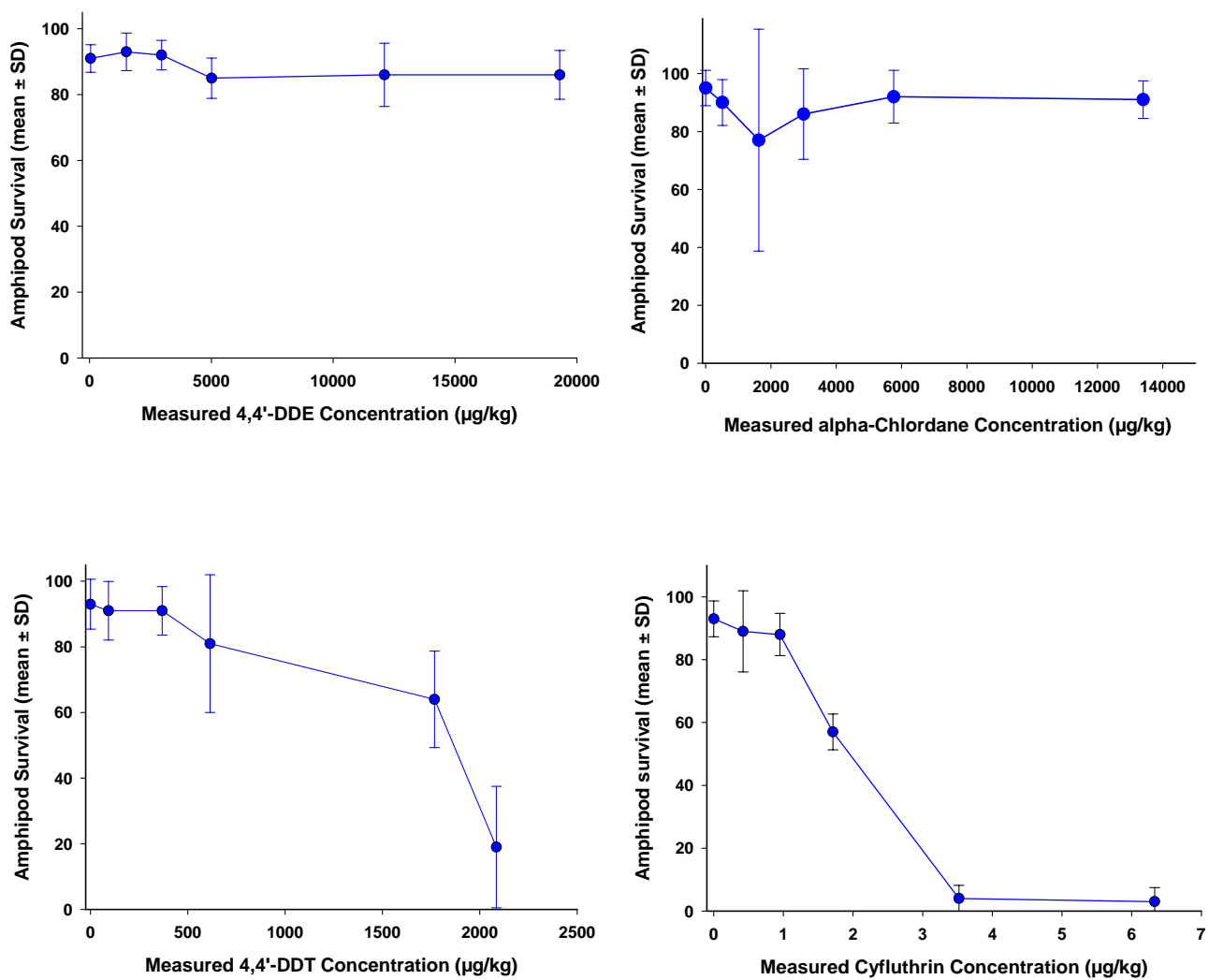


Figure 19. Dose-response plots for *E. estuarius* 10-day exposures to spiked sediments.

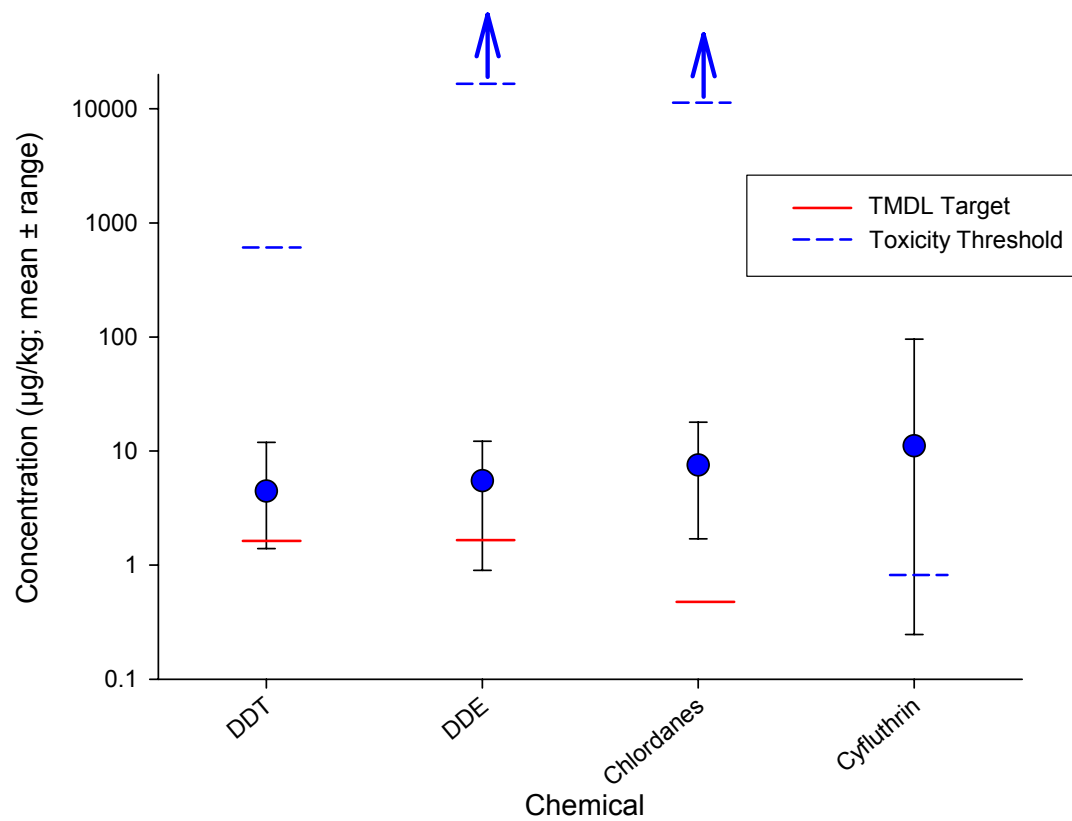


Figure 20. Relationship of toxicity threshold (NOEC) from spiked sediment tests to concentration measured in BCE sediments (mean ± range). Arrows indicate that the NOEC is a low estimate due to the lack of any toxicity in the sediments.

Table 9. Sediment toxicity thresholds (LC50) based on laboratory studies with sediment dwelling organisms. Data are expressed as µg/kg.

Chemical	Organism	Taxon	Habitat	LC50	Reference
DDTs					
DDD	<i>Hyalella azteca</i>	Amphipod	Freshwater	2600 ¹	Ingersoll et al. 2005
DDT	<i>Diporeia sp.</i>	Amphipod	Freshwater	12300	Lotufo et al. 2001
DDT	<i>Rhepoxynius abronius</i>	Amphipod	Marine	6180	Murdoch et al. 1997
DDT	<i>Eohaustorius estuarius</i>	Amphipod	Marine	554	Weston 1996
DDT	<i>R. abronius</i>	Amphipod	Marine	1036	Weston 1996
DDT	<i>Ampelisca abdita</i>	Amphipod	Marine	769	Weston 1996
DDT	<i>H. azteca</i>	Amphipod	Freshwater	1100	Lotufo et al. 2001
PCBs					
Aroclor 1242	<i>Crangon septemspinosa</i>	Shrimp	Marine	784	McLeese and Metcalfe 1980
Aroclor 1254	<i>R. abronius</i>	Amphipod	Marine	10800	Swartz et al. 1988
Aroclor 1254	<i>Microarthridion littorale</i>	Copepod	Marine	182000	DiPinto et al. 1993
PCB Mixture	<i>R. abronius</i>	Amphipod	Marine	25600	Murdoch et al. 1997
PCB Mixture	<i>Macoma nasuta</i>	Clam	Marine	810 ¹	Boese et al. 1995
PAHs					
Fluoranthene	<i>E. estuarius</i>	Amphipod	Marine	85300	Anderson et al. 2008
Fluoranthene	<i>A. abdita</i>	Amphipod	Marine	27600	Anderson et al. 2008
Fluoranthene	<i>R. abronius</i>	Amphipod	Marine	92680	Swartz et al. 1997
Acenaphthene	<i>R. abronius</i>	Amphipod	Marine	64680	Swartz et al. 1997
Phenanthrene	<i>R. abronius</i>	Amphipod	Marine	61880	Swartz et al. 1997
Phenanthrene	<i>Grandidierella japonica</i>	Amphipod	Marine	>30000	SCCWRP 1989
Pyrene	<i>R. abronius</i>	Amphipod	Marine	78680	Swartz et al. 1997
PAH Mixture	<i>Arenicola marina</i>	Polychaete	Marine	9242	Morales-Caselles et al. 2008
PAH Mixture	<i>Palaemonetes pugio</i>	Shrimp	Marine	6464	Wirth et al. 1998

¹Calculated from organic carbon normalized value assuming 1% total organic carbon.

IMPLICATIONS FOR MANAGEMENT OF BALLONA CREEK ESTUARY

The analyses conducted during this study have resulted in a greater understanding of the characteristics and causes of sediment toxicity in BCE. These results may be used in several ways to guide the development of a toxics management plan for the estuary and its watershed. Following is a summary of the major conclusions of the study and their implications for management.

- 1. Chemical contamination of BCE sediments is widespread and causing toxicity to sediment-dwelling organisms.** Every sampling event detected sediment toxicity to one or more marine species at multiple stations, and multiple contaminants were present at concentrations above background. These results support the continued listing of BCE as an impaired water body, with respect to toxic impacts on the organisms living in association with the sediment. The diversity of contaminants present indicates that there are multiple sources of contamination within the watershed.
- 2. Sediment quality in BCE shows high seasonal and spatial variability.** Sediment characteristics were found to vary markedly over short distances and time intervals within the estuary. Much of this variation was likely due to processes typical of estuaries, such as storm water flows, mixing of fresh and saltwater, and tidal water exchange. Consequently, sediment quality in BCE should be assessed based on measurements from multiple locations, rather than focusing on the conditions at a specific location.
- 3. Pyrethroids, and possibly other current use pesticides, are the principal cause of sediment toxicity in BCE.** Two independent lines of evidence indicated that pyrethroid pesticides are the dominant cause of sediment toxicity in BCE sediments: enhanced chemistry measurements and toxicity identification evaluations. Management actions that reduce the load of pyrethroids to BCE are likely to have the greatest benefit towards improving sediment quality in the estuary. Fipronil, another highly toxic pesticide, was also detected in BCE sediments at levels of possible concern. Additional monitoring and research focusing on the effects of fipronil to BCE sediment fauna is warranted.
- 4. The contaminants currently listed in the BCE TMDL are minor contributors to the observed sediment toxicity.** This finding suggests that reductions in the loads of legacy pollutants and trace metals will have little impact on BCE sediment toxicity, relative to the likely benefits of reducing loads of current use pesticides. Enhanced chemical analysis and toxicity identification evaluations indicated that PAHs, PCBs, chlordanes, and DDTs were not likely to be significant factors in BCE sediment toxicity. Some contribution of trace metals to the toxicity of sediment pore water extracted in the laboratory may be occurring, but in situ chemistry analyses indicate that the role of metals is likely to be minor at best.
- 5. The current management targets for BCE sediments are inaccurate.** The current targets established for improvement of BCE sediment quality have little predictive value, as they are far below levels of toxic impact and have little correspondence with the presence/absence of sediment toxicity. The TMDL target concentrations for metals do not compensate for variations in particle size or biological availability, increasing the likelihood that the cause and biological significance of changes in BCE sediment metals concentration will be misinterpreted. Trace organic toxicity thresholds are several orders of magnitude higher than

current TMDL target concentrations, indicating that such targets have little value for assessing sediment quality or monitoring the success of management actions.

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APPENDIX A: YEAR 1 PROGRESS REPORT

Sediment Toxicity Identification in Ballona Estuary

**Progress Report
April 16, 2008**

Sediment Contamination and Toxicity Survey

The objective of this task is to determine the toxicity of Ballona Estuary sediments at various locations and to different marine species. These data will be used to select locations for the toxicity identification evaluation (TIE) studies.

Sediment samples were collected from six different sites within Ballona Estuary by LAEMD on September 26 and October 3 of 2007 (Table 1, Figure 1). Each site was tested for toxicity by LAEMD using an amphipod whole sediment and an abalone sediment-water interface test. LAEMD found that five out of the six stations were toxic to the amphipod, *Eohaustorius estuarius* (Table 2). Station 1 showed a high percentage of amphipod survival while stations 2 through 6 showed low percentages of survival (Table 2). Stations 2 and 3 showed toxicity to the abalone, *Haliotis rufescens* (Table 3). A range of sediment organic enrichment and particle size was also present among the six stations. Stations 2 and 3 contained the greatest amounts of organic matter and highest proportion of fine sediments whereas Stations 4, 5 and 6 contained less than 10% fines (silt+clay) (Table 4). Based on these data, stations 2 and 4 were selected for TIE testing at SCCWRP to represent toxicity over range of sediment conditions. Additional sediment from stations 2 and 4 were collected by LAEMD with the assistance of SCCWRP staff on October 19, 2007 to use in the TIEs

Sediment samples from both collection events were also analyzed for a suite of trace metal and organic contaminants. Analyses of the samples from the first collection event for metal and trace organic priority pollutants were conducted by LAEMD. Chemical analyses of the second set of samples was conducted by CRG laboratory; these analyzes included organophosphate pesticides. Samples from both collection events were also analyzed by SCCWRP for a suite of additional current use pesticides that included Fipronil and its metabolites and commonly used pyrethroids. A summary of all chemistry data is included in the Appendix.

Toxicity Characterization

The objective of this task is to determine the general types of contaminants associated with sediment toxicity. These data will be used to refine the toxicity and chemistry analyses in subsequent tasks.

Bulk sediment collected on 10/19/07 from stations 2 and 4 were homogenized in the laboratory and placed into 4L HDPE jars. The samples were then stored in a walk-in refrigerator at 4°C until used in TIE experiments. The TIE characterization experiments included tests of both whole sediment and pore water. A variety of treatments were applied to each matrix type with the intent of characterizing the general chemical characteristics of the toxicants (Table 5).

Whole sediment TIE methods

A 10-day whole sediment TIE was conducted using the amphipod *E. estuarius*. The whole sediment TIE treatments included coconut carbon, cation exchange resin, Optipore beads, and piperonyl butoxide (PBO) (Table 5). Treatments for station 2 were conducted using site sediment concentrations of 25%, 50% and 100% in order to provide greater resolution of changes in toxicity. Station 4 treatments were conducted at sediment concentrations of 50% and 100%; a 25% concentration was not included because the prior LAEMD results indicated that this sample was not as toxic as station 2. Sediment was diluted using control sediment obtained from the amphipod collection site. Untreated site sediment at each concentration was also tested to provide a baseline for comparison with the TIE treatments. The control sediment was also tested with each TIE treatment as a blank to determine whether or not the treatments were a possible cause of toxicity. Three replicates were used for all treatments.

Sediment was passed through a 2 mm screen before testing began. Each treatment was conducted in 250 ml beakers containing approximately 40 ml of sediment and 200 ml of 20 ppt seawater. Ten amphipods were added to each lightly aerated beaker for 10 days under constant light and kept at a temperature of 15°C. Dissolved oxygen, pH, salinity and ammonia samples from overlaying water were taken at the beginning and end of the experiment from surrogate water quality beakers. Observations of amphipod mortality were made daily. At the end of the test, the surviving amphipods were counted to determine percentage survival.

Pore water TIE methods

A 10-day TIE experiment was also used to test the pore water from the two revisited Ballona Estuary stations. TIE treatments included EDTA, sodium thiosulfate (STS), piperonyl butoxide (PBO), C18 column extraction and cation resin exchange column extraction (Table 5). To obtain pore water, sediment was centrifuged at 3,000xg for 30 minutes. Pore water was treated with EDTA, STS and PBO at 25%, 50% and 100% for station 2 and 50% and 100% for station 4, using 20ppt laboratory seawater as the diluent. Pore water was run through C18 and cation resin exchange columns. For baseline determination, untreated pore water was tested at each concentration using 20 ppt seawater as the diluent. Samples of 20 ppt seawater were also treated with each TIE procedure for use as blanks to detect toxicity related to the treatment. Three replicates were used for each treatment.

Each treatment was conducted in a shell vial with 10 ml of sample at a temperature of 15°C. Five *E. estuarius* were added to each vial for 10 days under constant darkness without aeration. Dissolved oxygen, pH, salinity and ammonia samples were taken from overlying water at the beginning and end of the test from surrogate water quality vials for each site. Surviving amphipods were counted on days 4 and 10 to determine percentage survival.

Results for whole sediment

Station BCE 2. A dose response was observed in the baseline samples (Figure 2). A similar level of toxicity was observed at station 2 by both SCCWRP and LAEMD, showing very low percentages of amphipod survival (Table 2, Figure 2).

High amphipod survival was present in the coconut carbon treatment, suggesting a decrease in toxicity due to the binding of organic contaminants. Survival following cation exchange resin treatment appeared to be similar to the baseline, which suggests that metals were not a major cause of toxicity at station 2. However, there also was an additional increase in toxicity associated with the PBO treatments, indicating that pyrethroid insecticides may be contributing to toxicity at station 2. The Optipore treatment produced highly variable results and did not appear to reduce toxicity appreciably (Figure 2).

Station BCE 4. The 100% baseline sample produced approximately 70% amphipod survival (Figure 3), which indicated much less toxicity compared to the results from the toxicity survey (Table 2). Changes in the toxicity at station 4 may have been related to sediment particle size. There was a marked difference in particle size between the two samples, with a greater proportion of coarse sediments present in the September sample.

Amphipod survival was high in both the coconut carbon and cation resin exchange treatments (Figure 3). However, the relatively low toxicity in the baseline sediment limits the ability to determine whether the carbon and cation resin treatments were effective on this sample. Treatment of the sediment with PBO produced an increase in toxicity, similar to the pattern observed for station 2, again suggesting the presence of pyrethroid pesticides

Results for pore water

Station BCE 2. The pore water TIE results showed a similar pattern of toxicity characteristics as did the whole sediment analyses, suggesting that the toxic agent(s) are biologically available via porewater as well as through whole sediment. The 4-day exposure baseline samples showed a dose response with increasing mortality at both the 50% and 100% concentrations of baseline sediment (Figure 4). C-18 extraction appeared to remove the toxicity, but the EDTA and STS treatments were ineffective. An increase in pore water toxicity was observed at each of the PBO treatment concentrations.

The 10-day survival results were similar to those observed at 4 days (Figure 5). Partial effectiveness of C-18 extraction was observed and PBO treatment consistently increased toxicity. The EDTA and STS treatments produced inconsistent results; there was some reduction of toxicity in the 50% treatment, but greater toxicity at 100%. However, it is difficult to tell if EDTA had an effect on the sample because of the high variability of amphipod survival in the baseline treatment.

Station BCE 4. There was no substantial toxicity present in the baseline samples after 4 days of pore water exposure (Figure 6). Consequently, the effectiveness of the C-18, EDTA, and STS treatments could not be determined from the data. Toxicity was increased in both of the PBO treatments, consistent with the results observed in the whole sediment TIE. Greater toxicity was present in the 10-day baseline samples (Figure 7), which is consistent with the effects of exposure to a chemical stressor. The 10-day results confirmed those at 4-days, with PBO increasing the toxicity of the samples.

Toxicity Identification

Studies are in progress to confirm the Phase I toxicity characterization results and to provide greater specificity in identifying the probable cause of toxicity at station BCE 2. These studies include the development and application of additional TIE treatments that have been reported to be effective on pyrethroids. Confirmation of the toxicant characterization results includes two types of investigations: comparison toxicity units predicted from contaminant concentrations with those measured in the toxicity tests and verification of the effectiveness of selected TIE treatments on pyrethroids.

Preliminary TIE verification studies have confirmed that one type of pyrethroid (bifenthrin) is highly toxic to *E. estuarius* and that PBO treatment increases this toxicity. The dose response relationship of *E. estuarius* to bifenthrin spiked into seawater is shown in Figure 8. The toxicity response of *E. estuarius* to bifenthrin was increased with a longer exposure duration and $\geq 50\%$ mortality was produced by exposure to only 0.1 $\mu\text{g/l}$ of the compound. A separate experiment with bifenthrin confirmed that the PBO treatment used in the TIE increases toxicity of some pyrethroids. For example, addition of PBO to the test solutions resulted in a much higher percentage of amphipod mortality following 7 days of exposure to 0.05 $\mu\text{g/L}$ bifenthrin (Figure 9) than did exposure to bifenthrin without PBO. Note that toxicity was observed in the 10-day control samples, which contained PBO. This result indicates that PBO (an inhibitor of metabolism) has inherent toxicity to *E. estuarius*.

Similar work is in progress to investigate the effect of the PBO and other TIE treatments on pyrethroid toxicity to *E. estuarius*.

Table 1. Sediment collection and testing events.

Station	Toxicity Survey		Phase I TIE	
	Collection	Collection	Testing	
			Whole Sediment	Pore Water
<i>BCE1</i>	10/3/2007			
BCE2	9/26/2007	10/19/2008	10/26/2007	10/30/2007
BCE3	9/26/2007			
BCE4	9/26/2007	10/19/2008	10/26/2007	10/30/2007
BCE5	9/26/2007			
BCE6	9/26/2007			

Table 2. LAEMD toxicity survey results for *E. estuarius*. The control mean was 97%.

Station	Mean (% Survival)	Std. Dev.
<i>BCE-1</i>	89	11.94
BCE-2	3	6.71
BCE-3	0	0
BCE-4	16	8.22
BCE-5	18	4.47
BCE-6	8	4.08

Table 3. LAEMD toxicity survey results for *H. rufescens*. The dilution water control mean was 96.4% and the brine control mean was 97.3%.

Station	Mean (% Normal)	Std. Dev.
<i>BCE-1</i>	90.5	3.8
BCE-2	73.3	45
BCE-3	0	0
BCE-4	98.4	1.29
BCE-5	96.2	1.25
BCE-6	92.6	0.93

Table 4. Sediment characteristics for the toxicity survey stations.

Parameter	Units	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
TS	%	69.4	47.8	31.5	75.6	77.5	82.4
TOC	%	0.57	0.97	1.38	0.53	0.38	NA
Sand	%	80.15	65.04	43.24	46.23	91.34	17.49
Silt	%	17.39	30.53	51.77	6.21	0	0.37
Clay	%	2.53	4.45	5.01	0.78	0	0.05
Gravel	%	0	0	0	46.8	8.7	82.1
Fines (normalized to Sa+Si+Cl))	%	19.91	34.97	56.77	13.13	0	2.35

Table 5. Treatments used for whole sediment and pore water TIEs.

Treatment	Matrix	Purpose
EDTA	Water	Chelation of cationic metals (e.g. Zn, Cu)
Sodium thiosulfate (STS)	Water	Reducing agent for oxidizers (e.g. chlorine); reduces toxicity of some metals
C-18 column extraction	Water	Removal of non-polar organics
Cation exchange column extraction	Water	Removal of cationic metals
Coconut carbon	Sediment	Binding of organic contaminants
Cation exchange resin	Sediment	Binding of cationic metals
Piperonyl butoxide (PBO)	Water/ Sediment	Renders organophosphorus pesticides non-toxic; increases toxicity of pyrethroid pesticides
Optipore beads	Sediment	Binding of organic contaminants

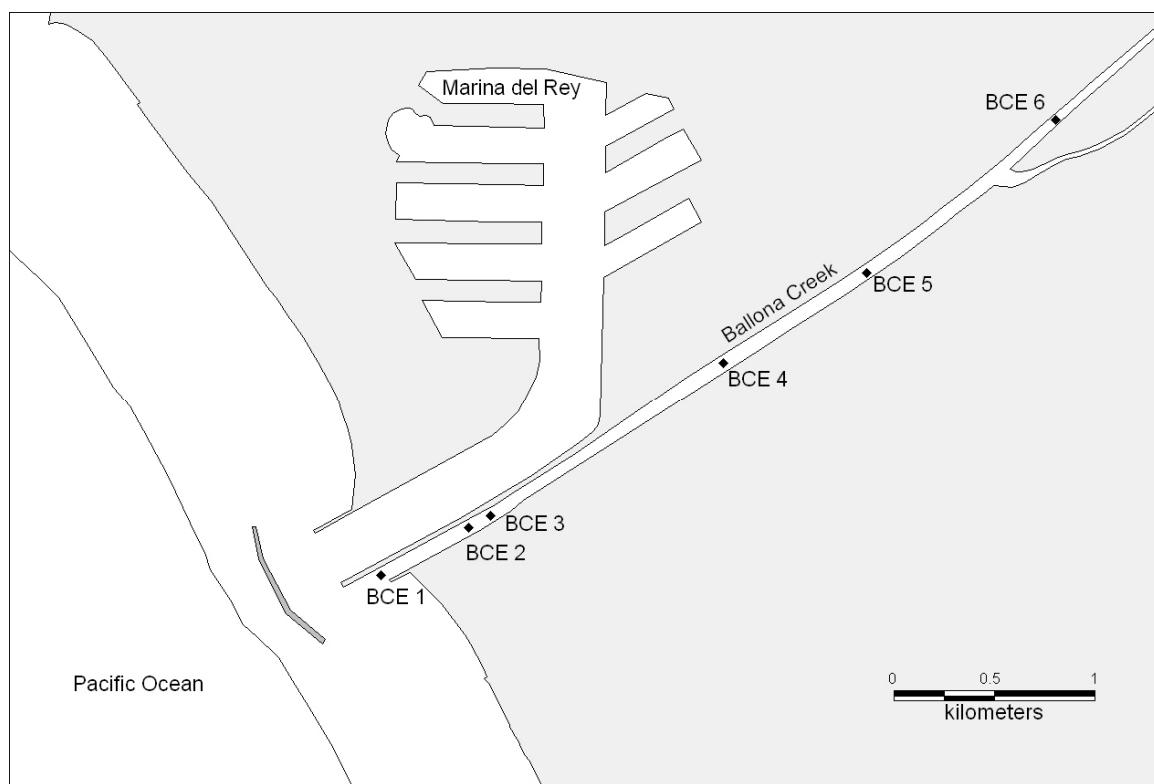


Figure 1. Ballona Creek sampling stations used for toxicity survey and TIE analyses.

BCE 2 Sediment TIE

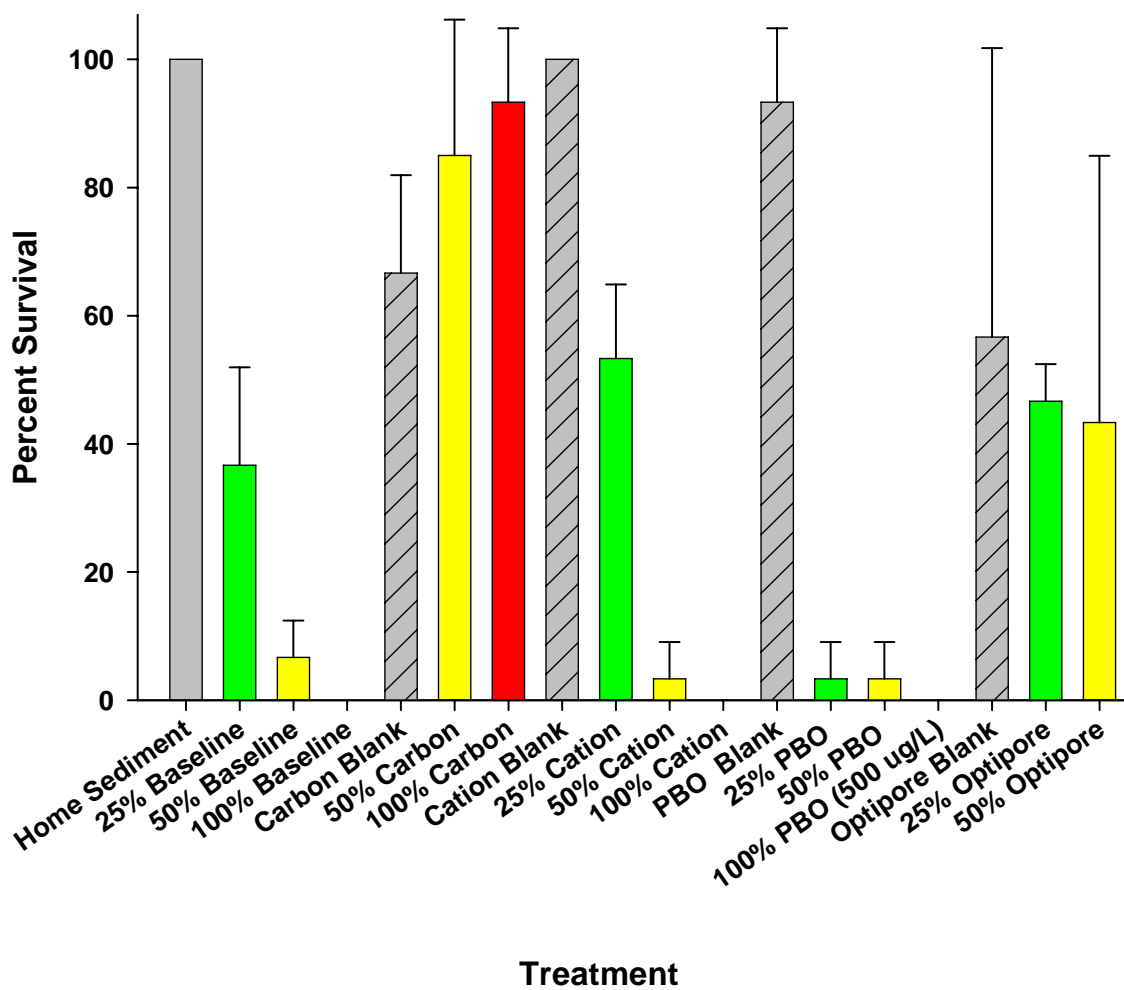


Figure 2. *E. estuarius* sediment TIE results for station BCE 2 collected 10/19/07. The 25% carbon and 100% Optipore treatments were not included in this test.

