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Spatial and temporal variations in silver contamination and toxicity in San Francisco Bay

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Abstract

Although San Francisco Bay has a "*Golden Gate*", it may be argued that it is the "*Silver Estuary*". For at one time the Bay was reported to have the highest levels of silver in its sediments and biota, along with the only accurately measured values of silver in solution, of any estuarine system. Since then others have argued that silver contamination is higher elsewhere (e.g., New York Bight, Florida Bay, Galveston Bay) in a peculiar form of pollution machismo, while silver contamination has measurably declined in sediments, biota, and surface waters of the Bay over the past two to three decades. Documentation of those systemic temporal declines has been possible because of long-term, ongoing monitoring programs, using rigorous trace metal clean sampling and analytical techniques, of the United States Geological Survey and San Francisco Bay Regional Monitoring Program that are summarized in this report. However, recent toxicity studies with macro-invertebrates in the Bay have indicated that silver may still be adversely affecting the health of the estuarine system, and other studies have indicated that silver concentrations in the Bay may be increasing due to new industrial inputs and/or the diagenetic remobilization of silver from historically contaminated sediments being re-exposed to overlying surface waters and benthos. Consequently, the Bay may not be ready to relinquish its title as the "*Silver Estuary*".

Keywords: Silver; San Francisco Bay; Pollution; Toxicity; Monitoring

1. Introduction

1.1. San Francisco Bay: the Silver Estuary

The story of silver contamination in San Francisco Bay (Fig. 1) is a unique and interesting one. While the Bay is best known for its Golden Gate Bridge (originally made golden by the sun reflecting off its toxic red lead paint), the Bay has since been distinguished by reports of unusually high level of silver concentrations in its sediments, biota, and water that have led to its characterization as the "*Silver Estuary*". Over two decades ago, silver concentrations of Bay sediments (Luoma and Cloern, 1982; Luoma et al., 1985) were found to be as high as 2.6 $\mu g\,g^{-1}$, more than 30-fold above the element's average crustal abundance (0.080 $\mu g\,g^{-1}$; Taylor and McLennan, 1985). During that period, silver concentrations were also found to be anomalously elevated in some of the Bay's benthic invertebrates: including tellenid clams, *Macoma balthica*, whose silver concentrations (7–120 $\mu g\,g^{-1}$ dry weight) exceeded those of clams from 37 European countries (Luoma and Cloern, 1982); and mussels, *Mytilus edulis* and *Mytilus californianus*, (Luoma and Cloern, 1982; Smith et al., 1986), whose silver concentrations were equal to or greater than those of mussels and clams from 63 estuaries in North America and northeast Pacific coastal waters (Goldberg et al., 1983). Although there were no published values for silver in any other estuarine waters for comparison in 1989, the highest total dissolved ($<0.45\,\mu m$) silver concentration (243 pM) measured in Bay waters at that time (Smith and Flegal, 1993) was determined to be two orders of magnitude greater than the baseline silver concentration (~1 pM) in surface waters of the North

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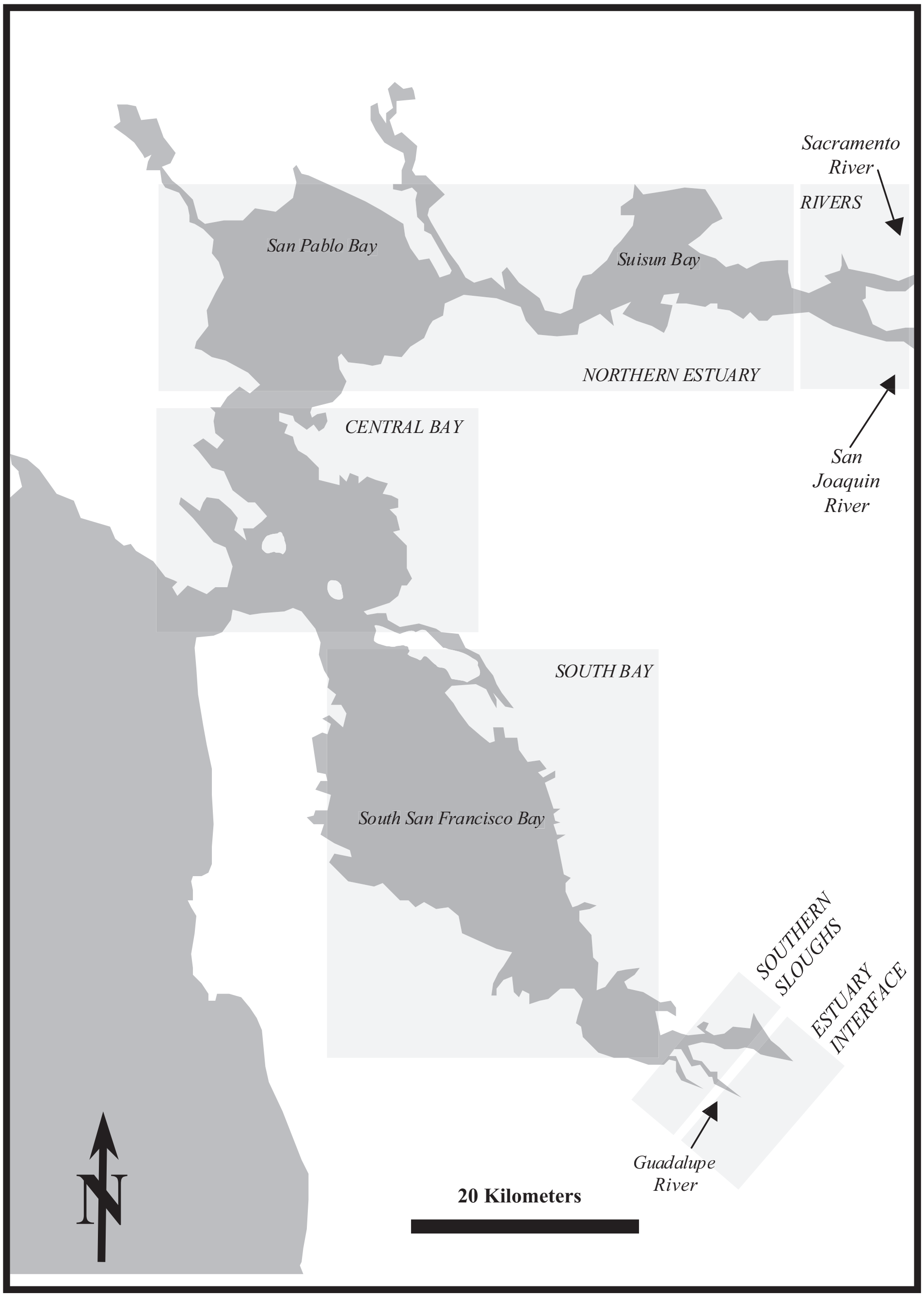

Fig. 1. Map of the San Francisco Bay estuarine system, showing hydrographic regions used in statistical analyses of spatial and temporal variations of silver concentrations in surface sediments.

