Investigations of Sediment Elutriate Toxicity at Three Estuarine Stations in San Francisco Bay, California

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Contents

Introduction

Since the San Francisco Regional Monitoring Program (RMP) bi-yearly sampling began in the winter of 1993, three stations have exhibited consistent toxicity to bivalves, and intermittent toxicity to amphipods. Significant toxicity to bivalves (*Mytilus galloprovincialis*) has been detected in all but one of the sediment elutriate samples from the Grizzly Bay, Sacramento River, and San Joaquin River stations. As part of the ongoing RMP sediment toxicity investigations, a characterization of the potential causes of toxicity began with Phase I Toxicity Identification Evaluations (TIEs) and chemical analyses. Initial TIE results and measurements of trace metals in sediment elutriates indicated trace metals were a potential cause of toxicity in samples from Grizzly Bay and San Joaquin River. TIE manipulations suggested an organic chemical might be the source of toxicity in Sacramento River sediment.

Because these sediments contain complex mixtures of contaminants, it was difficult to associate measured contaminants with toxicity using traditional statistical correlations. Although elevated pesticide and metal concentrations had been detected in some water column samples at these sites, sediment concentrations of organic chemicals and metals have not exceeded published sediment quality guidelines (e.g., ERMs) for any of the contaminants measured except for nickel. In addition, unionized ammonia and hydrogen sulfide measured during the toxicity tests did not exceed threshold effect concentrations for these sediment constituents.

The three stations in question are essentially freshwater stations, although there is some tidal influence in Grizzly Bay. Since the beginning of the RMP, overlying water salinity at the river stations ranged from 0 to 3‰ and salinity at Grizzly Bay ranged from 0 to 11‰. Because RMP samples have been tested with marine/estuarine species (i.e. bivalves), sediment elutriates were prepared by mixing the sediments with water at the test salinity of 28‰. It is not clear what effect elution of freshwater sediment with higher saline water had on chemical bioavailability or sediment toxicity. Generally, when metals in freshwater come in contact with higher salinity water, as in a river flowing into an estuary, they behave conservatively and the total metal concentrations are reduced through complexation with organic matter and particles (Van Den Berg, et al., 1990; L'Her Roux et al., 1998).

Toxicity Identification Evaluation Strategy

Investigations into potential causes of toxicity began with Phase I TIEs in 1996 and followed the timeline summarized in Table 1. As more information about the samples was discovered and new questions arose, the investigative strategy was altered to include TIE manipulations at the sediment-water interface, additional elutriate exposures in a freshwater matrix, and a novel approach for determining the cupric ion concentration in the samples. Because the samples had been consistently toxic year after year, there were no concerns about losing the toxicity signal. A potential drawback to continuing this investigation over multiple years was the transient nature of the sites. Seasonal changes in river flow and sediment deposition have altered the sediment characteristics and the concentration of sediment contaminants. Between 1993 and 1997 the percentage of the fine grained sediment fraction at Grizzly Bay generally remained above 90%, but the river sites ranged from 5 to 79% fines with no seasonal pattern. Metals such as copper maintained consistent concentrations in these sedi-

ments, but organic constituents such as PAHs and pesticides demonstrated seasonal patterns (SFEI, 1999). Varying concentrations of contaminants might have affected the interpretation of some TIE results.

After initial TIEs and chemical analyses were conducted on sediment elutriates; subsequent investigations emphasized metal toxicity with solid-phase TIE manipulations at the sediment-water interface, additional chemical analyses, and additional Phase I and II TIE manipulations of elutriate samples. Another set of Phase I elutriate TIEs was performed in April 1998 with additional metals analyses. Because copper concentrations were within the range toxic to bivalves and sample pH suggested ionic concentrations might have been elevated, ionic copper concentrations were measured in overlying water from sediment-water interface exposures that were conducted simultaneously with the TIEs. These concentrations were compared to a copper ion dose response curve. To determine the effects of manipulating freshwater samples with higher salinity water, copper ion concentrations were also measured in freshwater samples and additional exposures were conducted in 1999 using the freshwater organisms *Ceriodaphnia dubia* and *Selenastrum capricornutum*. Marine elutriates were also tested with the purple sea urchin, *Strongylocentrotus purpuratus*, whose larvae are less sensitive to some metals than *Mytilus*.

Methods

Elutriate Preparation and Chemistry

All toxicity testing and sample manipulations were conducted at the Marine Pollution Studies Laboratory at Granite Canyon (MPSL). Elutriate solutions were prepared by adding one part sediment to four parts Granite Canyon seawater in 1-liter borosilicate glass jars with Teflon-lined lids (1:4 volume to volume ratio, US EPA/ACOE, 1991). These mixtures were shaken vigorously for 10 seconds, then allowed to settle for 24 hours (Tetra Tech, 1986). The resulting supernatant was siphoned for use in toxicity testing, TIE manipulations and chemical analyses.

Elutriate metals extraction was conducted by Mike Gordon at Moss Landing Marine Laboratories, and analyses were conducted by Jon Goetzl at the Department of Fish and Game Trace Metals Analytical Facility. The liquid-liquid extraction method using APDC-DDDC-chloroform followed the procedure described by Bruland et al. (1979). Metals analyses conducted in 1998 and 1999 used Inductively Coupled Plasma Mass Spectrometry (US EPA method 1638). Trace organic analysis was conducted by Walter Jarman at the University of California, Santa Cruz, using standard RMP trace organics methods (SFEI, 1999).

