Technical Report 362
March 2002

Preliminary Characterization of Sediment Toxicity in the Chollas Creek Channel

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March 22, 2002

Technical Report #362

ABSTRACT

Stormwater discharges from Chollas Creek, a tributary of San Diego Bay, have been shown to be toxic to freshwater and marine aquatic life. Toxicant Identification Evaluation (TIE) studies indicate that organophosphate pesticides and zinc are responsible for the stormwater toxicity measured in laboratory tests. Sediment toxicity has also been measured in sediments collected from the outer portion of the Chollas Creek channel. However, no TIE studies have been conducted on these sediments to determine the cause of toxicity.

The objective of this study was to conduct preliminary TIE measurements on toxic sediments from the Chollas Creek channel. The results of this study were intended to address two questions: (1) Are sediment or pore water TIE methods useful for characterizing the toxicity of sediments in the study area? and (2) Is the channel sediment toxicity caused by a specific class of chemical?

Sediment from two sampling events (October 2000 and July 2001) were collected and tested for toxicity and TIE analysis. Pore water from the two October 2000 samples was not toxic to either amphipods or sea urchins and the TIE analyses were therefore not completed. Three samples (two channel stations and one reference station) from the July 2001 sampling were tested. Porewater and solid phase toxicity to amphipods was present at station C14 and porewater and sediment TIEs were conducted.

The TIE results yielded different patterns for pore water and sediment. Sediment toxicity was eliminated by treatment with activated carbon, while the toxicity of pore water was eliminated by both EDTA addition or solid phase extraction with a C-18 column. These preliminary results indicate that nonpolar organics are a key toxicant group in sediment and that metals and possibly organics may be important toxicants in pore water from the same station. Additional studies are needed to confirm the reproducibility of the patterns observed and to identify specific toxic constituents.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of the City of San Diego and Marine Environmental Consultants, Inc., who provided sediment samples for testing from the City's stormwater monitoring program. Valuable assistance to this project was also provided by the US Navy (SPAWAR), which provided sample collection and chemical analysis of some of the sediment samples.

The authors are indebted to the following SCCWRP personnel who assisted with the toxicity experiments: Jeff Brown, Ehren Doris, Kenna Koons, Kim Johnson, and Daniel Van.

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INTRODUCTION

The state of California's Bay Protection and Toxic Cleanup Program (BPTCP) has identified portions of the Chollas Creek channel as a toxic hotspot. This designation was based on the presence of benthic degradation, sediment toxicity, and elevated sediment contamination in the outer portion of the channel (Fairey *et al*. 1998). Additional studies conducted as part of the City of San Diego's stormwater monitoring program have confirmed the presence of sediment toxicity in the outer channel immediately following the storm season (URS/WCC 2000).

The Chollas Creek channel is listed as a 303(d) impaired water body. As a result, the San Diego Regional Water Quality Control Board has initiated TMDL and preliminary sediment clean up actions in the Chollas Creek watershed and channel. A key aspect of these activities is the identification of the cause of sediment toxicity in the Chollas Creek channel. This information is needed to guide source identification studies and to develop cleanup objectives for the area. The cause of sediment toxicity cannot be confidently determined from sediment contamination data alone, as the sediments are contaminated by an array of metals, PCBs, PAHs, and pesticides (SSC-San Diego 2000). These contaminants have multiple sources, including stormwater discharge and leaching from vessel coatings.

Toxicity Identification Evaluations (TIEs) have been shown to be effective in determining the cause of stormwater toxicity to aquatic life in the Chollas Creek watershed (SCCWRP 1999). These studies identified organophosphate pesticides and zinc as the primary toxic constituents in stormwater. It is not known whether these constituents are also responsible for the sediment toxicity observed in the Chollas Creek channel, as no sediment TIE studies have been conducted in the area. While standardized methods are available for conducting TIEs on stormwater and effluents (U.S. EPA 1991 and 1996), the methods for conducting sediment TIEs are still under development (Lebo *et al*. 1999, Burgess *et al*. 2000). It is not known whether a sediment TIE approach will be useful in investigating the cause of sediment toxicity in the Chollas Creek channel.

The objective of this study was to conduct preliminary TIE measurements on toxic sediments from the Chollas Creek channel. The results of this study were intended to address two questions:

- Are sediment or pore water TIE methods useful for characterizing the toxicity of sediments in the study area?
- Does the channel sediment toxicity appear to be caused by a specific class of chemical?

METHODS

Study Design

The research conducted in this project was organized into two phases, which were intended to coordinate with sediment studies conducted as part of the City of San Diego's stormwater monitoring program. The experimental plan was to conduct preliminary TIEs on samples of sediment from two stations monitored by the City in the fall of 2000 and spring of 2001. Porewater toxicity tests were conducted on the fall samples using two species and follow up toxicant characterization tests were planned to investigate any porewater toxicity present. Both sediment and porewater tests were planned for the spring sediment samples, which were expected to contain a greater magnitude of toxicity.

