



## A Review of Factors Influencing Measurements of Decadal Variations in Metal Contamination in San Francisco Bay, California

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**Abstract.** This review summarizes some of the principal results of systematic measurements of trace metal concentrations throughout San Francisco Bay that began in 1989, and that have yielded insights on the factors controlling temporal and spatial variations of those concentrations on seasonal to decadal time scales. Pronounced seasonal variation in some metal concentrations is associated with gradients in the system's hydrology and the diagenetic remobilization of metals from benthic sediments. Additional temporal variation is associated with interannual differences in hydrologic flushing (e.g., ENSO cycles) and episodic storm events. While intra- and inter-annual variabilities complicate assessments of long-term variations in metal concentrations, recent analyses using stable lead isotopic composition distributions and time-series models have deconvoluted decadal changes in lead and silver concentrations in the estuary. Decadal variations in concentrations of other contaminant metals (e.g., mercury) are now being characterized, as well as projections of future concentrations of other metals of concern (e.g., copper). These historic assessments and projections of trace metal variations attest to the importance of long-term, systematic monitoring programs to quantify past and future impacts on water quality in San Francisco Bay and other complex estuarine systems.

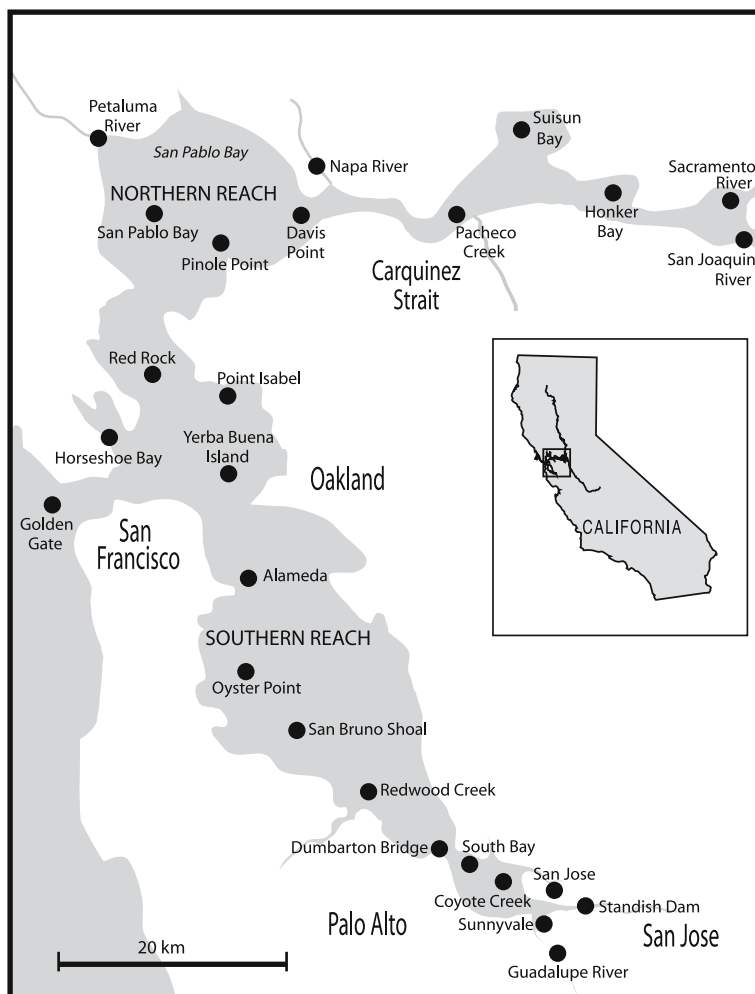
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### Introduction

Over the past five decades, billions of dollars have been spent to improve the water quality of San Francisco Bay (Fig. 1), where concentrations of some trace elements have approached or exceeded state and federal water quality criteria (Flegal et al., 1991, 1996; Thompson et al., 2000; Hoenicke et al., 2003; Sañudo-Wilhelmy et al., 2004).

Until recently, it has not been possible to quantify the beneficial impacts of most of those remediation efforts because sufficient, valid water quality data for toxic metal concentrations in the Bay have been lacking. These data are required to conduct time series analyses that distinguish pronounced seasonal and annual from decadal and centennial variations in the concentrations of trace elements in the Bay. However, with the availability of new, robust water quality data, these analyses have been made for lead and silver, and are now being made for mercury.

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*Figure 1.* Map of the San Francisco Bay estuary and tributaries showing the surface water sampling stations for the Regional Monitoring Program.

This review summarizes the results of measurements of long-term ( $\geq 10$  years) changes in trace metal concentrations in the Bay by first summarizing the difficulties of time-series calculations for this system. The difficulties include (1) the lack of sufficient accurate trace element data before the past decade; (2) the confounding effect of seasonal and annual variations in freshwater discharges on trace element concentrations in the system; and (3) incomplete records of historic and contemporary anthropogenic perturbations of trace element inputs to the system. We then show how those difficulties are now being resolved through the systematic, long-term regional data collection efforts, with rigorous quality assurance

and quality control protocols, of the San Francisco Bay Regional Monitoring Program (RMP). The results of this program enable both assessments of water quality changes over the past decade and projections of future water quality conditions under different environmental regimes.

## Background

### *Historic data*

Few data on trace element concentrations are available for San Francisco Bay waters before the 1990s, and almost all of these data are temporally

and spatially limited and their quality is suspect (Flegal et al., 1991). Most of the older values that had been reported in either peer-reviewed scientific journals or 'gray' literature are not reliable, because they (1) did not use currently accepted trace metal clean techniques, (2) were not corroborated by independent measurements, and (3) are inconsistent with more recent values obtained using more rigorous trace metal clean and quality control techniques.