Free copper ion concentrations were measured in overlying water from sediment-water interface exposures by determining copper complexation. Analysis was conducted by Heidi Zamzow at Moss Landing Marine Laboratories. Water was sampled from freshwater and marine sediment-water interface exposures. The analytical technique employed used flow injection analysis with chemiluminescent detection of a reaction between a copper-binding ligand and titrated copper (Zamzow, 1998). These analyses produced cupric ion concentrations for two of the marine samples and all of the freshwater samples. Additional analyses were conducted on spiked seawater samples in order to create a cupric ion dose-response curve for *Mytilus* larval development.

Table 1. Summary of testing conducted on River/Delta stations.

Date	Station	Exposure	Organism	Result	Chemical Analyses
August 1996	GB	TIE	Mytilus	EDTA treatment mitigates toxicity	Metals and Organics
		SWI	Mytilus	65% normal survival	
	SR	TIE	Mytilus	C18 Column treatment mitigates toxicity	Metals and Organics
		SWI	Mytilus	15% normal survival	
	SJR	TIE	Mytilus	Inconclusive	Metals and Organics
		SWI	Mytilus	46% normal survival	
August 1997	GB	SWI	Mytilus	19% normal survival	
		SWI/EDTA	Mytilus	76% normal survival – EDTA mitigates toxicity	
		FW Elutriate	Ceriodaphnia	100% survival	
	SR	SWI	Mytilus	57% normal survival	
		SWI/EDTA	Mytilus	57% normal survival	
		FW Elutriate	Ceriodaphnia	100% survival	
	SJR	SWI	Mytilus	28% normal survival	
		SWI/EDTA	Mytilus	60% normal survival – EDTA mitigates toxicity	
		FW Elutriate	Ceriodaphnia	100% survival	
February 1998	GB	SW Elutriate	S. purpuratus	98% normal development	
	SR	SW Elutriate	S. purpuratus	94% normal development	
	SJR	SW Elutriate	S. purpuratus	27% normal development	
April 1998	GB	TIE	Mytilus	EDTA and Cation Column mitigate toxicity	Metals
		SWI	Mytilus	28% normal survival	Cupric Ion
	SR	TIE	Mytilus	EDTA, STS, Cation Column, C18 Column mitigate toxicity	Metals
		SWI	Mytilus	32% normal survival	Cupric Ion
	SJR	TIE	Mytilus	Cation Column and C18 Column mitigate toxicity	Metals
		SWI	Mytilus	56% normal survival	Cupric Ion
February 1999	GB	FW Elutriate	Ceriodaphnia	92% survival	Metals
		FW Elutriate	Selenastrum	36% cell growth	
		SW Elutriate	Mytilus	0% normal survival	Metals
		SW Elutriate	S. purpuratus	96% normal development	
		SWI	Mytilus	18% normal survival	Metals
	SR	FW Elutriate	Ceriodaphnia	96% survival	Metals
		FW Elutriate	Selenastrum	180% cell growth	
		SW Elutriate	Mytilus	0% normal survival	Metals
		SW Elutriate	S. purpuratus	97% normal development	
		SWI	Mytilus	0% normal survival	Metals
	SJR	FW Elutriate	Ceriodaphnia	100% survival	Metals
		FW Elutriate	Selenastrum	107% cell growth	
		SW Elutriate	Mytilus	0% normal survival	Metals
		SW Elutriate	S. purpuratus	95% normal development	
		SWI	Mytilus	0% normal survival	Metals

Toxicity Identification Evaluations

Phase I TIE manipulations followed methods described by US EPA (1996). A brief description of the treatments follows. Filtration (0.45 mm glass fiber) removed contaminants associated with particles. Sample aeration was used to assess volatile constituents such as sulfide. Two different concentrations of EDTA were used to assess toxicity due to divalent cations. C18 solid-phase extraction columns were used to remove non-polar organic compounds. The C18 column was then eluted with methanol and the eluate was added back to clean dilution water to determine if C18-bound organics were toxic. Graduated pH adjustments (7.9, 8.1 and 8.4) were used to assess toxicity of ionic constituents such as ammonia. The addition of piperonyl butoxide (PBO) was used to test for the presence of metabolically activated pesticides such as Diazinon and other organophosphates.

As research into the causes of toxicity at these stations continued, additional Phase I and Phase II TIE manipulations were conducted. These TIEs emphasized treatments that would mitigate toxicity of divalent metals. Additional manipulations included a combination C18 Column/EDTA treatment that was used to remove mixtures of organic and metal contaminants. A Cation Exchange column was used to remove metal contaminants that were then eluted with acid and added back to clean dilution water for confirmation testing. All column samples for this phase of the study were pre-filtered (0.45 mm) so particulate-associated contaminants did not interfere with the interpretation of the results.

Each manipulation was conducted on multiple concentrations of sediment elutriate from each station and a control. Controls consisted of Granite Canyon seawater, adjusted to the appropriate salinity, and served as blanks for TIE treatments. TIE results were compared using analysis of variance between treatments within each elutriate concentration. Treatments were considered significantly different from the Baseline treatment at $p < 0.05$.

Sediment-Water Interface Exposures

In addition to elutriate exposures, bivalve larvae were exposed to solid-phase sediment using a sediment-water interface (SWI) exposure system (Anderson et al., 1996). This exposure system mimics situations that may occur in nature when negatively buoyant bivalve embryos contact sediment before hatching, and assesses toxicity of contaminants fluxed into overlying water. For this test, intact (unhomogenized) sediment cores were taken directly from the grab sampler. Intact cores were used rather than sediment homogenates in order to minimize artifacts caused by sediment mixing (Anderson et al., in press). This system allows for a more ecologically relevant exposure of epibenthic species, and comparison of test results allows evaluation of possible effects related to the elutriate preparation process. Cores were brought back to the laboratory on ice, prepared for testing by slowly adding 300 mL of overlying seawater, and equilibrated overnight under gentle aeration. Before test initiation, 25-mm mesh screen tubes were inserted into the core tubes containing the sediment, so that the screen was positioned about 1 cm above the sediment. Approximately 200 mussel embryos were pipetted into the screen tubes and exposed for 48 hours. Tests were terminated by removing the screen tube and rinsing larvae into vials that were fixed with 5% formalin. All normally developed larvae were counted in each test container to determine the percentage of embryos that developed into live normal larvae.