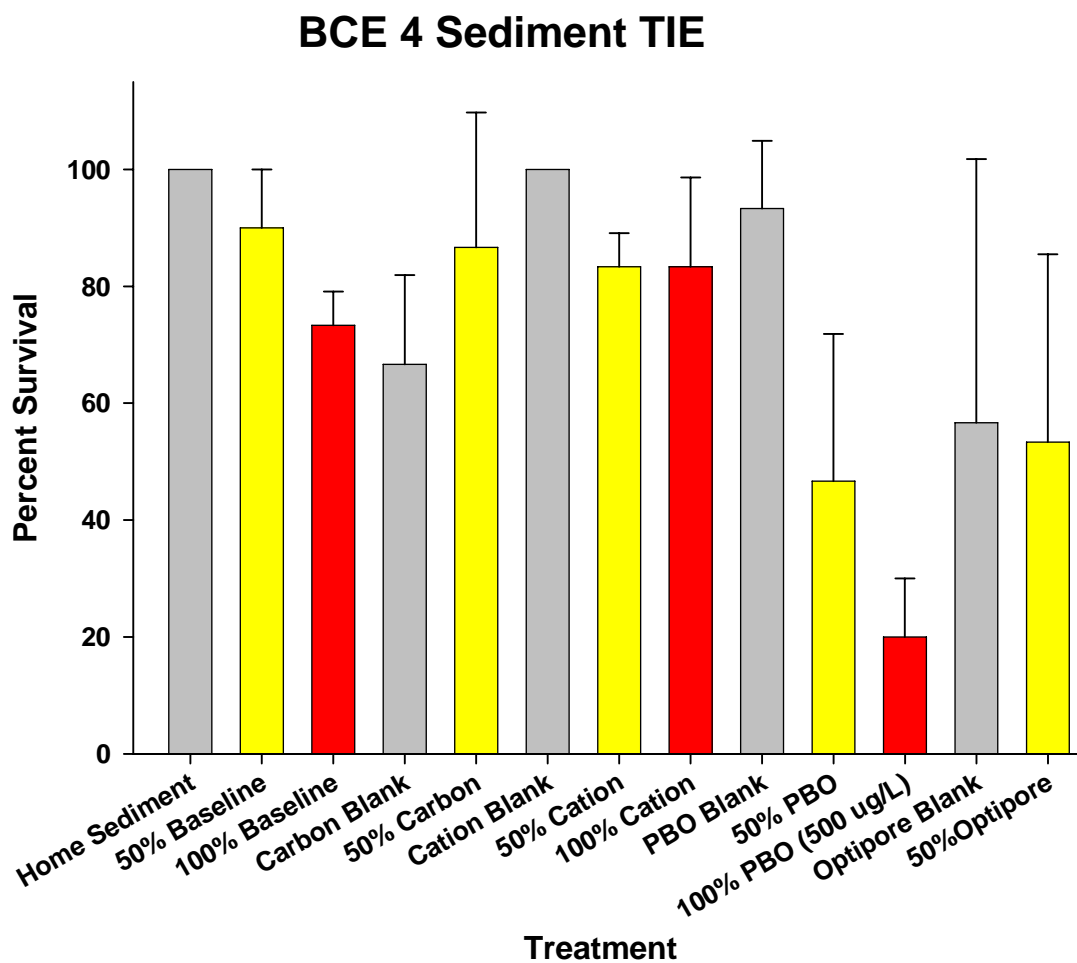


Figure 3. *E. estuarius* sediment TIE results for station BCE 4 collected 10/19/07. The 100% carbon and Optipore treatments were not included in this test.

BCE 2 Porewater TIE
***Eohaustorius estuarius* 4 Day Survival Results**

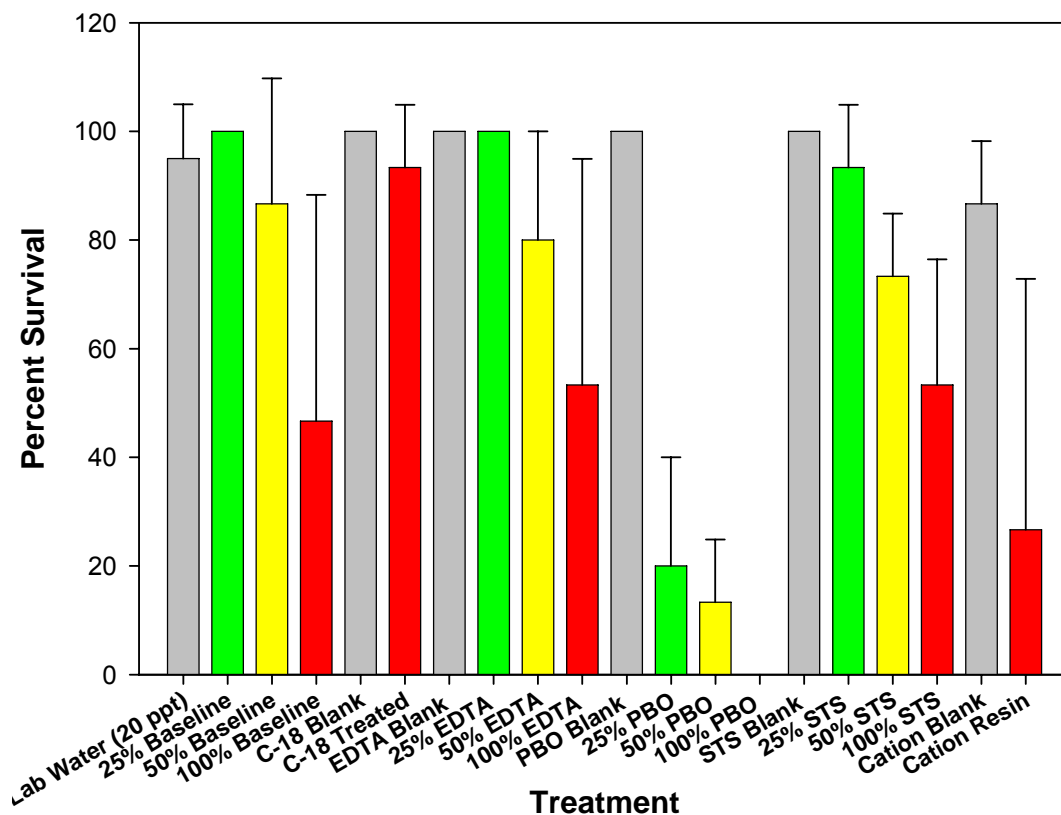


Figure 4. *E. estuarius* 4-day pore water TIE results for station BCE 2 collected 10/19/07.

BCE 2 Porewater TIE ***Eohaustorius estuarius* 10 Day Survival Results**

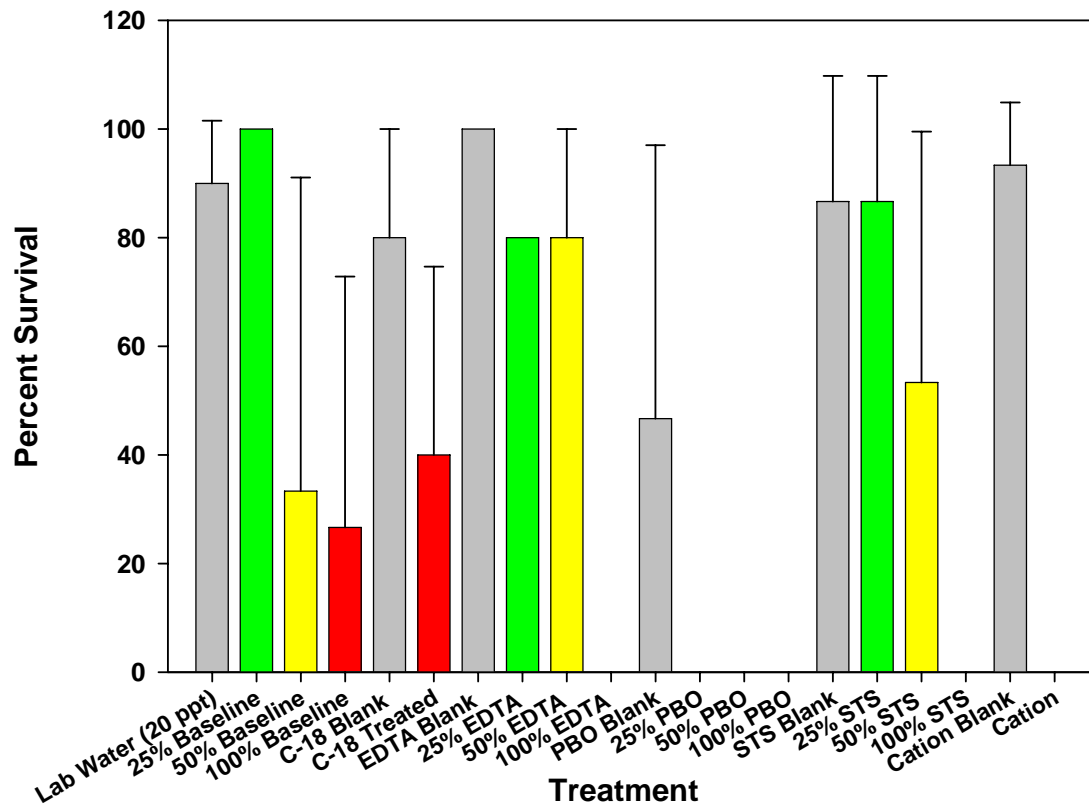


Figure 5. *E. estuarius* 10-day pore water TIE results for station BCE 2 collected 10/19/07.

BCE 4 Porewater TIE
***Eohaustorius estuarius* 4 Day Survival Results**

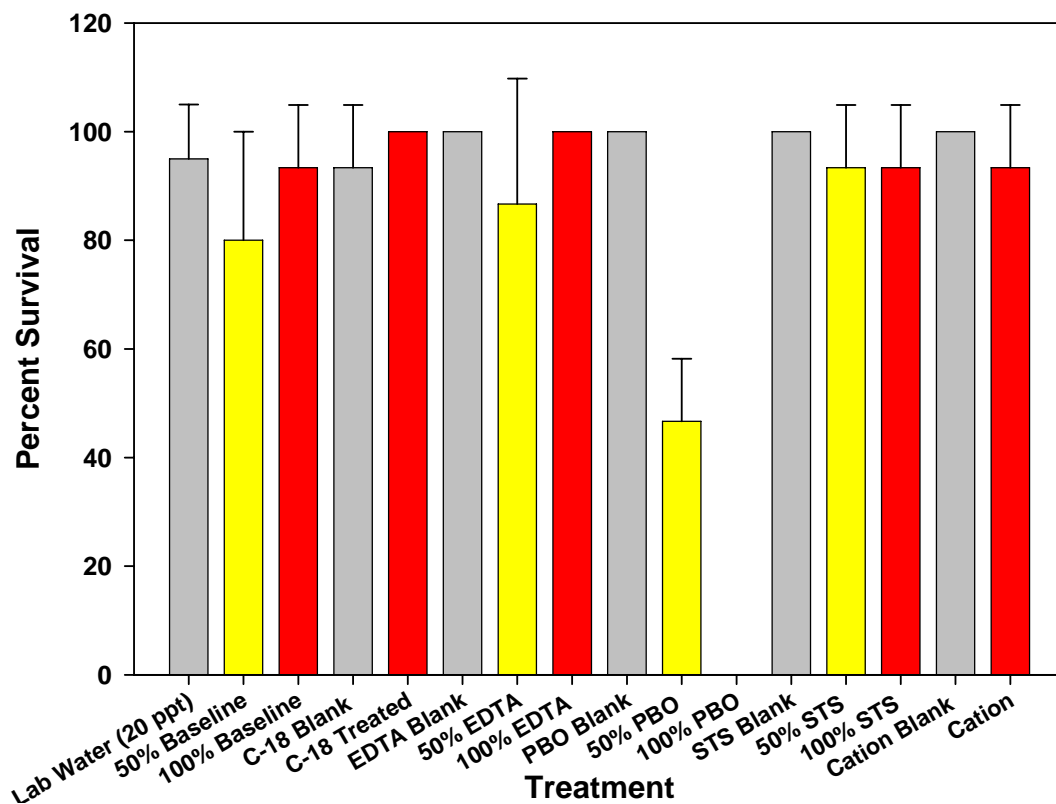


Figure 6. *E. estuarius* 4-day pore water TIE results for station BCE 4 collected 10/19/07.

BCE4 Porewater TIE
***Eohaustorius estuarius* 10 Day Survival Results**

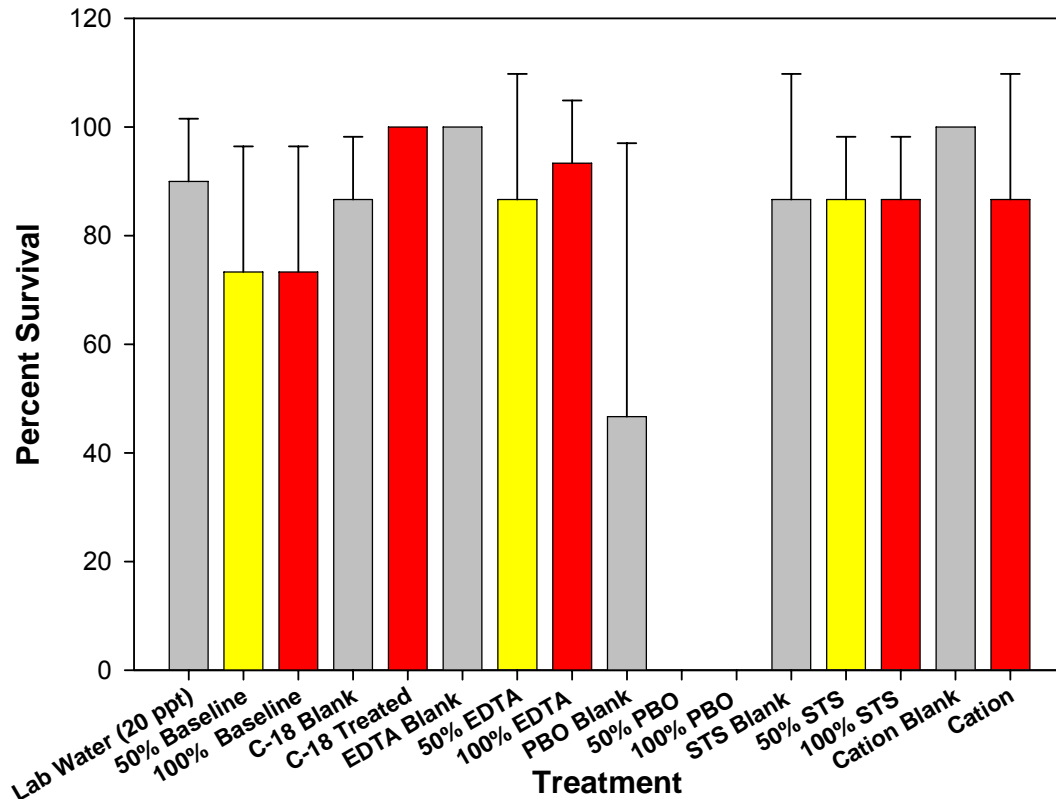


Figure 7. *E. estuarius* 10-day pore water TIE results for station BCE 4 collected 10/19/07.

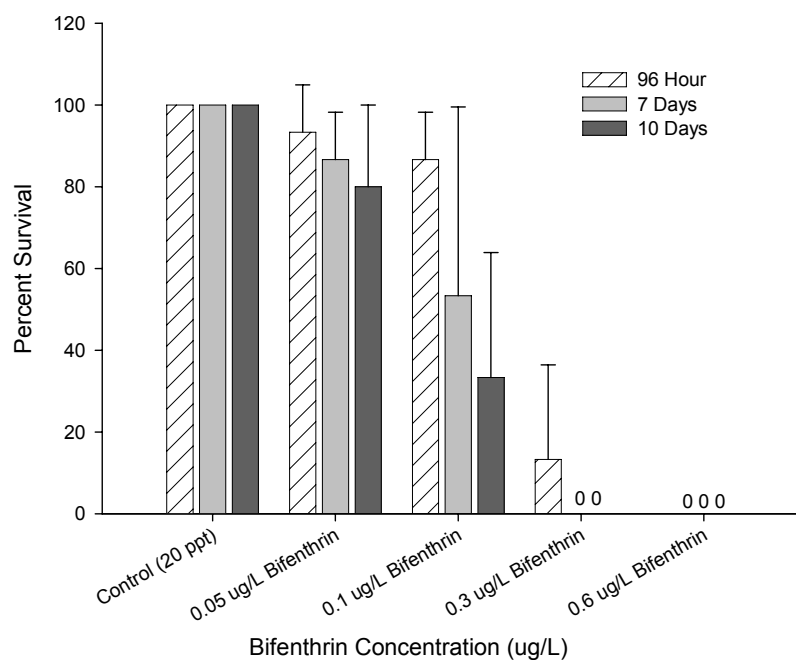


Figure 8. *E. estuarius* survival results for bifenthrin exposure in water. All concentrations are nominal values.

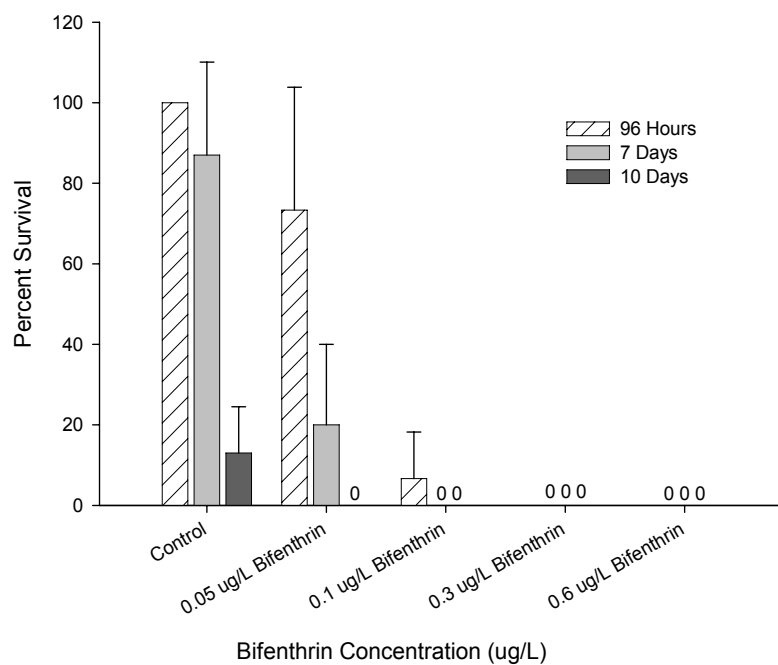


Figure 9. *E. estuarius* survival results for bifenthrin with PBO addition. All concentrations are nominal values.

APPENDIX

Sediment characteristics and concentrations of contaminants. All analyses for pyrethroids and Fipronil compounds conducted by SCCWRP. Analyses for other constituents in samples collected on 10/19 were conducted by CRG. All other data provided by LAEMD

Parameter	Unit	Station and Collection Date (2007)							
		BCE1 10/3	BCE2 9/26	BCE2 10/19	BCE3 9/26	BCE4 9/26	BCE4 10/19	BCE5 9/26	BCE6 9/26
%TS	%	69.4	47.8		31.5	75.6		77.5	82.4
%TOC	%	0.5770	0.969	23.98	1.38	0.533	0.26	0.381	NR
%Sand	%	80.15	65.04	58.04	43.24	46.23	68.62	91.34	17.49
%Silt	%	17.39	30.53	39.35	51.77	6.21	28.47	0	.37
%Clay	%	2.53	4.45	2.61	5.01	0.78	2.91	0	.05
%Gravel	%	0	0	NA	0	46.8	NA	8.7	82.1
% Fines normalized to Sa+Si+Cl	%	19.91	34.97	41.96	56.77	13.13	31.38	0.00	2.35
Cd	mg/kg	0.547	1.56	1.315	1.81	0.536	0.228	0.385	0.229
Cu	mg/kg	17.6	54.6	97.09	117	14.4	8.155	16.4	12.6
Mercury	mg/kg	0.0558	0.128	0.117	0.188	0.0651	0.025	0.0324	0.0268
Pb	mg/kg	30.3	52.1	69.95	66.7	11.3	10.49	15.2	4.93
Ag	mg/kg	0.563	1.40	1.344	1.60	0.190	0.144	0.306	<0.020
Zn	mg/kg	89.1	228	455.3	430	103	70.27	107	57.9
2,4'-DDE	ug/kg	<0.7	<0.7	ND	<0.7	<0.7	ND	<0.7	<0.7
4,4'-DDE	ug/kg	5.3	5.8	14	5.3	1.1	4.5	1.2	<0.6
2,4'-DDD	ug/kg	<1	<1	ND	<1	<1	ND	<1	<1
2,4'-DDT	ug/kg	<0.8	<0.8	ND	<0.8	<0.8	ND	<0.8	<0.8
4,4'-DDD	ug/kg	<1	<1	ND	<1	<1	ND	<1	<1
4,4'-DDT	ug/kg	<0.7	<0.7	ND	<0.7	<0.7	ND	<0.7	<0.7
A-Chlordane	ug/kg	3.00	<0.19	6.9	<0.19	<0.19	2.5	<0.19	<0.19
G-Chlordane	ug/kg	2.10	5.10	6.8	6.00	<0.18	2.9	<0.18	<0.18
Oxychlordane	ug/kg	<0.9	<0.9	ND	<0.9	<0.9	ND	<0.9	<0.9
A-Chlordene	ug/kg	NSA	NSA	NA	NSA	NSA	NA	NSA	NSA
G-Chlordene	ug/kg	NSA	NSA	NA	NSA	NSA	NA	NSA	NSA
Trans-Nonachlor	ug/kg	<0.16	<0.16	NA	<0.16	<0.16	ND	<0.16	<0.16
Cis-Nonachlor	ug/kg	<0.27	<0.27	ND	2.10	<0.27	NA	<0.27	<0.27

(Note: values that are revised from the original report are underlined.)

Station and Collection Date (2007)									
Parameter	Unit	BCE1 10/3	BCE2 9/26	BCE2 10/19	BCE3 9/26	BCE4 9/26	BCE4 10/19	BCE5 9/26	BCE6 9/26
Acenaphthylene	mg/kg	<0.26	<0.26	0.0248	<0.26	<0.26	0.0011	<0.26	<0.26
Acenaphthene	mg/kg	<0.28	<0.28	0.0135	<0.28	<0.28	ND	<0.28	<0.28
Fluorene	mg/kg	<0.29	<0.29	0.0248	<0.29	<0.29	0.0018	<0.29	<0.29
2-Chloronaphthalene	mg/kg	<0.24	<0.24	NA	<0.24	<0.24	NA	<0.24	<0.24
Naphthalene	mg/kg	<0.3	<0.3	0.0117	<0.3	<0.3	0.0011	<0.3	<0.3
2-Methylnaphthalene	mg/kg	<0.5	<0.5	0.0081	<0.5	<0.5	ND	<0.5	<0.5
Phenanthrene	mg/kg	<0.28	<0.28	0.679	<0.28	<0.28	0.0118	<0.28	<0.28
Anthracene	mg/kg	<0.26	<0.26	0.0832	<0.26	<0.26	0.0069	<0.26	<0.26
Fluoranthene	mg/kg	<0.26	<0.26	1.5973	<0.26	<0.26	0.0522	<0.26	<0.26
Pyrene	mg/kg	<0.27	<0.27	1.2078	<0.27	<0.27	0.0532	<0.27	<0.27
Benz(a)anthracene	mg/kg	<0.21	<0.21	0.2245	<0.21	<0.21	0.0326	<0.21	<0.21
Chrysene	mg/kg	<0.21	<0.21	0.6772	<0.21	<0.21	0.0413	<0.21	<0.21
Benzo(b)fluoranthene	mg/kg	<0.17	<0.17	0.3945	<0.17	<0.17	0.0333	<0.17	<0.17
Benzo(k)fluoranthene	mg/kg	<0.27	<0.27	0.384	<0.27	<0.27	0.0354	<0.27	<0.27
Benzo(a)pyrene	mg/kg	<0.18	<0.18	0.254	<0.18	<0.18	0.0334	<0.18	<0.18
Indeno(1,2,3-cd)pyrene	mg/kg	<0.2	<0.2	0.1764	<0.2	<0.2	0.0207	<0.2	<0.2
Dibenz(a,h)anthracene	mg/kg	<0.15	<0.15	0.0423	<0.15	<0.15	0.0062	<0.15	<0.15
Benzo(ghi)perylene	mg/kg	<0.18	<0.18	0.1547	<0.18	<0.18	0.017	<0.18	<0.18
Fipronil Desulfinyl	ug/kg	<u>≤0.05</u>	<u>≤0.05</u>	ND	<u>6.21</u>	<u>≤0.05</u>	ND	<u>≤0.05</u>	<u>≤0.05</u>
Fipronil Sulfide	ug/kg	<u>≤0.083</u>	<u>≤0.083</u>	ND	<u>≤0.083</u>	<u>1.53</u>	ND	<u>≤0.54</u>	<u>0.61</u>
Fipronil	ug/kg	<u>≤0.82</u>	<u>≤0.82</u>	ND	<u>≤0.82</u>	<u>≤0.82</u>	ND	<u>≤0.82</u>	<u>≤0.82</u>
Fipronil Sulfone	ug/kg	<u>1.20</u>	<u>3.77</u>	ND	<u>9.79</u>	<u>0.78</u>	ND	<u>1.77</u>	<u>≤0.52</u>
Bifenthrin	ug/kg	3.05	<u>26.6</u>	35.47	79.6	<u>3.64</u>	1.06	<u>4.57</u>	3.16
Fenpropathrin	ug/kg	<u>≤0.19</u>	<u>10.9</u>	18.64	21.1	<u>≤0.19</u>	ND	<u>≤0.19</u>	<u>≤0.19</u>
Lamda-Cyhalothrin	ug/kg	<u>≤0.04</u>	<u>4.98</u>	6.29	10.9	<u>≤0.04</u>	ND	<u>≤0.04</u>	<u>≤0.04</u>
Cis-Permethrin	ug/kg	3.94	<u>31.8</u>	45.34	100	<u>3.92</u>	1.85	<u>5.33</u>	2.86
Trans-Permethrin	ug/kg	2.99	<u>33.5</u>	46.37	88.3	<u>4.11</u>	2.29	<u>3.58</u>	4.38
Cyfluthrin	ug/kg	<u>≤0.94</u>	<u>55.7</u>	81.10	95.9	<u>≤0.94</u>	ND	<u>≤0.94</u>	<u>≤0.94</u>
Cypermethrin	ug/kg	<u>≤0.72</u>	<u>40.2</u>	51.76	58.9	<u>≤0.72</u>	ND	<u>≤0.72</u>	<u>≤0.72</u>
Esfenvalerate	ug/kg	<u>≤0.41</u>	<u>11.2</u>	14.00	25.7	<u>≤0.41</u>	ND	<u>≤0.41</u>	<u>≤0.41</u>
Deltamethrin	ug/kg	<u>≤0.09</u>	<u>8.14</u>	9.49	13.6	<u>≤0.09</u>	ND	<u>≤0.09</u>	<u>≤0.09</u>
Bolstar (Sulprofos)	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Chlorpyrifos	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Demeton	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Diazinon	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Dichlorvos	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Dimethoate	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Disulfoton	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Ethoprop (Ethoprofos)	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Renchlorphos	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Fensulfthion	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Fenthion	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Malathion	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Merphos	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Methyl Parathion	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Mevinphos (Phosdrin)	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Phorate	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Tetrachlorvinphos	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Tokuthion	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Trichloronate	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA

Parameter	Unit	Station and Collection Date (2007)							
		BCE1 10/3	BCE2 9/26	BCE2 10/19	BCE3 9/26	BCE4 9/26	BCE4 10/19	BCE5 9/26	BCE6 9/26
PCB008	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB018	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB028	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB031	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB033	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB037	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB044	ug/kg	NA	NA	ND	NA	NA	1.2	NA	NA
PCB049	ug/kg	NA	NA	ND	NA	NA	1.8	NA	NA
PCB052	ug/kg	NA	NA	ND	NA	NA	3	NA	NA
PCB066	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB070	ug/kg	NA	NA	ND	NA	NA	1.1	NA	NA
PCB074	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB077	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB081	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB087	ug/kg	NA	NA	ND	NA	NA	4.8	NA	NA
PCB095	ug/kg	NA	NA	3.1	NA	NA	6.7	NA	NA
PCB097	ug/kg	NA	NA	ND	NA	NA	7.1	NA	NA
PCB099	ug/kg	NA	NA	ND	NA	NA	5.1	NA	NA
PCB101	ug/kg	NA	NA	7.7	NA	NA	8.9	NA	NA
PCB105	ug/kg	NA	NA	ND	NA	NA	2.6	NA	NA
PCB110	ug/kg	NA	NA	4.9	NA	NA	10.1	NA	NA
PCB114	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB118	ug/kg	NA	NA	ND	NA	NA	9.8	NA	NA
PCB119	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB123	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB126	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB128	ug/kg	NA	NA	7.7	NA	NA	8	NA	NA
PCB138	ug/kg	NA	NA	ND	NA	NA	16.3	NA	NA
PCB141	ug/kg	NA	NA	ND	NA	NA	2.9	NA	NA
PCB149	ug/kg	NA	NA	3.8	NA	NA	7	NA	NA
PCB151	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB153	ug/kg	NA	NA	ND	NA	NA	8.3	NA	NA
PCB156	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB157	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB158	ug/kg	NA	NA	ND	NA	NA	3.2	NA	NA
PCB167	ug/kg	NA	NA	ND	NA	NA	2.4	NA	NA
PCB168+132	ug/kg	NA	NA	ND	NA	NA	5	NA	NA
PCB169	ug/kg	NA	NA	ND	NA	NA	2.1	NA	NA
PCB170	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB174	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB177	ug/kg	NA	NA	ND	NA	NA	5.3	NA	NA
PCB180	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB183	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB187	ug/kg	NA	NA	ND	NA	NA	1.3	NA	NA
PCB189	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB194	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB195	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB200	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB201	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB206	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
PCB209	ug/kg	NA	NA	ND	NA	NA	ND	NA	NA
Total PCBs	ug/kg	NA	NA	27.2	NA	NA	124	NA	NA

Station and Collection Date (2007)									
Parameter	Unit	BCE1 10/3	BCE2 9/26	BCE2 10/19	BCE3 9/26	BCE4 9/26	BCE4 10/19	BCE5 9/26	BCE6 9/26
PCB 1016	ug/kg	<7	<7	ND	<7	<7	ND	<7	<7
PCB 1221	ug/kg	<40	<40	ND	<40	<40	ND	<40	<40
PCB 1232	ug/kg	<12	<12	ND	<12	<12	ND	<12	<12
PCB 1242	ug/kg	<3	<3	ND	<3	<3	ND	<3	<3
PCB 1248	ug/kg	<26	<26	ND	<26	<26	ND	<26	<26
PCB 1254	ug/kg	<26	43	39.8	39	<26	82.2	<26	<26
PCB 1260	ug/kg	<11	<11	ND	<11	<11	ND	<11	<11

APPENDIX B: YEAR 2 PROGRESS REPORT

Sediment Toxicity Identification in Ballona Estuary

March 9, 2009

Introduction

This report describes the progress in Year 2 of studies to determine the cause of sediment toxicity that has been observed in the BCE. In 2007 (Year 1), toxicity testing by City of Los Angeles, Environmental Monitoring Division (CLA, EMD) with the amphipod *Eohaustorius estuarius* found toxicity at five of the six stations that were sampled (Figure 1). Additionally, testing with embryos of the abalone *Haliotis rufescens* at the sediment-water interface (SWI) indicated toxicity at two of the six stations. Based on these findings, additional samples were collected from stations

BCE 2 and BCE 4 for sediment toxicity identification evaluations (TIE) using *E. estuarius*. The TIE results indicated that a likely cause of toxicity at BCE 2 was pyrethroid pesticides. Due to changes in sediment composition and toxicity between the initial and TIE sampling, no source of toxicity could be identified for BCE 4.

Several questions either arose from the 2007 study or were left unanswered. What is the temporal variability in toxicity at each station? Can additional TIE methods verify pyrethroids as a source of toxicity? Do other chemicals listed in the toxicity TMDL contribute to the observed toxicity?

In 2008, additional TIE treatments and a second test species were employed in an effort to answer the questions stated above. The TIE methods used in 2007 were also repeated on one station to investigate temporal variability.

Methods

Study Design

As in 2007, preliminary testing of the sediment was conducted by CLA, EMD. Sediment samples were collected from six sites in the BCE by CLA, EMD on June 24 and 25 of 2008 for chemical and toxicity testing (Figure 1, Table 1). CLA, EMD performed toxicity tests using a 10-day survival test with *E. estuarius*, a SWI test with embryos of *H. rufescens*, and a pore water test using gametes of the purple sea urchin, *Strongylocentrotus purpuratus*.

Additional samples from all stations were collected on October 16, 2008 by CLA, EMD for whole sediment and pore water TIE testing and pyrethroid chemistry by SCCWRP. Based on the results from CLA, EMD, SCCWRP proceeded with TIE testing of stations BCE 2 and BCE 5 on October 21 and 24, 2008.