Consequently, comparable data on trace element concentrations in the Bay are, with few exceptions (e.g., Gordon, 1980; Cutter, 1989; Kuwabara et al., 1989), restricted to those in reports published since 1990. This relatively late date was well after efforts to reduce contaminant loadings to the Bay in the 1950s–1960s and also after the passage of the US Clean Water Act in 1972, which accelerated source control programs and the installation of secondary, advanced, and clarifying treatment facilities at publicly owned treatment works (POTWs) that reduced some metal loadings to the Bay by an order of magnitude or more (California Regional Water Quality Control Board, 1995). Although the impact of those source-control programs is evidenced in subsequent decreases in contaminant concentrations in sediment cores (e.g., Hornberger et al., 1999; Conaway et al., 2004), there is not – and can never be – a direct measure of contemporary changes in contaminant metal concentrations in Bay waters during that earlier period.

#### *Seasonal and annual variations in hydrology*

In addition to limited historic data, the effect of seasonal and annual variations of freshwater discharges to San Francisco Bay presents an additional difficulty in time-series analysis. The hydrology of the Bay is complex, with pronounced temporal and spatial gradients (Conomos, 1979; Kimmerer, 2002; Monismith et al., 2002). The Bay receives runoff from 40% of California's land area, with over 90% of that input from the Sacramento and San Joaquin rivers, which discharge into the northern region of the Bay. Conversely, less than 10% of the natural freshwater flow is into the southern region of the Bay.

Moreover, freshwater flows into the system are characterized by their seasonality and

interannual variability (Conomos, 1979; Kimmerer, 2002; Monismith et al., 2002). Relatively large discharges ( $> 10^3 \text{ m}^3 \text{ s}^{-1}$ ) occur during the winter and spring periods, and relatively small discharges ( $< 10^2 \text{ m}^3 \text{ s}^{-1}$ ) occur during the summer and fall periods. These pronounced seasonal differences are further confounded by marked (order-of-magnitude) interannual differences in freshwater discharges associated with El Niño Southern Oscillation (ENSO) cycles.

Difficulties of obtaining a representative sampling of metal concentrations in Bay waters during those different hydrologic regimes are illustrated in Fig. 2. This figure shows the two-week RMP sampling periods over the past decade superimposed upon freshwater discharges, ranging from 250 to 3250  $\text{m}^3 \text{ s}^{-1}$ , into the northern region of the estuary during that period. Because of disconnects between the collection periods and freshwater discharges, the water quality data obtained from the sampling periods often fail to accurately represent either average or extreme conditions. Therefore, seasonal, much less annual and decadal, variations in metal concentrations and fluxes in the Bay must be qualified by the limitations of the sampling program compared to the variability in the Bay's hydrology that strongly influences metal fluxes in the estuarine system.

#### *Anthropogenic inputs of metals to the system*

Large spatial variations in concentrations of some metals in San Francisco Bay waters also are partially due to historic and contemporary industrial fluxes of those metals to the system (Flegal et al., 1996). The Bay was heavily impacted by mercury and gold mining operations that began in the 1850s, and the legacy of those historic mining activities continues to account for much of the elevated concentrations of mercury in Bay sediments and surface waters (Conaway et al., 2003, 2004). Additionally, anthropogenic activities began contributing to the fluxes of some metals, notably lead in the 1800s (Hornberger et al., 1999; Ritson et al., 1999), while industrial fluxes of other metals (e.g., silver and copper) did not appear to become relatively important until much later (Hornberger et al., 1999). Consequently, there is no common industrial source or onset of metal contamination, which precludes simple

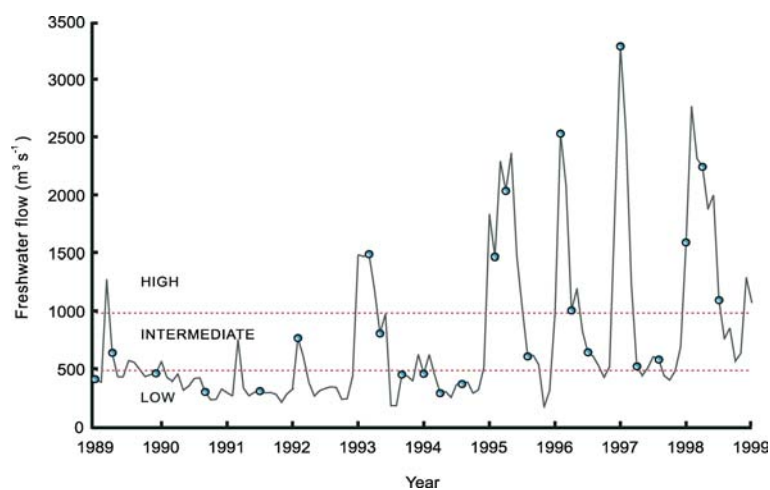


Figure 2. Sampling dates (○) in San Francisco Bay from 1989–1999, conducted as part of the Regional Monitoring Program and its precursor, plotted along with freshwater discharges ( $\text{m}^3 \text{s}^{-1}$ ) to the system during that period. While these and subsequent samplings have provided measures of seasonal and decadal variations of metal contamination in the Bay, the marked differences in freshwater flows during that period and during sample collections contribute to variability in the data and constrain time series models of changes in contaminant levels over the past decade.

normalizations to baseline reference concentrations or enrichment factors over the past two centuries.

The complexity and diversity of anthropogenic perturbations have increased over that period with the settling and industrial development of the Bay, which is now referred to as the 'Urban Estuary' (Nichols et al., 1986). Today, the Bay is surrounded by a megalopolis of approximately 7 million people (data are from the U.S. censuses 2000, compiled by staff of the Metropolitan Transportation Commission and the Association of Bay Area Governments). Furthermore, the Bay and its delta, which comprise 6% of California's area, are projected to contain 25% (10 million people) of the state's burgeoning population within two decades. At the same time, freshwater discharges to the Bay are increasingly being diverted to provide drinking water to two thirds of the state's population (22 million people) and to irrigate 4.5 million acres of farmland outside of its drainage basin (Knowles, 2002). All of those factors are contributing to the decreasing ability of the Bay to be purged of contaminants by large freshwater discharges, while the potential for contaminant metal loadings is increasing with the urbanization and industrialization of the state.