To determine if cation chelation could mitigate toxicity in SWI exposures, EDTA was added to overlying water in additional sediment cores. Cores of clean sand were also tested, with and without EDTA, as controls. Overlying water chemistry was not measured in these samples.

Freshwater Toxicity Tests

To investigate whether changes of sample salinity in the preparation of elutriates was affecting toxicity, freshwater elutriate tests were conducted using the cladoceran *Ceriodaphnia dubia* and the alga *Selenastrum capricornutum*. Elutriate samples were prepared as described above, but used moderately hard dilution water rather than 28‰ seawater (US EPA, 1993). Forty-eight-hour and 96-hour acute toxicity tests with *Ceriodaphnia* were conducted using neonates that were less than 24 hours old. Ninety-six hour acute toxicity tests were conducted using *Selenastrum* (US EPA, 1993). The results of these tests were compared to those of marine elutriate tests conducted with *Mytilus galloprovincialis* and the purple sea urchin, *Strongylocentrotus purpuratus* (US EPA, 1995). Sediment-water interface tests were also conducted using *M. galloprovincialis*.

Results

Results are presented in chronological order beginning with the first toxicity tests and chemical analyses conducted in 1996 (Table 1). Because significant toxic responses and toxicity mitigation generally occur within one or two concentrations of elutriate, data are represented graphically only for concentrations where TIE treatments mitigated toxicity

August 1996 TIEs and Chemical Analyses

Addition of EDTA significantly reduced toxicity of the 50% dilution of the Grizzly Bay elutriate sample (Table 1). These results suggest that divalent cations contributed to toxicity in this sample. It should be noted that the EDTA control was significantly more toxic than the Baseline control. Though this suggests EDTA toxicity in the full strength sample, in the 50% sample EDTA probably was not toxic due to dilution. The Column Eluate treatment was not significantly more toxic than the Eluate blank. This result corroborates the result from the C18 Column treatment: non-polar organic chemicals were probably not a cause of toxicity, since their potential removal from the sample by the column did not affect sample toxicity, and no toxic compounds could be eluted back off the column.

Passing the sample through the C18 Column significantly reduced toxicity of the 50% dilution of the Sacramento River elutriate sample (Table 1). Although the column removed some toxicity, no compounds were eluted off the column in toxic concentrations. Toxicity did not occur in the eluate treatment probably because the eluate concentrations were tested at 25% of the original elutriate strength in order to minimize toxicity associated with the methanol used to elute the column. Reduced toxicity in the Column treatment suggests that non-polar organic compounds might be the cause of some of the observed toxicity in the Baseline test.

Toxicity was not significantly mitigated in any of the TIE manipulations performed on the San Joaquin River sample. The ambient pH of the sample was well below the acceptable

limit for *Mytilus*. Graduated pH treatments did not mitigate toxicity, and toxicity also occurred in the SWI exposure where pH was within acceptable limits indicating that other factors were involved. There was slight but statistically insignificant mitigation of toxicity in the EDTA, Aeration and C18 Column treatments, perhaps indicating a combination of toxic contaminants.

Although analysis of selected metals in sample elutriates showed concentrations below the effect thresholds for Ag, Cd, and Zn, the Cu concentration approached the Lowest Observed Effect Concentration (LOEC) of 5.6 (Table 2). Pesticides, PCBs and PAHs in elutriates were below known effects thresholds for bivalve embryos (Table 3).

August 1997 Sediment-Water Interface Exposures

Sediment-water interface exposures conducted in August 1997 produced significantly toxic responses in samples from all three sites, with Grizzly Bay the most toxic at 19% normal development (Figure 1). The addition of EDTA to overlying water in the exposure system reduced toxicity in Grizzly Bay cores by 57% and San Joaquin River cores by 32%. There was no significant reduction of toxicity in the Sacramento River sample.

April 1998 TIEs and Chemical Analyses

TIE treatments were conducted on six concentrations of sediment elutriate. Results from the Cation Column Eluate are not presented because of significant blank toxicity. Unionized ammonia concentrations were below the effect threshold, but some pH levels were outside the acceptable range. Initial Baseline pH values for Grizzly Bay and San Joaquin River were below the tolerance threshold for *Mytilus*. However, pH could not have been the only cause of toxicity because other treatments with higher pH values had similar toxic responses.

Several treatments significantly reduced toxicity of the Grizzly Bay 25% elutriate sample (Figure 2). Filtration, EDTA treatments, the C18 Column with and without EDTA, and the Cation Column treatments were all significantly different from the Baseline treatment. Samples that were passed through the column treatments were all filtered. The C18 treat-

Table 2. Results of metals analysis for filtered and unfiltered elutriate samples and control water sampled in August 1996. [a]Martin *et al.* 1981, [b]MPSL unpublished data.

Station Name	Elutriate Matrix	Ag mg/L	Cd mg/L	Cu mg/L	Zn mg/L
Grizzly Bay	Filtered	0.0015	0.385	0.377	4.900
	Unfiltered	0.0131	0.398	2.520	6.350
Sacramento River	Filtered	0.0030	1.59	0.889	5.510
	Unfiltered	0.0052	1.52	2.100	7.210
San Joaquin River	Filtered	0.0026	0.172	0.170	3.930
	Unfiltered	0.0030	0.135	0.390	2.850
Control Water	Filtered	0.0029	0.067	0.042	2.030
	Unfiltered	0.0009	0.188	0.133	0.716
Mytilus LOEC			5600[b]	5.6[b]	
Mytilus EC50		14[a]	3530[b]	7.13[b]	175[a]

Table 3. Results of selected pesticide, PCB, and PAH analyses for elutriate samples and control water sampled in August 1996.