The study design was revised in the middle of the study due to a change in the stormwater monitoring program and the initiation of a spatial study of sediment quality in the study area. As a result, the spring 2001 sampling was not conducted as scheduled. The second phase of this project (sediment and porewater tests) was instead conducted on sediment samples collected in July 2001 as part of the spatial sediment quality study.

Sample Collection and Handling

The first set of sediment samples was collected on October 2, 2000. These samples were composite samples collected from stations 1 and 3 during the City of San Diego's stormwater monitoring program (Figure 1). Each sample was a composite of two grabs. The samples were stored in plastic bags at 4 °C. Each sample was homogenized with a plastic spoon and then a 300 ml portion was centrifuged at 3,000 x g for 30 minutes to extract the pore water. The pore water was transferred to a glass bottle and tested for toxicity the same day. The pore water tests were initiated on October 11.

The second set of samples was collected on July 18, 2001 as part of a spatial study of sediment quality offshore of Chollas Creek and Paleta Creek. Two samples from within the study area which demonstrated strong sediment toxicity (C01 and C14, Figure 1) and a reference station (R03) were collected using a grab sampler. The samples for TIE analysis were stored for approximately 1 month in 1 L HDPE containers at 4 °C. Pore water samples were extracted as described previously, except that sediment and pore water samples were handled in a nitrogen atmosphere. The samples were stored at 4 °C overnight and then tested for toxicity. The pore water and sediment toxicity tests were initiated on August 21.

Sea Urchin Fertilization Test

All pore water samples were evaluated for toxicity using the purple sea urchin fertilization test (U. S. EPA 1995). This test measures toxic effects on sea urchin sperm, which are expressed as a reduction in their ability to fertilize eggs. The test consisted of a 20 minute exposure of sperm to the samples. Eggs were then added and given 20 minutes for fertilization to occur. The eggs were then preserved and examined later with a microscope to assess the percentage of successful

fertilization. Toxic effects are expressed as a reduction in fertilization percentage. Purple sea urchins (*Strongylocentrotus purpuratus*) used in the tests were collected from the intertidal zone in northern Santa Monica Bay or from the central California coast. The tests were conducted in glass shell vials containing 10 mL of solution at a temperature of 15 ± 1 °C. Four replicates were tested at each of three sample concentrations (25, 50 and 100%). Dilutions were made by the addition of laboratory seawater.

A seawater control (0.45 µm and activated carbon filtered natural seawater from Redondo Beach) was included in each test series for quality control purposes. Water quality parameters (temperature, pH, ammonia, and salinity) were measured on the test samples to ensure that the experimental conditions were within desired ranges and did not create unintended stress on the test organisms.

Amphipod Survival Test

The amphipod survival test was used to evaluate toxicity of pore water samples from both collections and of whole sediment from the July 2001 sampling. The amphipods, *Eohaustorius estuarius*, were collected from Yaquina Bay near Newport, Oregon. The animals were held in the laboratory on their native sediment for up to a week before testing began. The pore water tests were conducted in glass vials containing 10 mL of solution at a temperature of 15 ± 1 °C. Five amphipods were added to each vial and were exposed for 96 hrs for the first sampling and 10 days for the second. Samples were tested at the 100% concentration only, with 3 or 5 replicates per sample.

The whole sediment testing was conducted in 250 ml glass beakers containing approximately 40 ml of sediment. Five amphipods were added to each beaker and were exposed for 10 days. The overlying water was adjusted to 20 g/Kg, the beakers were gently aerated and the exposures were conducted at 15 ± 1 °C. The beakers were monitored daily for visible changes to the sediment or death of the animals. At the end of the exposure period, the sediment from the beakers was passed through a sieve to recover the animals. The number of surviving animals was then assessed.

Pore Water Toxicity Characterization

Samples of pore water showing strong toxicity were treated with selected phase I TIE methods (Figure 2). Two treatments were applied to the sample: addition of ethylenediaminetetraacetic acid (EDTA) and extraction using a C-18 solid phase column. After treatment, the samples were tested for toxicity using the methods described above.

EDTA is an organic chelating agent that has a strong binding affinity for divalent metals, such as copper, nickel, lead, zinc, cadmium, and mercury. Metal that is bound to EDTA is essentially not biologically available to the toxicity test organisms and therefore cannot cause toxicity. For this experiment, a stock solution of EDTA was added to the samples to produce a final concentration of 60 mg/L. The EDTA was added at least one hour prior to the addition of the test organisms in order to allow sufficient time for chelation to occur.

