

Patterns and trends in sediment toxicity in the San Francisco Estuary

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Abstract

Widespread sediment toxicity has been documented throughout the San Francisco Estuary since the mid-1980s. Studies conducted in the early 1990s as part of the Bay Protection and Toxic Cleanup Program (BPTCP), and more recently as part of the Regional Monitoring Program (RMP) have continued to find sediment toxicity in the Estuary. Results of these studies have shown a number of sediment toxic hotspots located at selected sites in the margins of the Estuary. Recent RMP monitoring has indicated that the magnitude and frequency of sediment toxicity is greater in the winter wet season than in the summer dry season, which suggests stormwater inputs are associated with sediment toxicity. Additionally, spatial trends in sediment toxicity data indicate that toxic sediments are associated with inputs from urban creeks surrounding the Estuary, and from Central Valley rivers entering the northern Estuary via the Delta. Sediment toxicity has been correlated with a number of contaminants, including selected metals, PAHs and organochlorine pesticides. While toxicity identification evaluations (TIEs) suggest that metals are the primary cause of sediment toxicity to bivalve embryos; TIEs conducted with amphipods have been inconclusive.

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1. Introduction

Contaminants entering the San Francisco Estuary from river, urban, and industrial sources tend to become associated with sediments in this system (Shoelhammer, 2002). Sediment-associated pollutants may directly or indirectly impact benthic communities (Swartz et al., 1994; Hunt et al., 2001b; Thompson and Lowe, 2004), and are a primary source of tissue contamination in higher trophic level species (Fairey et al., 1997; see conceptual model by Thompson et al., in press). Widespread sediment toxicity has been documented in this estuary by monitoring studies begun in the middle 1980s by the National Oceanic and Atmospheric Administration (NOAA) and others, (Long et al., 1990; Chapman et al., 1987).

Prior to then, a number of earlier studies by the US Geological Survey documented sediment toxicity to resident infaunal species, such as the clam *Macoma balthica*. Reproductive effects on this species were linked to elevated metal concentrations associated with sewage treatment plant discharges in the southern Estuary (Hornberger et al., 2000). Similar studies showed growth and body condition effects in resident freshwater clam species in the northern Estuary (Johns and Luoma, 1990; Luoma et al., 1990).

In 1991, the San Francisco Bay Regional Water Quality Control Board (Regional Board) began pilot studies on contaminant concentrations and possible ecological effects in the Estuary as part of the Bay Protection and Toxic Cleanup Program (BPTCP). Sediment toxicity testing was an integral component of the BPTCP. Subsequent collaboration between waste dischargers, regulators, and other stakeholders resulted in establishment of the San Francisco Estuary Regional Monitoring Program (RMP) in 1993 and its design incorporated many of the monitoring components used in the BPTC.

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The primary objectives of the RMP are to measure contaminant concentrations in water, sediment, and tissues to provide information on the distribution of contaminants in the Estuary, and to document variation in contamination over time. This includes sediment toxicity tests, which serve as important contaminant effect measures in this program.

Regulatory agencies responsible for environmental management have combined information from laboratory toxicity tests, benthic community characterizations and chemical analyses of sediments and tissues to assess the ecosystem's health.

The Regional Board is responsible for protecting beneficial uses of water in the region, including maintaining water quality to support estuarine habitat. Water quality objectives to protect beneficial uses include numeric objectives for concentrations of contaminants, and narrative objectives for biological impacts. Narrative objectives require that all waters shall be maintained free of toxic substances in concentrations that produce detrimental effects in aquatic organisms. Narrative objectives further require that controllable water quality factors shall not cause a detrimental increase in concentrations of toxic substances found in bottom sediments or aquatic life.

Water and sediment toxicity tests have been used to monitor compliance with these objectives. Although there are no sediment quality objectives specific for California waters, published effects-based guidelines have been used to assess sediment contamination in the Estuary (Long et al., 1995). Sediment chemistry data from the RMP and the BPTCP have also been used to develop ambient sediment guidelines specifically for the San Francisco Estuary (Gandesbery and Hetzel, 1998). These values have been used to screen sites for further investigation by comparing sediment chemistry at stations of interest to ambient guideline values.

However, these guidelines are not based on biological effects. Statewide sediment quality objectives are now being developed for California (Bay et al., 2003), and this process includes evaluation of synoptic toxicity and chemistry data from the BPTCP and RMP. Given the lack of specific sediment quality objectives, the use of a triad approach of synoptic sediment toxicity tests, sediment chemistry, and benthic community analyses has been shown to be useful in providing a weight-of-evidence to inform management decisions regarding estuarine habitat quality.

This report is intended to synthesize results of past sediment toxicity investigations in the San Francisco Estuary and to summarize results of more recent unpublished studies. In addition to describing spatial and temporal patterns of impacts associated with sediment pollutants, we summarize what is known about the likely sources and causes of sediment toxicity. The emerging picture suggests that sediment toxicity continues to be widely observed, and is largely related to seasonal inputs of contaminant mixtures from urban creeks and storm water conveyances at the margins of the system, as well as from

Central Valley rivers via the Delta. These impacts are discussed in the context of evolving resource management issues in the San Francisco Estuary.