Station Name	Total PAH ng/L	Total PCB ng/L	Total DDT ng/L	Total Chlordane ng/L
Grizzly Bay	79.6	4.09	1.36	0.78
Sacramento River	5.5	3.29	0.80	0.40
San Joaquin River	4.1	10.60	0.46	0.40
Control Water	2.3	1.17	0.92	0

ments were not significantly different from the Filtration treatment indicating that the pre-filtration step probably caused the reduction in toxicity in these treatments. The C18 column can also remove metal chelates that are relatively non-polar (US EPA, 1991). The pre-filtered Cation Column treatment was significantly different from the Filtration treatment indicating that it had further reduced toxicity beyond the filtration step. Reduction of toxicity by the Cation column as well as the two EDTA treatments suggests that divalent cations contributed to the toxicity in this sample.

Toxicity was significantly reduced in the Sacramento River 25% elutriate by the Filtration treatment, both EDTA treatments, the Sodium Thiosulfate treatment, the C18 Column,

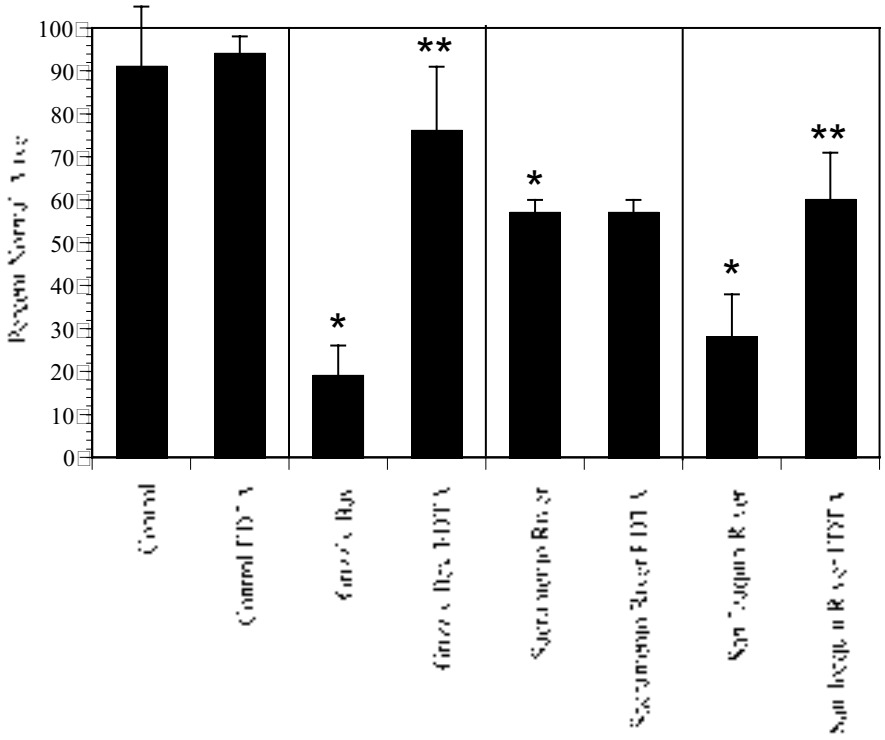

Figure 1. Results of EDTA treatments on overlying water from homogenized Sediment-Water Interface tests conducted on River Delta area samples (August 1997). Error bars indicate one standard deviation. Asterisk (*) indicates significant difference from control. Double asterisk (**) indicates significant differenct from non-EDTA treatment.