Toxicity Testing

Whole sediment

A 10-day whole sediment TIE was conducted using *E. estuarius*. Whole sediment TIE treatments included vigorous aeration, temperature reduction to 10°C, carboxyl esterase enzyme (CEE) addition, CEE with a temperature increase to 37°C, bovine serum albumin (BSA) addition, BSA addition with a temperature increase to 37°C, and addition of piperonyl butoxide (PBO), cation exchange resin, coconut carbon, and zeolite (Table 2). Amphipod collection site sediment (home sediment) was used for the negative controls. Home sediment was also treated with each TIE

manipulation to verify that the treatments themselves were not toxic. Untreated site sediment was tested at 100% and 50% concentrations to determine baseline toxicity, using home sediment as the diluent. Four replicates were tested for the controls and 100% baselines. Three replicates were tested for each of the remaining treatments.

Sediment was passed through a 2 mm screen before testing began. Each treatment was conducted in 250 ml beakers containing approximately 40 ml of sediment and 200 ml of 32 ppt seawater. Ten amphipods were exposed in each lightly aerated beaker for 10 days under constant light and at 15°C (10°C for the temperature reduction treatment). Four water quality parameters (dissolved oxygen, pH, salinity and ammonia) were determined in overlaying water at the start and end of the exposure from representative beakers for each treatment. At the end of the test, surviving amphipods were counted to determine percentage survival.

Pore water

Pore water was obtained by centrifuging sediment at 3,000xg for 30 minutes. Pore water TIE treatments for *E. estuarius* included the addition of CEE, BSA, PBO, sodium thiosulfate (STS) and EDTA to 100% and 50% pore water concentrations, using 32 ppt seawater as the diluent (Table 2). Undiluted pore water was also passed through solid phase extraction columns containing: cation exchange resin, C18, HLB, and zeolite. In addition a sequential cation exchange resin-C18 extraction was performed. Solid phase extracted pore water was then diluted to 50% and both the 100% and 50% concentrations were tested for toxicity. For the aeration treatment, samples were bubbled with air overnight and tested at both 50% and 100% concentrations. Samples of 32 ppt seawater were tested as controls. Untreated pore water was tested for baseline toxicity at both 100% and 50% concentrations. Four replicates were tested for the controls and 100% baselines. Three replicates were tested for each treatment.

The pore water samples were tested using a 10-day *E. estuarius* survival test. Exposures were conducted in shell vials with 10 ml of sample at 15°C (or 10°C for the temperature reduction TIE treatment). Five *E. estuarius* were added to each vial and tests were conducted under constant darkness without aeration. Dissolved oxygen, pH, salinity and ammonia samples were measured from surrogate water quality vials at the start and end for each exposure. Surviving amphipods were counted on days 4 and 10 to determine percentage survival.

In addition, a sea urchin fertilization test was conducted on pore water TIE samples. Each treatment was conducted in shell vials with 10 ml of sample at 15°C (or 10°C for the temperature reduction TIE treatment). Purple sea urchins were spawned to obtain gametes. The test was initiated with the addition of sea urchin sperm to each vial. Eggs were added twenty minutes after the sperm addition. After an additional twenty minutes, the test was terminated with the addition of buffered formalin to each vial. Dissolved oxygen, pH, salinity and ammonia samples were analyzed from surrogate water quality vials prior to the start of the test. Fertilized embryos were counted using an inverted microscope.

There was not enough pore water from BCE 2 to conduct the fertilization tests on all of the TIE manipulations. Treatments for BCE 2 included STS and EDTA additions as well as cation resin exchange and C18 column extractions. BCE 5 treatments included STS and EDTA additions and

cation exchange resin, C18, sequential cation exchange-C18 and zeolite column extractions. A vigorous aeration treatment sample was tested for BCE 2 at 100% and BCE 5 at 50% and 100%. Four replicates were used for the controls and three replicates were used for each treatment.

Chemistry

For the initial samples collected in June, CLA, EMD measured metals, chlorinated pesticides, PCBs and PAHs. SCCWRP measured pyrethroid pesticides, as well as fipronil and its metabolites, on the June and October 2008 samples.

Results

Initial Toxicity

The initial testing by CLA, EMD found five out of the six stations to be toxic (toxicity was defined as a 20% reduction in survival relative to the controls) to the *E. estuarius* survival test (Table 3). Only BCE 4 was not found to be toxic. Stations BCE 4, 5 and 6 were toxic to *H. rufescens* embryos. The pore water test indicated that stations BCE 5 and 6 reduced *S. purpuratus* fertilization.

Both the pattern of toxic stations and degree of toxicity were different from the 2007 results. In 2007, only BCE 1 was not toxic to *E. estuarius* and all of the toxic stations had survival less than 20%. In contrast, only BCE 5 elicited survival less than 40% in 2008. For the SWI testing, there was no overlap between the studies with regard to toxic stations, with only BCE 3 exhibiting toxicity in 2007.

TIE Testing

For BCE 2 whole sediment, the 100% baseline sample showed a low level of toxicity with 78% amphipod survival (Figure 2, Table A1). This is a substantial decrease in toxicity from what was observed for the initial testing (Table 3). Because of the low degree of toxicity, most of the TIE treatments did not provide useful information. However, there was an increase in toxicity with the addition of PBO in both the 100% and 50% concentrations. This enhancement of toxicity may indicate that pyrethroid pesticides are present in the sample. The temperature reduction treatment, which would also be expected to enhance toxicity in the presence of pyrethroids, however, showed no effect (Figure 2).

For BCE 5 whole sediment, there was no toxicity present in either the 100% or 50% baseline samples for the amphipod whole sediment test (Figure 3, Table A1). As noted for BCE 2, this represented a large decrease from the initial testing and thus most of the TIE treatments did not provide information due to the lack of baseline toxic response. Another similar result was observed for the PBO treatment which showed high toxicity at 100% and moderate toxicity at the 50% (Table A1) indicating the possibility of pyrethroid pesticides in the sample. There was also a slight decrease in survival associated with the temperature reduction treatment (Figure 3).

The pore water baseline test for the BCE 2 amphipod exposure indicated moderate toxicity (Figure 4, Tables A2 and A3). The C18 solid phase extract removed some of the toxicity, indicating organic compounds as the toxicant. None of the other toxicity removal techniques

were effective. Addition of PBO substantially increased toxicity (Figure 4), indicating pyrethroid pesticides as a cause of toxicity.

The pore water baseline test for the BCE 5 amphipod exposure showed complete mortality in the 100% sample and less than 20% survival at 50%. The only treatment that was effective on the 100% sample was the zeolite column extraction treatment (Figure 5). This treatment removes ammonia from the sample. Indeed, the treatments from BCE 5 had very high ammonia levels (Table A5); with the exception of the zeolite extraction, most treatments had un-ionized ammonia concentration values greater than 0.8 mg/L, the acceptable level for amphipod whole sediment exposures. The cation exchange and C18 columns were found to reduce toxicity in the 50% samples. While these treatments indicate metal and organic chemical causes of toxicity, it is also possible that these treatments were merely acting as filters to remove flocculent matter that was observed in the BCE 5 pore water. In the treatments that contained the flocculent (those that were not passed through a solid phase extraction column), movement of the amphipods seemed to be hindered by the material. It is therefore possible that the flocculent may have affected survival.

Pore water from BCE 2 did not cause any toxicity to sea urchin fertilization in the baseline sample (Table A6). This result is consistent with what CLA, EMD found in their initial testing (Table 3).

In contrast, the pore water from BCE 5 was highly toxic to the sea urchin test with no fertilization observed in any of the baseline concentrations (Table A6). None of the TIE treatments showed any effect. While flocculent material was present in these samples, none of samples which had the material removed by filtration (solid phase extraction columns) showed any fertilization. The fertilization test is less sensitive to ammonia than is the amphipod test and only a few samples exceeded the ammonia EC50 (1.1 mg/L un-ionized; Table A5), indicating that ammonia was not a significant confounding factor.

Chemistry

For the June 2008 sampling, each of the stations had an exceedance of at least one of the TMDL constituent target values (Table 4). Stations BCE 2 and BCE 5 had the most individual chemicals exceeding the target concentrations. The spatial pattern of exceedances differed somewhat from the 2007 survey, which found the greatest concentration to be at BCE 2 and BCE 3. Sediment grain size for each station also varied among surveys. For example, sediments from BCE5 went from 0% fines in 2007, to 53% in 2008 (Table 5). It is well known that trace contaminants are often associated with fine grained sediment.

Several pyrethroids and fipronil metabolites were detected at all stations in both June and October 2008 (Table A7). In addition, levels of individual and total pyrethroids were several fold higher than for fipronil and its metabolites. The number of detected pyrethroids at each station in 2008 was higher than for 2007, however the concentrations were generally lower than in 2007 (Table A8). As with the other chemicals, the spatial pattern of pyrethroid concentrations differed not only from 2007, but also for the June and October 2008 sampling events (Figures 6 and 7). The highest concentrations of pyrethroids were measured at BC 2 and BC 3 in 2007; in contrast, station BCE 5 had the highest concentrations in June 2008, whereas BCE 3 had the highest concentrations in October 2008 (Table A7).

Cis- and trans-permethrin and bifenthrin were the most abundant pyrethroids in the collected sediment samples. Cyfluthrin and cypermethrin were the next most abundant compounds. With the exception of a relatively high abundance of deltamethrin in the June 2008 BCE5 sample (Figure. 7), no obvious differences in pyrethroid relative abundance were noted across sites, or between sampling events.

Discussion

The Ballona Creek system appears to be spatially and temporally dynamic. Sediment characteristics, contaminant levels and distributions, and toxicity results were markedly different among stations and sampling events. For example, the sediment collected at BCE 5 in 2007, was coarse grained, showed no toxicity at the sediment-water interface and only exceeded the TMDL chemistry targets for PCBs. In 2008, the sediments collected at this station were fine grained (Table 5), had the highest SWI toxicity, and exceeded the TMDL targets for all the chemicals except PCBs and PAHs (Table 4). These changes are likely related to shifting zones of sediment deposition and scour as a result of wet season stormwater runoff and dry season tidal flows. In addition, small scale heterogeneity in sediment texture and contaminant levels cannot be discounted when resampling the same general areas, unless precise positioning is ensured and recorded.

The data indicate that there is little relationship between the total sediment concentration of the TMDL target contaminants and sediment toxicity in the BCE. Among the individual chemicals, a significant correlation between concentration and amphipod survival was present only for silver (Table 6). The TMDL target concentrations also showed little association with sediment toxicity. Between one and eight TMDL targets were exceeded at most of the stations in 2007 and 2008 (Table 4), but there was no correlation between amphipod survival and the number of exceedances or the magnitude of exceedance at a station, expressed as the mean TMDL target quotient (Table 6).

In the current study, an attempt was made to determine the likelihood of metals toxicity in the pore water by using the sea urchin fertilization test which is particularly sensitive to metals. However, the extreme toxicity of the station 5 sample prevented a definitive assessment. The TIE treatments have also not ruled out PAHs, PCBs, DDTs and chlordane as possible sources of toxicity, nor have they shown that these constituents are likely causes.

Another approach to determining the likelihood of chemicals causing toxicity is by comparing the concentrations present in the sediment to published toxicity thresholds. In the case of PAHs there are multiple guidelines to predict toxicity. The PAHs measured at most of the stations have been non-detectable, but the detection limits have been fairly high. For stations BCE 2 and BCE 4 in 2007, measurements were made with detection limits low enough to make the necessary calculations. Using multiple PAH guidelines (effects range median, threshold effects concentration, target lipid model, and equilibrium partitioning sediment benchmark) as lines of evidence, it seems unlikely that PAHs were a significant source of toxicity at either of these stations (Table 7). None of the guidelines were exceeded for BCE 2. For BCE 4, the guideline was only exceeded for the ESB at the 80% confidence level and above. To verify this finding, PAH analysis with sufficiently low detection limits should be performed at each station so that additional toxic unit comparisons can be made. In addition, there should be research to ensure that other classes of hydrocarbon pollutants (e.g. petroleum derived compounds) do not contribute to toxicity observed in these samples.

For the June 2008 sampling, PCBs did not exceed the TMDL target concentrations at any of the stations (Table 4). This class of contaminant is therefore an unlikely source of toxicity in the current set of samples.

The target value for total DDTs was exceeded at every station for the 2008 sampling (Table 4) and at three of the six sites in 2007. However, the total DDT concentrations in Ballona Creek are below ERM values and are also far below an estimated amphipod EC50 of 371 ug/g oc that was derived from field contaminated sediments (Table 8). Moreover, the trend in DDT levels did not coincide with *E. estuarius* survival; for BCE 5 (0% survival) DDTs were three times lower than in BCE 1-3 (72, 41, and 57% survival, respectively). Nonetheless, the potential for toxicity from DDTs should be further investigated.

Chlordane concentrations exceeded the TMDL target values at four of the six stations in 2008 (Table 4) and three of six in 2007. As was observed for DDTs, the level of chlordanes was two to three times lower in the sample exhibiting the highest sediment toxicity (BCE 5) than others (e.g. BCE1 and BCE 2). The effect of chlordane on the organisms used in our toxicity tests is not well established. Only one unpublished study has been conducted on *E. estuarius*, the results of which were inconclusive. More investigation into the possibility that chlordane is a source of toxicity is warranted.

The results of the TIE testing have had one very consistent theme both temporally and spatially; the indication that pyrethroid pesticides are a source of the observed toxicity. The main evidence for this has been that the addition of PBO usually increased toxicity, both in pore water and whole sediment samples (Tables 9 and 10). Treatments that are less specific, but indicate toxicity by organic compounds (coconut carbon, C18 extraction, and organic resin) have also been effective. Efforts to verify pyrethroids by using other TIE methods, such as carboxylesterase addition and temperature reduction have so far yielded inconsistent results. However, the effectiveness of these additional treatments for marine sediments has not been established.

The results to date provide two lines of evidence indicating that pyrethroids are a likely source of toxicity to Ballona Estuary sediments: the consistent increase in toxicity with PBO addition and the presence of high pyrethroid concentrations in sediment. The chemistry data are best interpreted using a Toxic Unit (TU) approach, where the sediment concentration of a contaminant is divided by its respective LC50 to determine the TU value. If the TUs are greater than one, then toxicity from the given chemical is likely. The sum of TUs for a group of related chemicals is also used to estimate the toxicity of the chemical mixture. One limitation to this approach is the lack of pyrethroid LC50 values for *E. estuarius*. However, several pyrethroid LC50s have been published for the freshwater amphipod *Hyaella azteca* and they can be used to estimate the likelihood of toxic effects to *E. estuarius*. The sum of pyrethroid TUs was greater than one for every sample analyzed in 2008, suggesting that pyrethroid pesticides were present in toxic amounts at all stations (Table 11). Among the individual pesticide compounds, bifenthrin, cypermethrin, and deltamethrin frequently contributed TUs greater than one (Table 11). Even though concentrations of cis- and trans-permethrin were consistently the highest among pyrethroids analyzed, the relatively low toxicity to *H. azteca* suggested that their toxic contributions in these sediments were low. Toxic thresholds specific to *E. estuarius* should be established for these compounds to verify their potential as the cause for toxicity at Ballona Estuary.

Fipronil and its metabolites were detected in both sets of samples collected in 2008. A recently published study has found that these compounds are toxic to a fresh water species at concentrations lower than those detected in Ballona Estuary. These constituents were not

detected in 2007, but this is likely due to improved analytical techniques. Additional research on the occurrence and toxicity of these compounds to *E. estuarius* should be conducted.

Recommendations

As noted in the discussion there are several issues with regard to toxicity in Ballona Creek sediments that need further investigation. To fill in some of these data gaps the following lines of investigation are recommended:

- Establish toxicity thresholds for *E. estuarius* to DDT compounds, chlordane, selected pyrethroid compounds, and fipronil using spiked sediment and water exposures
- Conduct further pore water TIE tests to determine the cause of toxicity to sea urchins.
- Quantify PAHs and total petroleum hydrocarbons at all stations using low detection limit methods and compare to guideline values.
- Assess the bioavailable fraction of candidate toxicants in sediment and pore water.

Table 1. CLA, EMD and SCCWRP sample collection and testing dates.

CLA, EMD				SCCWRP		
Station	Sample Collection	Testing		Sample Collection	Testing	
		Whole Sediment	SWI / Pore water		Whole Sediment	Pore Water
BCE1	6/25/2008	6/27/2008	6/26/2008	10/16/2008	10/24/2008	
BCE2	6/25/2008	6/27/2008	6/26/2008	10/16/2008	10/21/2008	10/24/2008
BCE3	6/25/2008	6/27/2008	6/26/2008	10/16/2008	10/24/2008	
BCE4	6/25/2008	6/27/2008	6/26/2008	10/16/2008	10/24/2008	
BCE5	6/24/2008	6/27/2008	6/26/2008	10/16/2008	10/21/2008	10/24/2008
BCE6	6/24/2008	6/27/2008	6/26/2008	10/16/2008	10/24/2008	

Table 2. Treatments used for whole sediment and pore water TIEs.

Treatment	Matrix	Purpose
Coconut carbon addition	Sediment	Binding of organic contaminants
Zeolite addition	Sediment	Removal of ammonia
Piperonyl butoxide addition (PBO)	Sediment	Renders organophosphorus pesticides non-toxic; enhances/increases toxicity of pyrethroid pesticides
Aeration	Water/Sediment	Removal of volatile compounds (e.g. sulfides)
Carboxylesterase (CEE) addition	Water/Sediment	Hydrolyzes pyrethroid pesticides
Bovine serum albumin (BSA) addition	Water/Sediment	Control for toxicants binding to carboxylesterase
Temperature reduction	Water/Sediment	Increases toxicity of pyrethroid pesticides
Sodium thiosulfate (STS) addition	Water	Reducing agent for oxidizers (e.g. chlorine)
Disodium Ethylenediaminetetraacetic acid (EDTA) addition	Water	Chelation of cationic metals (e.g. Zn, Cu)
C-18 column extraction	Water	Removal of non-polar organics
Cation exchange column extraction	Water	Removal of cationic metals
Hydrophilic-lipophilic balance column (HLB) extraction	Water	Removal of polar and non-polar organics
Zeolite column extraction	Water	Removal of ammonia

Table 3. Toxicity test results from initial sediment sampling of Ballona Creek in June 2008, conducted by CLA, EMD

Station	<i>E. estuarius</i>		<i>H. rufescens</i>		<i>S. purpuratus</i>	
	Whole Sediment		Sediment Water Interface		Porewater	
	Mean (% survival)	Std. Dev.	Mean (% normal)	Std. Dev.	Mean (% fertilized)	Std. Dev.
Control	100		95.4		99.8	
BCE1	72	12.1	96.8	1.4	99.5	1.0
BCE2	41	5.5	95.5	5.4	99.8	0.0
BCE3	57	16.8	93.7	2.3	100	0.0
BCE4	89	5.5	1.5	2.0	100	0.0
BCE5	0	0	0.0	0.0	0	0.0
BCE6	49	33.5	31.8	33.1	55.6	17.4

Table 4. Exceedances of Ballona Creek TMDL target concentrations from June 2008 (in gray). Metals concentrations are mg/kg and organic chemical concentrations are µg/kg.

Parameter	Target	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Amphipod % Surv.		72	41	57	89	0	49
Cadmium	1.2	0.7	1.0	0.5	0.3	2.0	0.1
Copper	34	38	57	14	12	164	9
Lead	46.7	31.7	74.2	18.6	10.3	62.4	3.6
Silver	1.0	0.3	0.6	0.3	0.1	1.3	0.1
Zinc	150	173	278	141	83	513	43.7
DDT's	1.6	23.8	23.9	18.7	2	7.2	4.7
Chlordane's	0.5	11.2	17.9	8.7	nd	5.7	nd
PCB's	22.7	15.3	21.7	7.8	0.8	8.3	nd
PAH's	4022	0.3	0.3	nd	nd	nd	nd

Table 5. Sediment physical parameters for June 2008 sediment samples.

	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
%Total Solids	61.8	39.2	72.8	76.4	23.4	74.8
%Total Organic Carbon	0.44	1.17	0.548	0.317	1.74	0.332
%Sand	84.8	66.6	97.7	93.4	46.6	11.4
%Clay	1.91	3.75	0.31	0.6	3.19	0.32
%Silt	13.3	29.8	2.07	5.99	50.4	5.89
%Gravel	0	0	0	0	0	82.4

Table 6. Spearman rank correlations of TMDL target chemical constituents with amphipod survival. PAH correlations could not be calculated due to lack of detectable concentrations.

Parameter	r	p
Cd	-0.536	0.066
Cu	-0.513	0.084
Pb	-0.347	0.253
Ag	-0.592	0.051
Zn	-0.526	0.075
ΣDDT	0.041	0.881
ΣChlordane	0.091	0.781
ΣPCB	-0.539	0.139
%Fines	-0.425	0.150
Number of Exceedances	-0.345	0.263
Mean TMDL Target Quotient	-0.025	0.921

Table 7. Toxicity guideline values for PAHs in Ballona Creek sediment samples from BCE 2 and BCE 4 collected in October 2007.

Guideline (units)	Threshold	BCE 2	BCE 4
LMW ERM (ng/g)	3160	845	23
HMW ERM (ng/g)	9600	3358	219
Sediment TEC (ug/g oc)	290	23	117
Target Lipid Model Sediment (TU)	1	0.0500	0.2350
ESB Toxic Units (TU)			
80% Confidence level	1	0.2135	1.0004
BCE 2 TOC=24%			
BCE 4 TOC=0.26%			

Table 8. Toxicity guideline values for total DDTs in Ballona Creek sediments from 2008

Guideline (units)	Threshold	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
ERM (ng/g)	46.1	23.8	23.9	18.7	2	7.2	4.7
Field Established Acute Amphipod EC50 (ng/g oc) (TU)	1	0.0146	0.0055	0.0092	0.0017	0.0011	0.0038

Table 9. Effectiveness of TIE treatments with *Eohaustorius estuarius* in whole sediment. Treatments that improved survival are given a “+”, those that decrease a “-“, and those with no effect a “0”. A “0+” or “0-“ indicates a marginal effect. Treatments where the effect was indeterminate are designed with a “?”.

Treatment	BCE2		BCE4	BCE5
	2007	2008	2007	2008
Piperonyl Butoxide Addition	-	-	-	-
Cation Exchange Resin (SIR 300)	0+	0	0+	?
Coconut Carbon	+	0	?	?

Table 10. Effectiveness of TIE treatments with *Eohaustorius estuarius* in pore water. Treatments that improved survival are given a “+”, those that decrease a “-“, and those with no effect a “0”. A “0+” or “0-“ indicates a marginal effect. Treatments not used on a given sample have an NA.

Treatment	BCE2		BCE4	BCE5
	2007	2008	2007	2008
Piperonyl Butoxide Addition	-	-	-	-
Cation Exchange Column	0	0	0+	+
C18 Column Extraction	0+	+	+	+
Sodium Thiosulfate addition	0	NA	0+	0
EDTA	0+	0	+	0+

Table 11. Estimated toxic units for pyrethroids in Ballona Creek sediments collected in 2008 for the freshwater amphipod *Hyalella azteca*.

(Note: values that have been revised from original progress report are underlined.)

	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
June 2008						
Bifenthrin	<u>3.63</u>	4.04	1.79	<u>1.70</u>	7.47	<u>3.82</u>
Lamda-Cyhalothrin	<u>0.46</u>	0.59	<u>0.37</u>	<u>0.28</u>	<u>1.76</u>	<u>0.80</u>
Permethrin	<u>0.60</u>	<u>0.60</u>	<u>0.50</u>	<u>0.30</u>	<u>0.70</u>	<u>0.50</u>
Cyfluthrin	<u>0.65</u>	<u>0.63</u>	<u>0.30</u>	<u>0.29</u>	1.40	<u>1.26</u>
Cypermethrin	<u>2.27</u>	3.24	1.63	<u>1.33</u>	<u>5.17</u>	<u>7.77</u>
Esfenvalerate	<u>0.03</u>	<u>0.03</u>	<u>0.02</u>	<u>0.02</u>	0.04	0.04
Deltamethrin	<u>0.98</u>	1.28	0.72	<u>0.60</u>	<u>3.54</u>	<u>1.33</u>
Total toxic units	<u>8.6</u>	<u>10.4</u>	<u>5.3</u>	<u>4.5</u>	<u>20.1</u>	<u>15.5</u>
October 2008						
Bifenthrin	<u>3.00</u>	<u>1.17</u>	<u>2.62</u>	<u>1.14</u>	<u>0.88</u>	<u>1.91</u>
Lamda-Cyhalothrin	<u>0.31</u>	0.13	0.35	<u>0.20</u>	0.12	<u>0.35</u>
Permethrin	<u>0.50</u>	<u>0.20</u>	<u>0.50</u>	<u>0.10</u>	<u>0.10</u>	<u>0.30</u>
Cyfluthrin	<u>0.60</u>	<u>0.18</u>	0.67	<u>0.26</u>	<u>0.20</u>	<u>0.46</u>
Cypermethrin	<u>2.56</u>	<u>0.87</u>	<u>2.83</u>	<u>0.71</u>	<u>0.42</u>	<u>1.55</u>
Esfenvalerate	0.01	0.01	0.02	0.01	0.00	0.02
Deltamethrin	0.09	<u>0.19</u>	0.16	0.07	0.04	<u>0.24</u>
Total toxic units	<u>7.1</u>	<u>2.8</u>	<u>7.2</u>	<u>2.5</u>	<u>1.8</u>	<u>4.8</u>

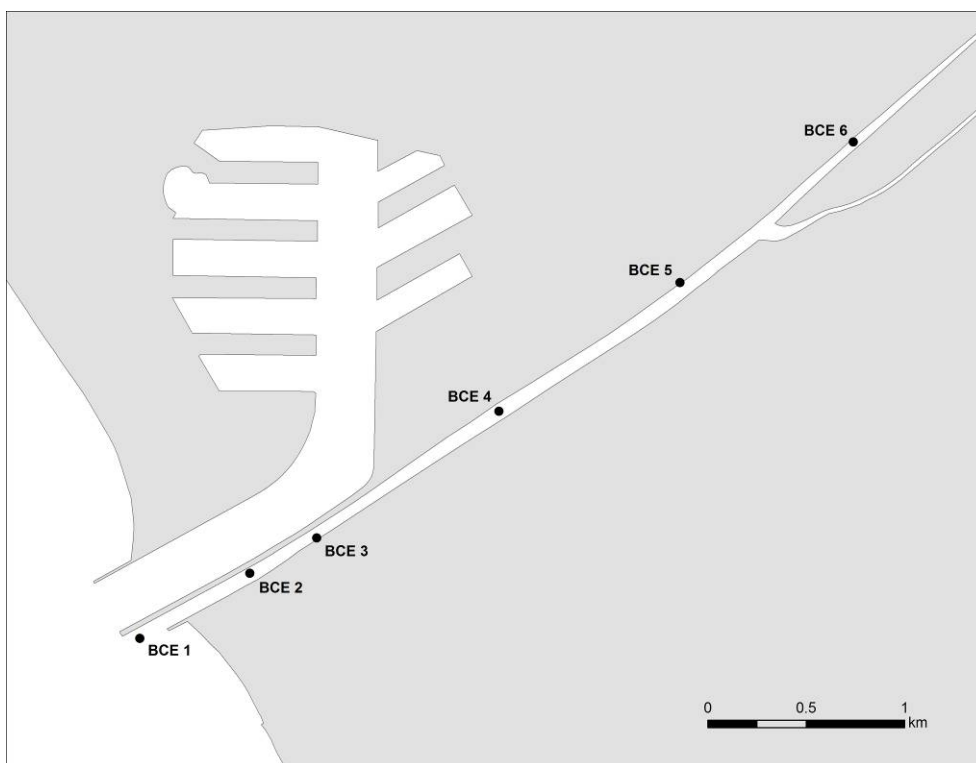


Fig 1. Ballona Creek sampling stations for October 2008.

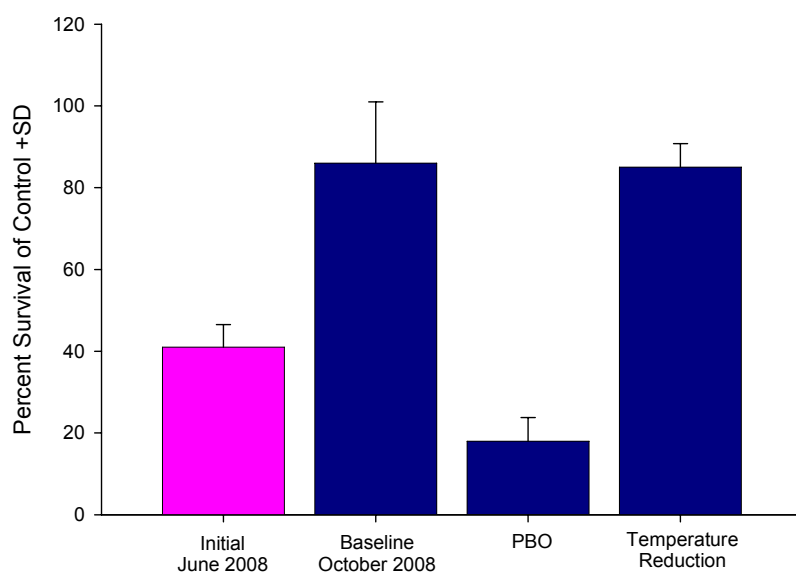


Figure 2. Percent survival of *E. estuarius* exposed to whole sediment (station BCE 2) before and after selected TIE treatments.

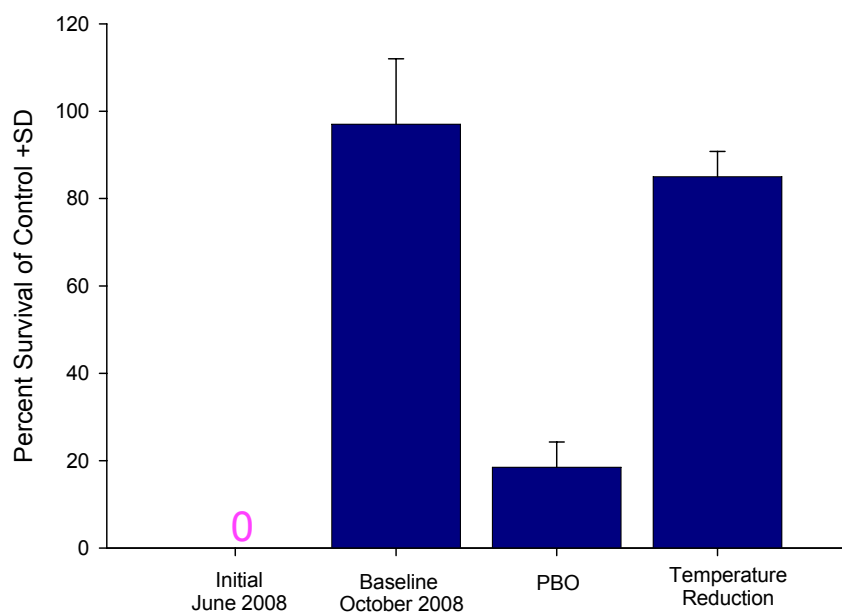


Figure 3. Percent survival of *E. estuarius* exposed to whole sediment (station BCE 5) before and after selected TIE treatments.