2. Methods

Sediment monitoring data from four related programs are summarized in this paper. The California BPTCP sampled sediments from 1991 and 1995. The San Francisco Estuary RMP began in 1993, monitoring many of the same sites as the BPTCP, as well as some new sites. The NOAA National Status and Trends Program (NST) sampled sediment in the summers of 2000 and 2001. The US Environmental Protection Agency's (EPA's) Environmental Monitoring and Assessment Program (EMAP) sampled sediments in summers of 2000 and 2001. Each program used similar methods. Detailed methods for sampling, toxicity testing, chemical and physical analyses have been reported elsewhere (RMP: Thompson et al., 1999; BPTCP: Hunt et al., 2001a,b; NST: National Oceanic and Atmospheric Administration (NOAA), 1991; EMAP: Weisberg et al., 1993).

A number of different sediment toxicity tests were conducted in the studies cited above. All solid-phase samples from studies conducted as part of the RMP and BPTCP were tested with the estuarine amphipod *Eohaustorius estuarius* using the 10-d growth and survival protocol (US Environmental Protection Agency, 1994). All solid-phase samples for studies conducted by NOAA NST and EPA EMAP were tested with the estuarine amphipod *Ampelisca abdita* using the 10-d growth and survival protocol (US Environmental Protection Agency, 1994). Both protocols are identical except for differing salinities and temperatures (*E. estuarius* = 20‰ @ 15 °C; *A. abdita* = 28‰ @ 20 °C). The EMAP stations were also tested with *E. estuarius* for comparison to *A. abdita*. All RMP samples were also tested with the 48-h embryo development protocol using mussels (*Mytilus galloprovincialis*). Mussel tests were conducted using sediment elutriates (water soluble fraction) with percent normal larval development as the endpoint (ASTM, 1991). Elutriate solutions were prepared by adding 100 g of sediment to 400 mL of clean sea water, shaking for 10 s, settling for 24 h, and decanting the eluate.

In addition to these toxicity tests, additional toxicity tests were used to assess sediment porewater toxicity as part of the NOAA NST study in 2000 and 2001. Porewater toxicity was assessed using the sea urchin (*Arbacia punctulata*) 48-h embryo development test, and the *A. punctulata* 1-h fertilization test (Carr et al., 2000). Some additional toxicity tests were also evaluated in the BPTCP study discussed below. Detailed methods for these additional tests are provided in Hunt et al. (2001a). Methods for toxicity identification evaluations (TIEs) conducted as part of BPTCP studies are reported in Hunt et al. (2001b). TIE methods used in RMP studies are described below.

2.1. Data analysis

Spatial and temporal trends in toxicity were first examined by graphing and mapping the data. Relationships between sediment contamination and amphipod toxicity were determined using principal components analysis (PCA), correlation analysis, and multiple regression (SAS Institute, 1995). Sediment chemical concentrations were compared to effects range median (ERM) sediment quality guideline values (Long et al., 1995). ERM values were also used to calculate a mean ERM quotient (mERMq; Long et al., 1998), as a means of evaluating concentrations of chemical mixtures.

In addition, effects of sediment contaminant mixtures in the NOAA NST 2000–2001 data set were investigated by correlating toxicity test results with the sediment quality guideline value SQGQ1, calculated according to Fairey et al. (2001). The SQGQ1 combines a number of different published guideline values including ERMs, probable effect levels (PELs), and consensus-based sediment quality guidelines. This measure has been demonstrated to be useful in predicting chemical mixtures

associated with amphipod mortality in laboratory tests (Fairey et al., 2001).

3. Results and discussion

3.1. Bay protection and toxic cleanup program studies

As part of the BPTCP, a series of sediment quality assessments were conducted in the 1990s to guide remediation and management of contaminated sediments in the bays and estuaries of California (Long and Wilson, 1997; Fairey et al., 1998, 2001; Anderson et al., 2001; Hunt et al., 2001a, b). One of the primary goals of the BPTCP was the identification of contaminated sites in need of management. BPTCP sediment work in San Francisco Bay was carried out in four phases: a pilot study to guide development of an RMP, an evaluation of candidate sediment toxicity reference sites, an extensive toxicity screening of the Bay margins, and an intensive evaluation of potential toxic hot spots.

In the pilot program conducted in 1991 and 1992, contaminants and toxicity were measured in sediments, sediment elutriates, and pore waters; and 15 toxicity test protocols were evaluated for use in sediment quality assessments (Flegal et al., 1994; Hunt et al., 1998). Samples were collected from marsh sites, bay sites, and along a contamination gradient in Castro Cove. These studies identified sites for future regional monitoring, and demonstrated the utility of several analytical methods, including trace metal analysis of porewater and sediment toxicity testing with selected protocols.

The BPTCP studies used a number of criteria to evaluate toxicity test protocols. The following tests were evaluated: homogenized sediment tests with the amphipods *A. abdita*, *Rhepoxynius abronius*, and *E. estuarius*, the polychaete *Neanthes arenaceodentata*, and the Leptostracan *Nebalia pugettensis*; intact sediment tests with *E. estuarius*; elutriate tests with *Atherinops affinis*, *Menidia beryllina*, *Crassostrea gigas*, and *Mytilus edulis*; porewater tests with *E. estuarius*, *C. gigas*, *M. edulis*, and *Strongyocentrotus purpuratus*; and sediment–water interface tests with *S. purpuratus*. The solid-phase sediment test with the amphipod *E. estuarius* was selected as an appropriate indicator species for regional monitoring because it consistently met test acceptability criteria, was capable of distinguishing between more and less contaminated sediments, and was tolerant of wide ranges of salinity and grain size. Elutriate, pore water, and sediment–water interface tests with mussel and sea urchin embryos also ranked well in terms of test performance, availability, sensitivity, and tolerance of natural sediment conditions (Hunt et al., 2001a, b).