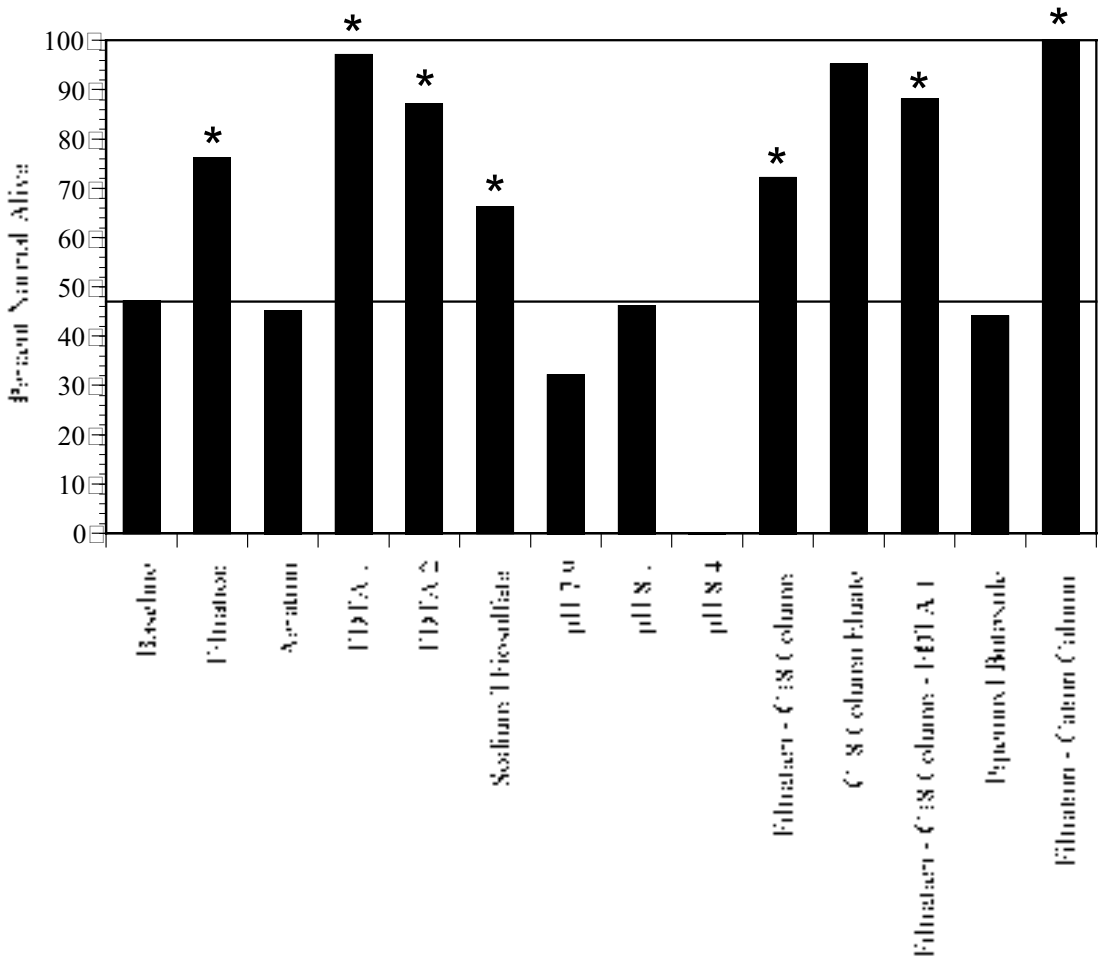

Figure 2. Results of TIE manipulations on 25% sediment elutriate from Grizzly Bay (April 1998). Asterisk (*) indicates a significant reduction of toxicity compared to Baseline treatment.

and the Cation Column (Figure 3). Removal of toxicity with the EDTA treatments and the Cation Column suggest that divalent cations might be a cause of toxicity. Removal of toxicity with the Sodium Thiosulfate treatment suggests removal of an oxidant or metal. Sodium Thiosulfate is a strong chelator of Cu, Cd, Hg and Ag chlorides (Hockett and Mount, 1996). Removal of toxicity by the Filtration treatment, along with the pre-filtration steps of the column treatments suggest that contaminants might also be particle-bound, but when the 50% elutriate concentration was examined, toxicity was significantly mitigated by both C18 Column treatments and not the Filtration treatment. Although the C18 Column removed some toxicity, no compounds were eluted off the column in toxic concentrations.

The C18 Column treatment and the Cation Column treatment significantly mitigated toxicity in the San Joaquin River 25% elutriate (Figure 4). Although the Filtration treatment and the EDTA treatments removed some toxicity, the differences were not statistically significant. The combined C18 Column/EDTA treatment did not remove toxicity. The pre-filtration step of the column treatments might be a factor in contaminant removal, but the additional removal of toxicity by the Cation Column in the 50% elutriate concentration suggests divalent cations as a source of toxicity. Partial reduction of toxicity by EDTA supports this hypothesis.