Pacific (Murozumi, 1981; Martin et al., 1983; Sañudo-Wilhelmy and Flegal, 1992). Therefore, it was not surprising that the introductory paragraph in Eisler's (1996) *Silver Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review* concluded with the statement:

> San Francisco Bay, for example, is impacted by discharges of silver in wastewater outfalls and from the diagenetic remobilization of silver from contaminated sediments in the estuary (Luoma and Phillips, 1988; Rivera-Duarte and Flegal, 1997a).

1.2. Sources of silver contamination in the Bay

As that conclusion indicates, the principal source of silver contamination in the Bay is relatively mundane and contemporary, compared to that of the most problematic contaminant in the Bay — mercury — which is primarily due to historic inputs from mercury and gold mining operations during the California Gold Rush that began over 150 years ago (Conaway et al., 2003). In contrast, extraordinarily high silver concentrations in the southern reach of the estuarine system, or South Bay, have been almost exclusively attributed to much more recent ($\leqslant$100 years) municipal and industrial waste water discharges (Luoma and Phillips, 1988), as observed elsewhere (Rutherford and Church, 1975; Bryan and Hummerstone, 1977; Martin et al., 1988; Sañudo-Wilhelmy and Flegal, 1991, 1992; Flegal and Sañudo-Wilhelmy, 1993; Bothner et al., 1994; Ravizza and Bothner, 1996; Sañudo-Wilhelmy et al., 1996).

Much of the silver contamination in the South Bay has been attributed to discharges from the Palo Alto Regional Water Quality Control Plant (PARWQCP), which has since been upgraded. Moreover, most of the silver being discharged from that plant was traced to effluent from a photographic processing plant, which has now been closed for over a quarter of a century (Squire et al., 2002). As a consequence of that closure, it has been possible to trace subsequent decreases in silver contamination in sediments and biota in an intertidal mudflat adjacent to that point source discharge in the South Bay. With additional analyses it has also been possible to chronicle concurrent declines of silver in sediments, water, and biota throughout the Bay over the past three decades — demonstrating the efficacy of wastewater discharge control efforts on silver contamination in the Bay.

Documentation of those declines in silver concentrations is complicated by ongoing fluxes of contaminant, as well as natural, silver to and within the Bay. Industrial fluxes, which include inputs from contemporary uses of the element in film processing, electroplating, electrical conductors, dental alloys, solder and brazing alloys, and applications as an antibacterial agent and in water purification (Purcell and Thomas, 1998), to the Bay have been declining over the past three decades as a result of decreased silver production, improved manufacturing techniques, increased reclamation, and advanced wastewater treatment throughout the system. Although the increasing trans-Pacific advection of industrial emissions of silver from fossil fuel combustion in Asia has recently been determined to be the principal source of silver contamination in the adjacent North Pacific (Ranville and Flegal, 2005), atmospheric inputs of silver to the Bay are still considered to be relatively inconsequential (<1% total flux; Squire et al., 2002). In contrast, the diagenetic remobilization of silver from historically contaminated sediments (Rivera-Duarte and Flegal, 1997b) appears to be an ongoing — and potentially increasing — problem. This problem is evidenced by some of the most recent measurements of silver concentrations in biota and surface waters of the Bay that are presented in this report, and by other reports of the erosion of relatively clean surface sediments and exposure of historically contaminated subsurface sediments in the Bay as its sediment budget becomes negative (Foxgrover et al., 2004).

1.3. *Silver toxicity in the Bay*

Concerns with silver toxicity (CAS Reg. No. 7440-22-4) are commonly limited to invertebrates and plants, because silver is a relatively rare element and not very toxic to humans or other vertebrates. Although found in trace levels in human tissues, it has no known physiologic function (ATSDR, 1990) and its presence in tissues is considered to be as a contaminant (RAIS, 2005). Exceptionally high levels of silver in humans (>1 g body burden) cause argyria, "*a gray or blue-gray, permanent discoloration of the skin and mucous membranes that is not a toxic effect per se, but is considered cosmetically disfiguring*" (RAIS, 2005). Silver has also been reported to cause mild allergic reactions from dermal exposures, respiratory tract irritation, impaired night vision, and abdominal pain from chronic inhalation; and unusually large internal doses of silver nitrate in humans have been reported to damage the gastrointestinal tract and cause abdominal pain, diarrhea, vomiting, shock, convulsions, and death. However, in the absence of adequate data, silver is not now classifiable as to human carcinogenicity.

In contrast, silver is highly toxic to micro-organisms and invertebrates. More than three decades ago, Bryan (1971) ranked it second only to mercury in its toxicity to marine invertebrates, and again ranked it as one of the three most toxic elements (the others being copper and mercury) to marine invertebrates in estuarine and marine waters one (Bryan, 1984) and two (Bryan and Langston, 1992) decades later. The relatively high toxicity of silver was subsequently corroborated by Eisler (1996), who reported that ionic silver (Ag^+) "*is one of the most toxic metals known to aquatic organisms in laboratory testing*", and more recently by Ratte (1999), who stated that ionic silver "*is one of the most toxic forms of a heavy metal, surpassed only by mercury and thus has been assigned to the highest toxicity class, together with cadmium, chromium(VI), copper and mercury.*"

These generalizations on the relative toxicity of silver to invertebrates are consistent with those of Luoma et al. (1995), which are more specific to the Bay. They noted that reported concentrations of silver toxicities to sensitive species and life stages of aquatic organisms were low ($\leqslant$130 nM) compared to reported dissolved (< 0.45 μm) silver concentrations in the Bay ($\leqslant$250 pM). They, however, indicated that laboratory measures of silver toxicity needed to be made using ambient silver concentrations in Bay waters to address sublethal and chronic toxicities within that system. As a result of the disparity between silver concentrations in laboratory and field studies, as well as the presence of confounding variables (e.g., the multiplicity of contaminants and other stressors) in the Bay, the extent — if any — of silver toxicity in the Bay has been difficult to resolve.

1.4. *Objectives*

The objectives of this report are two-fold. The first is to quantify temporal changes of levels of silver contamination in Bay water, sediments, and biota over the past few decades, since comparable data have been acquired. The second is to establish the current level of concern with silver toxicity, based on the most recent studies in the Bay and in controlled experiments.