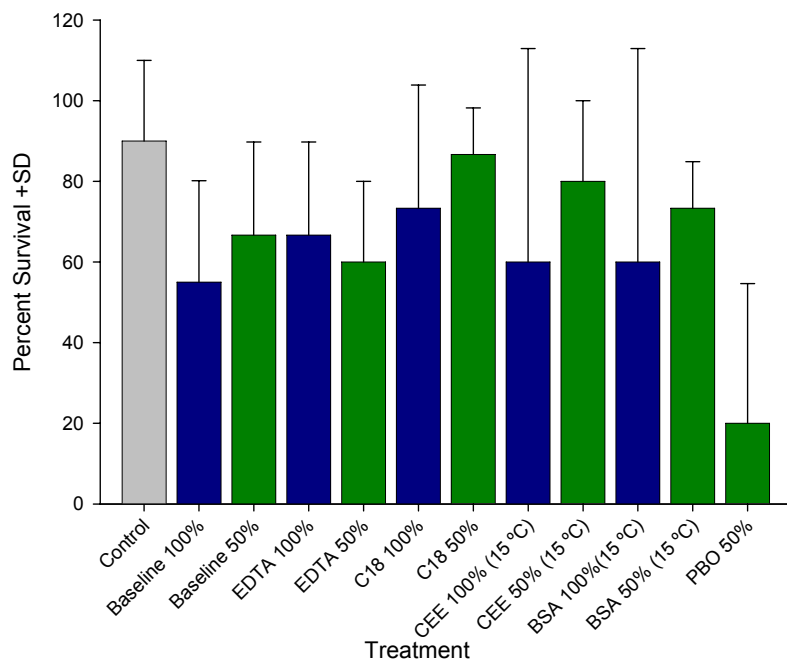


Figure 4. Percent survival of *E. estuarius* exposed to pore water (station BCE 2) before and after selected TIE treatments.

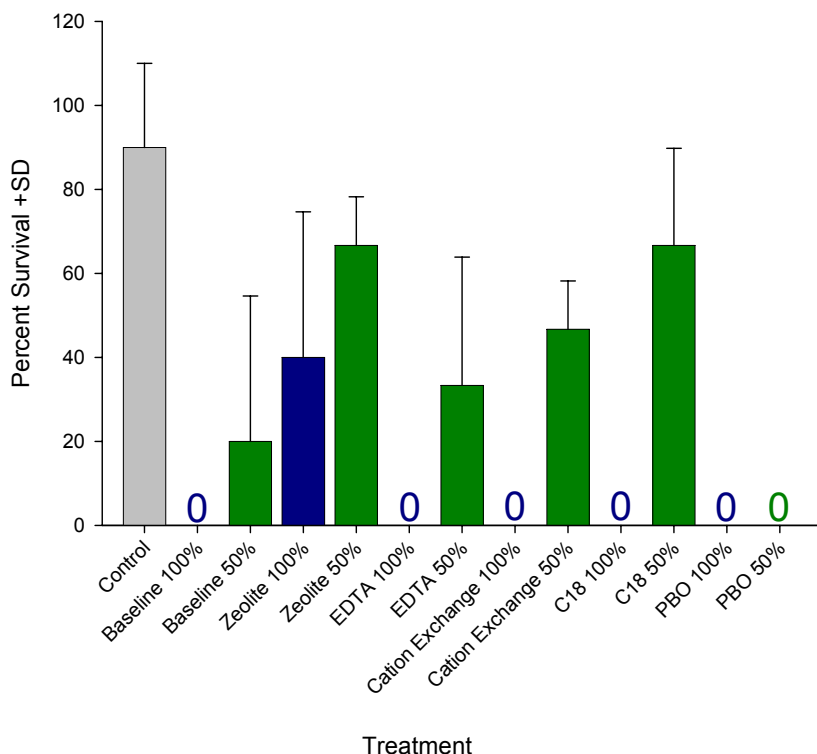


Figure 5. Percent survival of *E. estuarius* exposed to pore water (station BCE 5) before and after selected TIE treatments.

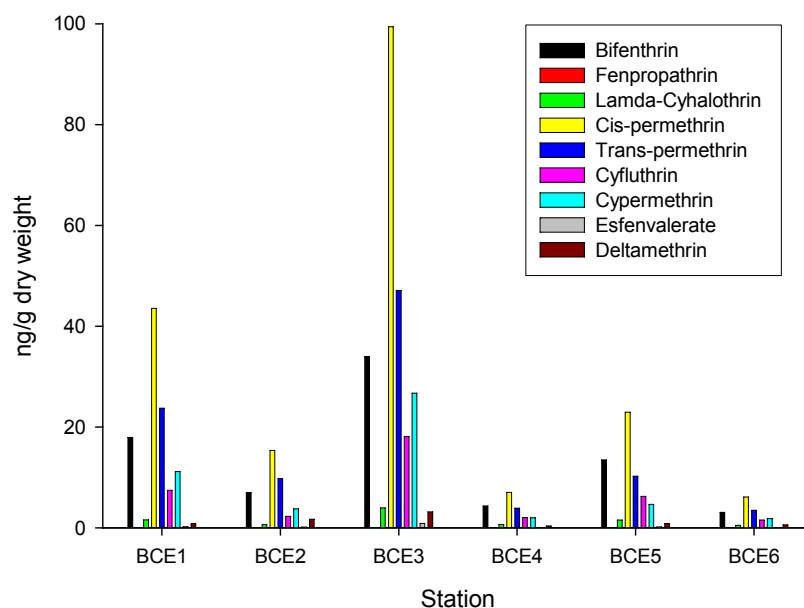


Figure 6. Pyrethroid concentrations in Ballona Creek sediments collected in October 2008. (Graph updated from previous progress report).

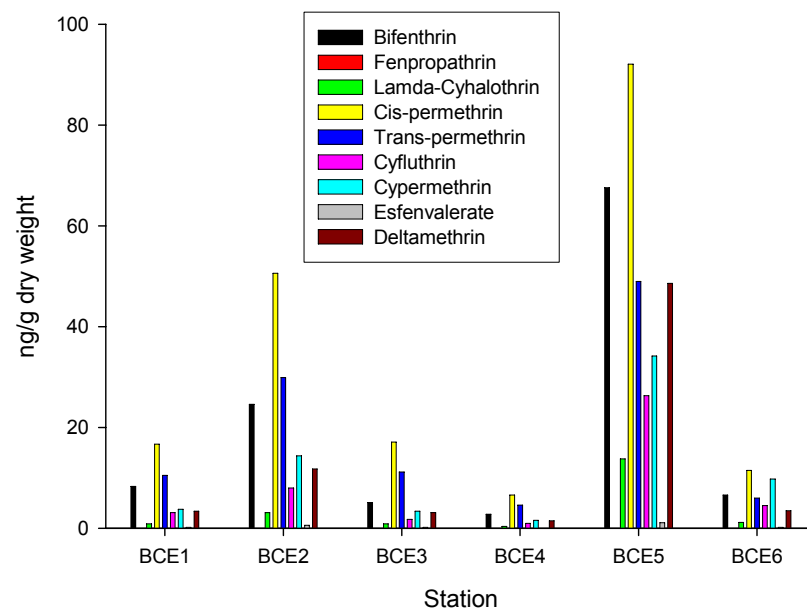


Figure 7. Pyrethroid concentrations in Ballona Creek sediments collected in June 2008. (Graph updated from previous progress report).

Appendices

Table A1. Survival of *E. estuarius* exposed to sediments from stations BCE 2 and BCE 5.

Treatment	Station BCE 2		Station BCE 5	
	Mean (% survival)	Std. Dev.	Mean (% survival)	Std. Dev.
Control	90	8.2	90	8.2
Baseline 100%	78	5.0	88	15.0
Baseline 50%	97	5.8	90	17.3
Baseline 25%	NA	NA	83	15.3
Temp. Reduction Blank	97	5.8	97	5.8
Temp. Reduction 100%	77	5.8	77	5.8
Temp. Reduction 50%	73	20.8	83	15.3
PBO Blank	93	11.6	93	11.6
PBO 100%	17	5.8	17	5.8
PBO 50%	50	10.0	47	41.6
Zeolite Blank	90	0.0	90	0.0
Zeolite 100%	80	0.0	83	5.8
Zeolite 50%	83	15.3	97	5.8
Aeration 100%	93	5.8	77	11.6
Aeration 50%	97	5.8	87	11.6
Cation exchange blank	97	5.8	97	5.8
Cation exchange 100%	87	11.6	77	15.3
Cation exchange 50%	87	15.3	97	5.8
Carbon Blank	67	49.3	67	49.3
Carbon 100%	83	15.3	90	10.0
Carbon 50%	93	5.8	90	10.0
CEE blank (15°C)	87	5.8	87	5.8
CEE 100% (15°C)	90	10.0	73	11.6
CEE 50% (15°C)	90	0.0	83	15.3
CEE blank (37°C)	87	15.3	87	15.3
CEE 100% (37°C)	67	11.6	50	30.0
CEE 50% (37°C)	90	10.0	83	15.3
BSA Blank (15°C)	93	11.6	93	11.6
BSA 100% (15°C)	83	11.6	87	11.6
BSA 50% (15°C)	90	0.0	83	11.6
BSA Blank (37°C)	93	5.8	93	5.8
BSA 100% (37°C)	77	5.8	70	26.5
BSA 50% (37°C)	90	10.0	90	0.0

NA= Not tested due to limited amount of sample

Table A2. Survival of *E. estuarius* exposed to pore water from stations BCE 2 and BCE 5 for 10-days.

Treatment	Station BCE 2		Station BCE 5	
	Mean (% survival)	Std. Dev.	Mean (% survival)	Std. Dev.
Control	90	20.0	90	20.0
Baseline 100%	55	25.2	0	0.0
Baseline 50%	67	23.1	20	34.6
Baseline 25%	73	23.1	67	30.6
Temp. Reduction Blank	NA	NA	60	40.0
Temp. Reduction 100%	NA	NA	0	0.0
Temp. Reduction 50%	NA	NA	0	0.0
PBO Blank	47	50.3	47	50.3
PBO 100%	NA	NA	0	0.0
PBO 50%	20	34.6	0	0.0
Zeolite Blank	NA	NA	60	34.6
Zeolite 100%	NA	NA	40	34.6
Zeolite 50%	NA	NA	67	11.6
Aeration Blank	80	0.0	80	0.0
Aeration 100%	60	20.0	0	0.0
Aeration 50%	53	11.6	0	0.0
CEE blank (15°C)	60	34.6	60	34.6
CEE 100% (15°C)	60	52.9	0	0.0
CEE 50% (15°C)	80	20.0	7	11.6
CEE blank (37°C)	NA	NA	53	23.1
CEE 100% (37°C)	NA	NA	0	0.0
CEE 50% (37°C)	NA	NA	7	11.6
BSA Blank (15°C)	93	11.6	93	11.6
BSA 100% (15°C)	60	52.9	0	0.0
BSA 50% (15°C)	73	11.6	20	20.0
BSA Blank (37°C)	NA	NA	40	34.6
BSA 100% (37°C)	NA	NA	0	0.0
BSA 50% (37°C)	NA	NA	40	20.0
Cation Exchange Blank	40	20.0	73	11.6
Cation Exchange 100%	33	41.6	0	0.0
Cation Exchange 50%	60	20.0	47	11.6
C18 Blank	60	34.6	80	20.0
C18 100%	73	30.6	0	0.0
C18 50%	87	11.6	67	23.1
HLB Blank	NA	NA	73	11.6
HLB SPE BCE 5 50%	NA	NA	53	41.6
Cation-C18 Exchange Blank	NA	NA	87	11.6
Cation-C18 Exchange 100%	NA	NA	0	0.0
Cation-C18 Exchange 50%	NA	NA	33	57.7
STS Blank	NA	NA	67	11.6
STS 100%	NA	NA	0	0.0
STS 50%	NA	NA	0	0.0
EDTA Blank	60	34.6	60	34.6
EDTA 100%	67	23.1	0	0.0
EDTA 50%	60	20.0	33	30.6

NA= Not tested due to limited amount of sample

Table A3. Survival of *E. estuarius* exposed to pore water from stations BCE 2 and BCE 5 for 4-days.

Treatment	Station BCE 2		Station BCE 5	
	Mean (% survival)	Std. Dev.	Mean (% survival)	Std. Dev.
Control	95	10.0	95	10.0
Baseline 100%	75	25.2	0	0.0
Baseline 50%	87	11.6	60	52.9
Baseline 25%	87	11.6	93	11.6
Temp. Reduction Blank	NA	NA	93	11.6
Temp. Reduction 100%	NA	NA	0	0.0
Temp. Reduction 50%	NA	NA	20	20.0
PBO Blank	93	11.6	93	11.6
PBO 100%	NA	NA	0	0.0
PBO 50%	80	0.0	87	11.6
Zeolite Blank	NA	NA	87	23.1
Zeolite 100%	NA	NA	67	11.6
Zeolite 50%	NA	NA	80	20.0
Aeration Blank	100	0.0	100	0.0
Aeration 100%	67	11.6	0	0.0
Aeration 50%	73	11.6	40	34.6
CEE blank (15°C)	87	11.6	87	11.6
CEE 100% (15°C)	73	30.6	0	0.0
CEE 50% (15°C)	93	11.6	27	46.2
CEE blank (37°C)	NA	NA	73	11.6
CEE 100% (37°C)	NA	NA	0	0.0
CEE 50% (37°C)	NA	NA	53	50.3
BSA Blank (15°C)	100	0.0	100	0.0
BSA 100% (15°C)	80	34.6	0	0.0
BSA 50% (15°C)	87	11.6	73	11.6
BSA Blank (37°C)	NA	NA	73	30.6
BSA 100% (37°C)	NA	NA	0	0.0
BSA 50% (37°C)	NA	NA	93	11.6
Cation Exchange Blank	60	20.0	87	11.6
Cation Exchange 100%	60	20.0	0	0.0
Cation Exchange 50%	73	23.1	87	11.6
C18 Blank	87	11.6	87	11.6
C18 100%	73	30.6	0	0.0
C18 50%	100	0.0	87	23.1
HLB Blank	NA	NA	80	0.0
HLB SPE BCE 5 50%	NA	NA	87	11.6
Cation-C18 Exchange Blank	NA	NA	100	0.0
Cation-C18 Exchange 100%	NA	NA	0	0.0
Cation-C18 Exchange 50%	NA	NA	53	41.6
STS Blank	NA	NA	87	11.6
STS 100%	NA	NA	0	0.0
STS 50%	NA	NA	20	20.0
EDTA Blank	73	23.1	73	23.1
EDTA 100%	73	11.6	0	0.0
EDTA 50%	80	20.0	67	11.6

NA= Not tested due to limited amount of sample

**Table A4. Unionized ammonia concentration of overlaying water in 10-day
E. estuarius exposed to sediments from stations BCE 2 and BCE 5.**

Treatment	Station BCE 2		Station BCE 5	
	Initial (mg/L)	Final (mg/L)	Initial (mg/L)	Final (mg/L)
Control	0.004	0.008	0.004	0.008
Baseline 100%	0.035	0.070	0.168	0.120
Baseline 50%	0.021	0.063	0.079	0.000
Baseline 25%	NA	NA	0.047	0.051
Temp. Reduction Blank	0.003	0.011	0.003	0.011
Temp. Reduction 100%	0.023	0.047	0.067	0.085
Temp. Reduction 50%	0.013	0.042	0.054	0.028
PBO Blank	0.005	0.000	0.005	0.000
PBO 100%	0.032	0.001	0.086	0.109
PBO 50%	0.014	0.000	0.087	0.013
Zeolite Blank	0.001	0.002	0.001	0.002
Zeolite 100%	0.000	0.030	0.063	0.045
Zeolite 50%	0.002	0.018	0.024	0.000
Aeration 100%	0.022	0.053	0.008	0.404
Aeration 50%	0.022	0.060	0.054	0.000
Cation exchange blank	0.003	0.001	0.003	0.001
Cation exchange 100%	0.015	0.091	0.061	0.075
Cation exchange 50%	0.015	0.069	0.080	0.067
Carbon Blank	0.011	0.012	0.011	0.012
Carbon 100%	0.027	0.096	0.117	0.223
Carbon 50%	0.024	0.054	0.060	0.083
CEE blank (15°C)	0.017	0.129	0.017	0.129
CEE 100% (15°C)	0.022	0.247	0.008	0.201
CEE 50% (15°C)	0.017	0.108	0.060	0.047
CEE blank (37°C)	0.081	0.106	0.081	0.106
CEE 100% (37°C)	0.006	0.237	0.193	0.332
CEE 50% (37°C)	0.092	0.152	0.151	0.249
BSA Blank (15°C)	0.007	0.036	0.007	0.036
BSA 100% (15°C)	0.019	0.171	0.077	0.109
BSA 50% (15°C)	0.018	0.118	0.063	0.101
BSA Blank (37°C)	0.029	0.109	0.029	0.109
BSA 100% (37°C)	0.013	0.252	0.302	0.495
BSA 50% (37°C)	0.057	0.213	0.097	0.119

Table A5. Un-ionized ammonia concentrations in pore water of *E. estuarius* exposed to pore water from stations BCE 2 and BCE 5 for 10-days. Note the initial data also represents the concentration in the purple sea urchin fertilization test.

Treatment	Station BCE 2		Station BCE 5	
	Initial (mg/L)	Final (mg/L)	Initial (mg/L)	Final (mg/L)
Control	0.000	0.122	0.000	0.122
Baseline 100%	NA	0.975	0.645	4.517
Baseline 50%	NA	0.487	0.555	1.684
Baseline 25%	0.037	0.324	0.259	0.714
Temp. Reduction Blank	NA	NA	0.000	0.045
Temp. Reduction 100%	NA	NA	1.355	1.847
Temp. Reduction 50%	NA	NA	0.807	0.674
PBO Blank	0.000	0.151	0.000	0.151
PBO 100%	NA	0.000	1.633	3.353
PBO 50%	NA	0.592	0.838	1.665
Zeolite Blank	NA	NA	0.010	0.184
Zeolite 100%	NA	NA	0.012	0.680
Zeolite 50%	NA	NA	0.007	0.533
Aeration Blank	NA	0.174	0.000	0.174
Aeration 100%	NA	0.797	3.785	4.078
Aeration 50%	NA	0.604	1.664	1.903
CEE blank (15°C)	0.007	0.393	0.007	0.393
CEE 100% (15°C)	NA	0.953	1.046	3.962
CEE 50% (15°C)	NA	0.505	2.424	2.451
CEE blank (37°C)	0.046	0.455	0.046	0.455
CEE 100% (37°C)	NA	NA	1.481	4.417
CEE 50% (37°C)	NA	NA	0.423	2.167
BSA Blank (15°C)	0.001	0.208	0.001	0.208
BSA 100% (15°C)	NA	1.247	1.979	4.978
BSA 50% (15°C)	NA	0.357	1.844	1.588
BSA Blank (37°C)	0.004	0.529	0.004	0.529
BSA 100% (37°C)	NA	NA	1.643	5.800
BSA 50% (37°C)	NA	NA	0.005	1.754
Cation Exchange Blank	0.000	0.372	0.008	0.171
Cation Exchange 100%	NA	0.971	0.807	4.123
Cation Exchange 50%	NA	0.485	0.297	1.346
C18 Blank	0.000	0.182	0.000	0.139
C18 100%	NA	0.732	2.024	3.652
C18 50%	NA	0.277	1.111	1.214
HLB Blank	NA	NA	0.018	0.161
HLB SPE BCE 5 50%	NA	NA	0.000	1.171
Cation-C18 Exchange Blank	NA	NA	0.000	0.168
Cation-C18 Exchange 100%	NA	NA	0.000	4.052
Cation-C18 Exchange 50%	NA	NA	0.903	1.990
STS Blank	0.000	0.188	0.000	0.188
STS 100%	NA	NA	1.677	3.620
STS 50%	NA	NA	0.791	1.884
EDTA Blank	0.000	0.261	0.000	0.261
EDTA 100%	NA	0.656	NA	4.228
EDTA 50%	0.430	0.443	NA	1.521

NA= Not tested due to limited amount of sample

Table A6. SCCWRP pore water toxicity test results with *S. purpuratus*. Stations BCE 2 and BCE 5.

Treatment	Station BCE 2		Station BCE 5	
	Mean (% fertilization)	Std. Dev.	Mean (% fertilization)	Std. Dev.
Control	98	3.2	98	3.2
Baseline 100%	98	1.0	0	0
Baseline 50%	100	0.7	0	0.6
Baseline 25%	NA	NA	0	0
Temp. Reduction Blank	NA	NA	99	0.6
Temp. Reduction 100%	NA	NA	0	0
Temp. Reduction 50%	NA	NA	0	0
Zeolite Blank	NA	NA	9	0.6
Zeolite 100%	NA	NA	0	0
Zeolite 50%	NA	NA	0	0
Aeration Blank	98	1.5	98	1.5
Aeration 100%	NC	NC	0	0
Aeration 50%	NA	NA	0	0
Cation Exchange Blank	90	10.6	63	3.2
Cation Exchange 100%	NC	NC	0	0
Cation Exchange 50%	NA	NA	0	0
C18 Blank	99	0.6	92	12.7
C18 100%	NC	NC	0	0
C18 50%	NA	NA	0	0
HLB Blank	NA	NA	97	1.2
HLB 100%	NA	NA	NC	NC
HLB 50%	NA	NA	NC	NC
Cation-C18 Exchange Blank	NA	NA	86	8.1
Cation-C18 Exchange 100%	NA	NA	1	1.0
Cation-C18 Exchange 50%	NA	NA	0	0.6
STS Blank	90	15.3	90	15.3
STS 100%	NC	NC	0	0
STS 50%	NA	NA	0	0
EDTA Blank	95	4.5	95	4.5
EDTA 100%	NC	NC	0	0
EDTA 50%	NA	NA	0	0

NA= Not tested due to limited amount of sample

NC= Not counted

Table A7. Fipronil and pyrethroid concentrations in sediments collected in 2008. Units are ng/g dry weight. Analysis performed by SCCWRP.

(Note: values that have been revised from original progress report are underlined).

Parameter	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
June 2008						
Fipronil desulfinyl	0.1	0.3	0.1	0.1	2.2	0.2
Fipronil sulfide	0.1	0.5	0.1	0.1	0.9	0.2
Fipronil	≤0.07	0.7	≤0.03	0.1	1.1	0.2
Fipronil sulfone	0.4	1.4	0.2	≤0.03	3.2	0.5
Total Fipronil	0.6	2.1	0.4	0.3	7.4	1.1
Bifenthrin	<u>8.3</u>	24.6	5.1	2.8	67.6	6.6
Fenpropathrin	ND	ND	ND	ND	ND	ND
Lamda-Cyhalothrin	<u>0.9</u>	3.1	0.9	0.4	13.8	1.2
Cis-permethrin	<u>16.7</u>	50.6	17.1	<u>6.6</u>	92.1	11.5
Trans-permethrin	<u>10.5</u>	29.9	11.2	4.6	49.0	6.0
Cyfluthrin	<u>3.1</u>	<u>8.0</u>	1.8	<u>1.0</u>	26.3	<u>4.5</u>
Cypermethrin	<u>3.8</u>	14.4	3.4	<u>1.6</u>	<u>34.2</u>	<u>9.8</u>
Esfenvalerate	<u>0.2</u>	<u>0.6</u>	<u>0.2</u>	<u>0.1</u>	1.1	0.2
Deltamethrin	<u>3.4</u>	11.8	3.1	<u>1.5</u>	<u>48.6</u>	3.5
Total Pyrethroids	<u>46.9</u>	<u>143</u>	<u>42.8</u>	<u>18.6</u>	<u>333</u>	<u>43.3</u>
October 2008						
Fipronil desulfinyl	0.17	0.04	0.10	0.04	0.24	0.05
Fipronil sulfide	0.18	0.04	0.12	0.04	0.18	0.06
Fipronil	≤0.06	≤0.03	≤0.07	≤0.02	≤0.09	≤0.03
Fipronil sulfone	0.43	0.12	0.45	0.08	0.35	0.12
Total Fipronil	0.78	0.20	0.67	0.16	0.77	0.23
Bifenthrin	17.9	6.99	34.0	4.37	13.5	3.08
Fenpropathrin	≤0.13	≤0.13	≤0.08	≤0.04	≤0.19	≤0.03
Lamda-Cyhalothrin	1.59	0.66	3.96	0.66	1.56	0.49
Cis-permethrin	43.6	15.4	99.4	7.05	23.0	6.12
Trans-permethrin	23.8	9.8	47.1	3.89	10.2	3.49
Cyfluthrin	7.48	2.28	18.1	2.04	6.23	1.55
Cypermethrin	11.18	3.8	26.7	2.00	4.68	1.83
Esfenvalerate	0.21	0.17	0.91	0.14	0.18	0.08
Deltamethrin	0.81	1.7	3.17	0.4	0.83	0.6
Total Pyrethroids	106	40.7	233	20.6	60.2	17.2

Table A8. Fipronil and pyrethroid concentrations in sediments collected in 2007. Units are ng/g dry weight. Analysis performed by SCCWRP.

(Note: values that have been revised from original progress report are underlined).

Parameter	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
Fipronil desulfinyl	<u>≤0.05</u>	<u>≤0.05</u>	<u>6.21</u>	<u>≤0.05</u>	<u>≤0.05</u>	<u>≤0.05</u>
Fipronil sulfide	<u>≤0.083</u>	<u>≤0.083</u>	<u>≤0.083</u>	<u>1.53</u>	<u>≤0.54</u>	<u>0.61</u>
Fipronil	<u>≤0.82</u>	<u>≤0.82</u>	<u>≤0.82</u>	<u>≤0.82</u>	<u>≤0.82</u>	<u>≤0.82</u>
Fipronil sulfone	<u>1.20</u>	<u>3.77</u>	<u>9.79</u>	<u>0.78</u>	<u>1.77</u>	<u>≤0.52</u>
Total Fipronil	<u>1.2</u>	<u>3.8</u>	<u>16.0</u>	<u>2.3</u>	<u>1.8</u>	<u>0.6</u>
Bifenthrin	3.05	<u>26.6</u>	79.6	<u>3.64</u>	<u>4.57</u>	<u>3.16</u>
Fenpropathrin	<u>≤0.19</u>	<u>10.9</u>	21.1	<u>≤0.19</u>	<u>≤0.19</u>	<u>≤0.19</u>
Lamda-Cyhalothrin	<u>≤0.04</u>	<u>4.98</u>	10.9	<u>≤0.04</u>	<u>≤0.04</u>	<u>≤0.04</u>
Cis-permethrin	3.94	<u>31.8</u>	100	<u>3.92</u>	<u>5.33</u>	2.86
Trans-permethrin	2.99	<u>33.5</u>	88.3	<u>4.11</u>	<u>3.58</u>	4.38
Cyfluthrin	<u>≤0.94</u>	<u>55.7</u>	95.9	<u>≤0.94</u>	<u>≤0.94</u>	<u>≤0.94</u>
Cypermethrin	<u>≤0.72</u>	<u>40.2</u>	58.9	<u>≤0.72</u>	<u>≤0.72</u>	<u>≤0.72</u>
Esfenvalerate	<u>≤0.41</u>	<u>11.2</u>	25.7	<u>≤0.41</u>	<u>≤0.41</u>	<u>≤0.41</u>
Deltamethrin	<u>≤0.09</u>	<u>8.14</u>	13.6	<u>≤0.09</u>	<u>≤0.09</u>	<u>≤0.09</u>
Total Pyrethroids	10.0	<u>223</u>	494	<u>11.7</u>	<u>13.5</u>	10.4

Table A9. Trace constituents in sediments collected in June 2008. Analysis performed by CLA, EMD. Values in gray exceed TMDL target concentrations.

Sample Date		6/25/2008	6/25/2008	6/25/2008	6/25/2008	6/24/2008	6/24/2008
Parameter	Unit	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
Cd	mg/kg	0.658	1.04	0.531	0.33	2.03	0.132
Cu	mg/kg	38.2	56.8	14	11.8	164	9.42
Mercury	mg/kg	0.0743	0.119	0.0393	0.0561	0.255	0.0145
Pb	mg/kg	31.7	74.2	18.6	10.3	62.4	3.58
Ag	mg/kg	0.33	0.65	0.278	0.137	1.32	0.071
Zn	mg/kg	173	278	141	83	513	43.7
2,4'-DDE	ug/kg	2.4	<0.7	<0.700	<0.7	<0.7	<0.700
4,4'-DDE	ug/kg	6.5	12.2	5.3	2	4.7	0.9
2,4'-DDD	ug/kg	<1.00	<1	<1.00	<1	<1	<1.00
2,4'-DDT	ug/kg	2.3	<0.8	<0.800	<0.8	<0.8	<0.800
4,4'-DDD	ug/kg	3	9	12	<1	<1	<1.00
4,4'-DDT	ug/kg	9.6	2.7	1.4	<0.7	2.5	3.8
Total DDTs		23.8	23.9	18.7	2	7.2	4.7
α-Chlordane	ug/kg	7	10.5	4.5	<0.19	5.7	<0.190
γ-Chlordane	ug/kg	4.2	7.4	4.2	<0.18	<0.18	<0.180
Oxychlordane	ug/kg	<0.900	<0.9	<0.900	<0.9	<0.9	<0.900
α-Chlordene	ug/kg	NSA	NSA	NSA	NSA	NSA	NSA
γ-Chlordene	ug/kg	NSA	NSA	NSA	NSA	NSA	NSA
Trans-Nonachlor	ug/kg	4.1	7.3	3.2	1	4.3	<0.160
Cis-Nonachlor	ug/kg	<0.270	5.9	<0.270	<0.27	1.5	<0.270
PCB 1016	ug/kg	<7.00	<7	<7.00	<7	<7	<7.00
PCB 1221	ug/kg	<40.0	<40	<40.0	<40	<40	<40.0
PCB 1232	ug/kg	<12.0	<12	<12.0	<12	<12	<12.0
PCB 1242	ug/kg	<3.00	<3	<3.00	<3	<3	<3.00
PCB 1248	ug/kg	<26.0	<26	<26.0	<26	<26	<26.0
PCB 1254	ug/kg	34	<26	<26.0	<26	26	<26.0
PCB 1260	ug/kg	19	37	12	<11	14	<11.0
Acenaphthylene	mg/kg	<.3	<.3	<.3		<.3	<0.300
Acenaphthene(ccc)	mg/kg	<.3	<.3	<.3		<.3	<0.300
Fluorene	mg/kg	<.4	<.4	<.4		<.4	<0.400
2-Chloronaphthalene	mg/kg	<.3	<.3	<.3		<.3	<0.300
Naphthalene	mg/kg	<.4	<.4	<.4		<.4	<0.400
2-Methylnaphthalene	mg/kg	<.7	<.7	<.7		<.7	<0.700
Phenanthrene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Anthracene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Fluoranthene(ccc)	mg/kg	0.281	0.251	<.2		<.2	<0.200
Pyrene	mg/kg	<.3	<.3	<.3		<.3	<0.300
Benz(a)anthracene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Chrysene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Benzo(b)fluoranthene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Benzo(k)fluoranthene	mg/kg	<.3	<.3	<.3		<.3	<0.300
Benzo(a)pyrene(ccc)	mg/kg	<.2	<.2	<.2		<.2	<0.200
Indeno(1,2,3-cd)pyrene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Dibenz(a,h)anthracene	mg/kg	<.2	<.2	<.2		<.2	<0.200
Benzo(ghi)perylene	mg/kg	<.2	<.2	<.2		<.2	<0.200

Table A9, continued.