The C-18 column treatment extracts nonpolar organic compounds from the sample. The C-18 column contains a resin that has a high binding affinity for nonpolar compounds, such as PAHs, PCBs, DDTs, and other organic pesticides. For the other treatment, approximately 100 ml of pore water was pumped through a 6 mL Varian Mega Bond Elut C-18 solid phase extraction column. The pore water was collected after passage through the column and tested for toxicity. The C-18 column also cross reacts with some inorganic compounds. For example, studies conducted at SCCWRP have demonstrated that copper and zinc may be removed by the C-18 column. The C-18 column may also remove other dissolved organic constituents from the sample that are not considered toxicants, such as humic acids.

Sediment Toxicity Characterization

Phase I sediment TIE manipulations were conducted on the whole sediment from each station from the July 2001 sampling. Three different manipulations were performed (Figure 2): addition of cation exchange resin, addition of charcoal, and aeration. After addition of the modifying agent for each treatment, the sample was stirred vigorously with a glass rod for 1 minute. Next, the samples were allowed to equilibrate overnight before addition of the animals. The samples were then tested for toxicity using the methods described above.

Cation exchange resin (ResinTech SIR-300) was added at a concentration of 20% by weight to an aliquot of the sediment sample. This resin has a strong binding affinity for copper, nickel, hexavalent chromium, lead, zinc, manganese, and cadmium. The cation exchange resin reduces metal toxicity of sediment by binding (and thus reducing the concentration of) metals dissolved in the pore water. Contact with pore water is considered to be the primary route of contaminant exposure in the 10-day amphipod toxicity test, so reducing pore water metal concentrations will reduce the toxicity of the sediment sample.

The charcoal treatment consisted of the addition of powdered coconut charcoal at a concentration of 15% by weight to the sediment sample. Many types of dissolved compounds, including nonpolar organics, bind to the very large surface area of the charcoal particles. Similar to the cation exchange resin, charcoal reduces the pore water concentration of various constituents, which reduces their ability to cause toxicity. Coconut charcoal contains a mixture of different types of binding sites and thus will bind many different types of compounds. In addition to trace organic contaminants (e.g, PAHs and DDTs) coconut charcoal also binds ammonia and humic material. very large surface area Organic chemicals bind with the charcoal making them biologically unavailable.

The aeration treatment consisted of 1 minute of vigorous stirring. This treatment was intended to increase the oxygen content of the sediment and reduce toxicity related to anoxic conditions, such as the generation of hydrogen sulfide. This treatment also served as a control for the cation exchange resin and charcoal treatments, which also used a similar amount of stirring to mix in the amendments.