2. Materials and methods

2.1. Overview

The United States Geological Survey (USGS) and the University of California, Santa Cruz (UCSC) base the following assessments of silver in Bay sediments, biota, and waters — along with its toxicity — on long-term, ongoing studies and monitoring. The latter is part of the San Francisco Bay Regional Monitoring Program (RMP), and the USGS is now coordinating many of its studies in the Bay with that program. Trace metal clean sampling and analytical protocols of both programs are briefly summarized in this report because details of those methodologies have been provided in numerous previous publications. The methodologies are organized from the earliest (sediments and biota) to the most recent (waters). There are two sets of sediment methodologies, those of the USGS and those of UCSC. Toxicity methodologies are, most appropriately, described following those of the biota since these are also being conducted by the USGS.

2.2. Sediments (USGS)

To chronicle historical inputs of silver into the Bay, the USGS (Hornberger et al., 1999b) analyzed cores from the Central Bay (CB90-12) and the northern reach of the estuary or North Bay, which includes Richardson Bay (RB92-3), San Pablo Bay (SP90-8), and Grizzly Bay (GB90-6). Sediment samples were collected using a gravity corer with a 363 kg weight sound. The cores were 9 cm in diameter and ranged from 0.5 to 2.5 m in length. Cores were split into a working half and an archive half and stored in a cold room until sampling. Samples were taken every 5–10 cm throughout the length of the core, depending on the suitability of the sediment.

Spatial and temporal variations in silver and other elemental concentrations of surface sediments have also been, and continue to be, systematically studied by the USGS in an intertidal mudflat in the South Bay in a long-term program (1977–present). The oxidized layer (~1–2 cm thick) of surface sediments are collected near-monthly from an intertidal mudflat ~1 km south of the wastewater discharge of the PARWQCP, where anomalously high silver concentrations were found in biota and sediments three decades ago (Luoma and Cloern, 1982; Luoma et al., 1985). Frequent sample collections and the long period of record have been instrumental in discerning differences between seasonal variation and inter-annual change. Some of those data (from 1977 to 1998) have been previously reported by Hornberger et al. (1999a, 2000), and more recent data have been reported by Moon et al. (2005).

All USGS sediment samples, whether from the North Bay historical coring study or from the South Bay long-term study, have been processed and analyzed similarly. Sediment samples are wet-sieved to $<64\,\mu m$, to reduce the most important grain size biases that can affect comparisons (Salomons and Forstner, 1984; Luoma, 1990) and dried. Each sieved sediment sample is then homogenized using a mortar and pestle, split into 0.5 g replicate aliquots, and placed into a scintillation vial. A 2-h extraction with weak acid (0.6 M HCl) is used to dissolve the "readily labile" or immediately "bioavailable" fraction of particulate silver. Two replicates of 0.5 g sediment aliquots per sampling site are digested at room temperature and filtered (0.45 μm).

Elemental concentrations, including that of silver, are then measured by graphite furnace atomic absorption spectrometry (GFAAS) using Zeeman background correction with calibration by the method of standard additions. Procedural blanks are analyzed concurrently, as are both internal standards and National Institute of Standards and Technology (NIST) standard reference materials (Sediment Standards 1646 and 2709) to assure the accuracy, precision, reproducibility, and comparability of the data.

2.3. Sediments (UCSC)

Sediment samples for the RMP have been collected from 26 sites, ranging from freshwater to salt water, along the middle or spine of the estuary from 1993 to the present. The sites were initially sampled biannually (winter and summer) from 1993 to 1999, but they have only been sampled annually since then because seasonal variability of elemental concentrations of sediments in the middle of the estuary is minimal.

Those sediments are also collected with a Young-modified Van Veen grab sampler. Duplicate grabs are made at each site, and 3–5-cm deep cores are extracted from each side of the grabs for complementary pore water chemistry measurements (pH, ammonia, and sulfides) after centrifugation aboard the research vessel. Sediment samples are collected with plastic compositing scoops from the top 5-cm of the replicate grabs and placed in acid-cleaned plastic containers. These samples are immediately frozen and stored until thawed for analysis.

Near-total concentrations of silver have been determined by GFAAS and/or high-resolution magnetic sector inductively coupled plasma mass spectrometry (HR ICP-MS) following an aqua regia digestion (Smith and Flegal, 1993; Squire et al., 2002), calibrated with NIST standard reference materials for sediments (1646 and 2709) and National Research Council of Canada (NRCC) reference sediments (BCSS-1, MESS-1, MESS-2, and PACS-1). These are defined as "near-total" concentrations because HF is not used to dissolve refractory aluminosilicates, which contain negligible (typically $<1\%$) amounts of silver in Bay sediments. But the essentially quantitative recoveries with these extractions are often markedly greater than those derived with the 2-h 0.6 M HCl leaches used in the preceding USGS measurements of "readily labile" concentrations of silver in sediments.

Ancillary measurements, used in the following statistical analyses, are also measured with established techniques (Squire et al., 2002). Grain size is determined, following a H_2O_2 digestion of organic material, by separating coarse and fine fractions, and then analyzing the fine fraction by X-ray transmission. Total inorganic carbon is determined by measuring the CO_2 evolved from dissolving the sediment in H_2SO_4, and total particulate carbon is determined by combustion in a high temperature (950°C) oxygen atmosphere. Total organic carbon (TOC) is then determined from the difference between those two prior measurements.

2.4. Biota

USGS studies of silver in Bay biota have focused on resident bivalves in both subtidal and intertidal habitats. In the northern reach of the Bay, *Corbula amurensis* have been collected from four subtidal sites (Mallard Island, Suisun Bay, CNWS, and Carquinez Strait) at near-monthly intervals from 1990 to the present. The sites are located in the ship channel where depths range from 8 to 20 m. Samples are collected with a Van Veen grab and depurated for 48 h, and clams ranging in size from 8 to 25 mm are separated into 1 mm size composites. A similar study is being conducted in the South Bay, as described by Hornberger et al. (2000). There, bivalves (*Macoma petalum*) are collected near monthly, concurrently with the sediments in the intertidal mudflat study described previously. Bivalves ranging (from 8 to 28 mm) are dug up from the mudflat, depurated for 48 h, and separated into 1 mm size composites.

Silver concentrations ($\mu g\,g^{-1}$) are determined with the method described in Brown and Luoma (1995). Briefly, the soft tissue is removed from the shell and combined within each replicate size composite. The tissue is dried, digested by reflux in concentrated HNO_3, reconstituted in 5% HCl, and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Silver concentrations measured in the bivalves after depuration reflect what is accumulated in the tissues, without influences from gut content (Brown and Luoma, 1995). Internal standards and NIST standard reference materials (Oyster Tissue 1566a and Mussel Tissue 2976) are used to assure accuracy and precision of the data.