Some of the complexity resulting from this urbanization is illustrated in Fig. 3. The figure shows the location of some of the more than 200 POTW and industrial plants that discharge directly into the Bay. It also shows the disparity in natural freshwater flows into the northern ( $\sim 90\%$ ) and southern ( $\sim 10\%$ ) regions of the estuary, which accounts for the pronounced differences in contaminant residence times between those two extremities. Conversely, 76% of the total POTW effluent released into the estuary enters the shallow waters (typically less than 2 m deep) of the southern region, and only 20% enters the waters of the northern region (Squire et al., 2002). As a consequence, the highest levels of metal contamination most often occur in the southern extremities of the Bay.

#### Temporal gradients in lead concentrations

Despite limited trace metal data prior to the 1990s, variations in hydrology, and anthropogenic perturbations to the system, temporal variations of some element concentrations have now been characterized by studies using rigorous quality control methods. Long-term (hundreds of years) gradients of lead deposition in the Bay were

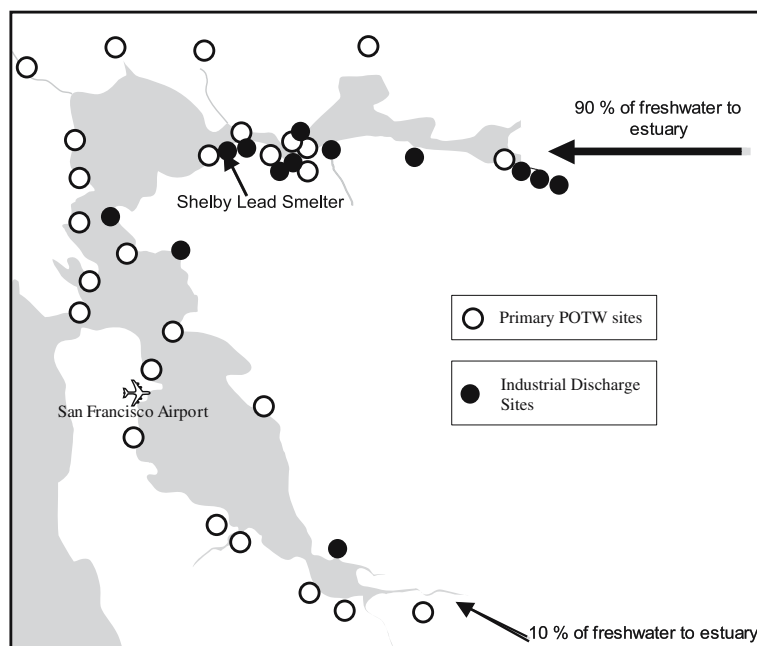


Figure 3. Map of San Francisco Bay with locations of major publicly operated treatment works (POTW) and industrial outfalls. Also shown are the relative amounts of wastewater discharged to the northern reach (20%), Central Bay (4%), and southern reach (76%) of the estuary; the natural freshwater discharges to the northern (90%) and southern (10%) of the estuary; and the location of the Selby lead smelter, which was a principal source of industrial lead fluxes to the estuary for nearly a century.

chronicled in sediment cores using both lead concentration (Hornberger et al., 1999) and isotopic composition ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ) analyses (Ritson et al., 1999). The perturbations date back to the California Gold Rush of 1849, when the source of sediments deposited in the Bay was altered by hydraulic mining. That activity altered lead isotopic compositions, but did not measurably change lead concentrations in Bay sediments. Later, when fossil fuel combustion increased within the Bay's drainage basin, both isotopic compositions and concentrations of lead in the sediments were affected. Industrial lead fluxes were then compounded with inputs from the Selby lead smelter, which went into operation in the later half of the 19th century. The smelter operations continued until 1970, thereby altering lead isotopic compositions and markedly elevating lead concentrations in the Bay and its watershed (Rabinowitz and Wetherill, 1972; Ritson et al., 1999; Steding et al., 2000). Other inputs of industrial lead, notably leaded gasoline, further altered lead isotopic compositions, and contaminant lead concentrations steadily increased until the 1980s,

when controls were placed on those emissions and the phase-out of leaded gasoline was being completed (Steding et al., 2000). Despite these controls and the passing of time, isotopic compositions of those diverse lead inputs are still evident in both Bay sediments and surface waters (Ritson et al., 1999; Dunlap et al., 2000; Steding et al., 2000) because of the recycling of contaminant lead between those phases within the Bay (Rivera-Duarte and Flegal, 1994; Ritson et al., 1999; Dunlap et al., 2000; Steding et al., 2000).