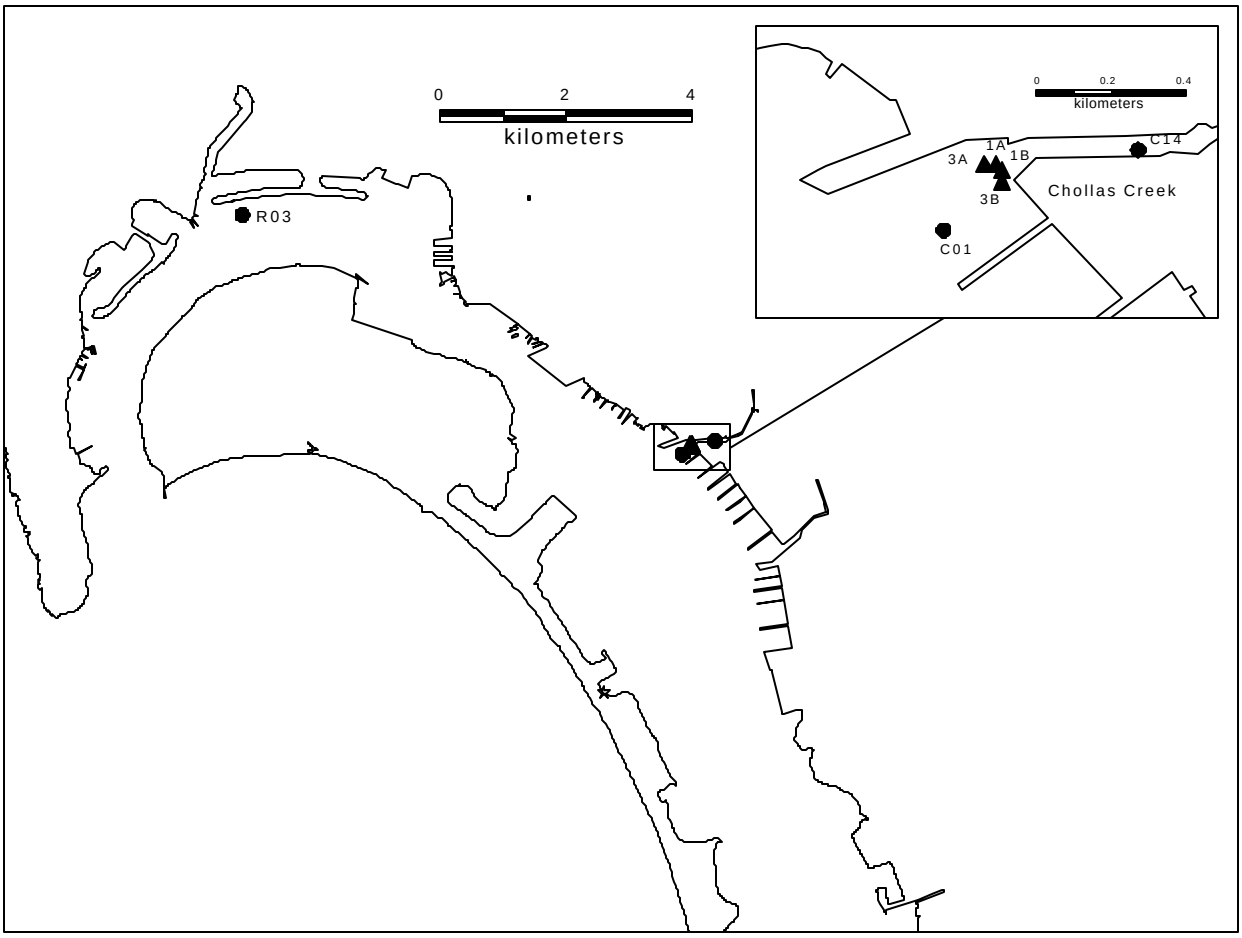

Figure 1. Location of sediment samples collected in October 2000 (triangles) and July 2001 (circles) for TIE.