To understand the sources of silver in the northern reach of the Bay, or North Bay, for this report, temporal patterns of silver tissue concentrations were compared with the temporal pattern of the hydrologic data from the river inflow from the Sacramento and San Joaquin Rivers at the head of the estuary. The hydrologic data, which yield estimates of net Delta outflow near Mallard Island, were derived by performing a water balance about the boundary of the Sacramento-San Joaquin Delta, taking Mallard Island as the western limit. The Interagency Ecological Program provided those data.

There are other ongoing, long-term measurements of silver accumulation in bivalves in the Bay. These include those of the state "*Mussel Watch*" program (Smith et al., 1986; Stephenson and Leonard, 1994), national "*Mussel Watch*" program (Goldberg et al., 1983; O'Connor, 1998; O'Connor and Lauenstein, 2006), and RMP (Gunther et al., 1999), which is based on the state and federal mussel watch programs. Previous reports of temporal and spatial variations of silver concentrations in biota in those studies are consistent with the following discussion of temporal and spatial variations in biota in the USGS studies. However, the latter studies are distinguished by: (1) the intensity of sampling and coverage over limited areas within the Bay and (2) the complementary studies of stress and/or sublethal toxicity of bivalves in those areas.

2.5. Toxicity

As just noted, the potential toxicity of silver in the Bay is determined by comparing tissue concentrations with reproductive activity in the bivalves, using protocols for collection and determination of reproductive stage detailed in Parchaso and Thompson (2002). Briefly, clams are collected for reproduction analyses concurrently with the clams collected for silver analyses. Clams used for reproduction analyses are preserved in 10% buffered formalin upon collection. In the laboratory, the soft tissue of each of those clams is removed and stored in 70% ethyl alcohol.

Tissues are prepared for bioassays using standard histological techniques. Each stained 10-μm thin section is examined with a light microscope and characterized by sex and developmental stage of the gonads. This characterization allows each specimen to be placed in one of five qualitative stages of gonadal development: inactive, active, ripe, spawning, and spent.

Frequently however, individuals are in transition between stages (i.e., active to ripe). To alleviate the difficulty of determining the stage of these individuals, the percentages of clams in the active, ripe and spawning stages are given positive values (multiplied by $+1$), while the percentages of clams in the inactive and spent stages are given negative values (multiplied by -1). These values are summed for each month at each station, and represent the "central tendency of reproduction". For example: a month with 30% active, 10% ripe and 70% inactive would be scored as -30%. The central tendency gives an indication of the reproductive state for the population sampled at that time. Data for reproduction are now available through 1997.

2.6. Water

As recently reported (Sañudo-Wilhelmy et al., 2004), the Bay is the only estuarine system in the United States, and quite likely the world, where silver and other dissolved metal concentrations have been systematically monitored over a protracted period (i.e., decades). The monitoring has been sustained since its inception in 1989, with routine collections at established stations along the length of the estuary, from the confluence of the Sacramento and San Joaquin rivers in the northern reach to the Central Bay, which discharges into the northeast Pacific, and into the South Bay. Again, details of that sampling program for silver have been provided in earlier reports (Smith and Flegal., 1993; Squire et al., 2002) and in a recent summary of the program's measurements of metals, including silver, in surface waters (Flegal et al., 2005). Therefore, the following brief descriptions of sampling and analytical protocols are provided to substantiate comparisons of the silver data from the Bay with those of other estuarine systems and time series analyses of temporal variations in total dissolved ($<0.45\,\mu$m) silver concentrations within the Bay.

All samples for analyses of total (unfiltered) and total dissolved ($<0.45\,\mu$m) silver concentrations in the Bay have been collected with the same procedures over the past two decades (1989–present), as part of the RMP (Flegal et al., 2005) and its forerunner (Flegal et al., 1991). Subsurface (1 m) waters are collected with a Teflon® (PFA) and C-Flex® peristaltic pumping system after it has been rigorously cleaned with high purity reagents (sub-boiling quartz distilled HNO_3 and HCl) and high purity (18.3 MΩ cm) water (Milli-Q®) and then conditioned with water at each sampling site. The pumping system is extended 5 m upstream from the research vessel for the collection of water that is passed through an acid-cleaned polypropylene filter cartridge ($<0.45\,\mu$m) into acid-cleaned polyethylene (LDPE) bottles. The sample bottles are immediately double-bagged in plastic, using clean hands/dirty hands procedures, and stored in larger plastic bags within plastic containers. This sampling system has been intercalibrated with other seawater sampling systems (Flegal and Stukas, 1987), as well as a pore water sampling system (Rivera-Duarte and Flegal, 1997b), to enable comparisons with other silver data.

Equally important, analyses of temporal changes at pM levels have also been enabled by extensively intercalibrated silver measurements over the past two decades, as with the preceding sediment and biota measurements that have been sustained over the past three decades. These water intercalibrations, with both field samples and a number of different reference materials for silver in estuarine and marine water (NIST SRM 1643d and National Research Council of Canada certified reference materials CASS-1, CASS-2, and CASS-3), have been especially important because of changes in both sample processing protocols and instrumentation during that period. Initial measurements were made by graphite furnace atomic absorption spectrometry (GFAAS) with a PerkinElmer 4100 GFAAS (Smith and Flegal, 1993), following preconcentration using a modified ammonium 1-pyrrolidine dithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) organic extraction (Bruland et al., 1985). The same wet chemistry was subsequently used in analyses with a PerkinElemer SIMMA GFAAS and then with a Finnegan ELEMENT HR ICP-MS (Squire et al., 2002). Most recently, the liquid/liquid organic extraction has been replaced by an online extraction using a mini-column packed with a strong anion exchange resin (Dowex 1-X8) in a flow-injection system to separate and concentrate silver from waters of varying salinity prior to determination by HR ICP-MS (Ndung'u et al., 2006).

2.7. Comparability of data

The following time series analyses of changes in silver concentrations in water, sediments, and biota are relatively unique to the Bay. Quantification of those temporal changes can only be made because of the (1) maintenance of a systematic sampling program for protracted periods, (2) use of rigorous trace metal clean sampling techniques that have been intercalibrated with other sampling methodologies, and (3) extensive use of analytical intercalibrations with field samples, procedural blanks, and reference materials with every sample collection, between every sample collection, and with the development of newer analytical protocols and instrumentation that are more sensitive, accurate, precise, and efficient.

But as previously noted, there are substantial differences in the rigor of the USGS (2-h 0.5 M HCl cold leach) and UCSC (~24-h conc. HNO_3:HCl boiling digestion) extractions of silver from Bay sediments. The former is designed to provide a measure of the "readily labile" or immediately "bioavailable" concentration of silver in sediments, while the latter is designed to provide a measure of the "near-total" concentration of silver in sediments. Since there is no simple ratio to normalize the two sets of data, direct comparisons between the USGS and UCSC measurements of silver in Bay sediments cannot be made. The following statistical analyses of the two sets of data also differ because of variations in their temporal sampling regimes and spatial gradients. However, as the following data show, temporal and spatial gradients of silver concentrations in Bay sediments derived from the two different sets of measurements are still relatively consistent. Moreover, those temporal and spatial variations of silver in sediments within the Bay are consistent with the following temporal and spatial variations of silver in biota and waters in the Bay, as well as those of silver toxicity within the Bay.