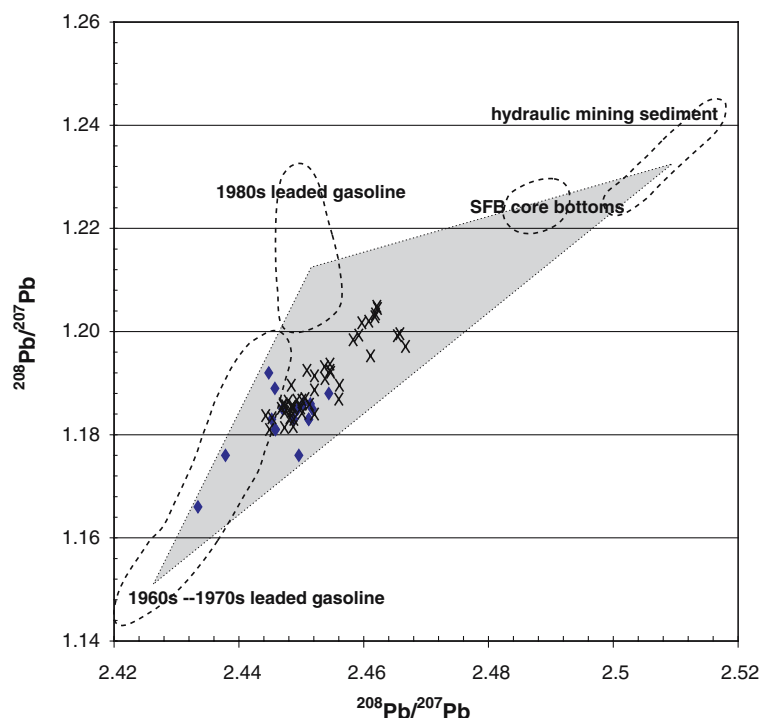
Because different sources of lead inputs to the Bay can be characterized by their isotopic composition ratios, those ratios have been used in mixing models to calculate decadal changes in industrial lead fluxes to San Francisco Bay waters (Steding et al., 2000). The models were used to resolve the apparent absence of decline in lead concentrations in Bay waters, even after (1) atmospheric emissions of industrial lead declined by two orders of magnitude with the elimination of leaded gasoline and (2) lead loadings to the estuary from POTW effluents were reduced 20-fold, to  $46 \text{ t year}^{-1}$  over the past three decades (Squire

et al., 2002). That apparent consistency in lead concentrations in the Bay was substantiated by the isotopic models, which indicated that historic fluxes of contaminant lead were still retained in the Bay and that there had been no measurable decrease in the ongoing flux of historic lead contamination from the watershed to the Bay over the past decade.

Some of those isotopic analyses are summarized in Fig. 4. The figure shows that the  $^{206}\text{Pb}/^{207}\text{Pb}$ : $^{208}\text{Pb}/^{207}\text{Pb}$  ratios of surface waters in the Bay over the past decade have consistently fallen between those of US leaded gasoline used during the 1960s–1980s and those of hydraulic mining sediments mobilized from the Sierra Nevada mountain range during the California Gold Rush dating back to the latter half of the 1800s. Comparison of the ratios of those historic sources with those of sediments and surface waters in the Bay indicate that most of the lead in those waters is a mixture of inputs of US gasoline lead from the

1960s–1970s and hydraulic mining sediments, rather than inputs from either more recent industrial emissions or natural sources.

The persistence of historic levels of lead in San Francisco Bay was corroborated by time-series models of total and dissolved ( $<0.45\ \mu\text{m}$ ) lead concentrations in San Francisco Bay waters measured for the RMP (Squire et al., 2002). These models were only possible because of the inter-annual consistency of the elemental analyses, demonstrated by the reproducibility of concurrent analyses of standard reference materials from each sampling period. Because of the heterogeneity of the Bay's physical transport processes and metal inputs, cluster analyses were needed to classify variables in different regions of the Bay based on their similarities, and then the primary factors controlling metal (i.e., lead) concentrations were identified. Using those primary controls on trace metal concentration, equations were fitted of the equation:



*Figure 4.* Lead isotopic compositions of historical inputs of natural and industrial lead to San Francisco Bay and current isotopic compositions of lead in surface sediments ( $\blacklozenge$ ) and surface waters ( $\times$ ) of the Bay. The shaded area represents a mixing triangle between historic and modern industrial inputs. This plot of isotopic compositions shows that historic industrial inputs still dominate lead concentrations in the Bay. The isotopic composition data are synthesized from reports by Ritson et al. (1999), Dunlap et al. (2000), and Steding et al. (2000).

$$x_j(t_k) = a_0 \left[ \prod_{i=1}^n \exp(a_i f_{ij}(t_k)) \right] \exp(bt_k)$$

with temporal signals using standard non-linear, iterative least squares regression of log-transformed data. Here the  $a_i$  are unknowns, the  $f_{ij}(t_k)$  are the  $n$  ( $= 1$  or  $2$ ) retained controls at collection site  $j$ ,  $t_k$  is the time of collection campaign  $k$ ,  $x_j(t_k)$  is trace metal concentration and  $b$  is an additional unknown quantifying the temporal decrease ( $b < 0$ ) or increase ( $b > 0$ ) in background level of the trace metal. The models were then checked for errors using a bootstrapping approach.

Again, the models corroborated isotopic composition analyses indicating that concentrations of both total and dissolved lead in the northern reach remained essentially constant over the past decade (1989–1999). The models showed that dissolved lead concentrations in the southern region also remained essentially constant over that period, despite a 40% decline in total lead concentrations in that region. As with the lead isotopic composition data, the persistence of elevated concentrations of lead in Bay waters (decadal mean of total dissolved lead =  $31 \text{ ng kg}^{-1}$ ) over the past decade compared to adjacent oceanic surface waters in the northeast Pacific ( $2.7 \text{ ng kg}^{-1}$ ) was attributed to (1) ongoing inputs from previous atmospheric depositions and industrial lead to its drainage basin slowly being advected into the estuary and (2) internal recycling of lead between the sediments and the water column within the Bay.

#### Temporal gradients in silver concentrations

In contrast to lead, comparable time-series models revealed marked declines in concentrations of dissolved silver in some parts of San Francisco Bay (Squire et al., 2002). Although there were (similar to lead) no quantifiable decreases in the concentrations of either dissolved or total silver concentrations in the northern region of the Bay over the past decade, marked decreases in concentrations of both dissolved (70%) and total silver (40%) in the southern region occurred during that time. These declines were attributed to the concurrent two-fold decrease in silver loadings from POTWs and a

comparable decline in the concentration of silver in surface sediments within the southern region of the Bay. The disparity in temporal changes in silver and lead concentrations in the Bay attests to the previously noted differences in historic and contemporary inputs of contaminant metals to the Bay.