Previous studies in the Estuary demonstrated the necessity for identifying suitable reference sites for comparison to test sites in sediment quality surveys (e.g., Long et al., 1990; Flegal et al., 1994). Such sites are necessary because evaluation of sediment toxicity often involves making comparisons between sites of interest and sites

thought to characterize regional conditions of minimal impact. The second phase of BPTCP studies in the San Francisco Estuary was conducted to meet the following two objectives: (1) identify reference sites that characterized the optimal ambient sediment quality existing in the Estuary, and (2) use data from the selected reference sites to establish standards against which to compare test site data for determination of significant sediment toxicity (Hunt et al., 2001a). Five sediment reference sites were selected on the basis of low concentrations of anthropogenic chemicals, distance from active contaminant sources, location in representative hydrographic areas of the Bay, and physical features characteristic of depositional areas (e.g., fine grain size and medium TOC). Three RMP sites that met the BPTCP reference site criteria were used to provide additional data to develop toxicity tolerance limits for the *Eohaustorius* amphipod test. The relative toxicity standards, or tolerance limits, were based on a confidence interval around a percentile of the reference data distribution (Smith, 2002). A detailed description of the derivation of tolerance limits based on reference site toxicity data is provided in Hunt et al. (2001a).

After sampling three field replicated stations at each reference site during three seasons, eight sites were found to meet program criteria for low contaminant concentrations and low toxicity, with grain size and total organic carbon characteristics similar to known contaminated sites. The primary toxicity tests, using amphipods and sea urchin embryos, produced rates of survival or normal development greater than 80% of the control response in 88% of the 149 tests. Tolerance limits representing the lowest 10th percentile of the reference data distribution (with 95% confidence) were: 70.9% survival for the amphipod *A. abdita*, 69.5% survival for the amphipod *E. estuarius*, 94.3% normal development for sea urchins in pore water, and 86.7% normal development for sea urchins at the sediment–water interface. The study indicated that when reference sites were well characterized and the assumptions of the tolerance limit method were carefully considered, this approach could effectively distinguish impacted conditions (Hunt et al., 2001a).

Having conducted a pilot regional monitoring project, evaluated toxicity test protocols, selected reference sites, and reviewed approximately 100 previous reports, the BPTCP began a directed toxicity screening of 127 sites around the margins of the Bay as part of the third phase of the study. These were sites where there was some evidence of elevated chemistry and/or toxicity, or where there were suspected sources of contaminants. This screening found that 21% of samples tested were toxic to amphipods, 31% of porewater samples were toxic to sea urchin embryos, and 33% were toxic to sea urchin embryos exposed at the sediment–water interface.

The final phase of the BPTCP was a confirmation phase, in which twelve stations were resampled and analyzed with the sediment quality triad approach (two toxicity tests, sediment chemistry, and benthic community analysis). Ten

of these stations were also analyzed for contaminant bioaccumulation, using 28-day laboratory exposures with the clam *Macoma nasuta*. A total of 46 stations were screened for a broad suite of trace metal and organic compounds, and a total of 143 samples were analyzed for mercury and PCBs, chemicals that were previously identified as elevated in Estuary fish tissues. Gradient studies were conducted at some confirmation sites to evaluate relationships between sediment chemistry and biological effects, and Phase I sediment TIEs were conducted at three sites.

The confirmation study identified several highly polluted locations that exhibited adverse biological effects, all located near the margins of the Estuary. A number of sites had high concentrations of chemical mixtures, numerous chemicals with concentrations above sediment quality guideline values, and significant benthic community impacts and/or toxicity. The sites exhibiting the highest chemical concentrations and greatest biological effects were: Stege Marsh, Mission Creek, Islais Creek, SF Central Basin, Point Portrero, Pacific Drydock, Oakland Fruitvale, Castro Cove, Peyton Slough, and San Leandro Bay (Fig. 1).

Statistical analyses indicated a number of chemicals that were both correlated with toxicity and found at concentrations exceeding ERM sediment quality guideline values. Mercury and total PCBs were found at elevated concentrations in a number of sediment samples analyzed in this study. Elevated tissue concentrations of PCBs were measured in clam bioaccumulation tests and sediment concentrations of mercury were significantly correlated with toxicity to sea urchin embryos in sediment–water–interface tests. However, mercury and PCBs co-occurred with numerous other contaminants in these samples and were not specifically identified as the cause of observed toxicity.

Chemicals commonly exceeding ERM guideline values included chlordanes, PCBs, DDTs, PAHs, dieldrin, copper, mercury, lead and zinc. Combined concentrations of chemical mixtures were high at many sites, with nine sites having mean ERM guideline quotients above the 95th percentile of the statewide distribution. Multivariate (PCA) analyses identified a suite of chemicals that both exceeded guideline values and were associated with toxicity. These included: total chlordanes and 2-methylnaphthalene (associated with amphipod toxicity); cadmium, copper, silver, and zinc (with sea urchin porewater toxicity); and cadmium, copper, and zinc (with sea urchin SWI toxicity). Nine chemicals or chemical classes were found at elevated concentrations in clam tissues when compared to clams exposed to control sediment: copper, lead, total chlordanes, total DDTs, dieldrin, total PCBs, LMW PAHs, HMW PAHs, and total PAHs (Hunt et al., 2001b).