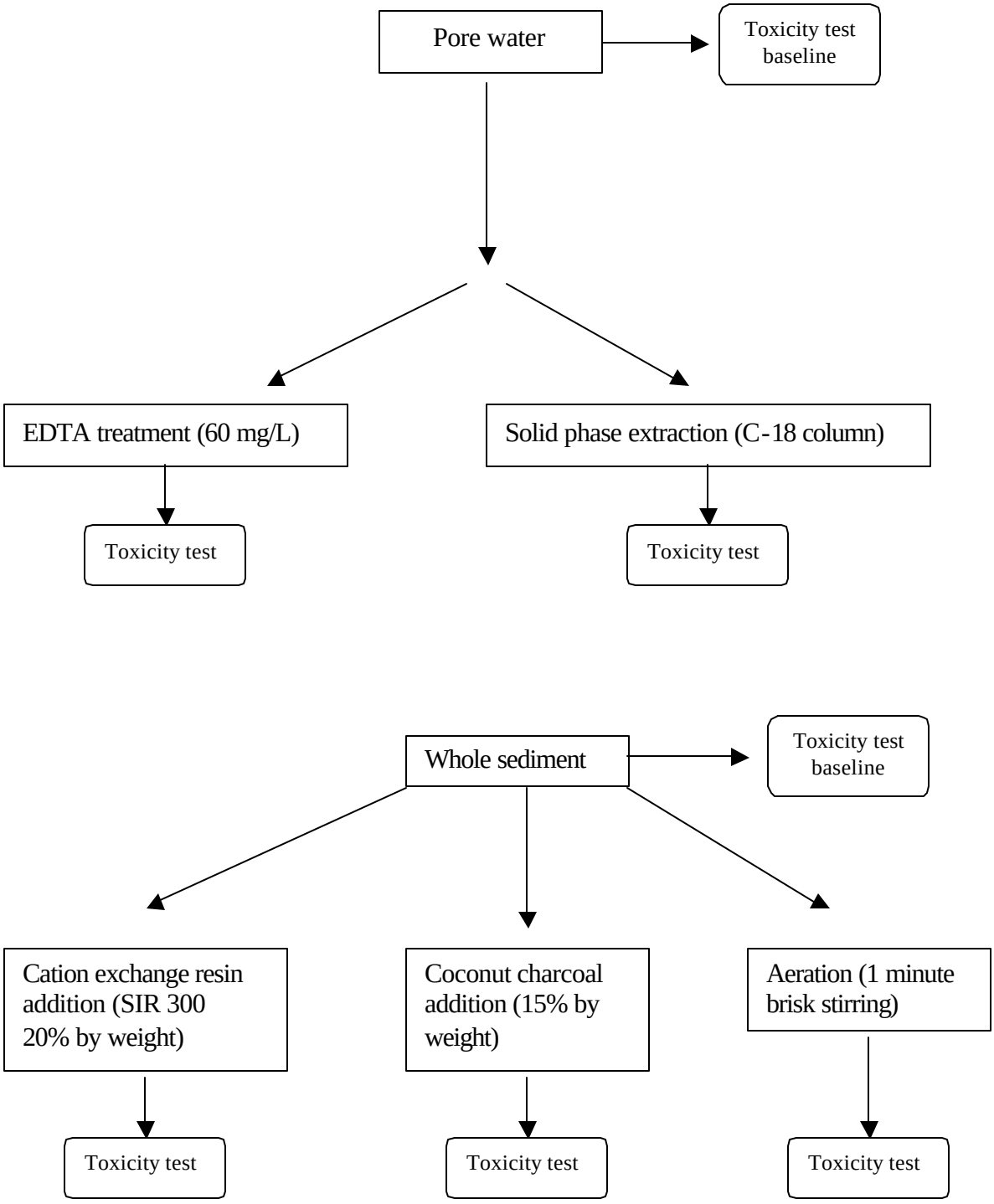

Figure 2. Toxicity characterization procedure for pore water and sediment.

RESULTS

October 2000 Pore Water

Samples of pore water from sediments collected in October 2000 were not toxic to sea urchins or amphipods. Sea urchin egg fertilization and amphipod survival percentages were greater than 90% for all samples and similar to the seawater control sample (Figure 3). TIE analyses were not conducted on these samples because there was no detectable toxicity.

July 2001 Pore Water

Severe toxicity was present in pore water collected in July 2001 from station C14, located near the mouth of Chollas Creek. There was only 27% amphipod survival in pore water from station C14 (Figure 4). No significant sediment or porewater toxicity was detected at the other stations (C01 or R03) or in the control samples. Toxicant characterization analyses were conducted on pore water from station C14.

Addition of EDTA or C-18 extraction eliminated the toxicity of porewater from station C14 (Figure 5). Both treatments had a similar effect, increasing amphipod survival from the baseline value of 27% to 93% (EDTA) or 100% (C-18).

July 2001 Sediment

Severe toxicity was also found in the whole sediment collected from C14. There was 0% amphipod survival in sediment from this station. No significant toxicity was observed at the other stations or in the controls. Whole sediment toxicant characterization analyses were performed on station C14 only.

Station C14 sediment toxicity was eliminated by one of the TIE treatments, addition of activated carbon (Figure 6). This treatment increased amphipod survival from the baseline value of 0% to 100%. The other two treatments, cation exchange resin addition or aeration, resulted in less than 15% amphipod survival. Samples of amphipod collection site sediment (control) treated with the cation exchange resin or aeration produced only minor changes in survival, indicating that the TIE treatments were compatible with the test species and laboratory system.

A summary of the chemical composition of the three sediment samples is shown in Table 1. The reference station (R03) contained the lowest concentration of constituents in most cases. Station C14, which was highly toxic, contained higher concentrations of Cd, Pb, Ni, Zn, PCBs, DDTs, and PAHs than stations C01 and R03.