#### Temporal gradients in mercury concentrations

Time series analyses of variations in mercury concentrations in San Francisco Bay waters are not yet completed, but the data required for these analyses are now becoming available. Mercury, like lead and silver, has a legacy of large contaminant fluxes to the Bay (i.e., spanning the past two centuries). Historic inputs of mercury are chronicled in radiocarbon-dated sediment cores and surface sediment distributions, which are reflected in surface water distributions (Choe and Gill, 2003; Choe et al., 2003; Conaway et al., 2003). Present atmospheric fluxes of industrial mercury to the system appear to be relatively substantial, as well (Steding and Flegal, 2002; Conaway et al., 2003). Consequently, resolving temporal variations in mercury concentrations in the Bay will be relatively more complex than it has been for lead and silver.

Still, historic inputs of mercury from industrial sources to the Bay have been documented in sediment cores from its northern (Hornberger et al., 1999) and southern (Conaway et al., 2004) regions (Fig. 5). Both sets of radiocarbon-dated cores contained baseline concentrations of  $60\text{--}70 \text{ ng g}^{-1}$ , that were consistent with concentrations in other relatively uncontaminated estuarine sediments. Values increased in the cores from southern ( $1200 \text{ ng g}^{-1}$ ) and northern ( $1000 \text{ ng g}^{-1}$ ) regions due to inputs from mercury mining and the use of mercury in gold mining, respectively, that began 150 years ago and continued into the latter half of the 1900s. Because of ongoing inputs from those historic activities and the reworking of Bay sediments – along with contemporary inputs from other industrial activities – surface sediment concentrations of mercury remain elevated relative to baseline conditions over most of the Bay, especially in its extreme southern region where historic and contemporary

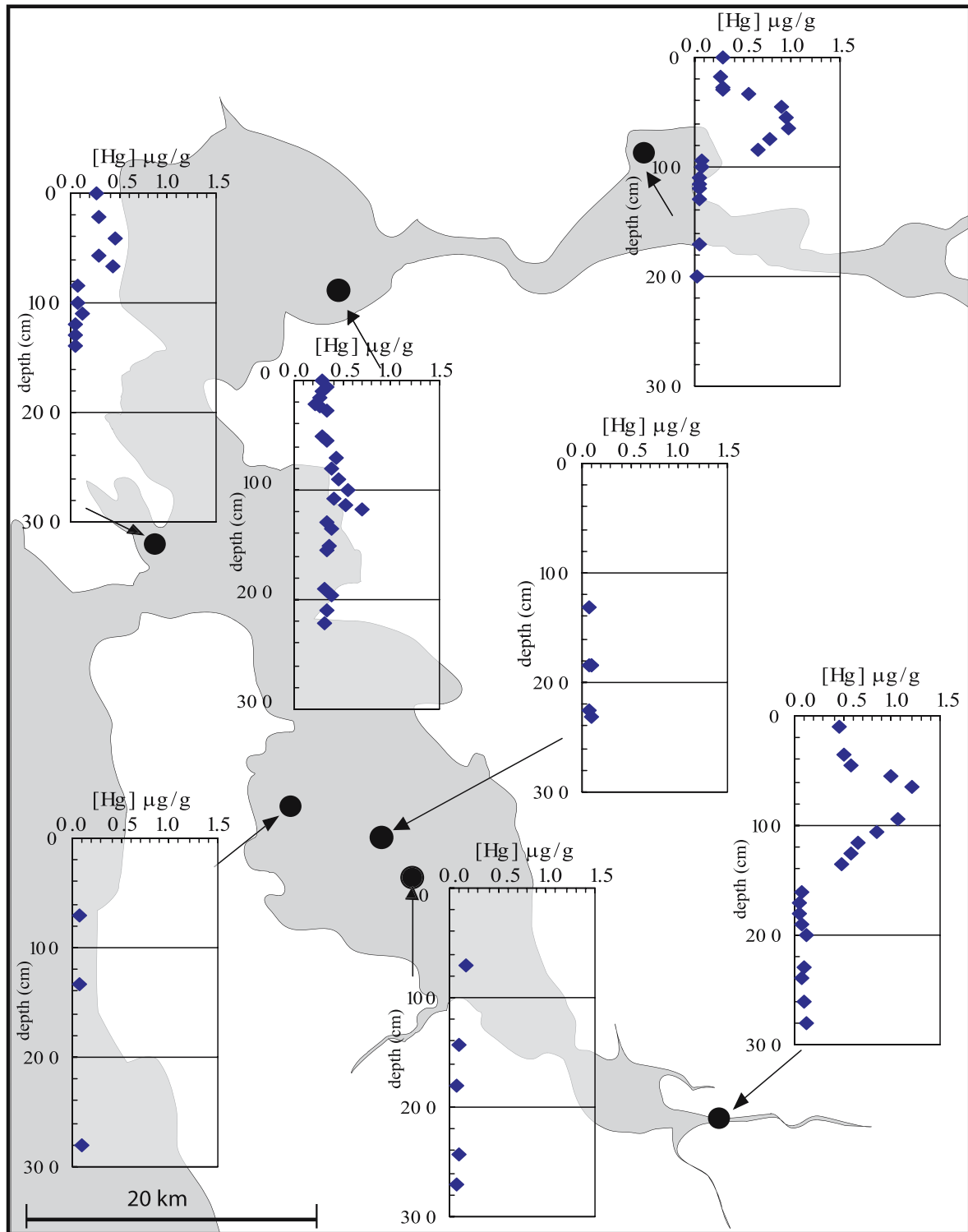


Figure 5. Mercury concentration ([Hg] in  $\mu\text{g g}^{-1}$ ) versus depth (cm) in sediment cores from locations in San Francisco Bay. Data from the 3 northern reach cores are from Hornberger et al. (1999), and data for other cores are from Conaway et al. (2004).



inputs of mercury from the New Almaden mining district are located.