Porewater TIEs were conducted in samples from Guadalupe Slough and Peyton Slough. Both sites were located on the Bay margin and received urban/industrial runoff. Toxicity of the Guadalupe Slough was

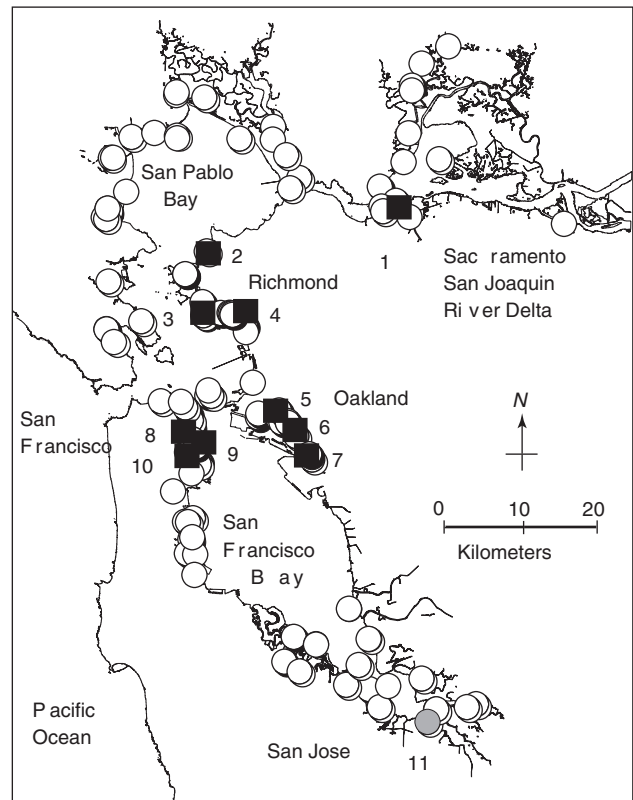


Fig. 1. Map of San Francisco Bay showing the location of 111 BPTCP stations screened for sediment toxicity (○), and the ten sites investigated in additional surveys and selected as candidate toxic hot spots (■). The ten candidate toxic hot spots were (1) Peyton Slough, (2) Castro Cove, (3) Point Potrero, (4) Stege Marsh, (5) Pacific Drydock, (6) Oakland-Fruitvale, (7) San Leandro Bay, (8) Mission Creek, (9) Central Basin, and (10) Islais Creek. Toxicity identification evaluations were conducted on porewater samples from Sites 1 and 11 (Guadalupe Slough), and gradient studies were conducted at Sites 1, 8, and 10.

reduced substantially 95% only by addition of EDTA, implicating trace metals as the cause of toxicity. In the Peyton Slough TIE, high toxicity was observed in pore water diluted to 15% strength in the initial test. Toxicity was reduced by addition of EDTA, addition of STS, filtration, and C-8 column extraction, and this information combined with chemical analyses of bulk-phase sediment from Peyton Slough indicated toxicity was likely due to high concentrations of copper, zinc, cadmium and other metals.

Stege Marsh samples were highly toxic (0% normal development) to sea urchins in sediment/water interface (SWI) exposures (Hunt et al., 2001b). As a TIE step, water overlying the intact sediment core was treated with EDTA, which partially reduced toxicity, indicating that trace metal flux from sediment into overlying water was partially responsible for that toxicity. However, the high toxicity of Stege Marsh samples was likely due to combined effects of the numerous metal and organic contaminants measured at very high concentrations in test sediments (Hunt et al., 2001b).

3.2. Regional monitoring program studies: 1993–2001

Beginning in 1993, the RMP evaluated toxicity of sediments to mussel embryos (*M. galloprovincialis*) and amphipods (*E. estuarius*) at 14 stations during wet (February–April) and dry (August–September) sampling periods. Like the BPTCP pilot RMP study, RMP stations were located along the center axis line running through the northern, central and southern regions of the Estuary. For each seasonal sampling period since 1993, the percentage of sediment samples that were toxic to at least one test organism ranged from 33% to 100%. Between 1997 and 2001, 63% of the sediment samples tested were toxic to at least one test organism (Fig. 2).

Patterns of toxicity differed with sediment and sediment elutriate tests. Certain stations were consistently toxic to bivalve embryos. These included Grizzly Bay and the river stations in the northern estuary, and the Coyote Creek and San Jose stations in the south bay (Fig. 3). Stations toxic to amphipods included Grizzly Bay, the Napa River, Yerba Buena Island, Redwood Creek and the South Bay.

Although there were no clear overall trends in toxicity, clear seasonal differences were observed (Fig. 3). The magnitude and frequency of sediment toxicity were greater in the Estuary during the winter seasons than in the summer seasons during this period. This seasonality



Fig. 2. Incidence of sediment toxicity to amphipods and bivalve embryos in samples collected by the RMP Status and Trends Program from 1997 to 2001.

suggests that storm water inputs were an important source of contaminants associated with sediment toxicity, particularly to amphipods. For example, 51% of the winter samples tested between 1993 and 1999 were toxic to amphipods, compared to only 16% of the summer samples Anderson et al. (2003).

Since 2000, the RMP shifted to dry season-only monitoring as part of a redesign of the status and trends component of the program. The switch to dry-season monitoring follows procedures used by the US EPA's EMAP. It is intended to assess long-term trends in contamination and toxicity, separate from any short-term seasonal effects caused by storm-water runoff.