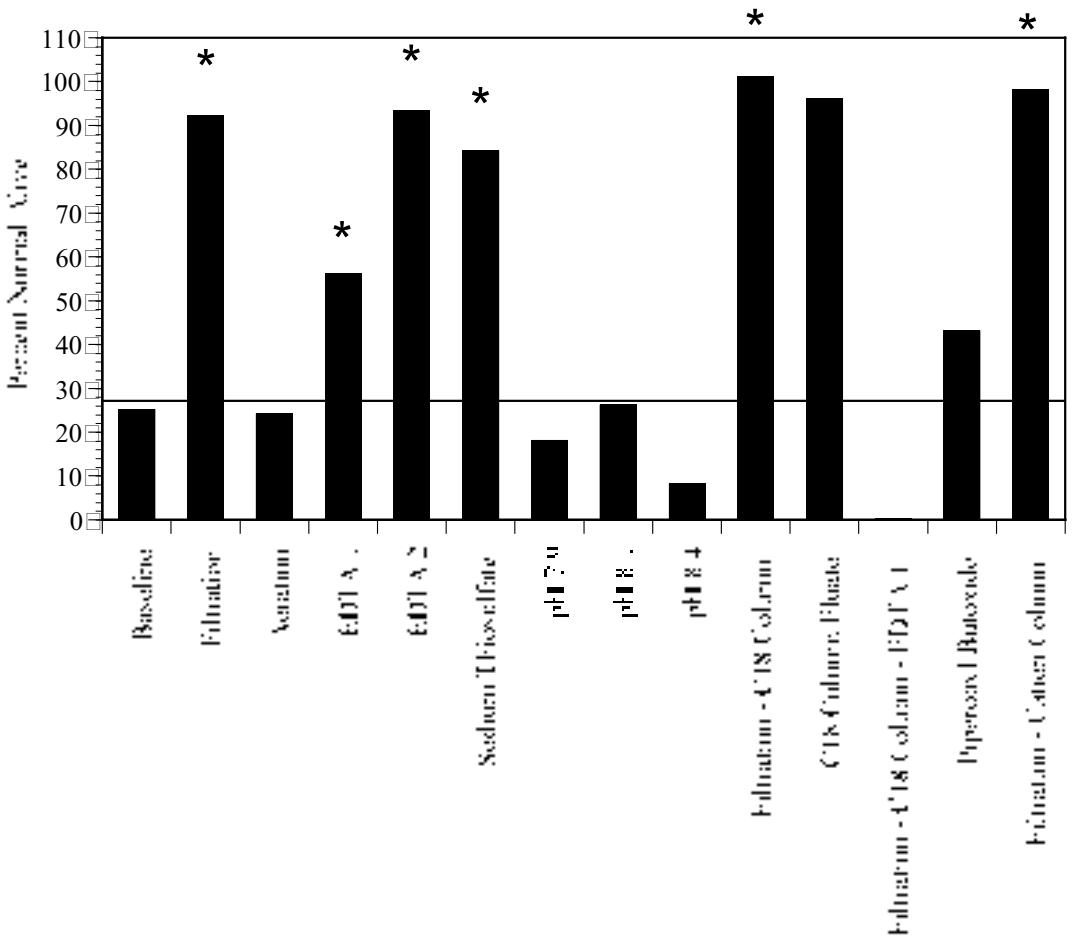

Figure 3. Results of TIE manipulations on 25% sediment elutriate from Sacramento River (April 1998). Asterisk (*) indicates a significant reduction of toxicity compared to Baseline treatment.

Selected metal concentrations in filtered elutriate samples were below the effect limits for Ag, Cd, and Zn, but the total Cu concentrations exceeded the LOEC value of 5.6 in samples from all three sites (Table 4, MPSL unpublished data).

April 1998 Sediment-Water Interface Exposures and Cupric Ion Analyses

Because previous chemical analyses of sediment elutriates indicated that copper concentrations were within the range toxic to mussel embryos at these stations, sediment overlying water from SWI cores was sampled to measure cupric ion concentrations. Sediment-water interface exposures were all significantly toxic to mussel larvae (Table 6). Cupric ion concentrations in the Grizzly Bay and San Joaquin River marine samples, and all three freshwater samples were successfully determined using flow injection analysis coupled with chemiluminescence detection (Table 6). Cupric ion concentrations in a laboratory reference toxicant test were also measured to create a cupric ion dose-response for mussel embryo-larval development. The cupric ion concentrations of the marine samples were below the cupric ion Lowest Observed Effect Concentrations (LOEC) for *Mytilus*. Cupric ion concentrations in fresh overlying water from SWI samples were higher than marine samples (Table 6).

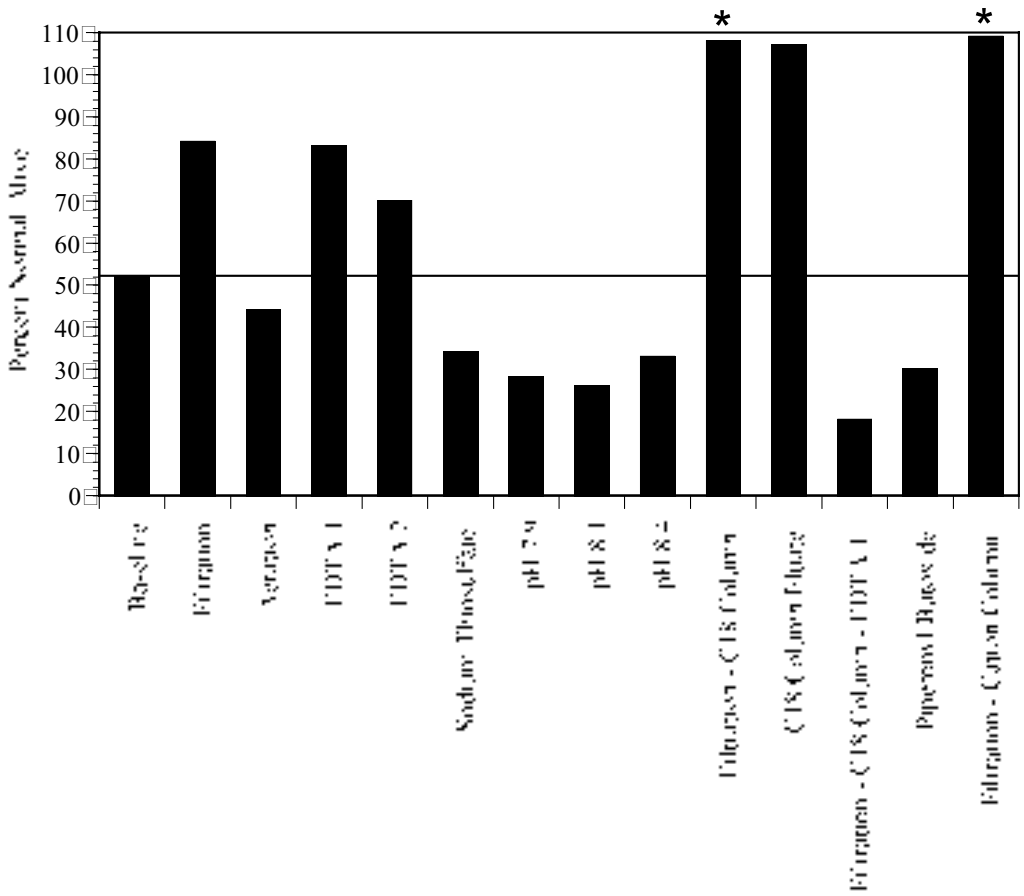

Figure 4. Results of TIE manipulations on 25% sediment elutriate from San Joaquin River (April 1998). Asterisk (*) indicates a significant reduction of toxicity compared to Baseline treatment.

February 1999 Freshwater and Marine Elutriate Tests and Metals Analyses

Elutriate samples were prepared with seawater and freshwater to determine if sample toxicity was significantly altered by salinity. Freshwater elutriate prepared with Grizzly Bay sediment was significantly toxic to the alga *Selenastrum* (Figure 5). No other freshwater toxicity was observed. Marine elutriates from all three sites were toxic to *Mytilus*, but none were toxic to purple sea urchin embryos. Significant toxicity was noted in the San Joaquin River sample when tested with purple sea urchin embryos in 1998 (Table 1). SWI exposures with *Mytilus* were also significantly toxic (Figure 5).