The distribution of mercury in surface sediments mirrors the distribution of mercury in surface waters of San Francisco Bay (Choe and Gill, 2003; Choe et al. 2003; Conaway et al., 2003) (Fig. 6). Concentrations of dissolved ( $<0.45 \mu\text{m}$ ) mercury are relatively high in the northern region ( $\sim 10 \text{ pM}$ ), relatively low in the Central Bay ( $\sim 2 \text{ pM}$ ), and relatively high in the southern region ( $\sim 10 \text{ pM}$ ). This distribution is, in part, comparable to those of lead and silver because of their similar biogeochemical cycles and historic industrial loadings in the Bay.

In addition to the contribution of mercury in sediments to the concentration of mercury in the water, there appears to be an increasing atmospheric flux of mercury to San Francisco Bay and its drainage basin from industrial emissions (Steding and Flegal, 2002). The atmospheric input is attributed primarily to local, regional, and global emissions of mercury from the combustion of fossil fuels. This attribution is based on preliminary measurements of mercury concentrations in precipitation along the California central coast, which range from 8 to 80 pM (average  $\approx 30 \text{ pM}$ ), compared to mercury concentrations in precipitation within the Bay, which range from 4 to 200 pM (average  $\approx 60 \text{ pM}$ ). That doubling in average mercury concentrations is ascribed to local and regional emissions of mercury and/or oxidants and surfaces to scavenge elemental mercury from the atmosphere within the Bay region.

Order-of-magnitude variations in mercury concentrations in both coastal and Bay precipitation is tentatively attributed to differences in trans-Pacific fluxes of contaminants (Steding and Flegal, 2002). These include emissions of mercury, oxidants, halogens, and particulates from fossil fuel combustion in Asia (e.g., mercury emissions from China from fossil fuel combustion are estimated to range from 1.6 to 2.2 Mmol year<sup>-1</sup>, which is approximately two times greater than US emissions, 0.78 Mmol year<sup>-1</sup>). Direct and indirect atmospheric inputs ( $\sim 10^1\text{--}10^2 \text{ kg year}^{-1}$ ) represent an important fraction of the total mercury flux ( $\sim 10^2\text{--}10^3 \text{ kg year}^{-1}$ ) to the Bay (Domagalski, 2001; Conaway et al., 2003). As a result, mercury concentrations in Bay waters may increasingly reflect atmospheric depositions from industrial

emissions outside of the system's drainage basin, which may at least partially mask reductions of industrial mercury emissions within that basin.

### Projections of future gradients in concentrations

Both the seasonal and decadal variations in fluvial inputs attest to the potential importance of hydraulic flushing on levels of metals in the Bay (Flegal et al., 1991). As previously observed, mass balance calculations indicate that only a small fraction (5–10%) of the leaded gasoline fallout from the late 1980s has been washed out of the San Francisco Bay's drainage basin (Steding et al., 2000). Furthermore, the inefficient removal of that lead from drainage basin soils and the persistence of historic depositions (1960–1980) of gasoline lead now found in the Sacramento and San Joaquin rivers' bed loads indicate that historic gasoline lead deposits may be retained in the basin for decades before they are flushed into the Bay. That projected persistence is in contradiction to reports of rapid (annual) decreases in lead contamination in rivers (e.g., Trefry et al., 1985), coastal waters (e.g., Sañudo-Wilhelmy and Flegal, 1994), and oceanic surface waters (e.g., Wu and Boyle, 1997) that have been positively correlated with reductions in aeolian emissions of industrial lead; but it is consistent with previous reports on the protracted biogeochemical cycling of <sup>210</sup>Pb in other estuarine systems (e.g., Turekian, 1977). Consequently, the systematic acquisition of lead concentration and isotopic composition data for San Francisco Bay over the past decade has enabled projections of future levels of lead contamination in the Bay that, while inconsistent with declines of lead contamination in other aquatic systems, are consistent with the biogeochemical cycling of aeolian lead depositions in estuarine systems – and therefore credible.

The acquisition of a decade of data for San Francisco Bay also enables projections of the impacts of current (Chen et al., 1996) and future (URS, 2003) processes on contaminant concentrations, as illustrated in Fig. 7. This figure shows the projected changes in copper concentrations in Bay waters after the proposed 1–3 km expansion of San Francisco airport runways into the Bay, based on a two-dimensional, free-surface flow