Certain stations in the Estuary have been consistently toxic to amphipods and mussel embryos since the program was redesigned. Samples from Grizzly Bay, the mouth of the Napa River, Redwood Creek, and the South Bay have been consistently toxic to amphipods. All samples collected in the northern Estuary (Grizzly Bay and the Sacramento and San Joaquin Rivers) have been toxic to mussels since 1994.

Analyses of contaminant associations with sediment toxicity have resulted in a variety of significant ($P < 0.05$) correlations using multiple regression analyses (Thompson et al., 1999). These are probably due, in part, to the complex mixtures of chemicals involved. For example, comparisons of the chemical and toxicity test data indicate that amphipod mortality correlates with mixtures of chemicals in sediments, as well as with specific metals (e.g., silver, cadmium), pesticides (e.g., chlordanes) and PAHs (Thompson et al., 1999).

ERM values were also used to calculate an mERMq. The concentration of each contaminant was divided by its ERM to produce a quotient, or proportion of the ERM. Quotients calculated for all contaminants in each sample were summed to produce a cumulative ERM 'index'. Since the number of contaminants measured by each monitoring program was slightly different, the summed quotients were divided by the number of contaminants whose ERMs were used to calculate each sum. To avoid weighting, only ERMs for low molecular weight PAHs (LPAHs), high molecular weight PAHs (HPAHs) and total DDT were used, instead of those for individual compounds or isomers. Using these criteria, Thompson et al. (1999) found that sediments with mERMq values greater than 0.22 were always toxic to *E. estuarius* in the Estuary sediments sampled from 1991 to 1996. These results were similar to those reported by Hunt et al. (2001b), who also found strong correlations ($P < 0.05$) between amphipod mortality and elevated concentrations of chlordanes, PAHs, and selected trace metals.

Hunt et al. (2001b) found that an average of 66% of samples were toxic to amphipods when mean ERMq values were between 0.22 and 0.50. These ERMq values are comparable to the mean ERMq where benthic community degradation is observed in Estuary field samples. Thompson and Lowe (2004) found that 63% of samples with

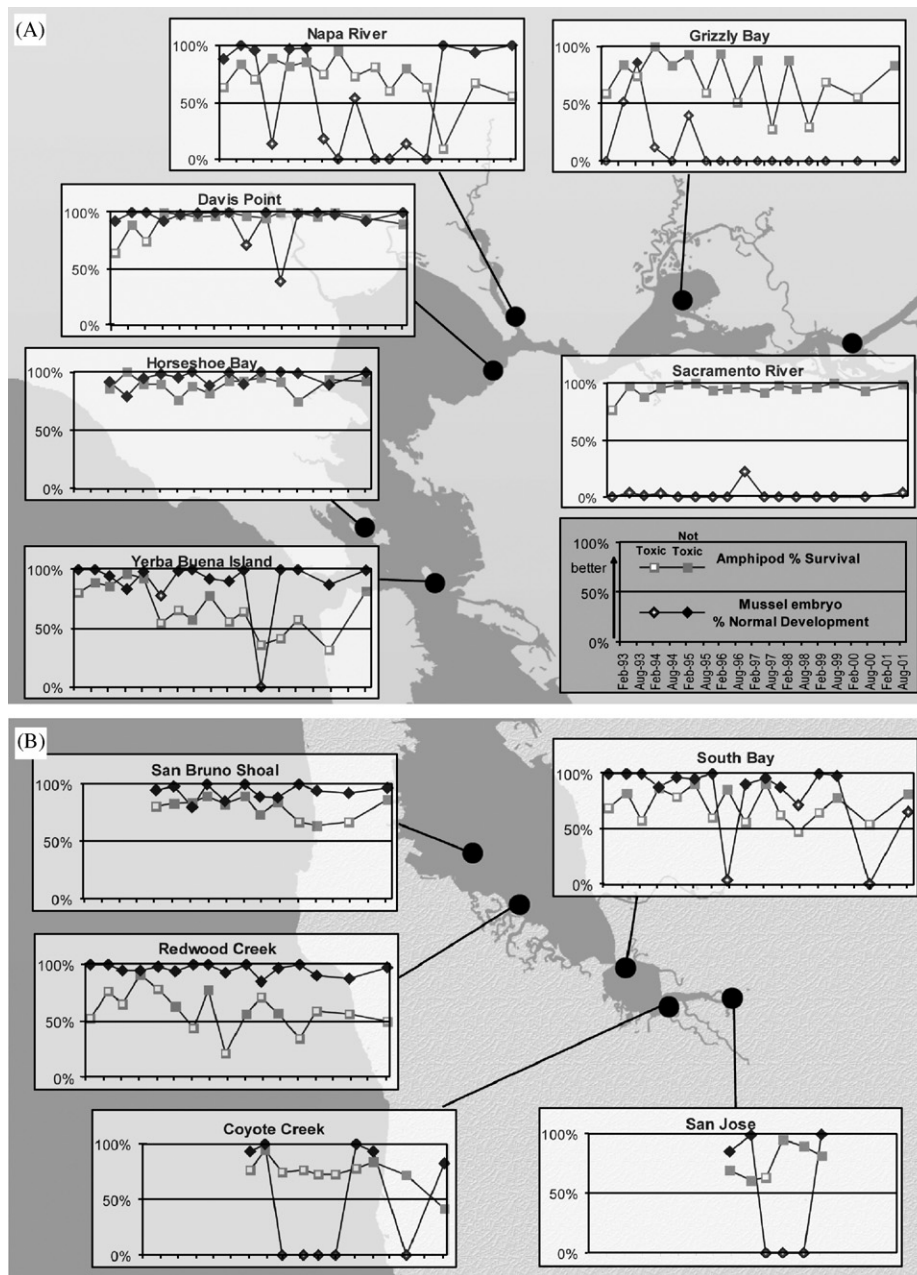


Fig. 3. Results of amphipod and bivalve embryo development toxicity tests showing magnitude of response and seasonal trends: (a) Northern and central Estuary stations; (b) Southern Estuary stations.