Selected metals were analyzed in freshwater and marine elutriate, and overlying water from SWI exposures. There was no obvious pattern in the concentrations of metals in the three matrices (Table 5). The highest concentrations from Grizzly Bay were found in freshwater elutriate, while Sacramento River and San Joaquin River had the highest concentrations in marine elutriate and in the marine SWI overlying water, respectively. Concentrations of Ag, As, Cr and Cu in marine salinity samples were close to, or below, background concentrations. Cd concentrations in freshwater samples were also close to background levels. The Cu concentration in freshwater elutriate from Grizzly Bay was above the EC50 for both freshwater test organisms, but only the *Selenastrum* demonstrated significant toxicity. Marine

Table 4. Results of metals analysis for filtered elutriate samples sampled in April 1998. [a]Martin et al. 1981, [b]MPS unpublished data.

Station Name	Ag mg/L	Al mg/L	As mg/L	Cd mg/L	Cr mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Ni mg/L	Pb mg/L	Zn mg/L
Grizzly Bay	0.55	5.8	44.2	1.77	8.9	9.6	19.9	22640	10.9	0.47	19.3
Sacramento River	0.069	14.3	33.2	1.45	15.9	9.1	47.3	12459	18.7	0.46	13.3
San Joaquin River	0.056	7.6	29.6	0.51	21.2	7.54	144.0	26028	23.7	0.34	15.0
Mytilus LOEC				5600[b]		5.6[b]					
Mytilus EC50	14[a]			3530[b]		7.13[b]					175[a]

copper concentrations were above the EC50s for marine organisms, but because the background concentration was so high these numbers are suspect.

Discussion and Conclusions

Two of the study sites are located in potentially high-energy river mouths. Sacramento River and San Joaquin River receive varying levels of sediment deposition depending on flow events. Grizzly Bay is also influenced by these rivers and by tidal action from San Pablo Bay. Seasonal sediment constituents vary and efforts to determine the causes of elutriate toxicity are confounded by this variability. Regardless of the transient nature of the study sites, the toxicity signal has remained consistently strong. Bi-yearly sampling has shown significant inhibition of embryo-larval development in all but one sample since 1993.

Although the river sites are fresh water and Grizzly Bay is heavily influenced by fresh water, the use of freshwater and marine test organisms with varying sensitivities has demon-

Table 6. Total, Labile and Cupric Ion concentrations (µg/L) for overlying water sampled from marine and freshwater sediment-water interface exposures, and a copper reference toxicant test. Asterisk (*) indicates sample not measured. Double asterisk (**) indicates No Observed Effect Concentration and Lowest Observed Effect Concentrations.

	Total Copper mg/L	Labile Copper mg/L	Cupric Ion mg/L	Larval Development (% normal alive)
Seawater SWI				
Grizzly Bay	1.099	0.464	0.018	28
Sacramento River	*	*	*	32
San Joaquin River	0.782	0.477	0.020	56
Control Water	0.070	0.032	0.001	73
Fresh Water SWI				
Grizzly Bay	0.635	0.483	0.044	
Sacramento River	0.508	0.534	0.048	
San Joaquin River	1.411	0.902	0.082	
Control Water	2.802	0.585	0.053	
Dose Response Concentration				
0 mg/L	0.235	0.083	0.004	80
1.8	1.595	0.496	0.022	81
3.2	3.438	1.957	0.085	89 NOEC**
5.6	5.103	2.898	0.126	78 LOEC**
10	9.843	7.403	0.322	1
18	18.206	15.315	0.666	0

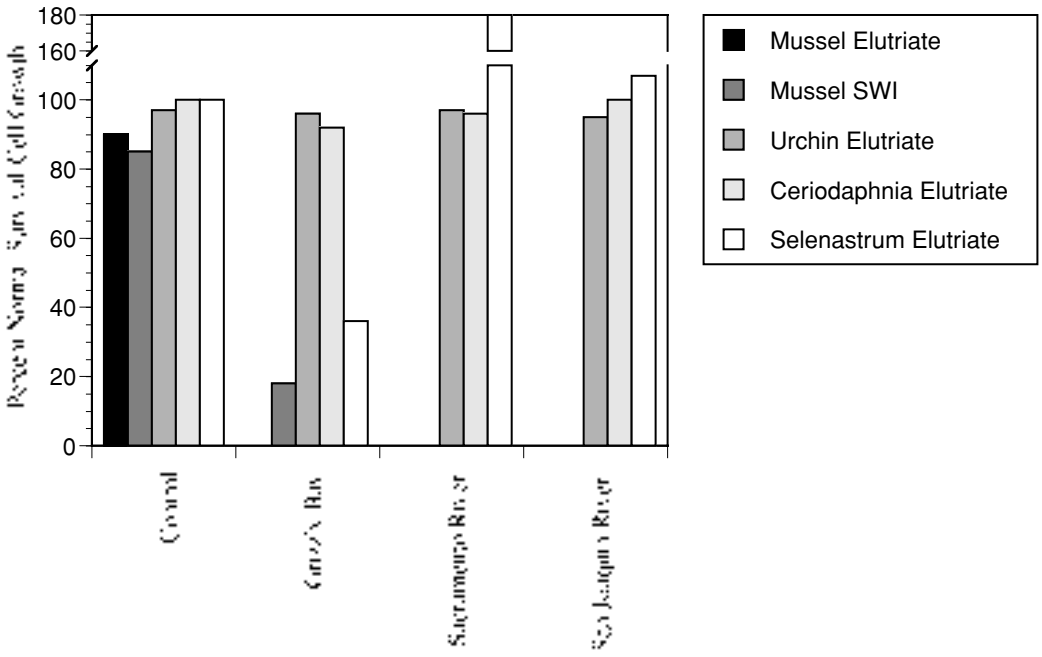

Figure 5. Results of marine and freshwater elutriate tests, and marine sediment-water interface tests (February 1999).

strated that toxicity is not simply an artifact due to adjusting the sample salinities. A significant reduction in the growth rate of *Selenastrum* was detected when this alga was exposed to freshwater elutriate prepared from Grizzly Bay sediment. Purple sea urchin larval development tests have been conducted twice with varying results suggesting that sediment constituents changed between sampling periods.