Sample Date		6/25/2008	6/25/2008	6/25/2008	6/25/2008	6/24/2008	6/24/2008
Parameter	Unit	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
PCB37	ug/kg	<1.7	<1.7	<1.7	<1.7	<1.7	<1.70
PCB44	ug/kg	<0.71	<0.71	<0.71	<0.71	<0.71	<0.710
PCB49	ug/kg	<0.72	<0.72	<0.72	<0.72	<0.72	<0.720
PCB52	ug/kg	<0.81	<0.81	<0.81	<0.81	<0.81	<0.810
PCB66	ug/kg	<0.68	<0.68	<0.68	<0.68	<0.68	<0.680
PCB70	ug/kg	<0.74	2.18	0.96	<0.74	<0.74	<0.740
PCB74	ug/kg	<0.71	<0.71	<0.71	<0.71	<0.71	<0.710
PCB77	ug/kg	<0.89	<0.89	<0.89	<0.89	<0.89	<0.890
PCB81	ug/kg	<0.87	<0.87	<0.87	<0.87	<0.87	<0.870
PCB87	ug/kg	<0.73	<0.73	<0.73	<0.73	<0.73	<0.730
PCB99	ug/kg	<0.71	<0.71	<0.71	<0.71	<0.71	<0.710
PCB101	ug/kg	1.76	2.89	1.38	<0.87	0.89	<0.870
PCB105	ug/kg	<0.65	<0.65	1.11	<0.65	<0.65	<0.650
PCB110	ug/kg	3.06	3.37	2	0.8	1.57	<0.700
PCB114	ug/kg	<0.62	<0.62	<0.62	<0.62	<0.62	<0.620
PCB118	ug/kg	2.89	3.89	<0.74	<0.74	1.55	<0.740
PCB119	ug/kg	<0.70	<0.70	<0.70	<0.70	<0.70	<0.700
PCB123	ug/kg	<0.74	<0.74	<0.74	<0.74	<0.74	<0.740
PCB126	ug/kg	<0.70	<0.70	<0.70	<0.70	<0.70	<0.700
PCB128	ug/kg	<0.83	0.89	<0.83	<0.83	<0.83	<0.830
PCB138	ug/kg	2.7	<1.4	<1.4	<1.4	1.5	<1.40
PCB149	ug/kg	2.86	3.98	1.12	<0.78	1.54	<0.780
PCB151	ug/kg	<0.72	<0.72	<0.72	<0.72	<0.72	<0.720
PCB153/168	ug/kg	2	3.16	1.21	<0.70	1.22	<0.700
PCB156	ug/kg	<0.63	<0.63	<0.63	<0.63	<0.63	<0.630
PCB157	ug/kg	<0.70	<0.70	<0.70	<0.70	<0.70	<0.700
PCB158	ug/kg	<0.49	<0.49	<0.49	<0.49	<0.49	<0.490
PCB167	ug/kg	<0.69	<0.69	<0.69	<0.69	<0.69	<0.690
PCB169	ug/kg	<0.71	<0.71	<0.71	<0.71	<0.71	<0.710
PCB170	ug/kg	<0.67	<0.67	<0.67	<0.67	<0.67	<0.670
PCB177	ug/kg	<0.67	<0.67	<0.67	<0.67	<0.67	<0.670
PCB18	ug/kg	<3.0	<3.0	<3.0	<3.0	<3.0	<3.00
PCB180	ug/kg	<0.65	<0.65	<0.65	<0.65	<0.65	<0.650
PCB183	ug/kg	<0.68	<0.68	<0.68	<0.68	<0.68	<0.680
PCB187	ug/kg	<0.70	<0.70	<0.70	<0.70	<0.70	<0.700
PCB189	ug/kg	<0.62	<0.62	<0.62	<0.62	<0.62	<0.620
PCB194	ug/kg	<0.62	<0.62	<0.62	<0.62	<0.62	<0.620
PCB201	ug/kg	<0.71	<0.71	<0.71	<0.71	<0.71	<0.710
PCB206	ug/kg	<0.62	1.4	<0.62	<0.62	<0.62	<0.620
Total PCBs		15.27	21.76	7.78	0.8	8.27	0
Sulfide (Dissolved)	mg/l	64.2	0.08	0.53	0.21	38	0.13
Dieldrin	ug/kg	1.8	1.80	2.6	<0.800	<0.800	<0.800

APPENDIX C: YEAR 3 PROGRESS REPORT

Sediment Toxicity Identification in Ballona Creek Estuary

Year 3 Progress Report

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September 14, 2010

INTRODUCTION

This report describes the progress in Year 3 (2009-2010) of studies to determine the cause of sediment toxicity that has been observed in the Ballona Creek Estuary. Previous years studies have found that sediment toxicity is common at the six total maximum daily load (TMDL) monitoring stations (Figure 1), but the magnitude and location is highly variable between sampling events. A high level of temporal and spatial variability has also been noted for physical parameters, such as grain size, and for the concentrations of chemical contaminants. One common finding in previous years is that pyrethroid pesticides are prevalent and a likely cause of toxicity.

Several questions were targeted for study in Year 3: 1) what is the cause of the pore water toxicity that has been observed using the sea urchin fertilization test? 2) are polycyclic aromatic hydrocarbons (PAHs) and other petroleum compounds present and possibly playing a role in sediment toxicity? 3) are metals and organic compounds present in the sediments bioavailable? 4) what are the toxicity thresholds for some of the organic compounds commonly detected in the Estuary? To answer these questions, three studies were conducted, two involving field sampling (Table 1) and the other a laboratory spiking study. The annual monitoring field study involved sampling at six stations in August and September 2009 to measure trace organic constituents and investigate the cause of pore water toxicity sea urchins using toxicity identification evaluation techniques (TIE). The bioavailability field study, in November and December of 2009, used the deployment of passive samplers to collect data on the concentrations of metals and organics in the sediment porewater *in situ*. Toxicity of the sediment and pore water was also evaluated as part of this study. The spiked sediment study investigated the toxicity threshold concentrations of DDT, DDE, chlordane, and cyfluthrin to the amphipod *Eohaustorius estuarius*. This amphipod has been used in previous toxicity studies of the Estuary. In addition to the work described above, the City of Los Angeles, Environmental Monitoring Division (CLA, EMD) conducted amphipod toxicity tests and TIEs on the samples collected in August and September; those data are not presented in this report.

This report describes the three studies separately, each with its own methods and results. A discussion section at the end summarizes the results from the three studies. Appendix tables follow the main report and contain data for the analyses conducted by SCCWRP.

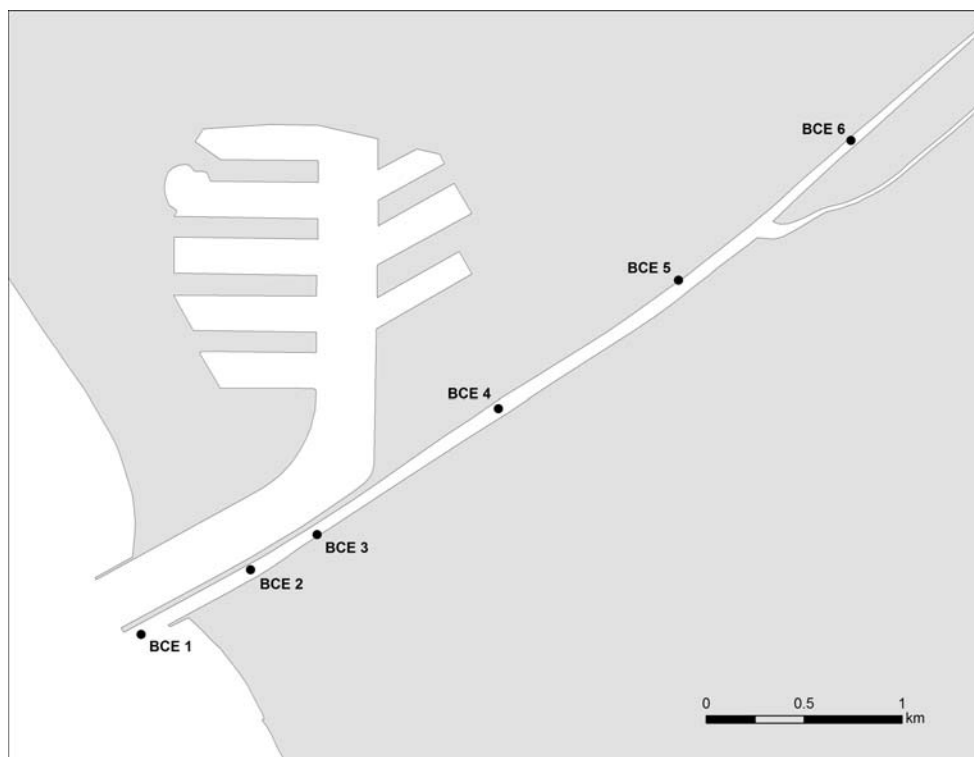


Figure 1. Ballona Creek Estuary sampling stations.

Table 1. Ballona Creek Estuary field sampling activities.

		Toxicity Testing				Chemical Analysis			
		Whole sediment		Pore water		AVS/SEM	Pore water metals	Passive Samplers	Whole Sediment
		TIE	Toxicity	TIE	Toxicity				
8/19/2009	1 through, 6	No	Yes ¹	No	No	Yes	Yes	No	Yes
9/21/2009	2 through 6	Yes ²	No	Yes ³	Yes	No	No	No	No
11/2/2009	1, 2, 3, 5	No	Yes	Yes	Yes	Yes	Yes	No	Yes
12/1/2009	1, 2, 3, 5	No	Yes	Yes	Yes	Yes	Yes	Yes ⁴	Yes

¹All stations by LA city.

²Stations 3 and 5, by CLA, EMD.

³Station 3 by SCCWRP.

⁴Sampled, but not all analysis completed.

ANNUAL MONITORING OF BALLONA CREEK ESTUARY

Methods

In August 2009, CLA, EMD did their annual sampling of six Ballona Creek Estuary monitoring stations (Figure 1). As part of that sampling, separate aliquots of sediment were taken for chemical analysis by SCCWRP of parameters that had not been previously measured. These additional analyses included:

- low detection limit polyaromatic hydrocarbons (PAHs) including alkylated compounds, which will allow for better comparison to sediment guideline values (USEPA 2003);
- sediment acid volatile sulfides and simultaneously extracted metals (AVS/SEM), which provides an indication as to whether sediment metals are biologically available (Ankley et al. 1996);
- black carbon, which is a portion of the sediment organic carbon that may tightly bind organic contaminants preventing them from being available for uptake by organisms (Vinturella et al. 2004);
- total petroleum hydrocarbons (TPH), which includes groups of compounds not normally quantified that may be important contributors to toxicity (Anson et al. 2008);
- pore water dissolved metals, which is the fraction of sediment metals that is most available for organism uptake.

As in previous years, CLA, EMD conducted other toxicity and chemical analyses on the same samples. Using the amphipod toxicity data generated by CLA, EMD from the August sampling, stations BCE3 and 5 were chosen to do follow up TIE testing on samples collected in September. CLA, EMD performed TIEs on whole sediment using the amphipod and SCCWRP tested pore water using the sea urchin fertilization test. Since planned sea urchin fertilization testing on the August samples by CLA, EMD had not been successful, additional samples were collected in September from BCE 2, 4 and 6, for testing by SCCWRP.

Pore water was obtained by centrifuging homogenized sediment at 3,000x g for 30 minutes. The supernatant water was removed by glass pipette and transferred to another centrifuge bottle. The extracted pore water was then centrifuged for another 15 minutes at 5,000x g to remove any fine particulates. The water was then transferred by glass pipette to glass Erlenmeyer flasks and stored at 5°C until used later in the day.

Sea urchin fertilization tests were conducted on the pore water samples (USEPA 1995). Samples were tested at 100%, 50% and 25% concentrations of pore water, diluted with laboratory seawater. Exposure chambers consisted of shell vials with 10 ml of sample at a temperature of 15°C. Purple sea urchins were spawned to obtain gametes. The test was initiated with the addition of sea urchin sperm to each vial. Eggs were added twenty minutes after the sperm addition. The test was terminated with the addition of buffered formalin to each vial. Dissolved oxygen, pH, salinity and ammonia samples were measured prior to the start of the test. Fertilized embryos were counted using an inverted microscope. One day prior to TIE testing, pore water samples of BCE3 and BCE5 were tested at a series of dilutions to determine the optimal concentration for the TIEs. The following day, TIEs were conducted on the pore water from BCE3 and BCE5 using these sea urchin fertilization test. Fertilization tests were conducted on dilutions of BCE 2, 4 and 6 concurrently with the TIE testing.

Freeze dried sediments were extracted by methylene chloride on a Dionex Accelerated Solvent Extraction 300 system. The extracts were concentrated and solvent exchanged into hexane. Copper powder was then added to remove sulfur. For analysis of TPHs, PAHs, PCBs and chlorinated pesticides, the extracts

were cleaned up on a silica/alumina column. For analysis of pyrethroids, fipronil, and fipronil degradates, the extracts were cleaned up on a Florisil column. The extracts were analyzed by GC/MS. Pyrethroids, fipronil, PCBs, and chlorinated pesticides were analyzed with negative chemical ionization mode. Total petroleum hydrocarbons and PAHs were analyzed with electron impact ionization mode.

Results

Toxicity

Initial sea urchin fertilization testing of BCE3 and 5 pore water determined that only BCE3 had substantial toxicity (Figure 2). BCE5 pore water was nontoxic at all concentrations. It was therefore decided that TIE testing on the following day would concentrate on BCE3. After conducting the TIE and subsequently counting the embryos, it was discovered that BCE3 was no longer toxic, but that BCE5 was quite toxic (Figure 3). However, there was not sufficient sample to conduct a second TIE on BCE5.

Testing of pore water from the other stations using the sea urchin fertilization test found that stations BCE5 and BCE6 were toxic for 100% pore water (Figure 4). BCE6 was also toxic at the 50% dilution (Appendix Table 1).

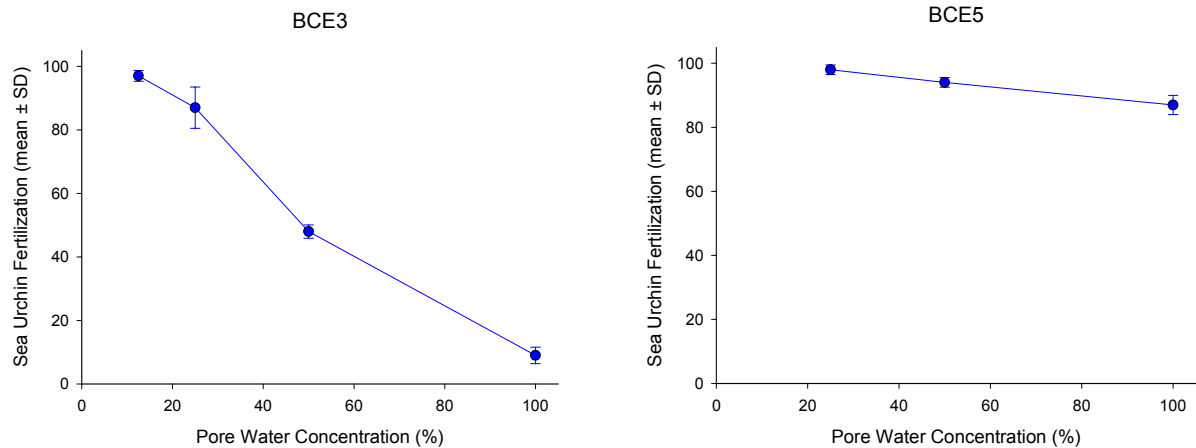
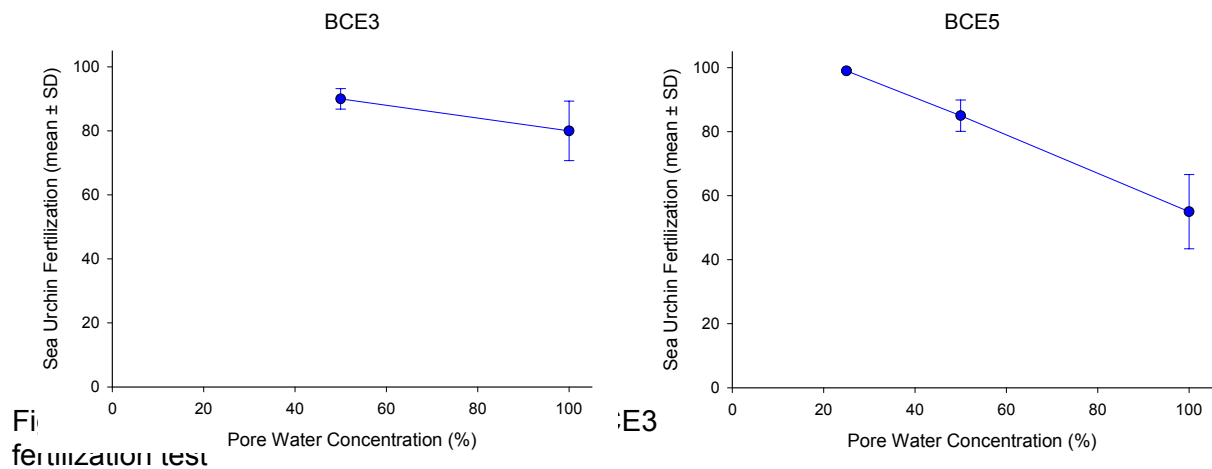


Figure 2. Results of initial testing of BCE3 and BCE5 pore water using the sea urchin fertilization test.



Fertilization test

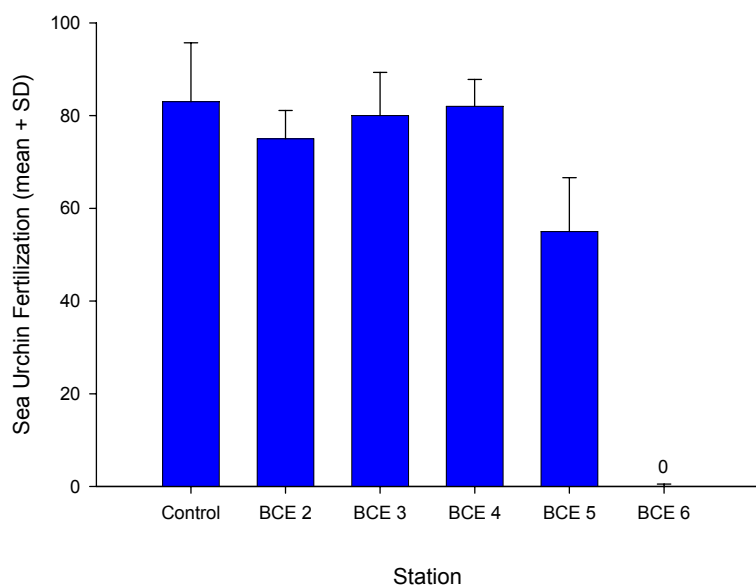


Figure 4. Results of sea urchin fertilization testing of Ballona Creek 100% pore water from the September 2009 sampling.

Chemistry

The sediments from all six stations were dominated by larger grained sediments (Table 2). Stations BCE1-3 all had greater than 80% sand, but no gravel, while BCE4-6 each had greater than 30% gravel. Total organic carbon was greater than 1% at BCE 2 and 3 and less than 1% at the remaining stations. Black carbon was similar at all stations except BCE1, which had nearly an order magnitude lower concentration.

Polyaromatic hydrocarbon compounds were detected at all six stations and had a wide range of concentrations, from 73.6 at BCE1 to 1723 $\mu\text{g}/\text{dry kg}$ at BCE3 (Table 2). The concentration of the sum PAHs did not exceed the TMDL target concentration at any station (Table 3). The concentration of TPH ranged from 58000 to 982000 $\mu\text{g}/\text{dry kg}$; about three orders of magnitude higher than the traditionally measured PAH compounds.

All three of the chlorinated organic compound groups on the TMDL list (chlordanes, DDTs and PCBs) were detected at every station (Table 2). Chlordane and DDTs exceeded the TMDL target concentration at all of the stations, while total PCBs exceeded the target only at BCE2 (Table 3).

Pyrethroid pesticides were detected at each of the stations, with BCE2 and 3 having the highest concentrations (Table 2). Permethrin compounds were the most prevalent of the pyrethroids at all stations except BCE1, followed by bifenthrin (Figure 5). Toxic unit calculations for the amphipod *E. estuarius* indicate that there was enough bifenthrin and/or cyfluthrin in the sediments at most of the stations to cause toxicity (Table 4).

Table 2. Summary of physical and chemical parameters for August 2009 sediment samples.

Parameter	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Sand (%)	83.6	80.3	83.4	61.2	47.2	10.7
Silt (%)	14.4	16.9	14.5	4.0	3.0	3.5
Clay (%)	2.1	2.8	2.2	0.4	0.4	0.3
Gravel (%)	0	0	0	34.4	49.5	85.5
TOC (%)	0.2	1.7	1.1	0.9	0.4	0.7
Black Carbon (%)	0.03	0.2	0.2	0.1	0.1	0.1
Sum PAH (µg/kg)	73.6	1507	1723	739	209	711
Total Petroleum Hydrocarbons (µg/kg)	58400	839000	982000	395000	210000	429000
Sum DDT(µg/kg)	7.36	11.1	8.85	2.38	3.17	2.20
Sum Chlordane (µg/kg)	2.79	24.1	19.8	6.87	4.77	4.47
Sum PCBs (µg/kg)	1.46	53.2	20.4	5.87	2.93	6.06
Sum Pyrethroids (µg/kg)	3.54	64.4	93.0	22.2	7.36	42.2
Sum Fipronils (µg/kg)	0.15	0.52	1.02	0.59	0.97	2.03

Table 3. Ballona Creek Estuary TMDL target concentration exceedances from 2009 (in gray). Concentrations are µg/kg.

Parameter	Target	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
DDTs	1.6	7.36	11.1	8.85	2.38	3.17	2.20
Chlordanes	0.5	2.79	24.1	19.8	6.87	4.76	4.47
PCBs	22.7	1.46	53.2	20.4	5.87	2.93	6.06
PAHs	4022	73.6	1507	1723	739	209	805

Table 4. Calculated toxic units for pyrethroids in Ballona Creek Estuary sediments collected in August 2009.

	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Bifenthrin	0.87	0.87	1.71	0.41	0.49	0.81
Cypermethrin	0.25	0.21	0.74	0.16	0.19	0.44
Permethrin	0.10	0.11	0.22	0.07	0.06	0.19
Cyfluthrin	1.27	0.70	2.16	0.92	0.41	1.56
Sum	2.49	1.89	4.83	1.56	1.15	3.00

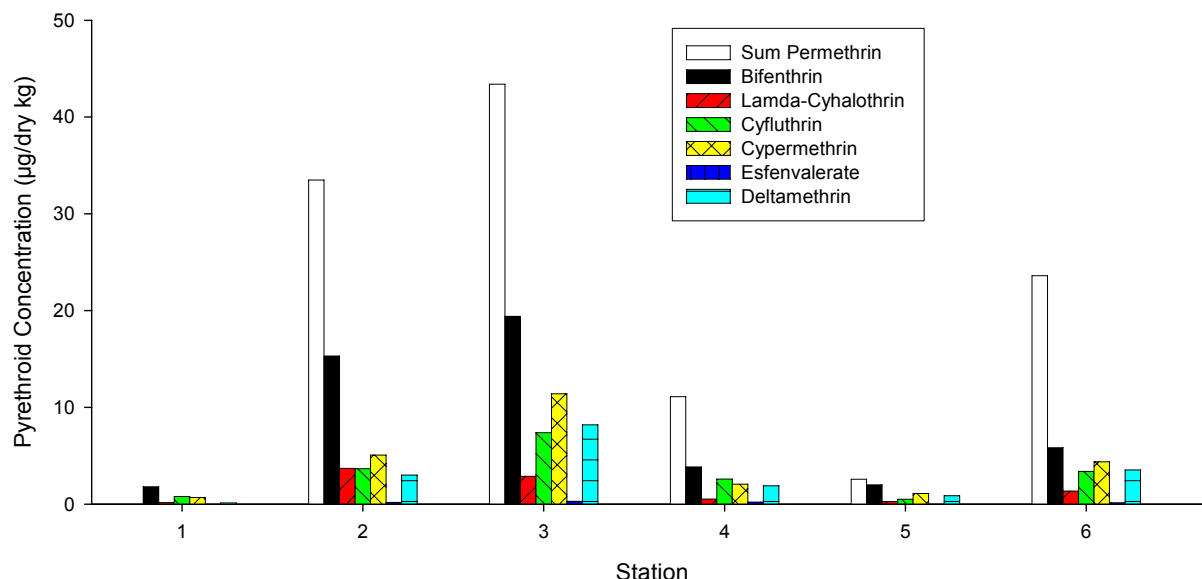


Figure 5. Concentrations of individual pyrethroid compounds in Ballona Creek Estuary sediments from the August 2009 sampling.

The phenylpyrazole insecticide fipronil and its degradation compounds were detected at all six stations (Table 2). The highest concentrations were observed at BCE6, 3, and 5, respectively. The majority of the compounds detected were the degradation products, rather than the parent compound (Figure 6). The threshold for toxicity of fipronil compounds to *E. estuarius* is unknown. However, fipronil and its degradates have been found to be toxic to fresh water midge larvae, *Chironomus tentans* at an LC50 of about 0.15 µg/g organic carbon (Maul et al. 2008). The parent compound and the degradation products fipronil-sulfide and fipronil-sulphone had very similar LC50s. The concentration of total fipronils at BCE6 on an organic carbon normalized basis was 0.29 µg/g OC; a concentration that would be expected to be toxic to *C. tentans*. In addition, fipronil toxicity to the freshwater amphipod *Hyalella azteca*, was found to be similar to some of the pyrethroid compounds, with a water LC50 of 0.54 µg/L (Lizotte Jr. et al. 2009).

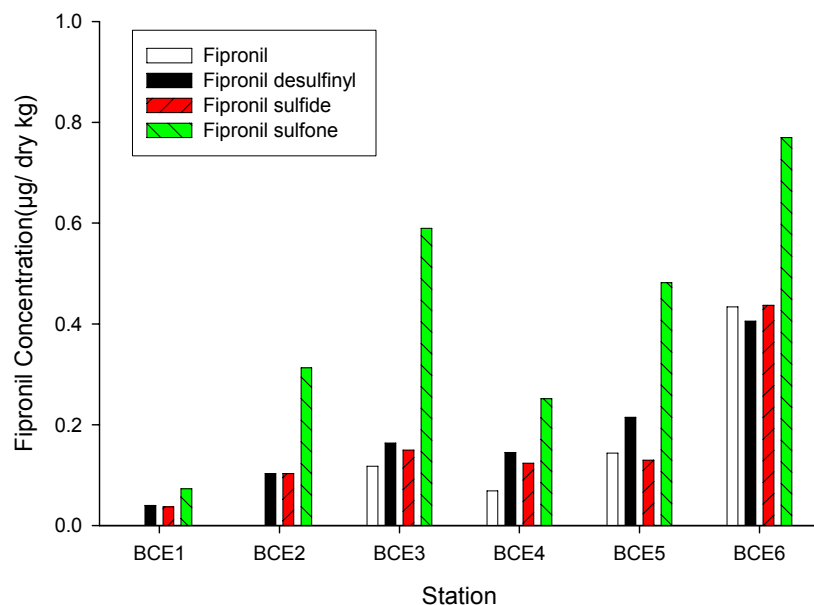


Figure 6. Concentrations of fipronil and its degradates in Ballona Creek Estuary sediments from the August 2009 sampling.

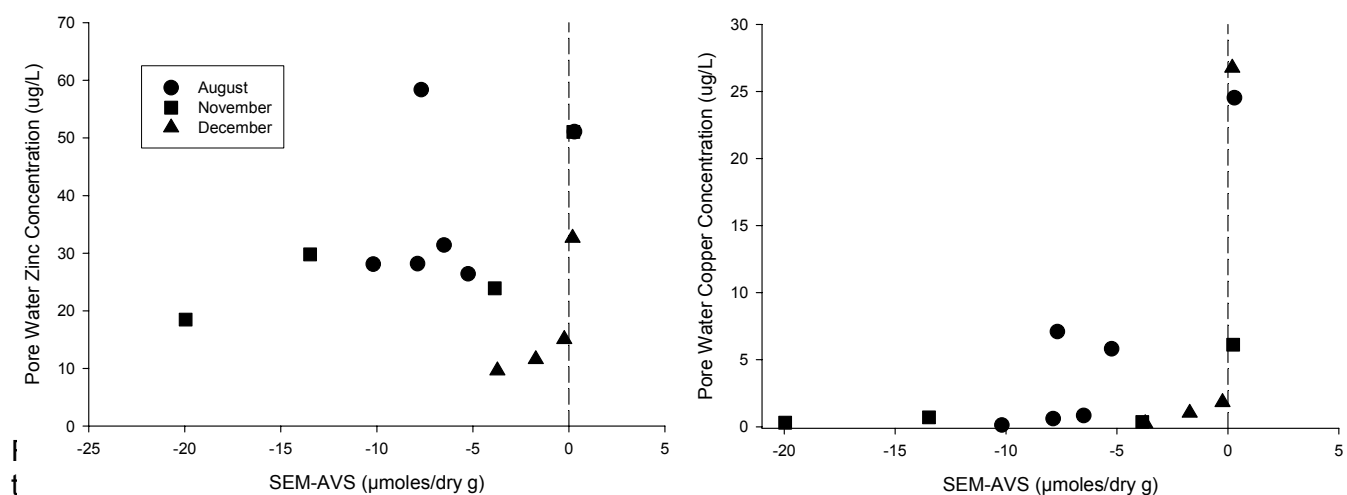
In order to determine if the concentrations of metals in the sediment are likely to be natural or anthropogenically enriched, an iron normalization calculation was performed (Schiff and Weisberg 1999). This procedure found that all of the TMDL target metals were enriched at BCE2 and 3 (Table 5). All except silver were enhanced at BCE1, 4 and, 5. Only copper and zinc were enriched at BCE6.

The concentration of metals in sediments does not necessarily predict their influence on sediment toxicity. Sulfides in the sediment can sequester the divalent metals cadmium, copper, lead, nickel and zinc, rendering them biologically unavailable. If the concentration of acid volatile sulfide (AVS), on a molar basis, exceeds the total concentration of simultaneously extracted divalent metals (SEM), then the metals are considered to be tightly bound to the sediments and not likely to be bioavailable. Sediment samples collected in 2009 were analyzed to determine the concentration of AVS and SEM. For the August sampling, only sediment from BCE5 had greater metals than sulfide concentration (Figure 7 and Appendix Table 2).

The main exposure route of metals for many animals that live in the sediment is considered to be uptake from the pore water. Therefore, samples of pore water extracted from the sediment by centrifugation were analyzed for dissolved metals. The concentrations were compared to values listed in the California Toxics Rule (CTR) for ambient waters, as no standards for pore water have been established. Only copper for BCE4, 5 and 6 exceeded the CTR concentration of 3.1 µg/L (Figure 8 and Appendix Table 2). The copper concentrations ranged from 0.13 µg/L at BCE1 to 24.5 µg/L at BCE5. The highest pore water metal concentrations were for zinc, which ranged from 26.4 µg/L at BCE4 to 58.4 µg/L for BCE6, but did not exceed the CTR of 81 µg/L at any station (Figure 9).

Table 5. Results of anthropogenic enrichment of metals analysis in Ballona Creek Estuary sediments. Values are the enrichment factors (ratio of observed to upper confidence bound of predicted background metal concentration); a value greater than 1 indicates enrichment.

	BCE1	BCE2	BCE3	BCE4	BCE5	BCE6
Cadmium	1.3	2.9	2.9	1.5	1.1	0.9
Copper	1.0	5.0	1.9	1.1	1.1	1.3
Lead	1.4	3.3	2.8	2.1	1.6	0.4
Zinc	1.2	2.8	2.8	1.9	2.0	1.2
Silver	0.2	2.1	1.2	0.6	0.4	0.5



concentration of total SEM minus the molar concentration of acid volatile sulfides. Values greater than 0 indicate the metal may be bioavailable. All samples greater than 0 were from BCE5.

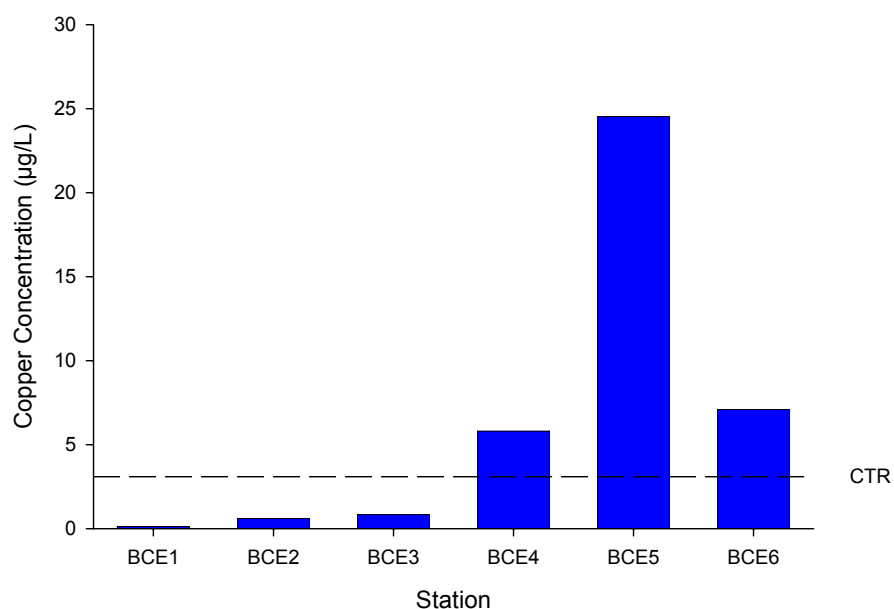


Figure 8. Pore water dissolved copper concentrations from sediment samples collected from Ballona Creek Estuary in August 2009. CTR=California Toxics Rule value for continuous concentration.