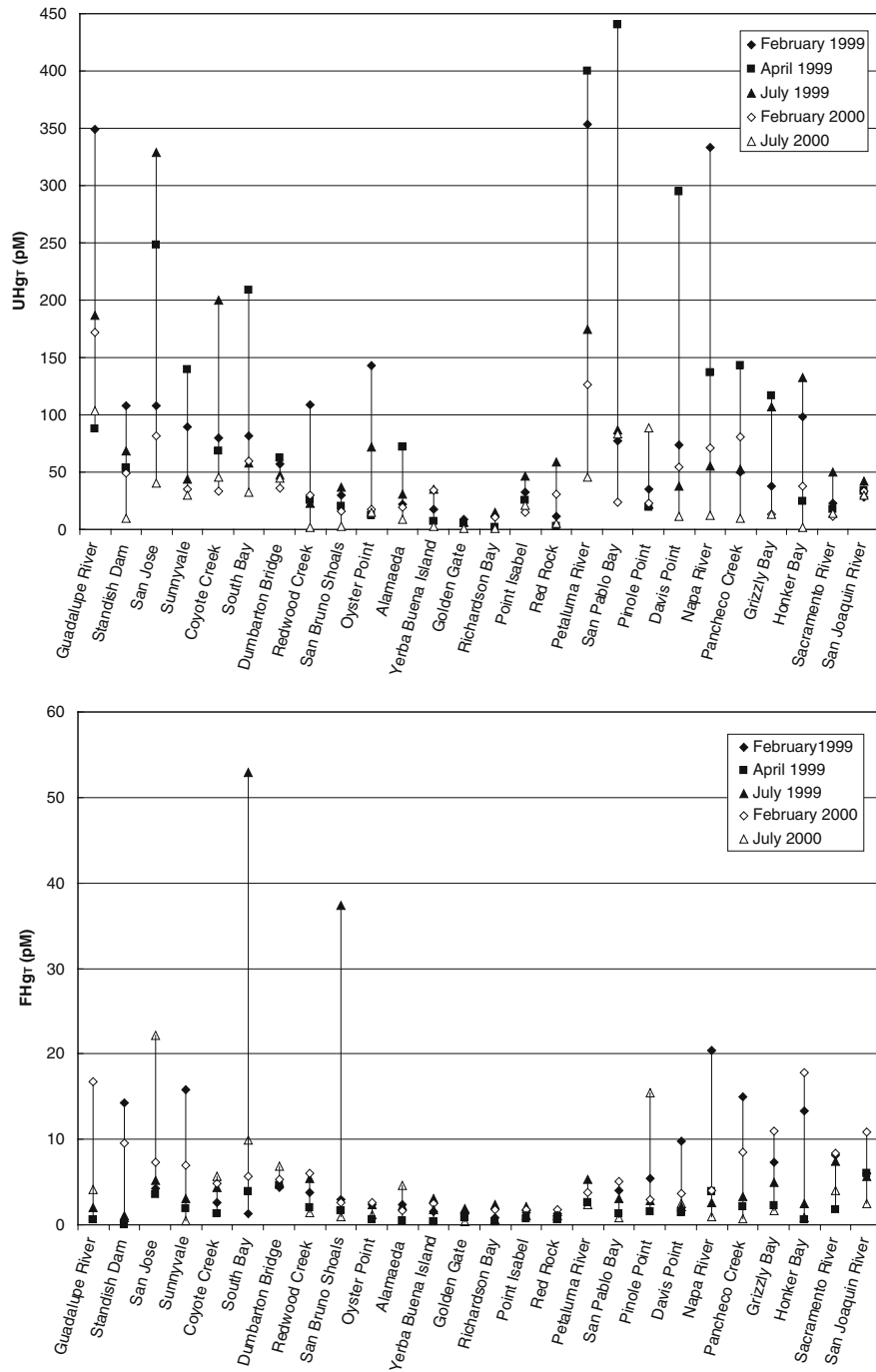


Figure 6. Surface water total mercury concentrations in picomolar (pM) in unfiltered (UHgr) and <math><0.45 \mu\text{m}</math> filtered (FHgr) waters from San Francisco Bay sites in 1999–2000 (from Conaway et al., 2003). Drop lines illustrate the differences in maximum and minimum values across seasons for each sampling location. Locations of sampling sites are shown in Fig. 1.

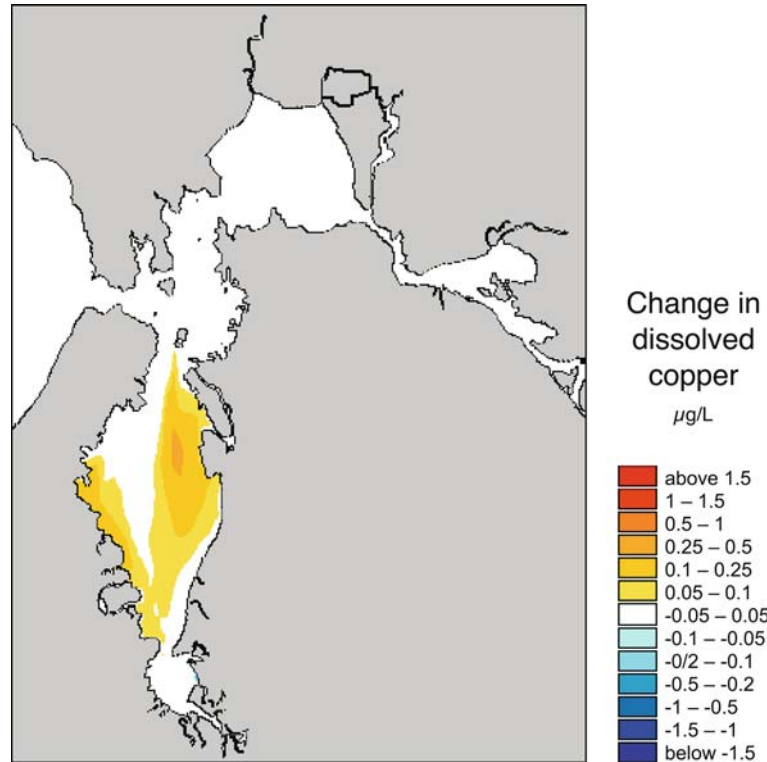


Figure 7. Model of changes in total dissolved ( $< 0.45 \mu\text{m}$ ) copper concentrations ( $\mu\text{g/l}$ ) in San Francisco Bay during the expansion of the San Francisco airport into the southern reach of the estuary (from T. Cooke, personal communication).

model (MIKE 21) that simulates hydraulics and associated phenomena in estuaries, and an associated module (ME) that incorporates the four primary processes governing dissolved metal concentrations in estuaries: (1) adsorption and desorption of metals, (2) sedimentation and resuspension of particulate metals, (3) diffusive transport of metals at the sediment/water interface, and (4) advective and dispersive transport of dissolved and particulate metals in the water column. Assuming the two-dimensional model is sufficient for modeling hydraulic processes in the Bay and the assumptions for the module are valid for copper in the Bay, the projection indicates that additional perturbations of the element's cycle in the Bay by the proposed expansion of the runway will be negligible. Of course, that and any other projection of the potentially adverse impact of such a large project needs to be carefully assessed prior to construction and, if built, tested after construction.