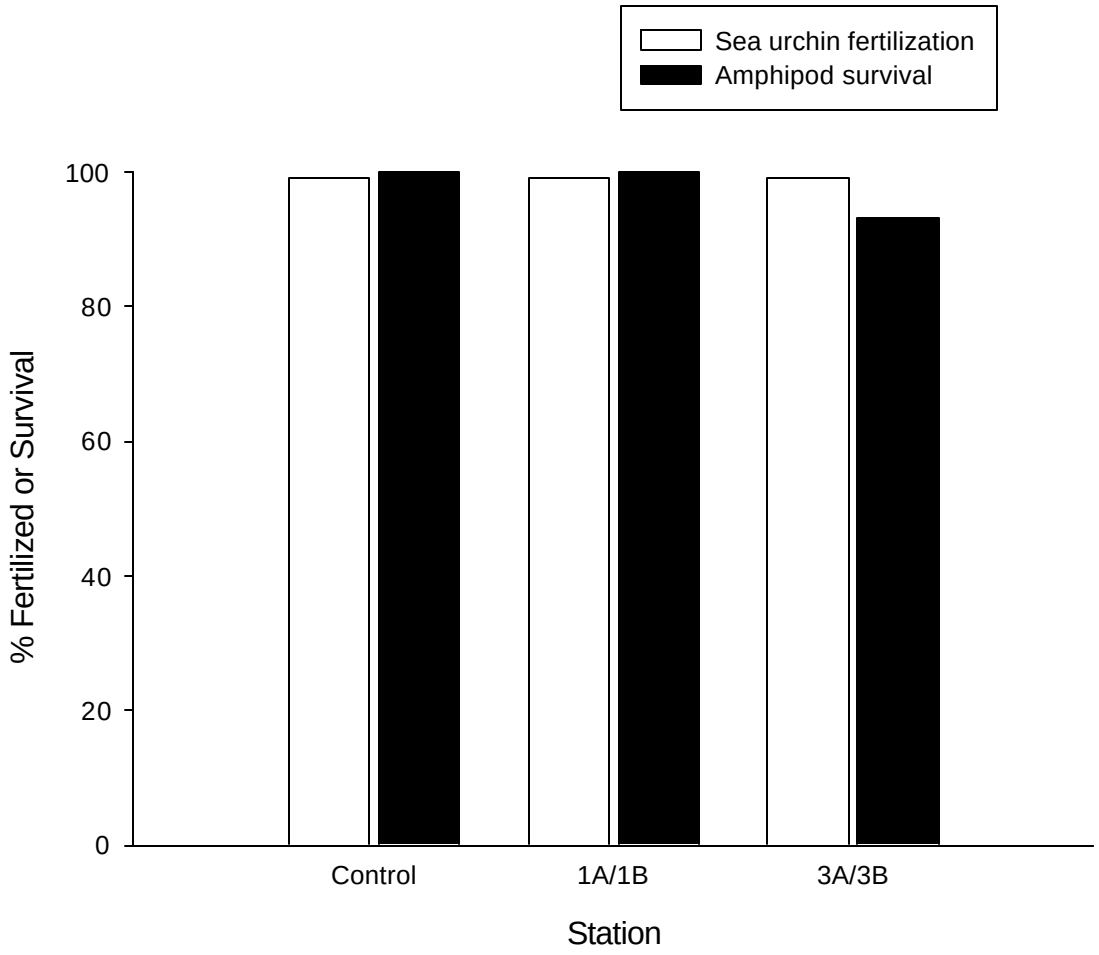

Figure 3. Results of sea urchin fertilization or amphipod survival tests of pore water from Chollas Creek channel sediments collected in October 2000.

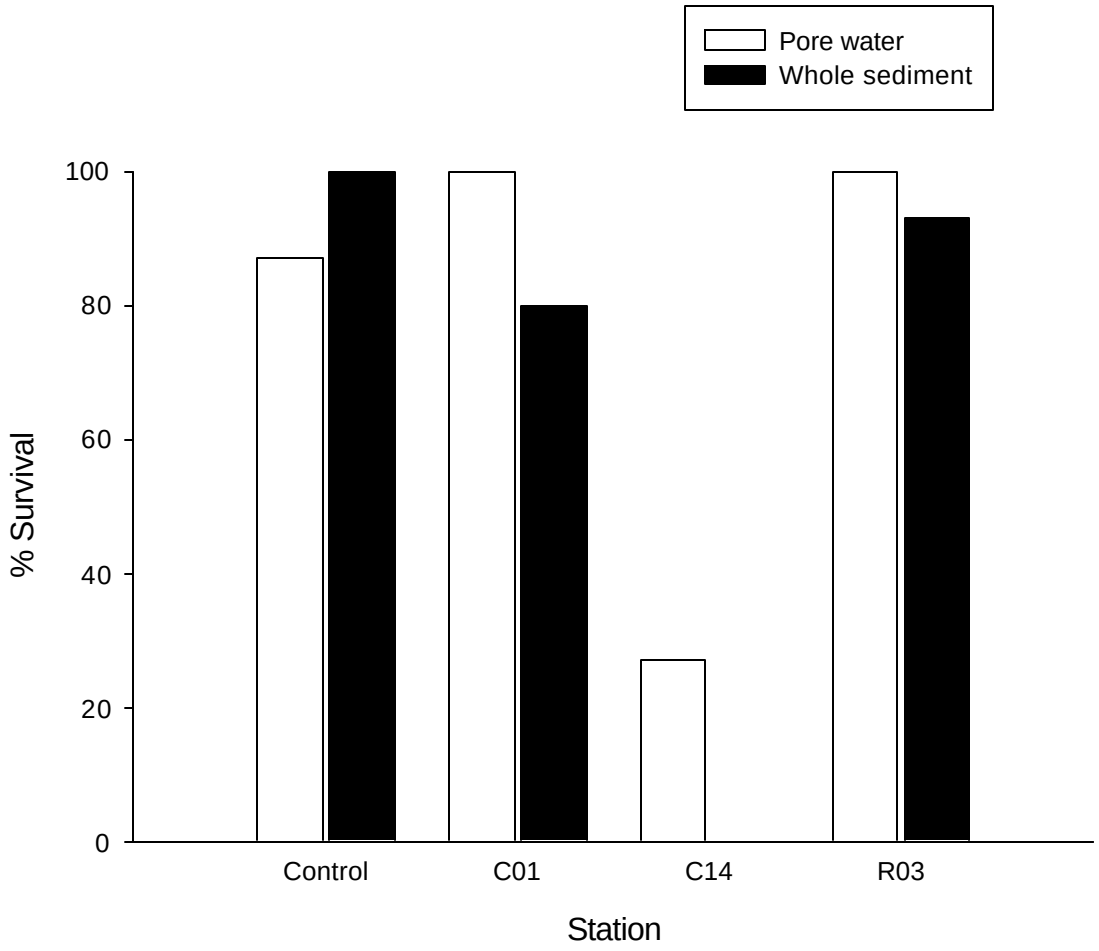

Figure 4. Results of solid phase and porewater amphipod toxicity tests conducted on samples collected in July 2001.