3. Results and discussion

3.1. Sediments

3.1.1. Temporal gradients of silver concentrations in sediment profiles in the North Bay

All USGS cores showed distinct contrasts in average ($x \pm \mathrm{sd}$) silver concentrations between uncontaminated intervals and intervals deposited after chemical disturbance of the sediments by human activities in the Bay (Hornberger et al., 1999b). Baseline concentrations ($0.09 \pm 0.02\,\mu\mathrm{g\,g}^{-1}$) in the deepest horizons of the Bay cores (pre-1850) are comparable to those in uncontaminated horizons of the reference core from Tomales Bay, California. Diffuse maxima in concentrations ($\geqslant 50\,\mu\mathrm{g\,g}^{-1}$) occur at depth (mid-1900s). While concentrations in more recent sediments ($\geqslant$1970) decrease, they still are 2–7-fold higher than the baseline level.

These vertical gradients evidence the persistent flux of industrial silver to Bay sediments from 1850 to the present. As previously noted, silver is a modern contaminant of interest because of its association with sewage discharges, and silver contamination associated with a point source discharge in the South Bay has been observed since the 1970s (Thomson et al., 1984; Luoma and Phillips, 1988; Smith and Flegal, 1993). In comparison, the highest silver concentrations in Bay cores are similar to the highest concentrations in Puget Sound, Washington, but less than the highest silver concentrations found in some other coastal systems (Daskalakis and O'Connor, 1995; Bricker, 1996; Huh, 1996) as shown in Table 1.

3.1.2. Temporal gradients in surface sediments in the South Bay

USGS time series analyses have shown that annual mean silver concentrations in surface sediment in their South Bay study site decreased by 3-fold between 1977 and 1998 (Fig. 2). Although concentrations were highest in 1979 ($1.62 \pm 0.42\,\mu\mathrm{g\,g}^{-1}$), they did not exceed the effects range-median (ERM) value of $3.7\,\mu\mathrm{g\,g}^{-1}$ (Long et al., 1995). Silver declined to the lowest levels in the mid-1990s (e.g., $0.20 \pm 0.14\,\mu\mathrm{g\,g}^{-1}$ in 1991). In the mid-1980s, annual mean silver concentrations declined to nearly half the ERL value of $1.0\,\mu\mathrm{g\,g}^{-1}$. Although significant decreases in silver and copper concentrations in the sediment did occur over time, concentrations for both metals are still 2–6-fold higher than regional background concentrations.

3.1.3. Spatial gradients in surface sediments throughout the Bay

To examine spatial distributions of silver in surface sediments throughout the Bay, data from the RMP sampling stations were grouped into six hydrographic regions: the Estuary Interface (two stations), Southern

Table 1
Comparison of silver concentrations in surface sediments ($\mu\mathrm{g\,g}^{-1}$, dry weight) in San Francisco Bay reported by the Regional Monitoring Program, with those reported by the USGS in South San Francisco Bay and by the NOAA National Status & Trends program in other locations around the US

	Location	Min	Max	Mean	Date of data	References
RMP	Lower South Bay	0.052	1.18	0.388	1993–2003	a
	Upper South Bay	0.064	0.588	0.317	1993–2001	a
	Central Bay	0.009	0.424	0.207	1993–2003	a
	San Pablo Bay	0.041	0.51	0.227	1993–2003	a
	Suisun Bay	0.029	0.361	0.184	1993–2003	a
	Sacramento River	0.036	0.129	0.074	1993–2003	a
	San Joaquin River	0.046	0.147	0.093	1993–2003	a
	Coyote Creek	0.063	1.8	0.543	1994–2002	a
	Guadalupe Creek	0.073	1.107	0.395	1994–2002	a
NOAA	Gulf of Mexico	0.003	2.2	0.136	1986–1997	b
	SF Bay	0.3	0.74	0.522	1986–1997	b
	Tomales Bay	0.12	0.54	0.211	1986–1997	b
	NW Coast (above SFB)	0.008	1.1	0.191	1986–1997	b
	SW Coast (below SFB)	0.02	4.1	0.507	1986–1997	b
	Hawaii	0.12	0.69	0.36	1986–1996	b
	Great Lakes	0.06	1.88	0.398	1993–1996	b
	NE Coast (above CB)	0.015	6.4	1.06	1986–1997	b
	SE Coast (below CB)	0.006	0.89	0.163	1986–1997	b
	Alaska	0.031	0.29	0.103	1986–1997	b
	Puerto Rico	0.04	0.214	0.132	1986–1996	b
USGS	South Bay mudflat	0.11	2.6	0.643	1977–2003	c

Data sources: (a) RMP, (b) NOAA, (c) Hornberger et al. (2000).*Abbreviations*: NW = northwestern, continental United States; SFB = San Francisco Bay; SW = southwestern, continental US; NE = northeastern, continental US; CB = Chesapeake Bay; SE = southeastern, continental US.