The importance of such projections has been further highlighted by a recent report of the potential adverse impacts of future changes in California's climate and water resources associated with global warming in the 21st century (Hayhoe et al., 2004). That study estimated ranges in sea level rise (9–41 cm) and changes in state-wide averages of temperature (+1 to +6 °C), precipitation (–157 to +38 mm), reservoir inflow (–30 to +12%) for years 2020–2049 and 2070–2099, relative to years 1961–1990, that would substantially reduce freshwater discharges and increase salinity within the Bay. Based on the preceding time-series analyses of changes in lead and silver concentrations in the Bay over the past decade, those reduced discharges would markedly decrease the system's capacity to flush contaminants being added to the system and increase the flux of contaminants from historically contaminated Bay sediments into overlaying waters. Consequently, future projections of the health of the Bay must

consider both (1) historic and contemporary contaminant loadings and (2) the consequences of less fresh water to flush the system due to an increasing population with proportionately greater demands for fresh water and less freshwater reserves due to global warming.

### **Complementary studies**

Whereas the preceding discussion has focused on spatial and temporal variations of trace metals in water samples collected over the past decade along a defined transect through the middle of the San Francisco Bay estuary, complementary studies have substantially improved our understanding of the cycling and bioavailability of those and other elements in Bay waters. These studies include other short-term and more spatially restricted investigations of elemental concentrations and speciation within the Bay. Among the most extensive of those studies have been those on the biogeochemical cycling and speciation of selenium by Cutter and his associates (Cutter, 1989; Cutter and San Diego-McGlone, 1990; Linville et al., 2002; Purkerson et al., in press); those on the speciation of copper, nickel and zinc by Bruland and his associates (Donat et al., 1994; Phinney and Bruland, 1997a, b; Beck et al., 2002a, b; Gee and Bruland, 2002); those on the complexation of metals in wastewater discharges to the Bay by Sedlak and his associates (Sedlak et al., 1997; Bedsworth and Sedlak, 1999a, b; Hsu and Sedlak, 2003); and those on the bioavailability of metals by Luoma and his associates (e.g., Luoma et al., 1998; Griscom et al., 2002). Others have reported on the biogeochemical cycling and/or speciation of chromium (Abu-Saba and Flegal, 1995, 1997; Abu-Saba et al., 2000), cobalt (Tovar Sanchez et al., 2004), lead (Kozelka et al., 1997); manganese (Roitz and Bruland, 1997; Roitz et al., 2002), mercury (Thomas et al., 2002; Choe and Gill, 2003; Choe et al., 2003), and silver (Smith and Flegal, 1993; Miller and Bruland, 1995) in the Bay, as well as on some multi-elemental studies (Kuwabara et al., 1989; Flegal and Sañudo-Wilhelmy, 1993; Wood et al., 1995; Sañudo-Wilhelmy et al., 1996). There have also been reports on trace metal concentrations in pore waters of Bay sediments (Rivera-Duarte and Flegal, 1994, 1997a, b, c; Rivera-Duarte et al., 1999;

Spinelli et al., 2002; Topping and Kuwabara, 2003). In addition, there is now a substantial amount of research on the bioavailability and toxicity of some trace elements (notably copper, nickel, and selenium) in Bay waters that has not been published in peer-reviewed articles, but has employed relatively rigorous trace metal clean techniques and sophisticated instrumentation.

Consequently, San Francisco Bay is now one of the most extensively studied estuaries in the world, for trace metals. This includes studies of biogeochemical cycles and speciation metals within the water column, which have been briefly noted, and a comparably large set of studies on trace metals in the Bay's sediments and biota, which is beyond the scope of this report. Still, our understanding of the biogeochemical cycling and toxicity of metals in the Bay is far from complete, and additional research is needed to accurately assess the health of the Bay and quantify the efficacy of efforts to improve that status.

### **Summary**

The systematic sampling and analysis of contaminant metal concentrations throughout San Francisco Bay over the past decade has enabled calculations of temporal changes in some of those concentrations. These include both measures of change over the past decade and projections of changes in future decades. Although there are limitations in these determinations, they are still more rigorous than those that could be made in any other estuary that we are aware of because the dataset for metal contamination is more systematic and extensive for the Bay than for any other estuary that we are aware of.

That rather disturbing observation that relatively little is known about temporal changes in metal concentrations in estuaries is based on our recent review of the status of research on toxic metals in US estuaries (Sañudo-Wilhelmy et al., 2004). We found that although the US Environmental Protection Agency (EPA, 2002), National Oceanographic and Atmospheric Administration (NOAA), and other environmental monitoring programs had contributed to extensive datasets on contaminant metal concentrations in some estuarine sediments (e.g., Daskalakis and O'Connor,

1995) and organisms (e.g., O'Connor, 2002), relatively limited datasets on contaminant metal concentrations are available for most other US estuaries. This determination was based on a bibliographic search of aqueous metal concentrations in estuaries listed in the EPA National Estuarine Program (28 estuaries) and NOAA Estuarine Research Reserve System (25 estuaries) that found a total of only 83 articles on published in peer-reviewed scientific journals between 1975 and 2002. Moreover, most (~70%) of those articles were for measurements in five estuaries (Delaware, Chesapeake Bay, Galveston Bay, Narragansett Bay, and San Francisco Bay); no articles had been published on contaminant metal concentrations in about half of the US estuaries. As a consequence, the degree of metal contamination in those estuaries remains unknown, and measures of changes in contaminant levels in almost all US estuaries – much less projections of future changes in those levels – are not possible.

Although we have not conducted a comparable bibliographic search on measures of contaminant metal concentrations in the world's estuaries, it is important to point out implications that our review of US estuaries may have for other aquatic systems worldwide. Although some of them, such as the Rhine River in Europe, have been investigated intensively, other urbanized estuaries, especially those in tropical regions and industrializing countries have received much less attention. Therefore, it is very important to begin obtaining reliable data to quantify the current health of those estuaries and model the impact of future perturbations caused by industrialization, alteration of freshwater discharges, and climate change.

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