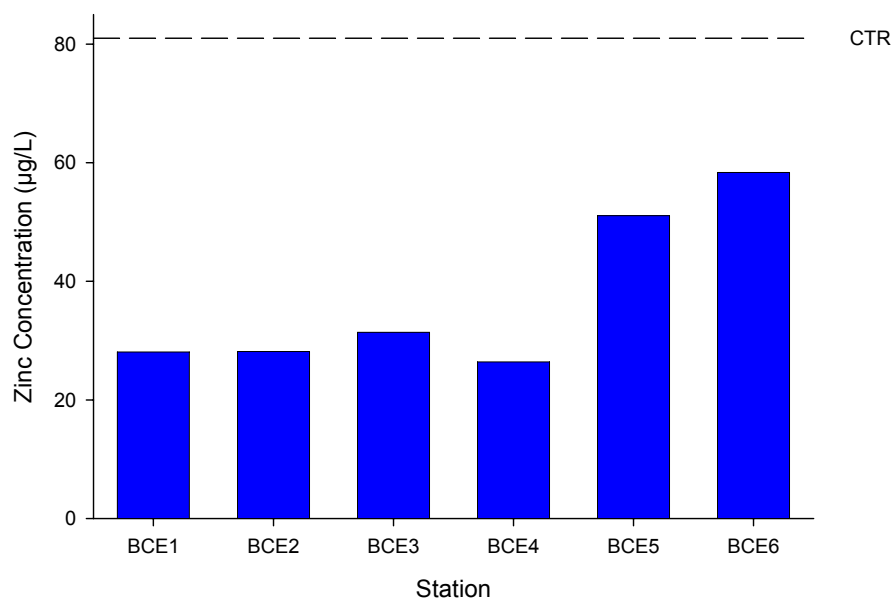


Figure 9. Pore water dissolved zinc concentrations from sediment samples collected from Ballona Creek Estuary in August 2009. CTR=California Toxics Rule value for continuous concentration.

PASSIVE SAMPLER STUDY

Methods

The *in situ* pore water concentrations of metals and organic compounds were measured at four monitoring stations in Ballona Creek Estuary (BCE1, 2, 3 and 5) in order to estimate bioavailable concentrations. At each station, a set of three peepers for sampling pore water metals and an apparatus containing passive sampling devices for sampling water column and pore water organic chemicals was deployed by diver on November 2, 2009. The samplers were retrieved by diver on December 1, 2009. Both at the time of deployment and retrieval, sediment samples were collected by the diver for amphipod survival and sea urchin fertilization toxicity testing, whole sediment chemistry (chlorinated pesticides, pyrethroids, fipronils, black carbon and TOC), grain size, AVS/SEM and pore water dissolved metals.

The peepers consisted of 50 mL low density-polyethylene snap cap vials with holes drilled in the lid. Deoxygenated, deionized water was used to fill the vial. A 0.45 μm pore-size polyether-sulfone (PES) filter membrane was placed over the vial opening and the perforated cap snapped closed (Figure 10). The vials were stored in deoxygenated, deionized water until deployment. Three peepers were buried approximately 5 cm below the sediment surface. At the end of the deployment period the peepers were removed from the sediment, gently rinsed with deionized water and the contents removed and filtered. A salinity measurement was made on a subsample and the remainder was analyzed for dissolved metals, each peeper being a replicate.

Solid-phase microextraction (SPME) fibers were deployed on a structure made of iron bar and wood (Figure 11). The fibers were housed inside copper tubes to prevent fouling. The tubes were attached to the structure so that when it was pushed into the sediment, the SPME housing would be about 5 cm into the sediment, with the wood resting on the sediment surface. At BCE1, 2, and 3, a second SPME was attached to a mast on the structure so that it was exposed to the water column. Because BCE5 is in shallow water, there was no mast on the structure for that station. Upon retrieval, the SPME fibers were immediately removed from the copper housing, rinsed with deionized water and placed in individual vials on ice. SPME fibers were manually injected into the GC inlet under splitless mode and thermally desorbed for 6 min at 280 °C. External calibration method was used for quantization of SPME measurements.

Pore water samples for toxicity testing and dissolved metals analysis were extracted from the sediment as previously described. Sea urchin fertilization tests on pore water were also performed as previously described, except that EDTA was added to a separate pore water aliquot to chelate divalent metals in order to determine the role of metals in toxicity.

Amphipod toxicity testing was conducted on the whole sediment and pore water using *Eohaustorius estuarius*. Whole sediment was tested in 1 liter jars with 2 cm of sediment and approximately 700 ml of overlying 20 ppt seawater with gentle aeration. There were five replicates from each station and 20 amphipods per replicate. The tests were conducted at 15°C under constant light. Pore water was tested in shell vials with 10 ml of sample. There were 5 replicates per station with 5 amphipods per replicate. The tests were conducted at 15°C under constant darkness. Water quality (pH, salinity, dissolved oxygen, and ammonia) was measured for both whole sediment and pore water tests at the beginning and end of the 10 day exposure period.



Figure 10. Peeper-style passive samplers used to collect pore water samples from Ballona Creek Estuary for trace metal measurement.

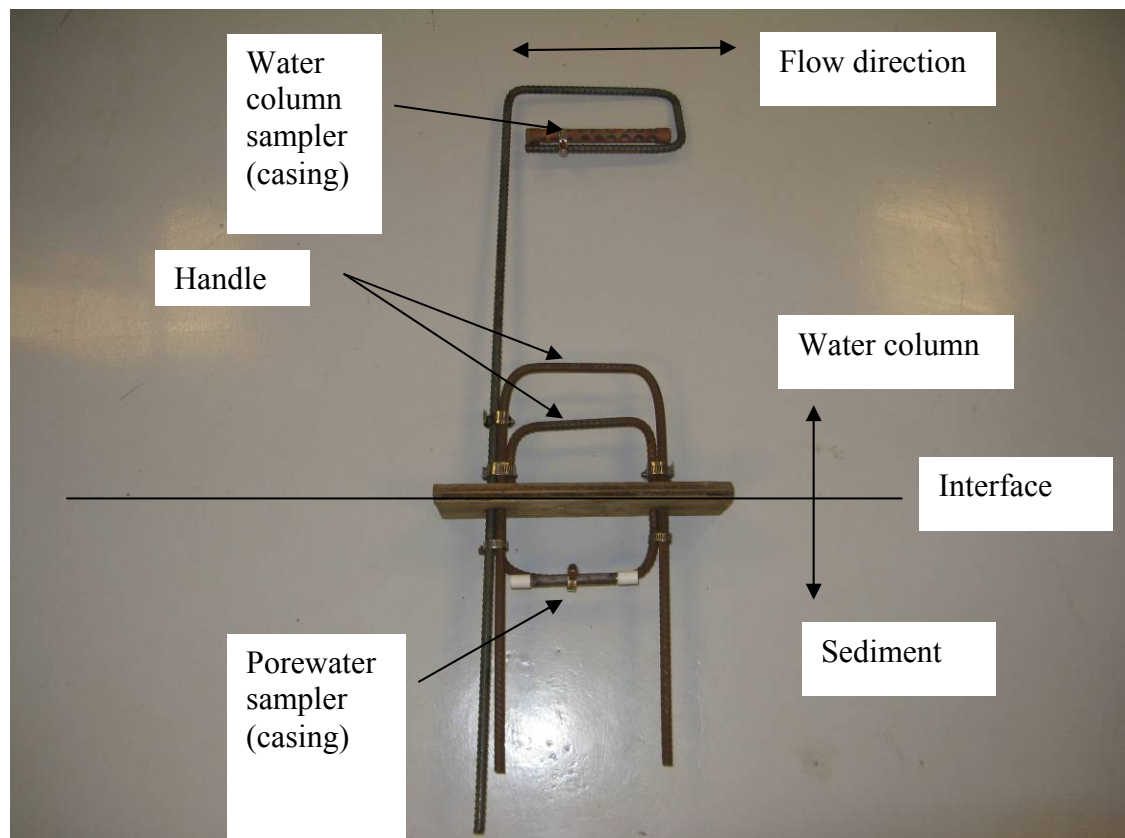


Fig.11. Trace organics passive sampler deployment fixture.

Results

Toxicity

Pore water toxicity testing with the purple sea urchin fertilization method identified toxicity at the time of passive sampler deployment for BCE1 and 5 (Figure 12). No toxicity was detected in the pore water extracted from sediments collected at the time of retrieval. The addition of EDTA to the pore water samples had a minimal effect on toxicity for BCE1. The toxicity of BCE5 pore water was eliminated by EDTA addition, indicating that cationic metals were likely causing the observed toxicity for this sample.

Whole sediment toxicity tests with amphipods found all stations to have substantial toxicity at both deployment and retrieval (Figure 13). The toxicity magnitude of toxicity was similar between the two samplings for most stations; station BCE5 had a greater magnitude of toxicity at retrieval than deployment. All pore water samples except the BCE5 sample at deployment had substantial toxicity to amphipods (Figure 14). The results were similar between sampling periods except for BCE5. Pore water toxicity for BCE5 changed from nontoxic to highly toxic between November and December.

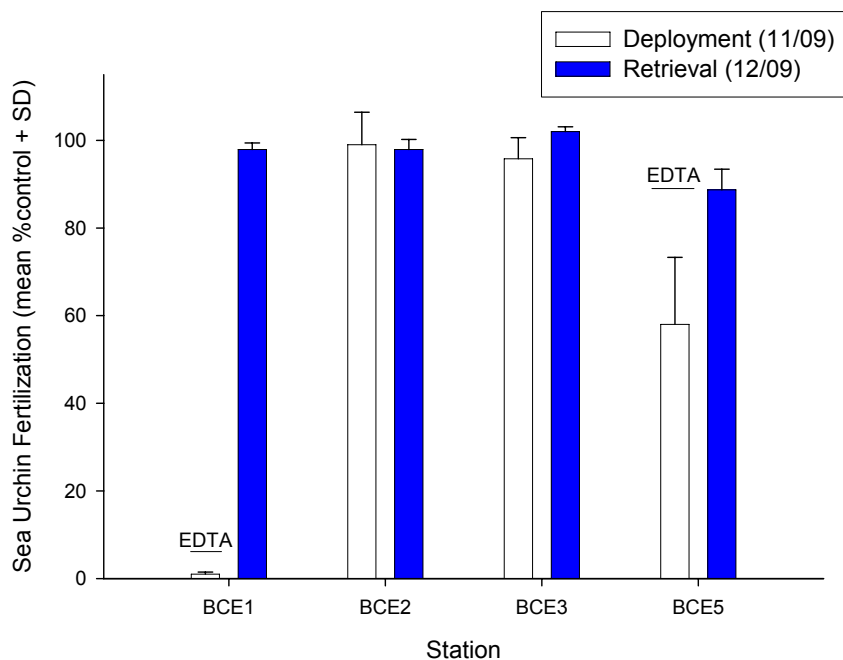


Figure 12. Results of sea urchin fertilization testing of Ballona Creek Estuary pore water samples from November and December 2009. The horizontal line above some bars indicates the fertilization percentage of the sample when EDTA was added. No change in fertilization with EDTA addition was present in samples without a line.

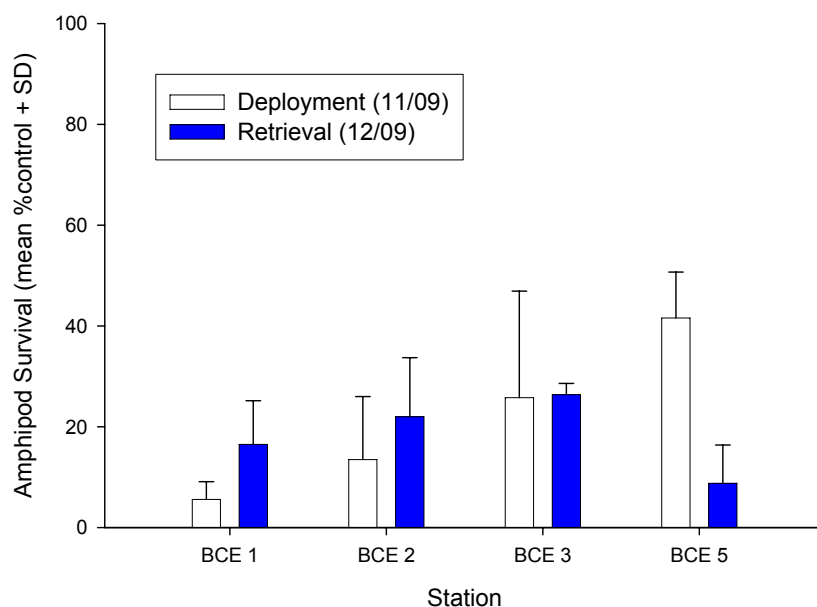


Figure 13. Results of amphipod 10-day survival testing of Ballona Creek Estuary whole sediment samples from November and December 2009.

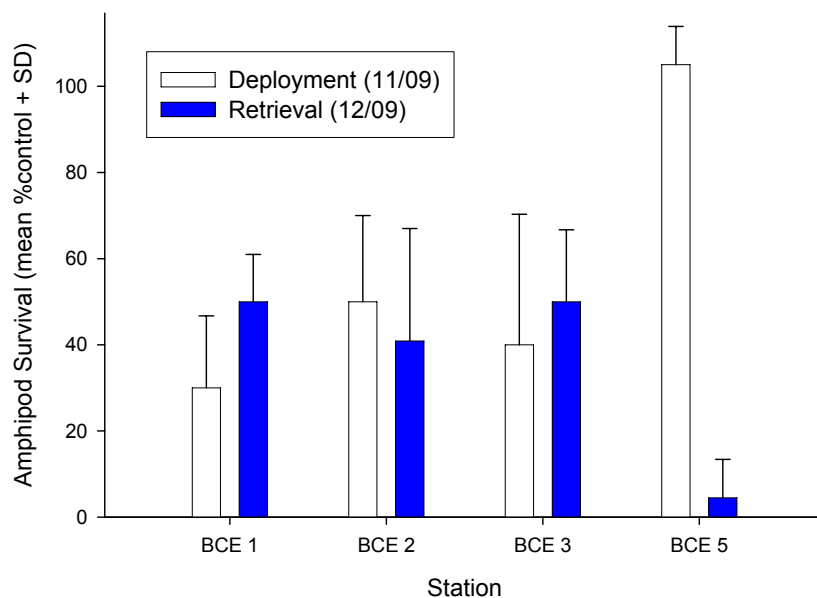


Figure 14. Results of amphipod 10-day survival testing of Ballona Creek Estuary pore water samples from November and December 2009.

Chemistry

Sediment grain size characteristics were similar between the deployment and retrieval of the passive samplers (Table 6). However, most stations had finer grain size and more TOC than in the August sampling. This is especially true for BCE1 and 2. For these two stations there was also an increase in sediment fines and/or TOC between deployment and retrieval. Organic constituents had higher concentrations than in August; most notably a more than 50 fold increase in the concentrations of pyrethroids and fipronils.

The SPME samplers detected all of the chemicals of interest in the water column and pore water from Ballona Creek Estuary, although the specific compounds detected varied by station (Table 7). Only PAHs were detected in the water column at BCE1, but this was in part due to the loss of one of the samplers which prevented some analyses. The other constituents except for fipronil were detected in the water column at the remaining stations. Pyrethroids and DDTs were not detected in the pore water from BCE1 and 2, but all constituents were detected at BCE3 and 5, although just above detection limits. None of the chemicals in the SPME samples were present at concentrations likely to cause toxicity.

At sample retrieval, the peepers from BCE1 could not be found by the diver. Visual evidence indicated that wave action had swept them away. A travel blank indicated possible zinc contamination in the peepers, so no peeper zinc data is presented. Concentrations of metals in the peeper samples were generally lower or similar to those measured in samples of extracted pore water from the same collection event (Appendix Tables 3 and 4). For example, nickel concentrations in the extracted pore water ranged from 1.6 µg/L at BCE2 deployment to 5.3 µg/L at BCE5 retrieval. The peepers had nickel concentrations ranging from 0.22 µg/L at BCE3 to 1.02 µg/L for BCE5. Conversely, cadmium in the pore water ranged from 0.005 µg/L for BCE1 deployment to 0.077 µg/L at BCE5 retrieval. The cadmium concentration in the peepers ranged from 0.012 µg/L for BCE3 to 0.15 µg/L for BCE5. Concentrations of metals in peepers were generally below levels expected to cause toxicity to either the purple sea urchin sperm or *E. estuarius*. Concentrations of zinc in the extracted pore water (Figure 15) were in the range reported to cause toxicity to sea urchin sperm (4 to > 100 µg/L) (Phillips et al. 1998), but no toxicity to sea urchins was detected in the samples at the end of deployment. One extracted pore water sample had an elevated copper concentration (BCE5, 26.8 µg/L) which was near the EC50 for purple sea urchin fertilization (32.7 µg/L, SCCWRP unpublished), but this sample was not toxic (Figures 12 and 16).

The pore water metals results were consistent with the results for the AVS and SEM analyses. All stations except BCE5 had AVS concentrations that exceeded the SEM (Figure 7 and Appendix Tables 3 and 4) and very low concentrations of dissolved metals were present. These results indicate that trace metals were unlikely to be biologically available in sediment pore water at concentrations of toxicological concern to marine life.

Table 6. Selected whole sediment chemistry data from Ballona Creek Estuary samples collected in November and December 2009.

Parameter	Deployment (11/09)				Retrieval (12/09)			
	BCE1	BCE2	BCE3	BCE5	BCE1	BCE2	BCE3	BCE5
Sand (%)	73.9	67.5	89.6	69.9	72.9	54.3	76.3	63.1
Silt (%)	25.2	32.6	10.2	25.8	26.1	42.4	22.6	32.0
Clay (%)	0.9	2.9	0.2	4.2	1.1	3.2	1.1	4.9
Gravel (%)	0.0	0.0	0.0	27.0	0.0	0.0	0.0	39.7
TOC (%)	1.8	2.3	0.5	0.3	2.2	4.3	0.7	0.3
Black Carbon (%)	0.3	0.4	0.2	0.2	0.5	0.6	0.2	0.2
Sum DDT(µg/kg)	9.16	16.3	2.75	0.00	6.54	10.8	8.78	0.00
Sum Chlordane (µg/kg)	16.7	27.6	11.8	2.70	14.8	22.4	15.5	2.70
Sum PCBs (µg/kg)	23.1	20.0	3.36	0.33	9.92	14.9	2.97	0.51
Sum Pyrethroids (µg/kg)	179	77.2	18.0	4.79	64.4	62.7	20.8	1.86
Sum Fipronils (µg/kg)	12.2	4.81	1.46	0.89	7.95	4.18	2.45	1.05

Table 7. Concentrations of trace organics measured using SPME devices deployed in Ballona Creek Estuary during November 2009.

Parameter	Water column				Pore water			
	BCE1	BCE2	BCE3	BCE5	BCE1	BCE2	BCE3	BCE5
Sum PAH (ng/L)	3.00	5.36	2.88	7.20	8.79	34.7	55.5	21.9
Sum DDT(ng/L)	NA	0.043	0.034	0.017	ND	ND	0.020	0.017
Sum Chlordane (ng/L)	NA	0.272	0.137	0.414	0.176	0.307	0.179	0.177
Sum PCBs (ng/L)	NA	0.031	0.029	0.041	0.000	0.028	0.105	0.005
Sum Pyrethroids (ng/L)	NA	0.077	0.02	0.148	ND	ND	0.038	0.009
Sum Fipronils (ng/L)	NA	ND	ND	5.55	0.767	2.30	0.462	6.58

NA = Not analyzed, SPME fiber broken

ND = Not detected

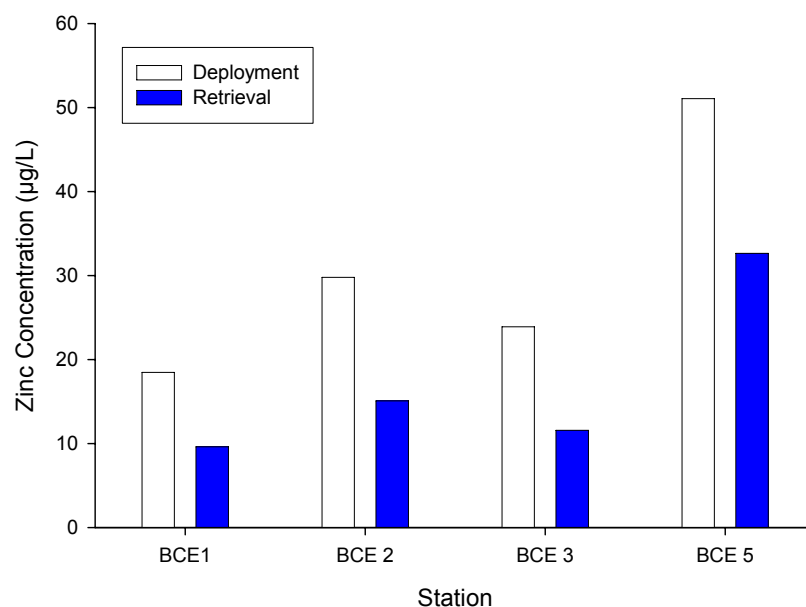


Figure 15. Concentration of dissolved zinc in pore water samples from Ballona Creek Estuary collected in November and December 2009.

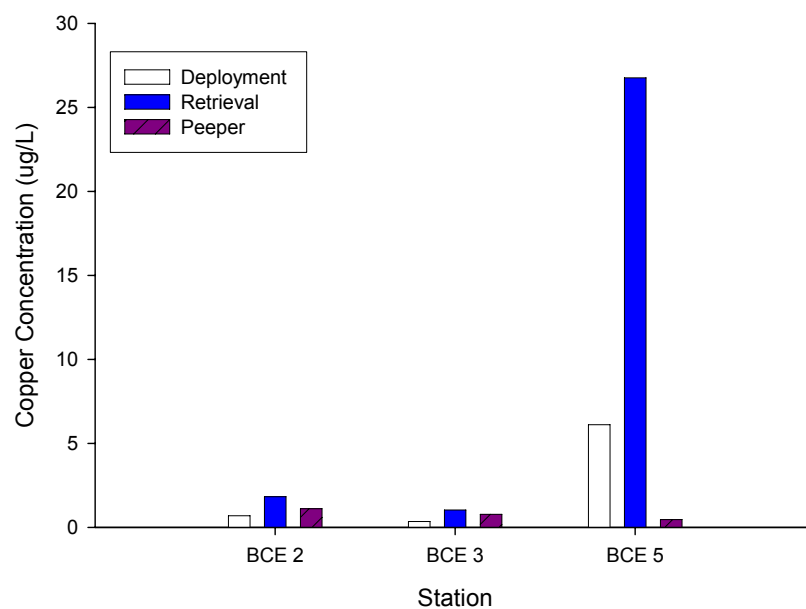


Figure 16. Concentration of dissolved copper in pore water and peeper samples from Ballona Creek Estuary in November and December 2009.

Spiked Sediment Tests

Methods

A series of spiked sediment experiments were conducted in order to establish toxicity thresholds for selected organic chemicals of concern for the Ballona Creek Estuary. Sediment used for spiking was collected by CLA, EMD from their NPDES monitoring station B5, located somewhat north and offshore of the mouth of Ballona Creek. This sediment had low contaminant concentrations and low toxicity. The TOC and grain size were 0.63% and 30% fines, respectively, similar to some sediments from Ballona Creek Estuary.

In separate experiments, batches sediment were spiked with 4,4' DDT, 4,4' DDE, alpha chlordane, and cyfluthrin. For each chemical, a range finding test was first performed to determine the appropriate concentration for final testing. The spiking procedure consisted of first making chemical stock solutions dissolved in acetone. A separate stock solution was made for each concentration such that the ratio of acetone carrier to sediment was the same for each treatment. For each sediment concentration, 10 grams of silica sand per 1.5 L of sediment was added to a glass jar. For each 10 grams of silica sand, 1 ml of stock solution was added to the sand by glass syringe. The open jar was placed in a fume hood for 1 hour for the acetone to evaporate. Sediment was then added to the jars. The jars were then placed on a roller table at 15°C in the dark for 24 hr. After the rolling period, the jars were stored at 5°C in the dark. Once a week during the 28 day equilibration period, the jars were rolled for 2 hr. At the end of the equilibration period a sample of each concentration was taken for chemical verification and the sediment was tested using the *E. estuarius* 10-day survival method described previously. Included in each exposure series was an acetone blank that consisted of 1 ml of acetone added to sand that was handled and tested in the same manner as the spiked sediments.

For chemicals that were found to be toxic when spiked onto sediment, a whole sediment TIE was conducted to verify that the results of the manipulations were as predicted in the literature for that chemical. The treatments included temperature reduction to 10°C, carboxyl esterase enzyme (CEE) addition, bovine serum albumin (BSA) addition, addition of piperonyl butoxide (PBO), cation exchange resin addition, coconut carbon addition, and zeolite addition (Table 8).

Results

Spiked sediment experiments with DDE and chlordane did not produce toxicity at any of concentrations tested (Figures 17 and 18). In each case, the highest concentration tested was more than two orders of magnitude greater than that present in Ballona Creek Estuary sediments (Appendix Table 2). The chemical concentrations for DDE and chlordane spiked sediments have not yet been analytically verified.

The DDT spiked sediment experiment produced a clear dose-response with a full range of toxicity (Figure 19). The lowest concentration at which toxicity was present was 2400 µg/dry kg. This concentration is about three orders of magnitude higher than that present in Ballona Creek sediments (Appendix Table 2). A TIE conducted on the 2400 µg/ kg DDT treatment produced results similar to those expected for this type of chemical. The carbon treatment completely removed toxicity (Figure 20). The PBO treatment slightly increased toxicity, as did the temperature reduction treatment. A partial reduction of toxicity was observed in the cation exchange resin, zeolite, and dilution treatments; this effect was attributed to the dilution of the spiked sediment as a consequence of adding the treatment materials. The carboxylesterase and BSA treatments had no effect. The DDT concentrations have not yet been analytically verified.

A steep dose-response was obtained in the cyfluthrin spiked sediment experiment. No toxicity was detected at 0.84 µg/kg and nearly complete mortality was produced by exposure to 3.5 µg/kg (Figure 21). The concentrations that are presented for cyfluthrin are the measured concentrations.

The cyfluthrin concentrations that were found to be toxic in the spiked sediment test are within the range that has been detected in Ballona Creek Estuary sediments (Figure 5). The TIE conducted on the 3.5

µg/kg concentration showed results that were similar to those obtained with Ballona Creek Estuary whole sediment. The carbon and the carboxylesterase treatments were the only treatments to substantially reduce toxicity (Figure 22). The temperature reduction and PBO treatments, which would be expected to increase toxicity, were inconclusive because there was no survival in the baseline sample.

Table 8. Description of whole sediment TIE treatments used on spiked sediments.

Treatment Details	Treatment Details	Purpose	Expected Result
Coconut carbon	15% by weight	Binding of organic contaminants	Decrease toxicity if organics are present
Cation exchange resin	20% by weight	Binding of cationic metals	Decrease toxicity if metals are present
Zeolite	20% by weight	Binding of ammonia	Decrease toxicity if ammonia is present
Dilution with control sediment	20% by weight	Control for physical manipulation of sediment	No to slight change in toxicity
Aeration of sediment	Manual mixing of sediment	Control for physical manipulation of sediment	No change in toxicity
Piperonyl butoxide (PBO)	400 µg/L	Inhibits pesticide metabolism	Decreases organophosphorus pesticide toxicity; increases toxicity of pyrethroid pesticides
Temperature reduction	10°C	Inhibits pesticide metabolism	Decreases organophosphorus pesticide toxicity; increases toxicity of pyrethroid pesticides
Carboxylesterase enzyme (CEE)	1.0 Units/ml - powderized form	Hydrolyzes pyrethroid pesticides	Decrease in toxicity if pyrethroid pesticides are present in the sample
Bovine serum albumin (BSA)	Match concentration to CEE enzyme addition	Control for nonspecific binding of toxicants to carboxylesterase	No change in toxicity

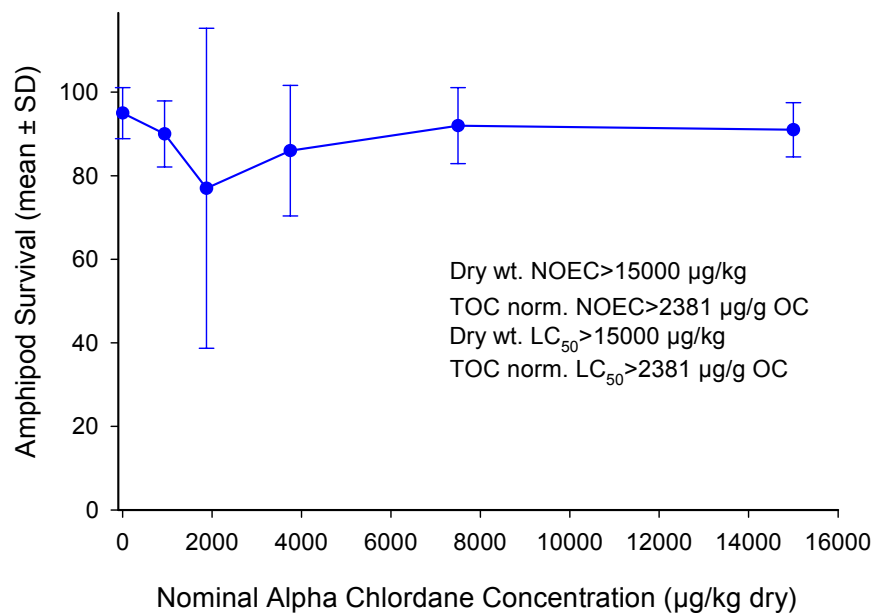


Figure 17. Response of *Eohaustorius estuarius* exposed to α -chlordane in sediment.

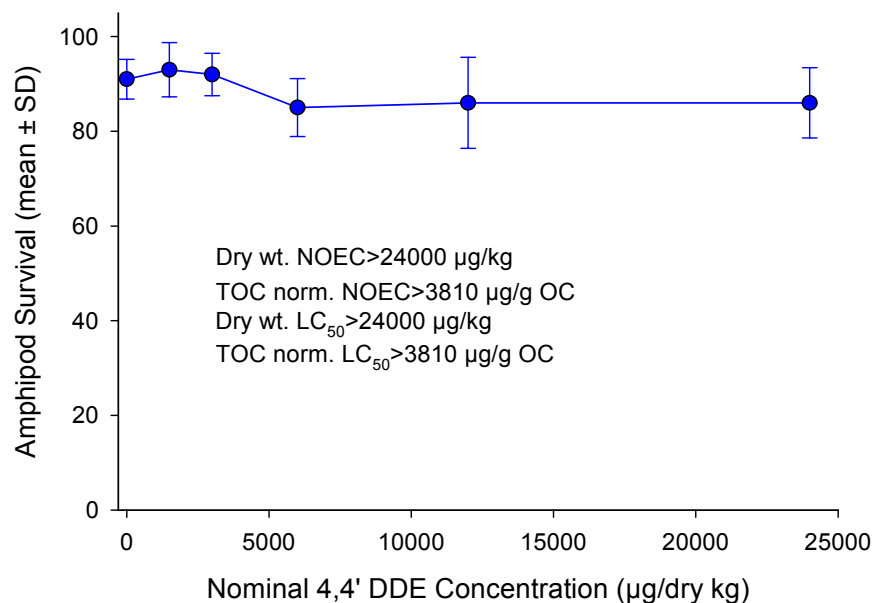


Figure 18. Response of *Eohaustorius estuarius* exposed to 4,4' DDE in sediment.

