Sediment Toxicity Identification Evaluations San Francisco Bay Regional Monitoring Program for Trace Substances

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Introduction

Sediment toxicity has been assessed at 14 Regional Monitoring Program (RMP) stations in both the winter and summer seasons since 1993. Amphipod mortality is measured in whole sediment samples using the estuarine amphipod *Eohaustorius estuarius*, and bivalve development is measured in sediment elutriates (sediment-water mixtures) and sediment-water interface exposures using embryos of the Bay mussel *Mytilus galloprovincialis*. Sediment toxicity test information is combined with chemical analyses, physical data, and in some cases, benthic community information to determine sediment quality in San Francisco Bay. Results of toxicity tests have indicated seasonal and spatial variability in toxic response, and these differ between the three toxicity test protocols. Consistent inhibition of bivalve embryo development has been observed at the three RMP river stations located in the northern reach of the Estuary. Seasonally variable mortality of amphipods has been observed at a number of stations, particularly those in the South Bay, and in some cases, stations in the northern Estuary.

One of the RMP goals is to investigate causes of sediment toxicity in order to identify chemicals of concern that may impact the estuary's ecosystem. Toxicity Identification Evaluation (TIE) procedures developed by the Environmental Protection Agency (Ankley *et al.* 1991, EPA 1996) have been used to demonstrate that metals (divalent cations) are most likely responsible for inhibited bivalve embryo-larval development in whole sediment (sediment-water interface) and sediment elutriate samples from the three North Bay river stations (Phillips *et al.* 2000).

Intermittent amphipod mortality has been observed at two RMP stations since toxicity tests were initiated in the winter of 1993: Redwood Creek (Station No. BA41) in the South Bay, and Grizzly Bay (Station No. BF21) in the northern Estuary. Using data from the RMP and the Bay Protection and Toxic Cleanup Program, Thompson *et al.* (1999) investigated the relationship between sediment contamination and amphipod mortality in San Francisco Bay using a combination of multivariate analyses (PCA) and regression techniques. These authors found that when considered on a bay-wide basis, amphipod mortality was significantly correlated with contaminant mixtures, as represented by a mean Effects Range Median Quotient value (mERMQ). When results were analyzed on a station-by-station basis, amphipod mortality at Grizzly Bay was correlated with chlordane, silver and cadmium, while PCA identified weak associations between mortality and bulk-phase chlordane and silver concentrations at Redwood Creek. Porewater and solid phase TIE studies were combined with chemical analyses of sediment, porewater and amphipod tissues using samples from Grizzly Bay and Redwood Creek (Anderson et al. 2000a). The results of these experiments suggested that amphipod mortality in samples from these stations was probably not due to non-polar organic chemicals. This report discusses results of additional experiments designed to identify chemicals responsible for mortality of amphipods and inhibition of bivalve embryonic development in Grizzly Bay sediment.

Bivalve TIE experiments

Previous experiments have indicated that cations are the cause of abnormal bivalve embryonic development in sediment elutriate and sediment-water interface exposures using Grizzly Bay sediment samples (Phillips *et al.* 2000a). Although elutriates from this station

consistently have measurable concentrations of a variety of trace metals, including copper, zinc, nickel and cadmium, it is not clear which of these metals are inhibiting bivalve development. Research is being conducted to investigate the toxicity of metal mixtures to determine how combinations of these metals may affect mussel and sea urchin embryonic development (Phillips et al. 2000b). Results of metal mixture experiments with mussel embryos were variable. Binary combinations of Cd+Zn, and Cu+Zn, and the trinary combination of Cd+Ni+Zn were less than additive for mussels; the combination of Cd+Cu+Ni was additive for mussels. Because Grizzly Bay sediment is contaminated by a complex mixture of moderate concentrations of metals (and trace organic compounds), it is difficult to determine whether toxicity of metal mixtures in elutriate samples from this station is consistent with that observed in laboratory spiking experiments.

In addition to investigations of effects of metal mixtures, techniques to separate individual metals from Grizzly Bay samples are also being developed. These experiments are designed to use a Supelco™ solid-phase cation exchange column to remove cations from (centrifuged) elutriate samples. Metals are then selectively eluted from the column using increasing molarities of hydrochloric (HCl) acid. Assuming cations have different binding affinities (copper>nickel>lead>zinc>cadmium), we are investigating the possibility of selectively extracting different metals bound to the column, so that we can determine which are contributing toxicity to Grizzly Bay elutriate samples. Preliminary experiments have been conducted with mixture of copper (20 µg/L), cadmium (5000 µg/L), nickel (1000 µg/L) and zinc (300 µg/L) spiked in seawater. In these experiments, 150 ml of the metal mixture was passed through the Supelco™ column. The column rinsate (post-column effluent) was then tested for toxicity with bivalve embryos to verify that all of the metal toxicity was removed. A series of increasing HCl concentrations were then passed through the column, and each HCl eluate was spiked into seawater to assess toxicity of the various fractions (pH of the spiked samples was adjusted to 8.0 with 1M sodium hydroxide). Four experiments were conducted and the results of these are given in Table 1. In the first experiment (Test 1) the column removed all of the toxicity of the metal mixture, and elution of the column with 1M HCl recovered toxicity. In the second experiment, various HCl molarities were used to elute the column. These results (Test 2) showed the majority of toxicity occurred in the 0.05M eluate; some toxicity was also recovered in the 0.5M eluate. Intermediate HCl molarities were tested in Test 3. In this experiment, there was 0% development in the 0.025M eluate fraction, and 46% development in the 0.5M fraction. Results of Test 4 also showed inhibition of development in the 0.025M fraction, but no significant toxicity in the other fractions. While the results of these preliminary experiments suggest some fractionation of sample toxicity, it is not clear if this is due to separation of metals. We have submitted a number of these samples for chemical analysis to determine if the four metals are eluting in the different HCl eluate fractions. The results of these analyses will be considered in the design of subsequent experiments with Grizzly Bay sediment elutriates.