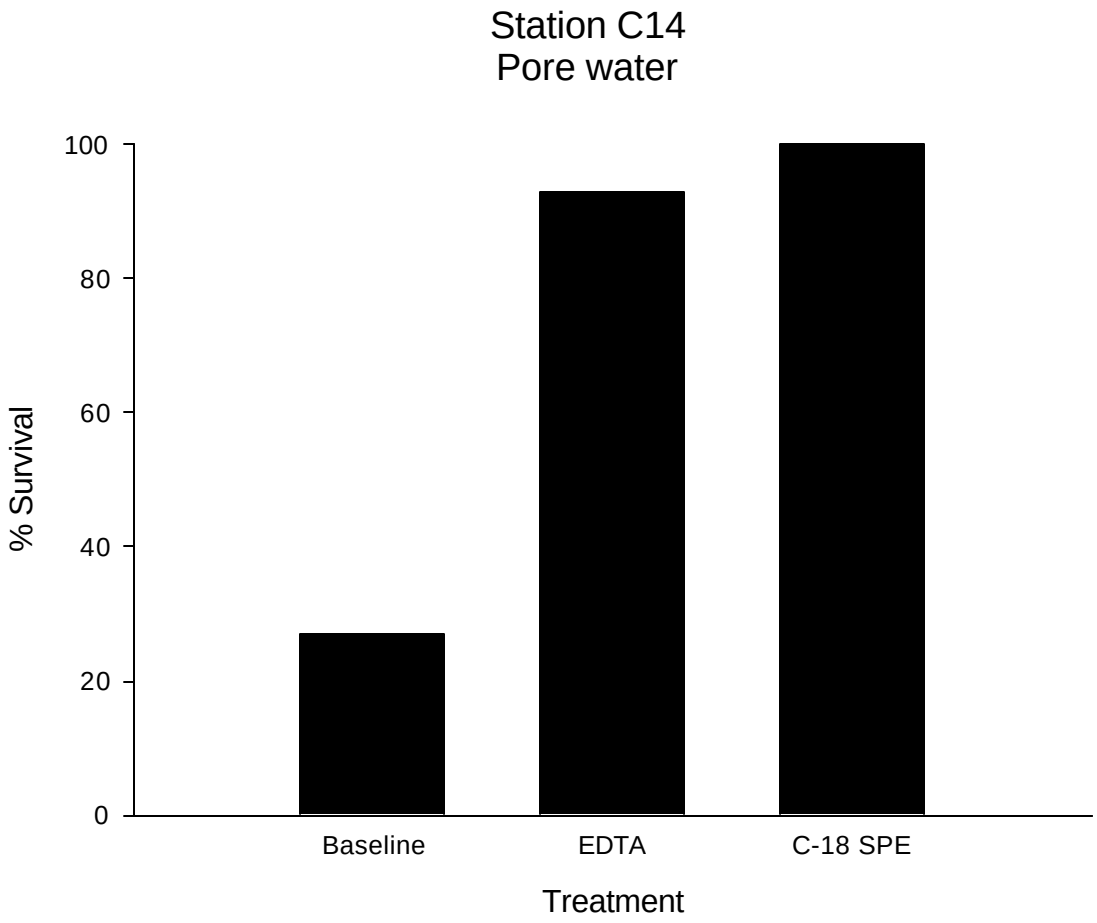

Figure 5. Response of amphipods to station C14 porewater TIE treatments.