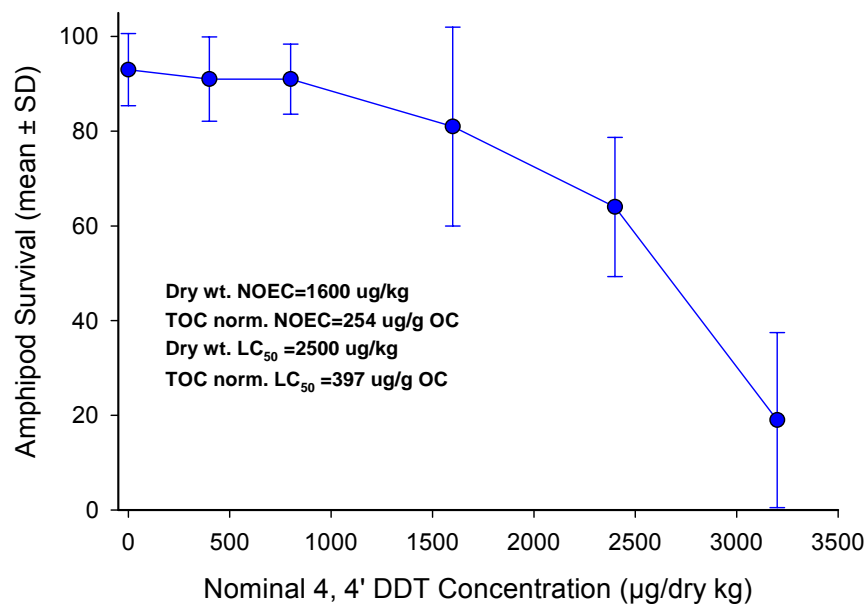


Figure 19. Response of *Eohaustorius estuarius* exposed to 4,4' DDT in sediment.

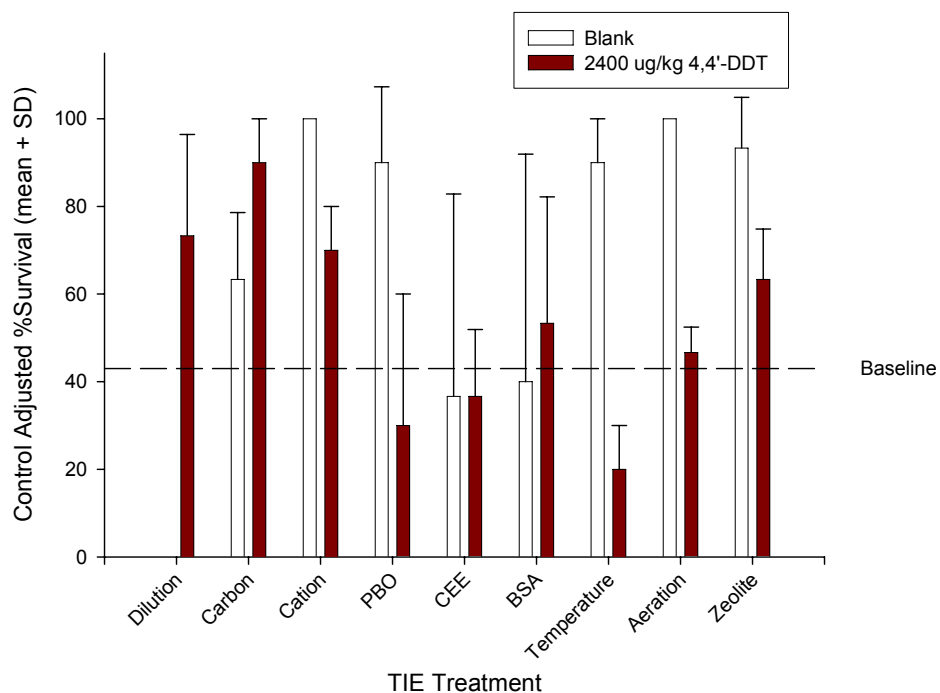


Figure 20. Results of *Eohaustorius estuarius* TIE conducted on sediment spiked with 4,4' DDT.

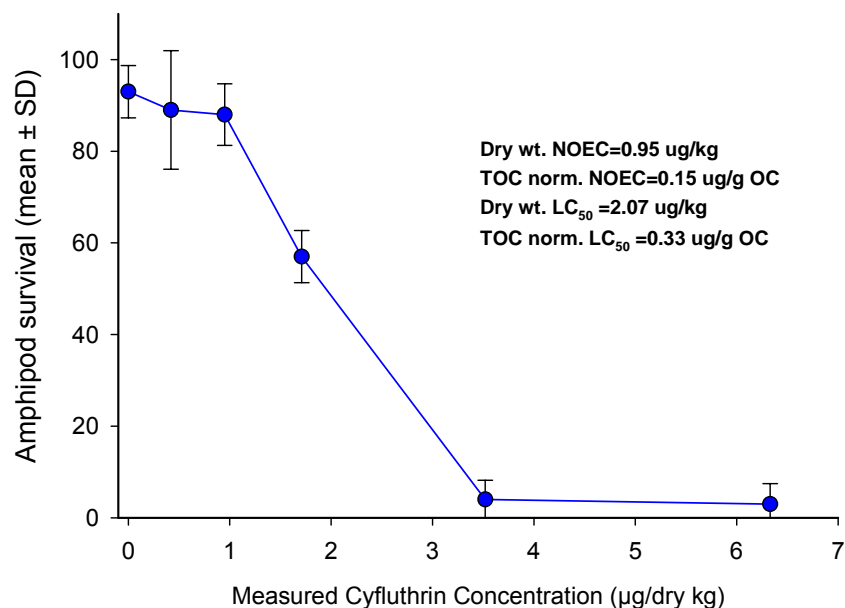


Figure 21. Dose-response plot of *Eohaustorius estuarius* exposed to cyfluthrin in sediment.

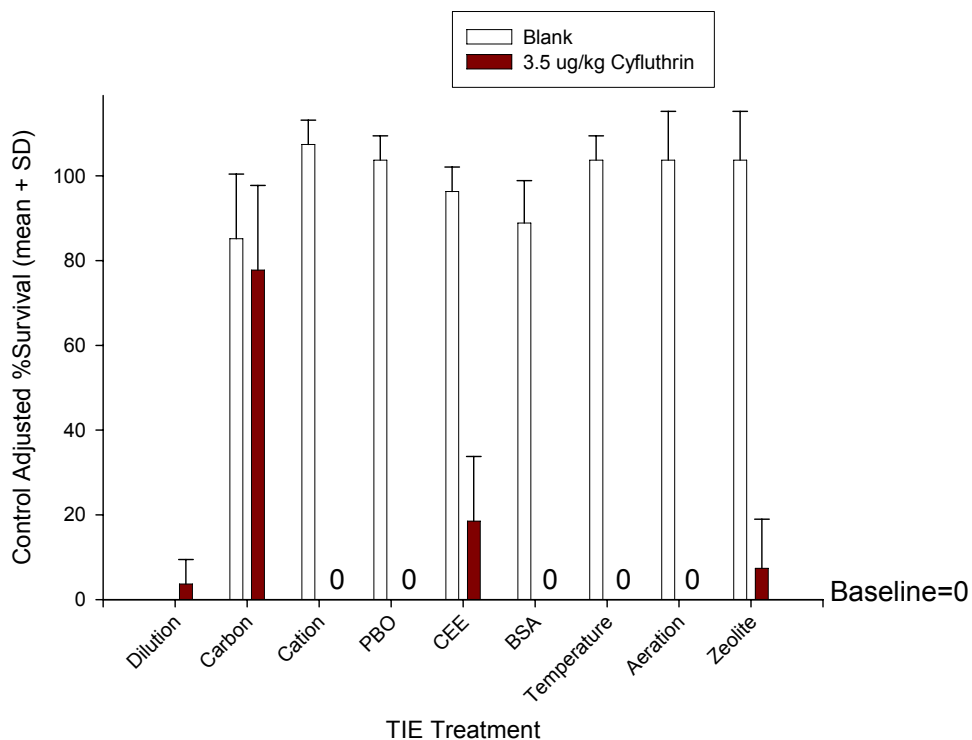


Figure 22. Results of TIE conducted on sediment spiked with cyfluthrin using the *Eohaustorius estuarius* 10 day survival test.

DISCUSSION

The main characteristic of the Ballona Creek Estuary system continues to be its dynamic nature. Again it was found that toxicity and chemistry changed over time and space; both between years and even within the four-month span during which sampling was conducted in 2009. Toxicity was found at BCE1 which in previous surveys has been rare. An example of the short term variability is the TOC content of the sediments. Sediment TOC content increased greatly at the two stations closest to the mouth of the estuary between August and November, while trending slightly downward at the upstream stations (Figure 23). This was accompanied by an increase in organic contaminants at BCE1 and 2. The short term changes may be due in part to runoff from an early season storm that occurred in mid-October that may have transported additional contaminants into the estuary.

Limited progress was made in determining the cause of pore water toxicity to the sea urchins in 2009. While the first round of TIE testing was inconclusive due to a change in toxicity, testing during the passive sampler study indicated that metals were causing pore water toxicity at BCE5. This is also the only station where AVS did not exceed SEM, indicating that increased concentrations of metals may be biologically available in the pore water. The cause of the toxicity that was observed in BCE1 remains unknown. Results from the AVS/SEM analysis and from the passive sampling indicate that any pore water metals toxicity that may exist for stations other than BCE5 may be an artifact of the pore water extraction method used in the laboratory. The AVS/SEM data indicate that it is unlikely that elevated concentrations of bioavailable trace metals were present in the pore water. The passive sampler data indicate that metals concentrations in the pore water were below levels expected to cause toxicity.

A complete set of PAH data with low detection limits was obtained for the first time. This allowed for a more detailed evaluation of the likelihood of PAHs contributing to sediment toxicity in Ballona Creek Estuary. PAH concentrations at all of the Ballona Creek Estuary stations were well below the thresholds for several sediment quality guidelines, indicating that PAHs are an unlikely source of toxicity (Table 9). However, total petroleum hydrocarbons were detected at concentrations that exceeded 100000 µg/kg at all stations except BCE1, and approached 1000000 µg/kg at BCE2 and 3 (Table 2). Recent research suggests that total petroleum hydrocarbons may contribute to sediment toxicity (Anson et al. 2008). However, the threshold of toxicity for total petroleum hydrocarbons to *E. estuarius* is unknown at this time.

Black carbon was measured in Ballona Creek Estuary sediments for the first time in 2009. This form of carbon binds organic contaminants more strongly than most other forms of organic carbon that are typically present in sediment. The ratio of black carbon to TOC in Ballona Creek Estuary sediments was similar to that reported for other areas (Vinturella et al. 2004). These black carbon values can be used in future calculations to refine estimates of the bioavailable fraction of organic contaminants in Ballona Creek Estuary sediments.

The SPME samplers detected low concentrations of organic contaminants in the water column and pore water of the estuary. At this time, the SPME data do not correspond to the pattern of toxicity observed in the estuary. Analyses of additional passive samplers are in progress in an effort to increase the sensitivity of the trace organics measurements. Results from these analyses are not yet available.

The spiked sediment exposure results are very useful for determining the likelihood that some of the TMDL target chemicals are contributing to toxicity. Sediment spiked with 4,4' DDE, 4,4' DDT or alpha chlordane were not toxic to *E. estuarius* at concentrations multiple orders of magnitude above those present in Ballona Creek Estuary sediments. It is therefore highly unlikely that these compounds are contributing significantly to the toxicity observed at the site. On the other hand, spiking with cyfluthrin found this pesticide to be toxic within the range of concentrations commonly encountered in Ballona Creek Estuary sediment. The determination of a threshold for cyfluthrin sediment toxicity to *E. estuarius* allows further confirmation that pyrethroid pesticides are likely the dominant cause of Ballona Creek Estuary sediment toxicity to this species. The sum of toxic units for the four pyrethroids for which there

is an *E. estuarius* sediment LC50 is greater than one for all locations monitored, indicating a high potential for toxic effects (Table 4). Several other pyrethroid compounds are also present in Ballona Creek Estuary sediments, lending further support to the conclusion that pyrethroid pesticides are the principal cause of sediment toxicity at this site.

Table 9. Comparison of Ballona Creek Estuary sediment PAH data to various sediment quality guidelines.

Guideline (units)	Threshold	BC1	BC2	BC3	BC4	BC5	BC6
LMW ERM ¹ (ng/g)	3160	5.14	54.8	59.0	28.0	8.07	32.6
HMW ERM ¹ (ng/g)	9600	18.5	516	597	219	48.9	263
Sediment TEC ² (ug/g oc)	290	21.2	53.7	95.4	50.7	27.4	65.8
Target Lipid Model ³ Sediment (TU)	1	0.043	0.072	0.116	0.067	0.035	0.082
ESB Toxic Units (TU) ⁴ 80% Confidence level	1	0.077	0.176	0.307	0.168	0.090	0.218

¹ (Long et al. 1995)

² (Swartz 1999)

³ (Di Toro and McGrath 2000)

⁴ (USEPA 2003)

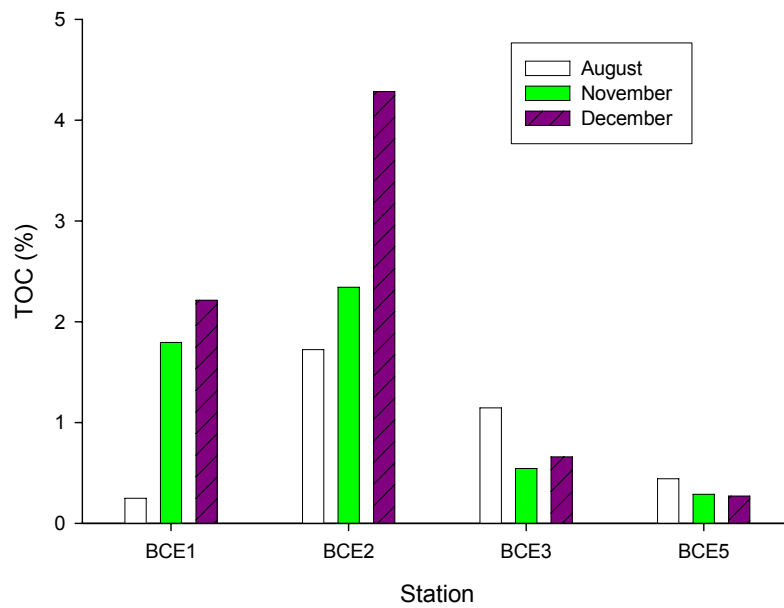


Figure 23. Temporal comparison of sediment TOC for Ballona Creek Estuary in 2009.

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Appendices

Table A-1. Pore water toxicity fertilization test results with *S. purpuratus*. Ballona Creek Estuary stations sampled in September 2009.

Treatment	BCE 2		BCE3		BCE 4		BCE 5		BCE 6	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std.	Mean	Std.	Mean	Std. Dev
Control	83	12.7	83	12.7	83	12.7	83	12.7	83	12.7
Baseline 100%	75	6.1	80	9.3	82	5.8	55	11.6	0	0.5
Baseline 50%	94	3.9	90	3.2	99	0.8	85	4.9	52	22.4
Baseline 25%	NA	NA	NA	NA	NA	NA	99	0.5	85	11.4
EDTA Blank	NA	NA	27	34.8	NA	NA	NA	NA	NA	NA
EDTA 100%	NA	NA	84	7.9	NA	NA	NA	NA	NA	NA
STS Blank	NA	NA	88	9.5	NA	NA	NA	NA	NA	NA
STS 100%	NA	NA	76	7.5	NA	NA	NA	NA	NA	NA
STS 50%	NA	NA	84	10.2	NA	NA	NA	NA	NA	NA
Zeolite Blank	NA	NA	63	28.8	NA	NA	NA	NA	NA	NA
Zeolite 50%	NA	NA	87	6.7	NA	NA	NA	NA	NA	NA
Aeration 100%	NA	NA	96	3.4	NA	NA	NA	NA	NA	NA
Cation Resin Blank	NA	NA	34	28.5	NA	NA	NA	NA	NA	NA
Cation Resin 50%	NA	NA	86	10.2	NA	NA	NA	NA	NA	NA
C18 Blank	NA	NA	94	7.2	NA	NA	NA	NA	NA	NA
C18 50%	NA	NA	83	12.8	NA	NA	NA	NA	NA	NA
C18 25%	NA	NA	92	6.5	NA	NA	NA	NA	NA	NA

NA = Not analyzed

Table A-2. Trace constituents in sediments and pore water collected in August 2009

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
Cadmium (SEM)	sediment	umol/dry	ND	ND	ND	ND	ND	ND
Copper (SEM)	sediment	umol/dry	ND	ND	ND	ND	0.0153	ND
Lead (SEM)	sediment	umol/dry	0.0049	0.0174	0.0162	0.0068	0.0145	0.0015
Nickel (SEM)	sediment	umol/dry	0.0085	0.0124	0.0136	0.0085	0.0059	0.0087
Zinc (SEM)	sediment	umol/dry	0.231	0.642	0.752	0.387	0.311	0.322
Total SEM	sediment	umol/dry	0.244	0.672	0.782	0.402	0.347	0.332
AVS	sediment	umol/dry	10.4	8.55	7.28	5.65	0.053	8.02
SEM/AVS	sediment	umol/dry	0.023	0.079	0.107	0.071	6.55	0.041
SEM-AVS	sediment	umol/dry	-10.2	-7.88	-6.50	-5.24	0.29	-7.69
Arsenic (As)	porewater	ug/L	12.8	2.82	3.41	4.66	4.77	3.92
Cadmium (Cd)	porewater	ug/L	0.047	0.093	0.05	0.069	0.106	0.07
Chromium (Cr)	porewater	ug/L	0.127	0.081	0.132	0.611	0.371	0.271
Copper (Cu)	porewater	ug/L	0.13	0.61	0.84	5.81	24.5	7.09
Lead (Pb)	porewater	ug/L	0.610	0.431	0.588	2.72	0.984	1.66
Nickel (Ni)	porewater	ug/L	2.18	1.51	2.62	6.97	15.3	2.51
Selenium (Se)	porewater	ug/L	1.19	0.40	0.68	0.85	2.07	0.50
Silver (Ag)	porewater	ug/L	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Tin (Sn)	porewater	ug/L	0.236	0.257	0.140	0.229	0.199	0.403
Zinc (Zn)	porewater	ug/L	28.1	28.2	31.4	26.4	51.1	58.4

Table A-2. Continued.

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
2,4'-DDE	sediment	ug/kg	0.645	≤0.370	0.388	<0.151	0.177	0.447
4,4'-DDE	sediment	ug/kg	6.71	11.1	8.46	2.38	2.99	1.75
2,4'-DDD	sediment	ug/kg	≤0.080	<1.026	<0.616	<0.308	<0.308	<0.308
2,4'-DDT	sediment	ug/kg	<1.67	<1.67	<1.00	<0.500	<0.500	<0.500
4,4'-DDD	sediment	ug/kg	<2.42	<2.42	<2.42	<0.727	<0.727	<0.727
4,4'-DDT	sediment	ug/kg	<4.44	<4.44	<2.667	<1.33	<1.33	<1.33
Chlordene	sediment	ug/kg	≤0.043	0.323	0.428	0.054	≤0.023	≤0.0160
Aldrin	sediment	ug/kg	≤0.007	≤0.037	≤0.0360	≤0.011	≤0.002	≤0.014
Chlorpyrifos	sediment	ug/kg	≤0.110	0.612	0.945	0.614	0.274	0.527
Oxychlordane	sediment	ug/kg	≤0.073	≤0.156	0.16	0.098	≤0.045	≤0.057
Heptachlor Epoxide B	sediment	ug/kg	≤0.314	0.452	0.230	0.131	0.096	0.179
Trans-Chlordane (Gamma)	sediment	ug/kg	0.758	7.32	5.59	1.72	1.34	0.984
Cis-Chlordane (Alpha)	sediment	ug/kg	1.01	8.92	6.91	2.36	1.80	1.57
DDMU	sediment	ug/kg	<2.42	<2.42	<1.455	<0.727	<0.727	<0.727
Trans-Nonchlor	sediment	ug/kg	0.732	4.61	3.79	1.31	0.899	0.829
Dieldrin	sediment	ug/kg	≤0.233	3.38	2.95	1.01	0.562	0.766
Endrin	sediment	ug/kg	<2.22	<2.22	<1.333	<0.667	<0.667	<0.667
Cis-Nonachlor	sediment	ug/kg	0.29	1.83	1.73	0.583	0.347	0.381
Naphthalene	sediment	ug/kg	1.60	4.88	4.24	2.19	0.468	1.26
2-Methylnaphthalene	sediment	ug/kg	≤0.785	2.47	1.53	1.10	≤0.296	0.58
1-Methylnaphthalene	sediment	ug/kg	≤0.459	≤1.238	≤0.812	≤0.568	≤0.189	≤0.365
Biphenyl	sediment	ug/kg	2.35	8.70	1.92	0.742	1.15	1.90
2,6-Dimethylnaphthalene	sediment	ug/kg	≤0.216	≤2.33	2.45	2.02	1.60	5.99
1,6-Dimethylnaphthalene	sediment	ug/kg	≤0.244	3.28	≤1.21	0.852	≤0.476	1.01
Acenaphthylene	sediment	ug/kg	≤0.071	1.44	1.70	0.899	≤0.129	0.52
1,2-Dimethylnaphthalene	sediment	ug/kg	≤0.143	0.996	0.712	0.482	0.448	0.98
Acenaphthene	sediment	ug/kg	≤0.038	1.18	1.59	0.843	≤0.157	0.78
2,3,5-Trimethylnaphtha...	sediment	ug/kg	≤0.5	≤0.670	0.515	0.387	0.321	0.54
Fluorene	sediment	ug/kg	≤0.269	2.89	2.79	1.93	0.798	2.07
Dibenzothiophene	sediment	ug/kg	1.45	7.56	6.91	4.14	2.49	4.39
Phenanthrene	sediment	ug/kg	3.54	37.2	41.0	19.35	5.66	19.31
Anthracene	sediment	ug/kg	≤0.129	4.72	6.12	2.50	0.300	2.41
3-Methylphenanthrene	sediment	ug/kg	3.508	13.4	16.9	2.43	5.92	12.18
2-Methylphenanthrene	sediment	ug/kg	3.20	11.6	18.4	6.57	4.88	9.35
2-Methylantracene	sediment	ug/kg	≤0.153	2.74	3.20	5.56	0.616	2.00
4H-Cyclopenta[def]phen...	sediment	ug/kg	0.365	7.38	7.68	5.42	0.668	4.12
9-Methylphenanthrene	sediment	ug/kg	3.80	10.2	10.7	2.61	6.49	10.4
1-Methylphenanthrene	sediment	ug/kg	2.68	7.96	9.87	0.711	4.76	7.64
3,6-Dimethylphenanthrene	sediment	ug/kg	≤0.267	0.998	1.05	0.535	0.446	0.98
1,7-Dimethylphenanthrene	sediment	ug/kg	1.54	10.0	1.95	2.83	10.3	18.9
Fluoranthene	sediment	ug/kg	4.97	113	113	55.8	9.33	44.8
Pyrene	sediment	ug/kg	5.06	110	117	60.7	11.0	48.4
11H-Benzo[b]fluorene	sediment	ug/kg	<2.17	9.03	8.11	2.05	≤0.524	3.91
(1+3)-Methylfluoranthene	sediment	ug/kg	1.32	13.3	14.4	3.46	2.26	11.8
Retene	sediment	ug/kg	6.93	28.1	28.5	9.52	9.04	15.0
4-Methylpyrene	sediment	ug/kg	2.82	31.5	34.2	15.2	6.27	16.0
1-Methylpyrene	sediment	ug/kg	1.33	17.1	17.9	8.39	3.08	8.97
Benzo[c]phenanthrene	sediment	ug/kg	1.69	32.5	34.1	18.7	2.85	10.8
Cyclopenta[cd]pyrene	sediment	ug/kg	1.43	45.4	43.9	34.4	3.05	18.2
Benzo[a]anthracene	sediment	ug/kg	2.92	36.9	35.7	19.8	5.06	15.83
Chrysene	sediment	ug/kg	5.52	92.7	105	51.8	9.55	38.9
3-Methylchrysene	sediment	ug/kg	3.30	51.4	61.6	21.8	13.5	29.84
6-Methylchrysene	sediment	ug/kg	0.590	11.8	12.2	13.7	3.05	5.79
Benzo[b+k]fluoranthene	sediment	ug/kg	2.16	72.1	86.1	38.8	5.26	29.65
Benzo[a]fluoranthene	sediment	ug/kg	<1.06	27.4	40.0	15.6	<0.319	13.6
Benzo[e]pyrene	sediment	ug/kg	2.81	71.9	85.9	36.1	9.72	31.5
Benzo[a]pyrene	sediment	ug/kg	≤1.14	58.7	76.2	31.0	5.33	28.4
Perylene	sediment	ug/kg	3.46	53.4	51.0	38.0	16.5	24.1
9,10-Diphenylanthracene	sediment	ug/kg	<1.03	3.8	5.24	0.752	1.47	3.65

Table A-2 Continued

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
Dibenz[a,j]anthracene	sediment	ug/kg	<1.53	14.1	21.2	6.73	1.24	7.18
dibenzo[a,h]anthracene...	sediment	ug/kg	≤2.18	105	150	≤0.329	8.60	48.1
Benzo[b]chrysene	sediment	ug/kg	<2.89	22.4	37.5	19.4	2.60	15.2
Picene	sediment	ug/kg	<1.51	40.5	62.6	9.31	2.90	16.1
Benzo[g,h,i]perylene	sediment	ug/kg	4.85	134	157	91.6	14.8	50.5
Anthanthrene	sediment	ug/kg	<10.7	176	187	74.5	15.5	69.1
Fipronil desulfinyl	sediment	ug/kg	0.040	0.103	0.164	0.145	0.215	0.406
Fipronil sulfide	sediment	ug/kg	0.037	0.103	0.15	0.124	0.130	0.437
Fipronil	sediment	ug/kg	<0.069	≤0.057	0.118	0.069	0.144	0.434
Fipronil sulfone	sediment	ug/kg	0.073	0.313	0.590	0.252	0.482	0.770
Bifenthrin	sediment	ug/kg	1.79	15.3	19.4	3.84	2.00	5.83
Lamda-Cyhalothrin	sediment	ug/kg	0.146	3.70	2.87	0.517	0.265	1.35
Cis-permethrin	sediment	ug/kg	≤3.6	21.4	23.2	6.24	2.56	13.7
Trans-permethrin	sediment	ug/kg	<7.74	12.1	20.2	4.86	≤1.79	9.90
Cyfluthrin	sediment	ug/kg	0.785	3.67	7.38	2.58	0.506	3.38
Cypermethrin	sediment	ug/kg	0.695	5.07	11.4	2.05	1.09	4.39
Esfenvalerate	sediment	ug/kg	≤0.02	0.173	0.296	0.206	0.066	0.135
Deltamethrin	sediment	ug/kg	0.123	3.01	8.20	1.89	0.869	3.53
PCB18	sediment	ug/kg	≤0.060	≤0.496	≤0.300	≤0.180	≤0.199	0.335
PCB28	sediment	ug/kg	<0.86	≤0.476	≤0.382	≤0.167	≤0.195	0.266
PCB52	sediment	ug/kg	≤0.188	1.29	0.970	0.600	≤0.194	0.386
PCB49	sediment	ug/kg	≤0.175	0.951	1.27	0.295	0.344	0.428
PCB44	sediment	ug/kg	≤0.0947	1.98	2.84	0.904	1.02	1.243
PCB37	sediment	ug/kg	<1.66	<1.66	<0.996	<0.498	<0.498	<0.498
PCB74	sediment	ug/kg	<2.42	≤0.742	≤0.260	≤0.134	<0.727	<0.727
PCB70	sediment	ug/kg	<3.33	≤2.57	≤1.09	≤0.310	<1	<1
PCB66	sediment	ug/kg	<3.33	≤1.48	≤0.526	≤0.157	<1	<1
PCB101	sediment	ug/kg	≤0.236	4.94	1.50	0.361	≤0.175	0.306
PCB99	sediment	ug/kg	<1.78	2.13	<1.07	≤0.192	≤0.093	≤0.047
PCB119	sediment	ug/kg	<0.523	≤0.213	<0.314	≤0.020	<0.157	<0.157
PCB87	sediment	ug/kg	<1.48	2.70	≤0.701	≤0.164	<0.444	≤0.081
PCB110	sediment	ug/kg	≤0.279	7.31	1.99	0.568	≤0.294	0.451
PCB81	sediment	ug/kg	<0.199	<0.199	<0.119	<0.06	<0.06	<0.06
PCB151	sediment	ug/kg	≤0.043	0.572	0.252	0.068	≤0.035	≤0.057
PCB77	sediment	ug/kg	<0.296	≤0.267	≤0.160	≤0.047	≤0.018	≤0.043
PCB149	sediment	ug/kg	≤0.166	3.61	1.35	0.313	0.176	0.268
PCB123	sediment	ug/kg	≤0.050	0.672	0.184	0.065	0.035	0.049
PCB118	sediment	ug/kg	0.243	5.59	1.54	0.432	0.192	0.327
PCB114	sediment	ug/kg	≤0.017	0.266	0.07	0.022	≤0.009	0.016
PCB153/168	sediment	ug/kg	0.243	3.62	1.30	0.348	0.194	0.296
PCB105	sediment	ug/kg	0.14	3.61	1.02	0.293	0.132	0.239
PCB138	sediment	ug/kg	0.283	5.30	1.85	0.486	0.268	0.422
PCB158	sediment	ug/kg	≤0.036	0.642	0.18	0.06	0.037	0.053
PCB187	sediment	ug/kg	0.073	0.599	0.376	0.108	0.059	0.09
PCB183	sediment	ug/kg	0.037	0.333	0.184	0.051	0.027	0.044
PCB126	sediment	ug/kg	≤0.007	≤0.070	≤0.034	≤0.014	≤0.007	≤0.011
PCB128	sediment	ug/kg	≤0.083	1.84	0.612	0.161	0.084	0.146
PCB167	sediment	ug/kg	≤0.017	0.336	0.122	0.032	0.016	0.029
PCB177	sediment	ug/kg	≤0.040	0.406	0.232	0.058	0.028	0.053
PCB200	sediment	ug/kg	≤0.007	0.043	0.03	≤0.010	≤0.004	≤0.005
PCB156	sediment	ug/kg	0.043	0.971	0.284	0.068	0.036	0.065
PCB157	sediment	ug/kg	≤0.013	0.186	0.066	≤0.014	≤0.007	0.015
PCB180	sediment	ug/kg	0.15	1.48	0.891	0.241	0.115	0.229
PCB170	sediment	ug/kg	0.077	0.878	0.45	0.117	0.058	0.116
PCB201	sediment	ug/kg	0.053	0.356	0.314	0.089	0.047	0.077

Table A-2 Continued

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 4	BCE 5	BCE 6
PCB169	sediment	ug/kg	≤0.007	≤0.037	<0.022	≤0.040	<0.014	≤0.003
PCB189	sediment	ug/kg	≤0.010	0.067	0.03	≤0.008	≤0.005	≤0.007
PCB194	sediment	ug/kg	0.05	0.319	0.262	0.069	0.035	0.067
PCB206	sediment	ug/kg	0.063	0.249	0.226	0.066	0.031	0.046

ND=Not Detected

Table A-3. Trace constituents in sediments and pore water collected in November 2009.