The initial pH of the elutriate samples in the bi-yearly toxicity tests was generally low enough to cause the observed toxicity (Phillips et al., 1997). Initial pH values during these tests have ranged from 6.20 to 7.74, with abnormal development being observed in range-finding tests below 7.50. Although the pH value of Grizzly Bay and San Joaquin River elutriate samples were low enough to cause the observed toxicity in the baseline TIE tests, manipulations of sample pH would have mitigated toxicity if pH was the only factor contributing to abnormal development. Toxicity was also observed in SWI exposures where overlying water pH was within tolerance limits.

The TIE manipulations on sediment elutriate samples and sediment-water interface exposures indicate divalent cations are the likely cause of toxicity at the three river delta sites. EDTA and the Cation Column treatments successfully removed toxicity to some degree in all three samples. The C18 Column also removed toxicity from the Sacramento River sample indicating that non-polar organic contaminants could also be contributing to toxicity at this site. Chemical analyses of sediment elutriate samples have demonstrated variable concentrations of trace metals that have generally been below the effect thresholds of the test organism. Copper concentrations have been near or above the effect threshold on several occasions, but copper is probably not the only cause of toxicity. Other metals may have contributed to toxicity through additivity. Masnado et al. (1995) found that combinations of metals with concentrations below NPDES water quality permit limits were toxic to *Ceriodaphnia dubia*.

Table 5. Results of metals analysis for filtered freshwater and marine elutriate samples and marine overlying water samples from SWI exposures. All samples collected in April 1998. [a] Martin et al. 1981, [b] MPSL unpublished data.

Station Name	Test Matrix	Ag µg/L	Al µg/L	As µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Mn µg/L	Ni µg/L	Pb µg/L	Zn µg/L
Grizzly Bay	Fresh Elutriate	0.21	8931	5.99	0.15	39.9	47.1	479	48.7	15.8	53.4
	Marine Elutriate	ND	75.3	48.4	1.6	7.8	12.1	10101	20.2	ND	ND
	Marine SWI	ND	174	31.1	0.31	5.41	9.44	52.5	10.3	0.2	5.22
Sacramento River	Fresh Elutriate	0.01	232	1.08	0.016	1.23	2.42	8.6	3.8	0.56	0.24
	Marine Elutriate	ND	12.4	56.2	1	15.9	15.9	923	21.8	ND	ND
	Marine SWI	ND	ND	33.4	0.38	10.9	11.6	174	16.3	ND	ND
San Joaquin River	Fresh Elutriate	0.03	919	9.42	0.11	2.4	10.6	160	4.97	2.79	0.43
	Marine Elutriate	ND	16.5	51.4	0.09	11.8	14.9	4167	16.5	0.12	ND
	Marine SWI	1.15	151	78.5	1.61	9.33	14.7	19.8	24.9	11	15.8
Control Water	Fresh	ND	4.92	ND	0.031	0.44	0.74	0.43	1.63	0.073	ND
	Marine	0.46	5.43	52.8	0.27	13.6	13.3	0.2	7.09	0.43	ND
Ceriodaphnia EC50	Fresh						17.6[b]				
Selenastrum EC50	Fresh						25.6[b]				
S. purpuratus EC50	Marine				436[b]		17.6[b]				95.9[b]
Mytilus EC50	Marine	14[a]			3530[b]		7.13[b]				175[a]

Combinations of cadmium and copper can have a synergistic effect while combinations of these metals with zinc can have an antagonistic effect (MPSL, unpublished data). The toxicity of metals in combination is part of a continuing State Water Board study at MPSL.

Because copper concentrations were high enough to cause some of the observed toxicity, the free copper ion concentrations in sediment-water interface exposures were analyzed. When SWI cupric ion concentrations were compared to a cupric ion dose response it was determined that the concentrations of free copper ion were approximately 15% of the cupric ion LOEC value. Cupric ion concentrations from the current dose-response experiment were compared to measurements taken by Rivera et al. (1999) using a copper-ion-selective electrode. The cupric ion EC50 value generated from this project compared favorably to those generated by Rivera et al. (1999). Interference was encountered when measuring the cupric ion concentration in the Sacramento River marine sample. Although the source of the interference was not determined, it may have been additional divalent cations or an organic contaminant. Interference due to organic contaminants agrees with TIE results that also suggested the presence of organic contaminants in the Sacramento River samples.

To further pursue the causes of toxicity in these samples, specific procedures that isolate and add back metals will be conducted using a cation exchange column. After metals are removed with the column, they will be serially eluted from the column using different strengths of a weak acid solution. Each fraction will be tested for toxicity to bivalves and measured chemically to determine the concentrations of metals. Toxicity and chemistry results can then be compared to those of a spiked experiment to determine what metals are contributing to toxicity.

While experimental, this technique holds promise to improve our ability to separate the relative contributions of a mixture of toxic metals in sediment elutriate samples.

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