mean ERMq values between 0.147 and 0.635 (using a modified calculation of the ERMq) had degraded benthic communities. While the studies cited above sometimes used different combinations of ERM guidelines in their calculation of the ERMq, all showed effect thresholds around ERMq values of 0.2.

3.3. RMP toxicity identification evaluations (TIEs)

TIEs are considered an important tool to support sediment quality management in the San Francisco Estuary. Where the TIE process can identify the specific chemicals responsible for sediment toxicity, further in-

vestigations may be used to identify sources of these contaminants, and appropriate source control procedures can then be implemented. For example, as part of BPTCP activities in the northern Estuary, Hunt et al. (2001b) used TIEs in samples from Peyton Slough to indicate that divalent cations were responsible for toxicity to sea urchin embryos. Analyses of sediments from this site showed elevated concentrations of copper, zinc, and cadmium. When combined as a weight-of-evidence with the other sediment quality triad data, TIEs serve as an important tool to inform the regulatory process.

Since the beginning of the RMP, several stations have demonstrated consistent or seasonal toxicity to amphipods

and bivalves, and TIEs have been used to investigate causes of sediment toxicity at a number of these stations. The TIE process is designed to proceed in three phases: characterization, identification, and confirmation (United States Environmental Protection Agency, 1996). Since 1996, TIEs have been conducted on sediment elutriate samples from eleven stations that were toxic to bivalve embryos.

Phillips et al. (2003) used Phase I TIE procedures to demonstrate that sediment elutriate toxicity to bivalve embryos in Grizzly Bay sediment was caused by cationic metals. They also found that addition of the chelate EDTA to overlying water in Grizzly Bay sediment core tubes reduced toxicity to bivalve embryos exposed at the sediment–water interface. Then, Phase II TIE procedures using sediment elutriate combined serial elutions of a cation exchange column with increasing hydrochloric acid concentrations with toxicity tests and chemical analyses of the different eluates. These results demonstrated that toxicity to bivalves was most likely caused by copper (Phillips et al., 2003).

A number of additional Phase I TIEs were conducted at RMP stations located throughout the Estuary. In the majority of cases, toxicity to bivalve embryos was reduced by treatments that reduce bioavailability of divalent cations (i.e., EDTA, STS, Cation column; Table 1). Analyses of total metal concentrations in these samples have consistently shown, however, that metals were well below published effect thresholds for toxicity to *Mytilus* embryos. Thus, there has been a clear trend of divalent cations contributing to inhibition of bivalve embryo development, but in most cases, specific metal(s) have not been identified.

These results are consistent with TIE evidence from Peyton and Guadalupe Slough, which also suggested

porewater toxicity to sea urchin embryos was caused by divalent cations (Hunt et al., 2001b). In some cases, TIE evidence has indicated other non-metal constituents were responsible for elutriate toxicity (Phillips et al., 2000). For example, TIE evidence suggested particles and organic chemicals may have been partially responsible for toxicity in the Sacramento and San Joaquin River samples tested in 1998 (Table 1).

Solid-phase TIEs have been conducted on sediment from two stations, Redwood Creek and Grizzly Bay. Solid-phase treatments used a variety of published methods, including addition of cation exchange resin to reduce metal bioavailability and addition of powdered coconut charcoal to reduce trace organics bioavailability (Burgess et al., 2000; Ho et al., 2004). Sediment was also leached in weak acid (0.5 M HCl) to remove weakly bound metals, and concentrations of metals and organics were analyzed in amphipod tissues after exposure to acid-treated sediment. Because unionized ammonia is a common toxic constituent of sediments, unionized ammonia concentrations were measured in all samples for comparison to toxicity thresholds. In the TIE results discussed below, unionized ammonia concentrations were always well below toxicity thresholds for test organisms in these studies.

Information from solid-phase TIE treatments combined with concentrations of trace organics measured in tissues of sediment-exposed amphipods indicated that non-polar organic compounds were probably not the primary cause of acute toxicity of Grizzly Bay sediments to amphipods (Anderson et al., 2001). Addition of a metal-binding resin and coconut charcoal did not reduce toxicity of Grizzly Bay sediment. Solid-phase toxicity of this sediment was reduced considerably after leaching the sediment with 0.5 M HCl. Combined with chemical analyses of treated

Table 1

Summary of sediment elutriate bivalve embryo TIE results from the San Francisco Regional Monitoring Program. Black cells indicate treatments that significantly reduced toxicity, gray cells indicate treatment was conducted but did not reduce toxicity, and open cells indicate treatment was not conducted