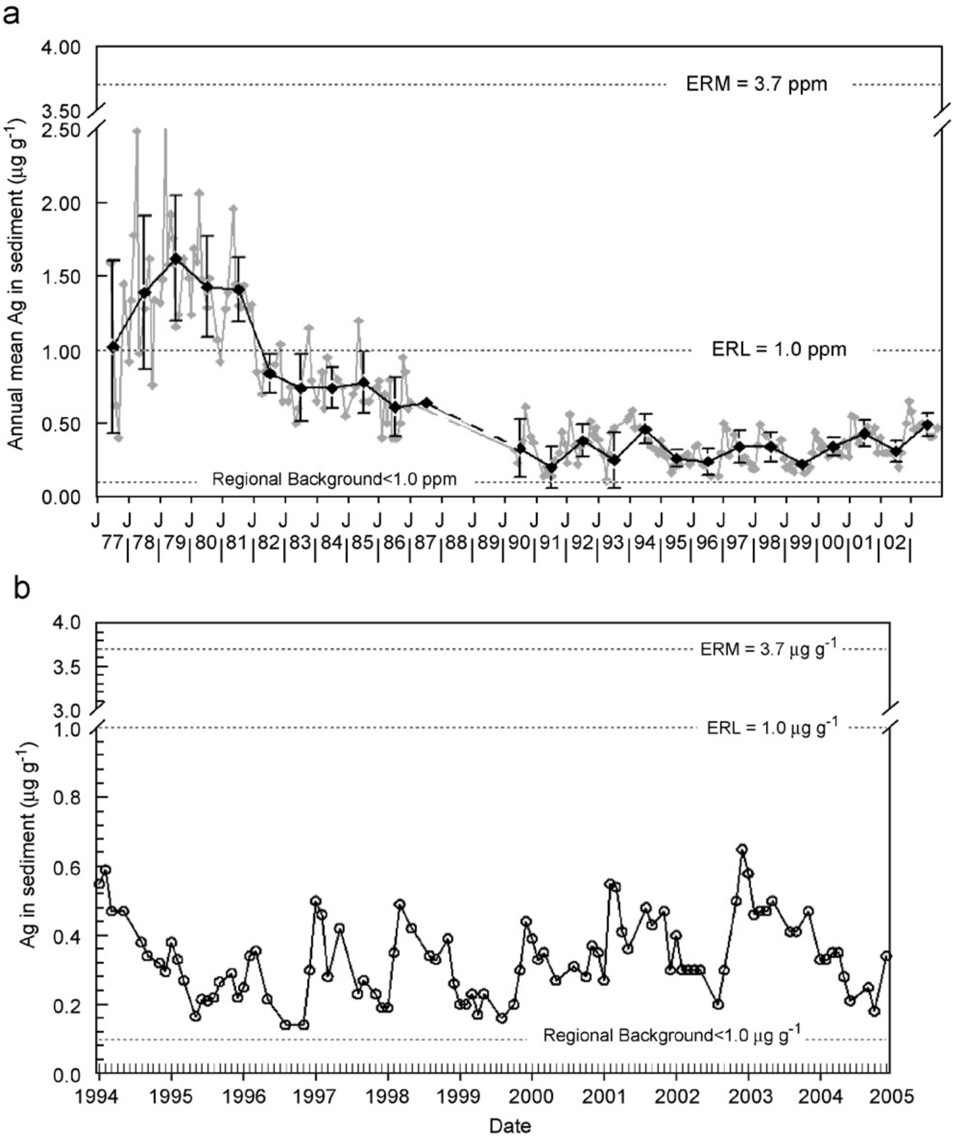

Fig. 2. (a) Long-term (1977–2002) variations in silver concentrations of surface sediments ($\mu g\,g^{-1}$ dry wt) in an intertidal mudflat in the southern reach of the estuary or South Bay and (b) shorter term temporal variations in those sediments from 1994 to 2004, when concentrations were still 2–6 times higher than background levels (from Moon et al., 2005). Effects range-median (ERM) = $3.7\,\mu g\,g^{-1}$ dry wt. (from Long et al. (1995).

Sloughs (two stations), South Bay (seven stations), Central Bay (five stations), North Bay (eight stations), and Delta (two stations), as characterized by the San Francisco Estuary Institute (2001). Comparisons between these estuarine regions, as well as sampling seasons and individual sampling stations, were conducted using the non-parametric Kruskal–Wallis test for multiple comparisons (Zar, 1984). If the null hypothesis, stating that the sample distributions were from the same population, was rejected ($P<0.05$), then a non-parametric multiple comparison for unequal sample sizes was performed on the ranks using Tukey's honestly significant difference (HSD) test. Concentrations below the method detection limits (MDLs) were replaced with one half the MDL for statistical analyses. As previously indicated, no significant seasonal difference was found between the wet (winter) and dry (summer) sampling periods ($H=0.82$, $\mathrm{df}=1$, $P=0.365$).

In contrast, significant differences were found in silver concentrations among the six regions of San Francisco Bay ($H=145.31$, $\mathrm{df}=5$, $P<0.0005$), as shown in Table 2. Silver concentrations in the Estuary Interface, South Bay, and Southern Slough sediments were significantly higher, concentrations in Central Bay and North Bay sediments were intermediate and significantly different from those of other regions, and concentrations in River sediments were significantly lower than those of all the other regions. Ranking by median concentration was the Estuary Interface ($0.43\,\mu g\,g^{-1}$) > South Bay ($0.36\,\mu g\,g^{-1}$) > Southern Sloughs ($0.35\,\mu g\,g^{-1}$) > Northern Estuary ($0.21\,\mu g\,g^{-1}$) > Central Bay ($0.20\,\mu g\,g^{-1}$) > Rivers ($0.065\,\mu g\,g^{-1}$). Significant differences in silver concentrations were also found

Table 2
Statistical analysis of temporal variations of silver concentrations in surface sediments in San Francisco Bay, 1993–2001

						Durbin–Watson (OLS Model)	
Segment	Code	Station	*P*	*n*	adj-r^2	*d*	Interpretation
Rivers	BG20	Sacramento River	0.505	15	0.000	2.647	Inconclusive
Rivers	BG30	San Joaquin River	0.365	15	0.000	1.797	Accept null
Northern Estuary	BF40	Honker Bay	0.485	13	0.000	2.646	Accept null
Northern Estuary	BF21	Grizzly Bay	**0.011**[a]	15	0.355	2.317	Accept null
Northern Estuary	BF10	Pacheco Creek	0.120	15	0.112	1.196	Inconclusive
Northern Estuary	BD50	Napa River	**0.030**[a]	17	0.228	2.214	Accept null
Northern Estuary	BD41	Davis Point	0.586	17	0.000	2.047	Accept null
Northern Estuary	BD31	Pinole Point	**0.005**[a]	15	0.426	1.759	Accept null
Northern Estuary	BD22	San Pablo Bay	<**0.0005**[a]	16	0.572	2.085	Accept null
Northern Estuary	BD15	Petaluma River	0.317	13	0.008	2.714	Inconclusive
Central Bay	BC60	Red Rock	0.812	13	0.000	2.403	Accept null
Central Bay	BC41	Point Isabel	0.214	15	0.048	1.882	Accept null
Central Bay	BC32	Richardson Bay	**0.003**[a]	15	0.475	2.002	Accept null
Central Bay	BC21	Horseshoe Bay	0.210	15	0.050	1.685	Accept null
Central Bay	BC11	Yerba Buena Island	**0.049**[a]	14	0.226	1.807	Accept null
South Bay	BB70	Alameda	0.285	13	0.021	1.719	Accept null
South Bay	BB30	Oyster Point	<**0.0005**[a]	15	0.729	2.028	Accept null
South Bay	BB15	San Bruno Shoal	**0.011**[a]	13	0.405	2.121	Accept null
South Bay	BA41	Redwood Creek	0.070	15	0.172	1.712	Accept null
South Bay	BA30	Dumbarton Bridge	**0.026**[a]	15	0.273	2.168	Accept null
South Bay	BA21	South Bay	**0.028**[a]	15	0.267	2.227	Accept null
South Bay	BA10	Coyote Creek	0.062	11	0.260	2.175	Accept null
Southern Sloughs	C-3-0	San Jose	0.104	14	0.138	2.501	Accept null
Southern Sloughs	C-1-3	Sunnyvale	0.710	12	0.000	2.596	Accept null
Estuary Interface	BW10	Standish Dam	0.464	10	0.000	2.425	Accept null
Estuary Interface	BW15	Guadalupe River	0.936	8	0.000	2.164	Accept null