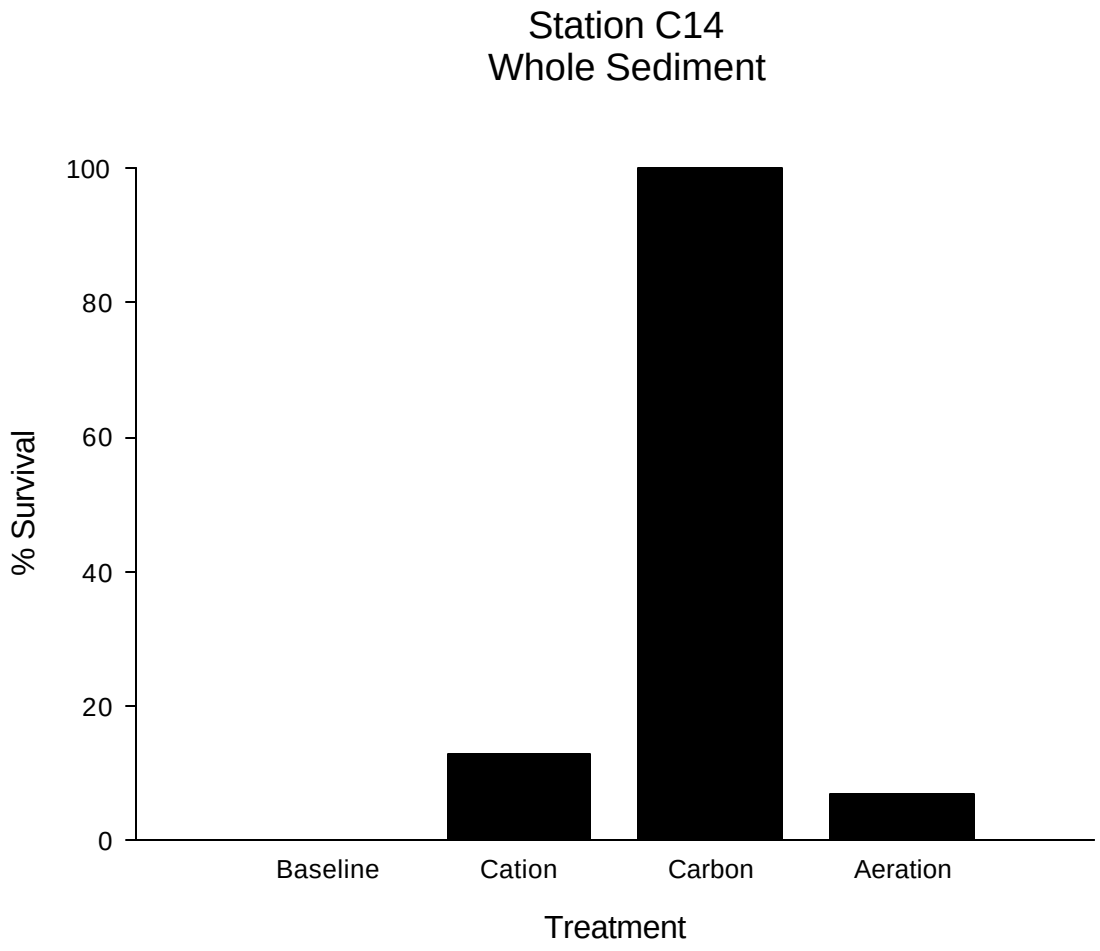

Figure 6. Response of amphipods to station C14 sediment TIE treatments.

Table 1. Contaminant concentrations (dry weight basis) of sediments collected in July 2001.

Constituent	C01	C14	R03
Al (ug/g)	74750	71700	73900
Sb (ug/g)	2.7	2.66	0.561
As (ug/g)	11.55	9.41	5.55
Ba (ug/g)	487	477	528
Be(ug/g)	1.26	1.17	1.12
Cd(ug/g)	0.414	1.37	0.288
Cr (ug/g)	56.8	51.6	42.2
Cu(ug/g)	140	94.9	43.3
Fe (ug/g)	41650	41900	29950
Pb (ug/g)	75.8	103	23.2
Ni (ug/g)	17.2	22.8	11.2
Hg (ug/g)	0.418	0.235	0.25
Ag (ug/g)	0.7	0.461	0.384
Se (ug/g)	0.336	0.45	0.18
Zn (ug/g)	234	347	114
Total PCBs (ug/Kg)	190	212	26.8
Total DDTs (ug/Kg)	28.7	242	2.52
Total PAHs (ug/Kg)	7206	16159	1179

DISCUSSION

The results of this study indicate that sediment TIEs are useful for helping to identify the cause of sediment toxicity in the Chollas Creek channel. TIE manipulations of both pore water and sediment from station C14 eliminated the toxicity, demonstrating that both of these exposure matrices are useful for continued research. The effectiveness of the carbon and EDTA treatments, along with chemistry data showing elevated contaminant concentrations at station C14, provide support for a hypothesis that the sediment toxicity at this station is due to elevated concentrations of contaminants, rather than grain size or organic enrichment factors.

Both metal and organic toxicants appear to be producing toxicity near the mouth of Chollas Creek. This conclusion is supported by the elimination of sediment toxicity by the addition of activated carbon (effective on nonpolar organics) and by the effectiveness of EDTA addition (complexes trace metals) to porewater. The effectiveness of the C-18 column extraction procedure in eliminating toxicity suggests that nonpolar organics may also play a role in station C14 porewater toxicity.

Definitive statements regarding the cause of sediment toxicity in the Chollas Creek channel cannot be made, based solely upon these results. Additional studies are needed to confirm the reproducibility of the patterns observed with these samples and to identify specific toxic constituents.

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