Station Name/ Number	Year	Elutriate TIE Treatments							
		Aeration	Particle Removal	EDTA	STS	C18 Column	C18 EDTA	Graduated pH	Cation Column
Grizzly Bay BF21	1996								
	1998								
	2001								
Sacramento River BG20	1996								
	1998								
	2004								
San Joaquin River BG30	1996								
	1998								
	2004								
Coyote Cr./BA10	2002								
Yerba Buena/BC11	2002								
Lower So. Bay/ 011	2003								
Suisun Bay/ 011	2003								
Suisun Bay/ 013	2003								
Suisun Bay/ 015	2004								

and untreated sediments and of amphipod tissues after weak acid leaching, these results suggested that the most likely cause of amphipod toxicity in sediment from Grizzly Bay was an acid-soluble contaminant, such as a metal (Hunt et al., 2005). However, all metal concentrations in this sample were well below published ERM guidelines. Except for specific hot spot sites near the margins of the system (e.g., Hunt et al., 2001b), sediments in the Estuary are generally contaminated by complex mixtures of moderate concentrations of chemicals, resulting in lower magnitude toxicity. Moderate toxicity due to complex mixtures has complicated the TIE process because the procedures work best when there is a strong response in the baseline (untreated) sample. Despite this limitation, causes of elutriate and sediment toxicity in some samples have been characterized into broad classes of chemicals, such as toxicity to bivalves caused by cationic metals (Table 1).

3.4. Summary of NOAA-EMAP amphipod toxicity test results

In 2000, NOAA initiated a 2-year study to measure biological effects associated with sediment contamination in San Francisco Bay as part of the NST. This study was conducted in collaboration with the US EPA's EMAP and the San Francisco Estuary RMP. Toxicity tests using the amphipod *A. abdita* were conducted at 198 stations in two summer sampling periods in 2000 and 2001. During this study, toxicity at a subset of 48 stations was also assessed using the estuarine amphipod *E. estuarius*, as part of EPA funded research to compare the two amphipod species for use in future coastal monitoring efforts on the west coast.

These studies were designed to meet the following objectives: (1) to determine the incidence and severity of sediment toxicity based on bioassays with different species; and (2) to investigate the relationships between amphipod survival, bulk-phase contaminant concentrations, sediment physico-chemical properties, and indicators of macrobenthic community structure.

Sediments from 3 out of 198 stations (1.5%) were significantly ($P < 0.05$) toxic to *A. abdita*. Within the *A. abdita* and *E. estuarius* shared data set, no samples were toxic to *A. abdita*, while 32 of 48 samples (67%) were toxic to *E. estuarius*. PCA indicated that *A. abdita* survival was not correlated with any of the chemical or physical variables (Table 2).

Analyses showed that three factors accounted for the majority of variability in the dataset that included the *E. estuarius* toxicity test results, but no contaminants were significantly correlated with amphipod survival. *E. estuarius* survival was negatively correlated with fined grain sediments and TOC, but not bulk-phase contaminants (Table 2). Because contaminants co-occur with fined grain sediments and elevated TOC, it was not possible to resolve the relative effects of these variables on amphipod survival. Many stations with relatively fined grained sediments were observed to have high (>90%) amphipod survival (MPSL, 2003), and previous research has demonstrated that *E. estuarius* can tolerate up to 70% clay with negligible effects (Tay et al., 1998). Percent clay did not exceed 35% in any of the samples measured, so it unlikely this sediment constituent played a role in amphipod survival.

The reason for the observed difference in response between the two species is not clear, but one possibility

Table 2
Results of principal components analysis for amphipod survival and selected chemical and physical parameters

	<i>A. abdita</i> results			<i>E. estuarius</i> results		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
Amphipod survival	0.054	-0.366	-0.178	-0.096	-0.029	-0.617
Cadmium	0.720	0.031	-0.228	0.728	0.052	-0.124
Copper	0.641	0.129	0.277	0.631	0.125	0.245
Lead	0.871	0.178	-0.111	0.880	0.195	-0.059
Mercury	0.786	-0.019	0.037	0.788	0.004	0.047
Silver	0.745	-0.084	0.015	0.724	-0.067	0.181
Zinc	0.852	0.155	0.280	0.829	0.166	0.302
Total DDT	0.275	0.580	-0.237	0.273	0.612	-0.201
Total chlordane	-0.007	0.944	0.030	-0.040	0.944	0.084
Dieldrin	0.170	0.955	-0.047	0.144	0.968	0.009
Total PCB	0.700	0.320	-0.299	0.716	0.347	-0.227
Total organic carbon	0.733	0.150	0.427	0.696	0.145	0.469
Total PAH	0.066	0.018	-0.689	0.095	0.050	-0.534
SQGQ1	0.118	0.948	0.004	0.082	0.953	0.101
Fines	0.548	0.044	0.668	0.483	0.030	0.755
Variability	33.6	22.5	10.0	32.6	22.3	11.8
<i>n</i>	198			48		
Regression <i>p</i>						0.010

Component loadings greater than 0.40 were considered significant based on Tabachnik and Fidell (1996) and these are indicated in bold.

may be differences in amphipod behavior. *A. abdita* are tube-dwelling amphipods that form a mucus-lined tube that is irrigated primarily with surface water while the animal is feeding (Robson, 1990). This tube is usually constructed within the first few hours after the animals are introduced to the test sediment. In contrast, *E. estuarius* are free-burrowing deposit feeders that presumably have greater exposure to contaminants in interstitial water (DeWitt et al., 1989).