Region	*P*	*n*	adj-r^2
Rivers	0.230	30	0.017
Northern Estuary	<**0.0005**[a]	121	0.197
Central Bay	**0.001**[a]	72	0.141
South Bay	<**0.0005**[a]	97	0.313
Southern Sloughs	0.255	26	0.014
Estuary Interface	0.859	18	0.000

Data from the RMP sampling stations were grouped into six hydrographic regions: the Estuary Interface (two stations), Southern Sloughs (two stations), South Bay (seven stations), Central Bay (five stations), Northern Estuary (eight stations), and Rivers (two stations), as characterized by the San Francisco Estuary Institute (2001).

[a] Significant decrease in silver concentration.

among the individual stations ($H = 226.48$, df $= 25$, $P < 0.0005$). Median Red Rock (0.015 μg g^{-1}), Sacramento River (0.048 μg g^{-1}), Pacheco Creek (0.055 μg g^{-1}), Davis Point (0.067 μg g^{-1}), San Joaquin River (0.081 μg g^{-1}), and Honker Bay (0.14 μg g^{-1}) sediment silver concentrations were significantly lower compared to those at other stations.

The significantly higher silver concentrations in the Estuary Interface, South Bay, and Southern Slough sediments are likely due to a combination of hydrological conditions, effects from relatively higher influence from the Sacramento and San Joaquin rivers, and the proximity to less heavily populated, urbanized, and industrialized regions of the estuary, hence a reduced potential for silver loadings from municipal and industrial wastewater effluents.

3.1.4. Temporal gradients of silver in surface sediments throughout the Bay

Variation in long-term sediment silver concentration trends may be influenced by sediment characteristics. For example, sediments with more fines (silt and clay) and high total organic carbon (TOC) generally have higher contaminant concentrations than sandy and low TOC sediments (Luoma, 1990; Horowitz, 1991). Therefore, relationships between the transformed silver concentrations, grain size (% clay, % fines, and % silt), and TOC were evaluated with Pearson's correlation coefficients.

These evaluations showed a significant positive relationship between silver and the proportion of clay measured in the sediment samples ($r = 0.515$, $P < 0.0005$, $n = 364$). Linear regression analysis revealed that percent clay accounted for approximately 35% of the variation in transformed silver concentrations: log $(X+1)$ transformed in an attempt to normalize regression residuals (adj-$r^2 = 0.348$, $P < 0.0005$, $n = 364$). A general linear model (GLM) analysis of covariance (ANCOVA) showed a significant difference among the slopes of the regression lines for the individual sampling stations ($F_{25,312} = 2.82$, $P < 0.0005$, $n = 364$). Therefore, the individual station regression lines, instead of a common regression slope, were used to normalize the data (Hebert and Keenleyside, 1995).

Silver concentrations at each station were normalized for percent clay using linear regression analysis. Percent clay was the independent variable and silver the dependent variable. Residuals from this analysis represent the variation in the silver concentration that remains after the influence of percent clay has been removed. Temporal trends were then examined for each station by conducting an *M*-estimation robust regression technique — iteratively reweighted least squares (Chatterjee and Machler, 1997) — using the residuals from the linear regression analysis as the dependent variable, and sampling date as the independent variable. Combining individual station residuals permitted the examination of temporal trends by region.

The presence of first-order autocorrelation was investigated using a Durbin–Watson test on the residuals from a linear regression analysis conducted prior to the robust regression. Insufficient evidence was found to reject the null hypothesis of no autocorrelation. It was assumed that a significant ($P < 0.05$) positive slope indicated an increase in silver concentrations at the station over time; a significant negative slope indicated a decrease over time; and a lack of significance in slope indicated no detectable change in silver concentration.

Based on those assumptions, significant decreases in sediment silver concentrations were observed at the South Bay, Dumbarton Bridge, San Bruno Shoal, Oyster Point, Yerba Buena Island, Richardson Bay, San Pablo Bay, Pinole Point, Napa River, and Grizzly Bay stations, while no detectable changes in sediment silver concentrations were found at the other 16 stations (Table 2). Grand mean-adjusted silver concentrations were estimated based on the robust regression analyses, to have decreased 24% in the Northern Estuary from 0.30 to 0.23 $\mu g\,g^{-1}$; while silver concentrations were estimated to have declined from 0.25 to 0.19 $\mu g\,g^{-1}$ (a 24% decrease) in the Central Bay and 49% in the South Bay from 0.33 to 0.17 $\mu g\,g^{-1}$. The decline in surface sediment concentrations, especially in the South Bay, is primarily attributed to the marked decrease in silver loadings from at least one wastewater treatment plant (PARWQCP) in the area (Squire et al., 2002). Consequently, the temporal decline of silver concentrations of surface sediments throughout the Bay observed in the RMP measurements (Fig. 3), parallel those in the USGS measurements in both vertical profiles in the northern reach of the Bay and a highly impacted region within the southern reach of the Bay.

3.2. Biota

3.2.1. Spatial distribution of silver in the North Bay

The predominance of point source discharges of silver to the Bay was further indicated by the spatial distribution of silver concentrations in *C. amurensis* in the northern reach of the estuarine system or North Bay (Fig. 4). That distribution evidenced a local or site-specific source occurred in the middle region of the study area. On all time scales (monthly, annual means, or means for the decade), the highest silver tissue concentrations in *C. amurensis* occurred at two intermediate sites (Carquinez Strait and CNWS). When data from all 10 years were aggregated, mid-estuary silver concentrations in clams were significantly ($P < 0.05$) higher (two-fold) than in clams at either end of the USGS transect (Mallard Island and San Pablo Bay). The central estuarine peak made detection of impacts easier, because there was not a co-variance with factors like salinity or carbon/organic matter input from river flows.

3.2.2. Temporal gradients in the South Bay and North Bay

Mean annual concentrations of silver in *M. petalum* in the southern reach of the estuary or South Bay showed a strong trend of declining concentrations from the 1970s to 1991 (Fig. 5), despite high, distinctly seasonal, intra-annual variability (Cain and Luoma, 1990). The magnitude of seasonal variation, represented by the error bars, is a product of seasonal tissue growth and tissue metal concentrations. This variation is proportionately consistent among years (Hornberger et al., 1999a, 2000). The highest annual mean ($x \pm$ sd) concentration of silver in *M. petalum* during the study period was $109 \pm 41\,\mu g\,g^{-1}$ in 1980; while silver concentrations then decreased to $3.7 \pm 0.8\,\mu g\,g^{-1}$ in 1998.