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
Cadmium (SEM)	sediment	umol/dry g	ND	ND	ND	ND
Copper (SEM)	sediment	umol/dry g	ND	ND	ND	0.0065
Lead (SEM)	sediment	umol/dry g	0.0041	0.0073	0.0041	0.0062
Nickel (SEM)	sediment	umol/dry g	0.0219	0.0177	0.004	0.0043
Zinc (SEM)	sediment	umol/dry g	0.532	0.533	0.174	0.238
Total SEM	sediment	umol/dry g	0.558	0.558	0.182	0.255
AVS	sediment	umol/dry g	20.5	14.0	4.04	0.021
AVS/SEM	sediment	umol/dry g	0.027	0.040	0.045	12.2
SEM-AVS	sediment	umol/dry g	-20.0	-13.5	-3.86	0.23
Arsenic (As)	porewater	ug/L	4.51	3.06	3.51	1.95
Cadmium (Cd)	porewater	ug/L	0.005	0.009	0.009	0.061
Chromium (Cr)	porewater	ug/L	0.368	0.169	0.179	0.098
Copper (Cu)	porewater	ug/L	0.31	0.70	0.36	6.12
Lead (Pb)	porewater	ug/L	0.169	0.287	0.279	0.176
Nickel (Ni)	porewater	ug/L	1.92	1.61	2.26	2.40
Selenium (Se)	porewater	ug/L	0.05	0.05	0.03	0.37
Silver (Ag)	porewater	ug/L	NA	NA	NA	NA
Tin (Sn)	porewater	ug/L	NA	NA	NA	NA
Zinc (Zn)	porewater	ug/L	18.5	29.8	23.9	51.1
Sulfide	porewater	mg/L	0.03	0.04	0.01	0.01
2,4'-DDE	sediment	ug/kg	0.507	0.640	<0.44	<0.176
4,4'-DDE	sediment	ug/kg	5.38	8.22	2.75	≤0.445
2,4'-DDD	sediment	ug/kg	0.774	2.41	<0.385	<0.154
2,4'-DDT	sediment	ug/kg	<1.33	<6.66	<6.66	<2.67
4,4'-DDD	sediment	ug/kg	2.50	6.26	≤1.94	<1.40
4,4'-DDT	sediment	ug/kg	<1.33	<6.66	<6.66	<2.67
2,4'-DDE	SPME/WC	ng/L	NA	<0.002	<0.002	<0.002
4,4'-DDE	SPME/WC	ng/L	NA	0.043	0.034	0.017
2,4'-DDD	SPME/WC	ng/L	NA	<0.006	<0.006	<0.006
2,4'-DDT	SPME/WC	ng/L	NA	<0.043	<0.043	<0.043
4,4'-DDD	SPME/WC	ng/L	NA	<0.072	<0.072	<0.072
4,4'-DDT	SPME/WC	ng/L	NA	<0.05	<0.05	<0.05

Table A-3. Continued.

Sample Date Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
Chlordene	sediment	ug/kg	0.35	0.678	0.395	0.059
Aldrin	sediment	ug/kg	0.059	≤0.04	≤0.03	≤0.004
Chlorpyrifos	sediment	ug/kg	0.401	0.567	0.26	≤0.036
Oxychlordane	sediment	ug/kg	0.192	0.29	≤0.09	<0.096
Heptachlor Epoxide B	sediment	ug/kg	0.298	0.372	<0.19	<0.076
Trans-Chlordane (Gamma)	sediment	ug/kg	4.20	7.22	3.46	0.885
Cis-Chlordane (Alpha)	sediment	ug/kg	5.99	10.1	4.38	1.10
DDMU	sediment	ug/kg	<0.952	<4.76	<4.76	<1.904
Trans-Nonchlor	sediment	ug/kg	3.58	5.83	2.29	0.521
Dieldrin	sediment	ug/kg	<0.056	<0.28	≤0.02	<0.112
Endrin	sediment	ug/kg	<0.526	<2.63	<2.63	<1.052
Cis-Nonachlor	sediment	ug/kg	1.62	2.55	1.01	0.166
Chlordene	SPME/WC	ng/L	NA	<0.001	<0.001	<0.001
Aldrin	SPME/WC	ng/L	NA	<0.001	<0.001	<0.001
Chlorpyrifos	SPME/WC	ng/L	NA	0.062	0.026	0.175
Oxychlordane	SPME/WC	ng/L	NA	0.002	<0.002	0.003
Heptachlor Epoxide B	SPME/WC	ng/L	NA	<0.03	<0.03	<0.03
Trans-Chlordane (Gamma)	SPME/WC	ng/L	NA	0.022	0.013	0.016
Cis-Chlordane (Alpha)	SPME/WC	ng/L	NA	0.043	0.030	0.044
DDMU	SPME/WC	ng/L	NA	<0.038	<0.038	<0.038
Trans-Nonchlor	SPME/WC	ng/L	NA	0.013	0.007	0.011
Dieldrin	SPME/WC	ng/L	NA	0.12	0.056	0.158
Endrin	SPME/WC	ng/L	NA	<0.204	<0.204	<0.204
Cis-Nonachlor	SPME/WC	ng/L	NA	0.01	0.005	0.007
Fipronil desulfinyl	sediment	ug/kg	2.20	0.705	0.186	0.100
Fipronil sulfide	sediment	ug/kg	1.21	0.524	0.184	0.092
Fipronil	sediment	ug/kg	0.798	0.422	0.082	0.036
Fipronil sulfone	sediment	ug/kg	8.02	3.16	1.01	0.664
Bifenthrin	sediment	ug/kg	25.3	14.3	4.16	0.684
Fenpropathrin	sediment	ug/kg	<0.0115	<0.0115	<0.0115	<0.0115
Lamda-Cyhalothrin	sediment	ug/kg	2.43	1.84	0.538	0.182
Cis-permethrin	sediment	ug/kg	61.5	24.0	5.27	1.52
Trans-permethrin	sediment	ug/kg	49.9	19.0	4.40	1.41
Cyfluthrin	sediment	ug/kg	8.30	4.48	1.21	0.247
Cypermethrin	sediment	ug/kg	21.6	8.21	1.58	0.533
Esfenvalerate	sediment	ug/kg	0.558	0.249	0.074	0.021
Deltamethrin	sediment	ug/kg	9.86	5.02	0.774	0.187
Fipronil desulfinyl	SPME/WC	ng/L	NA	≤0.423	<0.438	4.058
Fipronil sulfide	SPME/WC	ng/L	NA	≤0.071	≤0.051	0.375
Fipronil	SPME/WC	ng/L	NA	<0.847	<0.847	≤0.456
Fipronil sulfone	SPME/WC	ng/L	NA	≤0.135	≤0.073	1.119
bifenthrin	SPME/WC	ng/L	NA	0.013	0.009	0.036
Fenprothrin	SPME/WC	ng/L	NA	<0.001	<0.001	<0.001
Lambda-cyfluthrin	SPME/WC	ng/L	NA	0.002	<0.0003	0.006
Cis-permethrin	SPME/WC	ng/L	NA	0.018	<0.0001	0.02
Trans-permethrin	SPME/WC	ng/L	NA	0.017	<0.0001	0.015
cyfluthrin-1	SPME/WC	ng/L	NA	0.012	<0.001	0.017
Cypermethrin-1	SPME/WC	ng/L	NA	0.015	0.004	0.025
Esfenvalerate	SPME/WC	ng/L	NA	<0.0001	<0.0001	<0.0001
Deltamethrin	SPME/WC	ng/L	NA	<0.002	<0.002	<0.002
PCB74	sediment	ug/kg	<0.179	<0.22	<4.54	<1.82
PCB70	sediment	ug/kg	0.642	<0.698	<1.85	<0.74
PCB66	sediment	ug/kg	<0.391	<0.500	<2.94	<1.18

Table A-3. Continued.

Sample Date Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
PCB101	sediment	ug/kg	1.96	1.60	<0.56	<0.061
PCB99	sediment	ug/kg	0.794	<0.76	<0.305	<0.488
PCB119	sediment	ug/kg	<0.077	<0.310	<0.495	<0.198
PCB87	sediment	ug/kg	0.975	<0.823	<0.285	<0.626
PCB110	sediment	ug/kg	2.50	2.30	<0.834	<0.069
PCB81	sediment	ug/kg	<0.058	<0.29	<0.29	<0.116
PCB151	sediment	ug/kg	0.464	0.378	0.11	<0.02
PCB77	sediment	ug/kg	0.111	<0.11	<0.035	<0.15
PCB149	sediment	ug/kg	1.87	1.84	<0.435	<0.21
PCB123	sediment	ug/kg	0.272	0.285	<0.065	<0.008
PCB118	sediment	ug/kg	2.00	1.80	0.540	0.051
PCB114	sediment	ug/kg	0.090	0.085	<0.01	<0.008
PCB153/168	sediment	ug/kg	2.21	2.20	0.505	0.065
PCB105	sediment	ug/kg	1.07	0.978	0.305	<0.032
PCB138	sediment	ug/kg	2.70	2.66	0.639	0.077
PCB158	sediment	ug/kg	0.313	0.328	0.09	0.01
PCB187	sediment	ug/kg	0.516	0.688	0.14	0.024
PCB183	sediment	ug/kg	0.27	0.325	0.07	0.012
PCB126	sediment	ug/kg	0.025	<0.03	<0.005	<0.018
PCB128	sediment	ug/kg	0.733	0.685	0.165	<0.02
PCB167	sediment	ug/kg	0.151	0.15	0.035	<0.004
PCB177	sediment	ug/kg	0.293	0.37	0.085	<0.012
PCB200	sediment	ug/kg	0.033	0.045	<0.01	<0.002
PCB156	sediment	ug/kg	0.394	0.352	0.08	0.01
PCB157	sediment	ug/kg	0.082	0.095	0.03	<0.004
PCB180	sediment	ug/kg	1.11	1.49	0.300	0.049
PCB170	sediment	ug/kg	0.612	0.602	0.145	0.016
PCB201	sediment	ug/kg	0.372	0.497	0.11	0.016
PCB169	sediment	ug/kg	0.044	0.03	<0.005	<0.002
PCB189	sediment	ug/kg	0.034	0.03	0.015	<0.004
PCB194	sediment	ug/kg	0.306	0.3175	<0.015	<0.006
PCB206	sediment	ug/kg	0.169	<0.015	<0.015	<0.006
PCB18	SPME/WC	ng/L	≤0.006	≤0.006	≤0.006	≤0.008
PCB28	SPME/WC	ng/L	≤0.006	≤0.024	≤0.005	≤0.007
PCB52	SPME/WC	ng/L	≤0.006	≤0.009	≤0.004	≤0.008
PCB49	SPME/WC	ng/L	≤0.004	≤0.006	≤0.002	≤0.006
PCB44	SPME/WC	ng/L	≤0.006	≤0.008	≤0.005	0.017
PCB37	SPME/WC	ng/L	≤0.002	<0.041	≤0.008	<0.041
PCB74	SPME/WC	ng/L	NA	<0.045	<0.045	<0.045
PCB70	SPME/WC	ng/L	NA	<0.018	<0.018	<0.018
PCB66	SPME/WC	ng/L	NA	<0.025	<0.025	<0.025
PCB101	SPME/WC	ng/L	NA	0.007	0.008	≤0.004
PCB99	SPME/WC	ng/L	NA	<0.011	<0.011	<0.011
PCB119	SPME/WC	ng/L	NA	<0.004	<0.004	<0.004
PCB87	SPME/WC	ng/L	NA	<0.013	<0.013	<0.013
PCB110	SPME/WC	ng/L	NA	≤0.008	≤0.006	≤0.005
PCB81	SPME/WC	ng/L	NA	<0.002	<0.002	<0.002
PCB151	SPME/WC	ng/L	NA	<0.0006	0.001	0.001
PCB77	SPME/WC	ng/L	NA	<0.002	<0.002	<0.002
PCB149	SPME/WC	ng/L	NA	≤0.004	≤0.003	<0.005
PCB123	SPME/WC	ng/L	NA	0.001	<0.0006	<0.0006
PCB118	SPME/WC	ng/L	NA	0.004	0.003	0.003
PCB114	SPME/WC	ng/L	NA	<0.0004	<0.0004	<0.0004
PCB153/168	SPME/WC	ng/L	NA	0.005	0.004	0.003
PCB105	SPME/WC	ng/L	NA	0.002	0.001	0.001
PCB138	SPME/WC	ng/L	NA	0.005	0.003	0.003

Table A-3. Continued.

Sample Date Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
PCB158	SPME/WC	ng/L	NA	<0.0002	<0.0002	<0.0002
PCB187	SPME/WC	ng/L	NA	<0.0005	0.002	0.001
PCB183	SPME/WC	ng/L	NA	0.001	0.001	0.001
PCB126	SPME/WC	ng/L	NA	<0.0003	<0.0003	<0.0003
PCB128	SPME/WC	ng/L	NA	0.001	0.001	0.001
PCB167	SPME/WC	ng/L	NA	<0.0003	<0.0003	<0.0003
PCB177	SPME/WC	ng/L	NA	0.001	0.001	0.001
PCB200	SPME/WC	ng/L	NA	<0.0009	<0.0009	<0.0009
PCB156	SPME/WC	ng/L	NA	<0.0003	<0.0003	<0.0003
PCB157	SPME/WC	ng/L	NA	<0.0003	<0.0003	<0.0003
PCB180	SPME/WC	ng/L	NA	0.002	0.002	0.003
PCB170	SPME/WC	ng/L	NA	0.001	0.001	0.001
PCB201	SPME/WC	ng/L	NA	≤0.001	≤0.001	0.002
PCB169	SPME/WC	ng/L	NA	<0.0003	<0.0003	<0.0003
PCB189	SPME/WC	ng/L	NA	<0.0005	<0.0005	<0.0005
PCB194	SPME/WC	ng/L	NA	0.001	0.001	0.001
PCB206	SPME/WC	ng/L	NA	≤0.001	≤0.001	0.002

NA = Not analyzed

ND = Not detected

Table A-4. Trace constituents in sediments and pore water collected in December 2009.

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
Cadmium (SEM)	sediment	umol/dry g	ND	ND	ND	ND
Copper (SEM)	sediment	umol/dry g	ND	ND	ND	0.0156
Lead (SEM)	sediment	umol/dry g	ND	0.0023	0.0029	0.0027
Nickel (SEM)	sediment	umol/dry g	0.0064	0.0088	0.0033	0.0036
Zinc (SEM)	sediment	umol/dry g	0.0186	0.270	0.143	0.174
Total SEM	sediment	umol/dry g	0.025	0.281	0.149	0.196
AVS	sediment	umol/dry g	3.75	0.52	1.87	ND
AVS/SEM	sediment	umol/dry g	0.0067	0.54	0.080	ND
SEM-AVS	sediment	umol/dry g	-3.72	-0.24	-1.72	0.20
Arsenic (As)	porewater	ug/L	4.68	1.59	2.87	3.52
Cadmium (Cd)	porewater	ug/L	0.016	0.032	0.063	0.077
Chromium (Cr)	porewater	ug/L	0.24	0.094	0.15	0.144
Copper (Cu)	porewater	ug/L	0.26	1.83	1.04	26.8
Lead (Pb)	porewater	ug/L	0.203	0.315	0.468	0.174
Nickel (Ni)	porewater	ug/L	1.64	2.22	2.58	5.30
Selenium (Se)	porewater	ug/L	0.03	ND	0.02	ND
Silver (Ag)	porewater	ug/L	NA	NA	NA	NA
Tin (Sn)	porewater	ug/L	0.087	0.079	0.119	0.055
Zinc (Zn)	porewater	ug/L	9.62	15.1	11.6	32.6
Sulfide	porewater	mg/L	0.34	0.10	0.09	0.08
Arsenic (As)	field peeper	ug/L	NA	1.29	0.49	1
Cadmium (Cd)	field peeper	ug/L	NA	0.038	0.012	0.15
Chromium (Cr)	field peeper	ug/L	NA	0.273	0.275	0.168
Copper (Cu)	field peeper	ug/L	NA	1.11	0.78	0.47
Lead (Pb)	field peeper	ug/L	NA	0.065	0.01	0.04
Nickel (Ni)	field peeper	ug/L	NA	0.506	0.223	1.02
Selenium (Se)	field peeper	ug/L	NA	NA	NA	NA
Silver (Ag)	field peeper	ug/L	NA	0.08	0.07	0.057
Tin (Sn)	field peeper	ug/L	NA	0.164	0.151	0.130
Zinc (Zn)	field peeper	ug/L	NA	CT	CT	CT
2,4'-DDE	sediment	ug/kg	0.307	≤0.37	<0.44	<0.176
4,4'-DDE	sediment	ug/kg	5.35	7.08	8.18	≤0.509
2,4'-DDD	sediment	ug/kg	<0.077	<0.385	0.597	<0.154
2,4'-DDT	sediment	ug/kg	<1.33	<6.66	<6.66	<2.67
4,4'-DDD	sediment	ug/kg	1.76	3.76	≤1.77	<1.40
4,4'-DDT	sediment	ug/kg	<1.33	<6.66	≤0.493	<2.67
2,4'-DDE	SPME/PW	ng/L	≤0.001	<0.002	<0.002	<0.002
4,4'-DDE	SPME/PW	ng/L	<0.012	≤0.008	0.040	0.017
2,4'-DDD	SPME/PW	ng/L	<0.006	<0.006	<0.006	<0.006
2,4'-DDT	SPME/PW	ng/L	<0.043	<0.043	<0.043	<0.043
4,4'-DDD	SPME/PW	ng/L	<0.072	<0.072	<0.072	<0.072
4,4'-DDT	SPME/PW	ng/L	<0.05	<0.05	<0.05	<0.05
Chlordene	sediment	ug/kg	0.154	≤0.025	≤0.015	≤0.004
Aldrin	sediment	ug/kg	<0.027	≤0.085	<0.135	<0.054
Chlorpyrifos	sediment	ug/kg	0.0995	≤0.07	≤0.10	≤0.036
Oxychlordane	sediment	ug/kg	0.1205	≤0.16	<0.24	<0.096
Heptachlor Epoxide B	sediment	ug/kg	0.166	0.19	≤0.134	<0.076
Trans-Chlordane (Gamma)	sediment	ug/kg	3.39	5.92	3.93	0.751
Cis-Chlordane (Alpha)	sediment	ug/kg	5.17	7.91	4.84	0.990
DDMU	sediment	ug/kg	<0.952	<4.76	<4.76	<1.90
Trans-Nonchlor	sediment	ug/kg	3.09	5.22	2.47	0.583
Dieldrin	sediment	ug/kg	1.32	0.874	3.26	0.118

Table A-4. Continued.

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
Endrin	sediment	ug/kg	<0.526	<2.63	<2.63	<1.05
Cis-Nonachlor	sediment	ug/kg	1.35	2.30	1.02	0.210
Chlordene	SPME/PW	ng/L	<0.001	<0.001	<0.001	<0.001
Aldrin	SPME/PW	ng/L	<0.001	<0.001	<0.001	<0.001
Chlorpyrifos	SPME/PW	ng/L	0.032	0.108	0.0565	0.087
Oxychlordane	SPME/PW	ng/L	≤0.001	<0.002	0.002	<0.002
Heptachlor Epoxide B	SPME/PW	ng/L	0.043	0.062	<0.03	<0.03
Trans-Chlordane (Gamma)	SPME/PW	ng/L	0.004	0.003	0.012	0.002
Cis-Chlordane (Alpha)	SPME/PW	ng/L	0.018	0.020	0.028	0.018
DDMU	SPME/PW	ng/L	<0.038	<0.038	<0.038	<0.038
Trans-Nonchlor	SPME/PW	ng/L	0.003	0.003	0.008	0.003
Dieldrin	SPME/PW	ng/L	0.074	0.109	0.069	0.065
Endrin	SPME/PW	ng/L	<0.204	<0.204	<0.204	<0.204
Cis-Nonachlor	SPME/PW	ng/L	0.002	0.002	0.005	0.002
Fipronil desulfinyl	sediment	ug/kg	1.31	0.389	0.255	0.094
Fipronil sulfide	sediment	ug/kg	0.69	0.254	0.19	0.064
Fipronil	sediment	ug/kg	0.43	0.613	0.349	0.227
Fipronil sulfone	sediment	ug/kg	5.53	2.93	1.65	0.661
Bifenthrin	sediment	ug/kg	8.36	11.6	3.41	0.592
Fenprothrin	sediment	ug/kg	<0.023	<0.115	<0.115	<0.046
Lamda-Cyhalothrin	sediment	ug/kg	1.11	1.33	0.409	0.060
Cis-permethrin	sediment	ug/kg	17.6	16.8	6.12	0.665
Trans-permethrin	sediment	ug/kg	17.6	16.0	5.27	<0.012
Cyfluthrin	sediment	ug/kg	4.71	4.58	2.35	<0.03
Cypermethrin	sediment	ug/kg	7.99	6.47	2.27	0.424
Esfenvalerate	sediment	ug/kg	0.26	0.269	0.100	0.030
Deltamethrin	sediment	ug/kg	6.70	5.59	0.918	0.084
Fipronil desulfinyl	SPME/PW	ng/L	0.635	1.66	0.741	4.517
Fipronil sulfide	SPME/PW	ng/L	0.132	0.314	0.182	1.00
Fipronil	SPME/PW	ng/L	<0.847	<0.847	<0.847	≤0.391
Fipronil sulfone	SPME/PW	ng/L	≤0.128	0.33	≤0.113	1.06
bifenthrin	SPME/PW	ng/L	<0.003	<0.003	0.012	<0.003
Fenprothrin	SPME/PW	ng/L	<0.001	<0.001	<0.001	<0.001
Lambda-cyfluthrin	SPME/PW	ng/L	<0.0003	<0.0003	0.001	<0.0003
Cis-permethrin	SPME/PW	ng/L	<0.0001	<0.0001	0.020	<0.0001
Trans-permethrin	SPME/PW	ng/L	<0.0001	<0.0001	0.022	<0.0001
cyfluthrin-1	SPME/PW	ng/L	<0.001	<0.001	0.005	0.001
Cypermethrin-1	SPME/PW	ng/L	<0.0003	<0.0003	0.007	0.004
Esfenvalerate	SPME/PW	ng/L	<0.0001	<0.0001	<0.0001	<0.0001
Deltamethrin	SPME/PW	ng/L	<0.002	<0.002	<0.002	0.004
PCB74	sediment	ug/kg	≤0.266	<4.54	<4.54	<1.82
PCB70	sediment	ug/kg	<0.37	<0.37	<1.85	<0.74
PCB66	sediment	ug/kg	<0.588	≤0.27	<2.94	<1.18
PCB101	sediment	ug/kg	0.770	1.19	≤0.373	≤0.082
PCB99	sediment	ug/kg	0.213	<0.47	≤0.194	<0.488
PCB119	sediment	ug/kg	<0.099	<0.495	<0.495	<0.198
PCB87	sediment	ug/kg	0.528	≤0.65	<1.56	<0.626
PCB110	sediment	ug/kg	0.574	1.31	≤0.478	≤0.144
PCB81	sediment	ug/kg	<0.058	<0.29	<0.29	<0.116
PCB151	sediment	ug/kg	0.364	0.315	0.110	<0.026
PCB77	sediment	ug/kg	<0.075	≤0.075	<0.375	<0.15
PCB149	sediment	ug/kg	0.892	1.37	≤0.453	≤0.054
PCB123	sediment	ug/kg	0.133	0.195	≤0.055	≤0.012

Table A-4. Continued.

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
PCB118	sediment	ug/kg	1.04	1.35	0.398	0.084
PCB114	sediment	ug/kg	0.0438	0.08	≤0.02	<0.022
PCB153/168	sediment	ug/kg	1.01	1.57	0.453	0.092
PCB105	sediment	ug/kg	0.575	0.774	0.254	0.038
PCB138	sediment	ug/kg	1.28	1.96	0.627	0.124
PCB158	sediment	ug/kg	0.152	0.230	0.060	0.012
PCB187	sediment	ug/kg	0.255	0.540	0.144	0.022
PCB183	sediment	ug/kg	0.115	0.225	0.060	0.012
PCB126	sediment	ug/kg	0.0123	≤0.015	<0.045	<0.018
PCB128	sediment	ug/kg	0.350	0.530	0.164	0.038
PCB167	sediment	ug/kg	0.0694	0.090	0.025	≤0.004
PCB177	sediment	ug/kg	0.138	0.270	0.075	≤0.012
PCB200	sediment	ug/kg	0.0168	0.045	≤0.015	≤0.002
PCB156	sediment	ug/kg	0.184	0.225	0.065	0.012
PCB157	sediment	ug/kg	0.0355	0.070	≤0.015	≤0.004
PCB180	sediment	ug/kg	0.505	1.03	0.264	0.038
PCB170	sediment	ug/kg	0.267	0.505	0.134	0.024
PCB201	sediment	ug/kg	0.177	0.405	0.119	0.012
PCB169	sediment	ug/kg	0.0142	0.025	≤0.01	<0.01
PCB189	sediment	ug/kg	0.0149	0.025	0.015	<0.006
PCB194	sediment	ug/kg	0.114	0.275	<0.015	<0.006
PCB206	sediment	ug/kg	0.100	0.240	<0.015	<0.006
PCB18	SPME/PW	ng/L	≤0.022	≤0.011	0.044	≤0.017
PCB28	SPME/PW	ng/L	≤0.016	≤0.008	≤0.02	≤0.012
PCB52	SPME/PW	ng/L	≤0.011	≤0.008	0.018	≤0.012
PCB49	SPME/PW	ng/L	≤0.008	≤0.003	≤0.008	≤0.004
PCB44	SPME/PW	ng/L	≤0.011	≤0.008	0.021	≤0.014
PCB37	SPME/PW	ng/L	≤0.013	≤0.005	<0.041	<0.041
PCB74	SPME/PW	ng/L	<0.045	<0.045	<0.045	<0.045
PCB70	SPME/PW	ng/L	<0.018	<0.018	<0.018	<0.018
PCB66	SPME/PW	ng/L	<0.025	<0.025	<0.025	<0.025
PCB101	SPME/PW	ng/L	<0.006	≤0.002	0.008	≤0.003
PCB99	SPME/PW	ng/L	<0.011	<0.011	<0.011	<0.011
PCB119	SPME/PW	ng/L	<0.004	<0.004	<0.004	<0.004
PCB87	SPME/PW	ng/L	<0.013	<0.013	<0.013	<0.013
PCB110	SPME/PW	ng/L	<0.009	≤0.002	≤0.006	<0.009
PCB81	SPME/PW	ng/L	<0.002	0.002	<0.002	<0.002
PCB151	SPME/PW	ng/L	<0.0006	0.001	0.001	<0.0006
PCB77	SPME/PW	ng/L	<0.002	≤0.001	<0.002	<0.002
PCB149	SPME/PW	ng/L	<0.005	<0.005	<0.005	<0.005
PCB123	SPME/PW	ng/L	<0.0006	0.001	0.001	<0.0006
PCB118	SPME/PW	ng/L	<0.0005	0.002	0.003	0.001
PCB114	SPME/PW	ng/L	<0.0004	0.001	<0.0004	<0.0004
PCB153/168	SPME/PW	ng/L	<0.0005	0.003	0.003	0.002
PCB105	SPME/PW	ng/L	<0.0006	0.001	0.002	<0.0006
PCB138	SPME/PW	ng/L	<0.0006	0.001	0.0025	<0.0006
PCB158	SPME/PW	ng/L	<0.0002	0.001	<0.0002	<0.0002
PCB187	SPME/PW	ng/L	<0.0005	0.001	0.002	0.001
PCB183	SPME/PW	ng/L	<0.0006	0.001	0.001	<0.0006
PCB126	SPME/PW	ng/L	<0.0003	0.001	<0.0003	<0.0003
PCB128	SPME/PW	ng/L	<0.0007	0.001	0.001	<0.0007
PCB167	SPME/PW	ng/L	<0.0003	0.001	<0.0003	<0.0003
PCB177	SPME/PW	ng/L	<0.0008	0.001	0.001	<0.0008
PCB200	SPME/PW	ng/L	<0.0009	0.001	<0.0009	<0.0009
PCB156	SPME/PW	ng/L	<0.0003	0.001	<0.0003	<0.0003
PCB157	SPME/PW	ng/L	<0.0003	0.001	<0.0003	<0.0003

Table A-4. Continued.

Parameter	Matrix	Unit	BCE 1	BCE 2	BCE 3	BCE 5
PCB180	SPME/PW	ng/L	<0.0005	0.002	0.002	0.001
PCB170	SPME/PW	ng/L	<0.0007	0.001	0.001	<0.0007
PCB201	SPME/PW	ng/L	<0.0012	≤0.001	0.002	≤0.001
PCB169	SPME/PW	ng/L	<0.0003	0.001	<0.0003	<0.0003
PCB189	SPME/PW	ng/L	<0.0005	0.001	<0.0005	<0.0005
PCB194	SPME/PW	ng/L	<0.001	0.001	0.002	<0.001
PCB206	SPME/PW	ng/L	<0.002	≤0.001	0.002	≤0.001

NA = Not analyzed

ND = Not detected

CT = Blank Contaminated

Table A-5. Pore water fertilization test results with *S. purpuratus*. Ballona Creek Estuary stations sampled in November 2009.

Treatment	BCE 1		BCE 2		BCE 3		BCE 5	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Control	96	3.1	96	3.1	96	3.1	96	3.1
Baseline 100%	1	0.5	95	7.4	92	4.8	58	15.3
Baseline 50%	37	16.2	98	1.4	98	1.4	96	3.3
Baseline 25%	87	12.3	96	1.4	92	0.7	NC	NC
Baseline 12.5%	96	1.5	95	2.1	89	11.3	NC	NC
EDTA Blank	81	21.8	81	21.8	81	21.8	81	21.8
EDTA 100%	8	3.7	94	2.1	94	7.1	90	3.5
EDTA 50%	36	13.1	95	3.1	98	0.7	97	3.8
EDTA 25%	93	6.8	93	7.8	92	7.0	NC	NC
EDTA 12.5%	NC	NC	80	5.7	96	0.7	NC	NC

NC = Not counted

Table A-6. Pore water fertilization test results with *S. purpuratus*. Ballona Creek Estuary stations sampled in December 2009.

Treatment	BCE 1		BCE 2		BCE 3		BCE 5	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Control	97	1.6	97	1.6	97	1.6	97	1.6
Baseline 100%	95	1.5	95	2.3	99	1.1	86	4.7
Baseline 50%	NC	NC	NC	NC	NC	NC	NC	NC
Baseline 25%	NC	NC	NC	NC	NC	NC	NC	NC
Baseline 12.5%	NC	NC	NC	NC	NC	NC	NC	NC
EDTA Blank	NC	NC	NC	NC	NC	NC	NC	NC
EDTA 100%	NC	NC	NC	NC	NC	NC	NC	NC
EDTA 50%	NC	NC	NC	NC	NC	NC	NC	NC
EDTA 25%	NC	NC	NC	NC	NC	NC	NC	NC
EDTA 12.5%	NC	NC	NC	NC	NC	NC	NC	NC

NC = Not counted

Table A-7. Whole sediment and pore water toxicity test survival results for *E. estuarius*. Ballona Creek Estuary stations sampled in November 2009.

Treatment	BCE 1		BCE 2		BCE 3		BCE 5	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Sediment								
Control	89	19.2	89	19.2	89	19.2	89	19.2
Baseline 100%	5	3.5	12	12.5	23	21.1	37	9.1
Pore water								
Control	80	14.1	80	14.1	80	14.1	80	14.1
Baseline 100%	24	16.7	40	20.0	32	30.3	84	8.9
Baseline 50%	68	41.5	64	21.9	68	30.3	72	41.5
Baseline 25%	60	14.1	80	20.0	68	22.8	92	11.0

Table A-8. Whole sediment and pore water toxicity test survival results for *E. estuarius*. Ballona Creek Estuary stations sampled in December 2009.

Treatment	BCE 1		BCE 2		BCE 3		BCE 5	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
Sediment								
Control	91	10.8	91	10.8	91	10.8	91	10.8
Baseline 100%	15	8.7	20	11.7	24	2.2	8	7.6
Pore water								
Control	88	11.0	88	11.0	88	11.0	88	11.0
Baseline 100%	44	16.7	36	26.1	44	16.7	4	8.9
Baseline 50%	88	17.9	88	26.8	76	8.9	76	16.7
Baseline 25%	88	11.0	88	11.0	76	21.9	92	11.0