These species have also demonstrated variable sensitivity to single contaminants in water-only exposures. *A. abdita* is more sensitive to cadmium than *E. estuarius* (ASTM, 2000), and more sensitive to ammonia (Kohn et al., 1994), but both species have similar sensitivities to fluoranthene (ASTM, 2000; Boese et al., 1997). Schlekot et al. (1995) reported that *A. abdita* was somewhat more sensitive to Black Rock Harbor sediment than *E. estuarius*, but found that tests with both species resulted in similar rankings of this sediment as toxic or non-toxic. Weston (1995) used spiked-sediment tests with cadmium, DDT, and crude oil to compare responses of *Eohaustorius* and *Ampelisca* and found that *Ampelisca* was more sensitive to cadmium, *Eohaustorius* was more sensitive to DDT, and both species demonstrated comparable sensitivity to crude oil. Anderson et al. (1999) demonstrated increasing toxicity to *E. estuarius* along a pesticide contamination gradient in Moss Landing Harbor (CA) where no toxicity to *A. abdita* was detected. TIEs and chemical analyses suggested that toxicity of Moss Landing Harbor sediment was due to non-polar organic compounds, most likely organochlorine pesticides (Anderson et al., 1999).

3.5. NOAA/EMAP porewater toxicity studies 2000–2001

In addition to the amphipod tests, toxicity of sediment pore water was assessed using the sea urchin *A. punctulata* (Carr, 2002). Two endpoints were measured in 199 samples: fertilization and embryo-larval development (Carr et al., 2000). Tests were conducted using 100% (undiluted), 50% and 25% porewater concentrations. The results indicated widespread porewater toxicity to this species relative to a laboratory seawater control, particularly to sea urchin embryo development. In these tests, 82%, 49%, and 23% of the porewater samples were toxic to sea urchin development at the 100%, 50%, and 25% concentrations, respectively.

Although some of the toxicity to embryo development was attributed to unionized ammonia, toxicity persisted in many samples when ammonia was diluted below toxic thresholds, suggesting that other contaminants besides ammonia were contributing to the toxicity observed in these samples (Carr, 2001a, b, 2002). Sixty-three of the 199 pore water samples (32%) were toxic using the fertilization endpoint in the undiluted pore water, and some toxicity was observed in the 50% and 25% pore water dilutions.

4. Summary and future research

A number of monitoring programs conducted over the past 15 years have shown that San Francisco Estuary sediments remain toxic to a variety of test species. Current RMP summer monitoring continues to show moderate toxicity to amphipods at selected stations. The sampling approach for the current RMP incorporates a probabilistic sampling design where the margins of the Estuary are better represented, and this will allow a more accurate assessment of the spatial representation of sediment toxicity. Spatial patterns of toxicity from BPTCP and RMP monitoring suggest a higher magnitude of toxic effects occurs in samples collected near urban creeks at the margins of the Estuary, and in the northern Estuary adjacent to Delta inputs. This pattern is supported by seasonal monitoring conducted by the RMP, which has shown greater toxicity in the winter sampling period, and suggests stormwater inputs are an important source of toxicity in the Estuary.

Several lines of evidence suggest toxicity of San Francisco Estuary sediments is probably due to chemical mixtures rather than single pollutants. Amphipod mortality has been shown to be significantly correlated with organochlorine pesticides (e.g., chlordane, DDT), PAHs, and selected metals (Swartz et al., 1994; Thompson et al., 1999; Hunt et al., 2001b). Amphipod mortality in this system has been correlated with mixtures of chemicals quantified as mERMq values (Thompson et al., 1999; Hunt et al., 2001b). The range of mean ERMq values corresponding to amphipod toxicity is similar to the range associated with benthic community impacts (Thompson and Lowe, 2004).

TIEs with bivalve and sea urchin embryos have largely implicated divalent cations, and copper has been shown to inhibit embryo development in Grizzly Bay sediments (Phillips et al., 2003). TIEs with amphipods have been inconclusive using traditional EPA methods, although toxicity of Grizzly Bay sediment to amphipods was significantly reduced with weak-acid leaching (Hunt et al., 2005). While the combined evidence suggests a number of contaminants are associated with sediment toxicity in the Estuary, management decision-making will require more focused TIE studies that identify specific chemicals responsible for toxicity.

Recognizing the connection between source watersheds and Estuary sediments, a recent pilot project was initiated to sample six urban creeks which are proximate to Estuary stations demonstrating consistent sediment toxicity (San Francisco Estuary Institute, unpublished data). Samples are being collected in winter and spring to account for stormwater contributions to toxicity. Additional goals of this study are to measure concentrations of emerging chemicals of concern in watersheds of the Estuary (e.g., pyrethroid pesticides), and to conduct toxicity tests and TIEs in freshwater sediments of these creeks, and at the confluences of the creeks and the Estuary. This study is

designed to provide resource managers with more information on the relative toxicity and contamination of sediments entering the system from urban creek sources.

Studies are also being conducted to further investigate the relative sensitivities of the amphipods *A. abdita*, a resident species, and *E. estuarius*, a non-resident species that is used as the RMP's primary sediment toxicity indicator in the Estuary. Additional studies will include investigations between toxicity test results, benthic community characterizations, chemical analyses and TIEs at sites demonstrating defined contamination gradients. In addition to investigations of the influence of winter stormwater on sediment toxicity at the margins of the Estuary, emphasis is being placed on better understanding the relationship between laboratory sediment toxicity test results and impacts on resident benthic invertebrates in this system (see Thompson et al., in press). These studies are designed to provide linkages between these indicators, to evaluate Estuary-specific and statewide sediment quality objectives, and to provide resource managers with additional data on causes of benthic community impairments in the Estuary.

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