Amphipod TIE experiments

Results of previous TIEs demonstrated that amphipod toxicity in Grizzly Bay sediment samples was greater in whole-sediment exposures than in porewater exposures. These results suggest that sediment ingestion may be the primary exposure pathway at this sight.

Table 1. Results of metal elution experiments using the Supelco™ cation exchange

	Test 1		Test 2		Test 3		Test 4	
Treatment	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Control	0.95	0.05	0.80	0.06	0.96	0.06	0.79	0.04
Sample	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Column Control	1.02	0.04	0.82	0.04	0.93	0.04	0.80	0.05
Column Sample	0.95	0.08	0.82	0.09	0.94	0.07	0.86	0.05
Eluate Control	1.03	0.06	0.85	0.08	0.90	0.13	0.85	0.04
Column Acid Control							0.83	0.18
Eluate Sample 0.001M			0.81	0.04				
Eluate Sample 0.005M			0.81	0.05				
Eluate Sample 0.010M			0.81	0.12	0.87	0.04	0.83	0.07
Eluate Sample 0.015M							0.73	0.05
Eluate Sample 0.020M							0.82	0.09
Eluate Sample 0.025M					**0.00**	**0.00**	**0.20**	**0.03**
Eluate Sample 0.030M							0.76	0.05
Eluate Sample 0.035M							0.78	0.04
Eluate Sample 0.040M							0.85	0.06
Eluate Sample 0.045M							0.82	0.06
Eluate Sample 0.050M			**0.00**	**0.00**	0.87	0.05	0.76	0.02
Eluate Sample 0.075M					0.92	0.06		
Eluate Sample 0.100M			0.83	0.05	0.90	0.05	0.79	0.04
Eluate Sample 0.250M					0.86	0.05		
Eluate Sample 0.450M							0.80	0.04
Eluate Sample 0.500M			**0.69**	**0.12**	**0.46**	**0.23**	0.83	0.08
Eluate Sample 0.550M							0.86	0.05
Eluate Sample 1M	**0.00**	**0.00**	0.82	0.03	0.91	0.05	0.85	0.09

Information from solid-phase TIEs combined with measures of trace organic tissue concentrations in sediment-exposed amphipods suggest that non-polar organic compounds were probably not the primary cause of acute toxicity. Subsequent experiments were designed to reduce whole-sediment trace metals concentrations to determine if these are a significant source of amphipod mortality at this station. Toxicity of Grizzly Bay sediment to amphipods was assessed by adding 20% wet weight cation exchange resin (Resin Tech SIR-300 iminodiacetate Na form) to the sample and stirring the mixture for 24 hours at 15°C on a ball roller. This resin (particle size ~ 20-30 mesh) has been demonstrated to have a high affinity for soluble cations in porewater, and also may strip particle bound metals (Burgess *et al.* 2000). Dilution effects due to the 20% addition of the resin were accounted for by adding 30 mesh reference sand to Grizzly Bay sediment. The results of this experiment demonstrated a significant reduction in Grizzly Bay sediment toxicity with the addition of the cation resin (Figure 1). However, the fact that the reference sand also significantly reduced toxicity suggests that this was due to dilution of the sample rather than reduced cation bioavaliability. No chemical analyses of the various sediment treatments were conducted so it is not clear how effective the cation resin was in reducing bulk-phase metals. Additional experiments designed to assess metal-associated toxicity of Grizzly Bay sediments to amphipods will be conducted using samples collected in the RMP winter sampling period. These will include additional cation resin experiments, and weak-acid leaching experiments to reduce bulk-sediment metal concentrations.

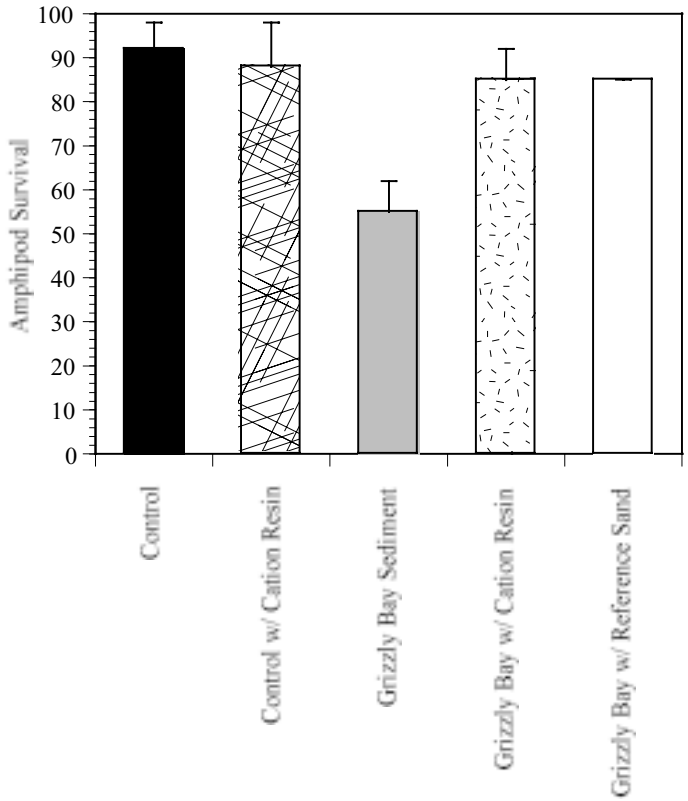

Figure 1. Results of Grizzly Bay solid-phase cation TIE.

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