Notably, the annual mean concentrations of silver in *M. petalum* appeared to respond rapidly to the treatment upgrades that occurred at the PARWQCP in the 1970s. For example, mean concentrations of silver declined more than 50% between 1980 ($109 \pm 41\,\mu g\,g^{-1}$) and 1982 ($45 \pm 22\,\mu g\,g^{-1}$) after the first phase of plant improvements. They again declined $>50\%$ between 1987 ($55 \pm 30\,\mu g\,g^{-1}$) and 1989 ($11 \pm 7\,\mu g\,g^{-1}$), after the second phase of improvements, and have remained relatively low since then.

Bioaccumulated concentrations of silver in *M. petalum* were significantly ($P < 0.05$) related to sediment metal concentrations among all data (Hornberger et al., 2000). This relationship appeared to be driven primarily by the high concentrations observed in the sediment between 1977 and 1988. There was no significant ($P < 0.05$) relationship in the 1989–1998 data alone, when sediment metal

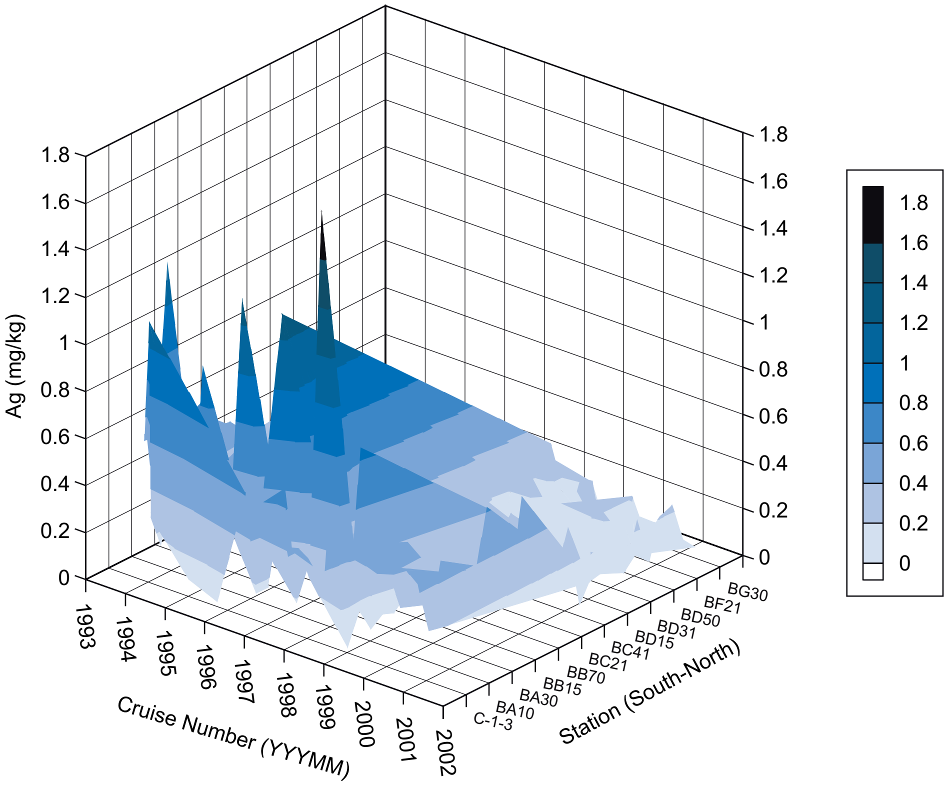

Fig. 3. Spatial and temporal variations in silver concentrations (mgkg^{-1} dry wt) of surface sediments in the San Francisco Bay estuary sampled during the Regional Monitoring Program.

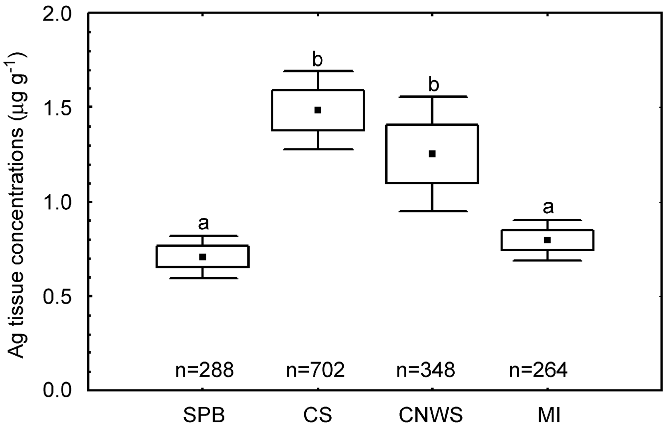

Fig. 4. Spatial distribution of silver concentrations in *Corbicula amurensis* (µg g^{-1} dry wt.) from 1990 to 1999, indicating an internal source of silver in the northern reach of the San Francisco Bay estuarine system.

concentrations were low. Concentrations of silver in *M. petalum* between 1977 and 1998 were also linked to metal loads from the PARWQCP, but this relationship can only be tested from 1989 to 1998 because of the absence of reliable silver loading data prior to 1989. Still, it is reasonable to assume that the relationship was strong prior to 1989 since the PARWQCP was the primary source of silver loadings to the mudflat (Thomson et al., 1984).

Although that study site near the PARWQCP was characterized by only moderately contaminated sediment, as defined by Long et al. (1995), severe silver contamination in the tissues of *M. petalum* occurred in the late-1970s and early-1980s (Thomson et al., 1984). Silver contamination was also documented in resident biota elsewhere in the South Bay in the 1980s (Luoma et al., 1985; Cain and Luoma, 1990), but to a lesser extent than at this site. Inputs from other dischargers in the South Bay do not greatly influence that site (Luoma et al., 1998; Luoma and Phillips, 1988), although all inputs of industrial silver *in toto* probably generate regional-scale contamination. These declines are also consistent with the reports of declining silver concentrations in transplanted mussels (*Mytilus californianus*) in the South Bay at a California mussel watch station between 1977 and 1990 (Stephenson and Leonard (1994), at other California state mussel watch stations and RMP stations throughout the estuary (Gunther et al., 1999), and at other national mussel watch stations around the country (Daskalakis et al., 1997).

In contrast, temporal variation in silver accumulation in *C. amurensis* in the North Bay appear to be partly driven by the hydrology in that part of the estuary, as shown in the study by Brown et al. (2003) which occurred over a period of extreme year-to-year differences in weather and hydrodynamics (Fig. 6). They determined the variability of silver concentrations was related to the pattern of

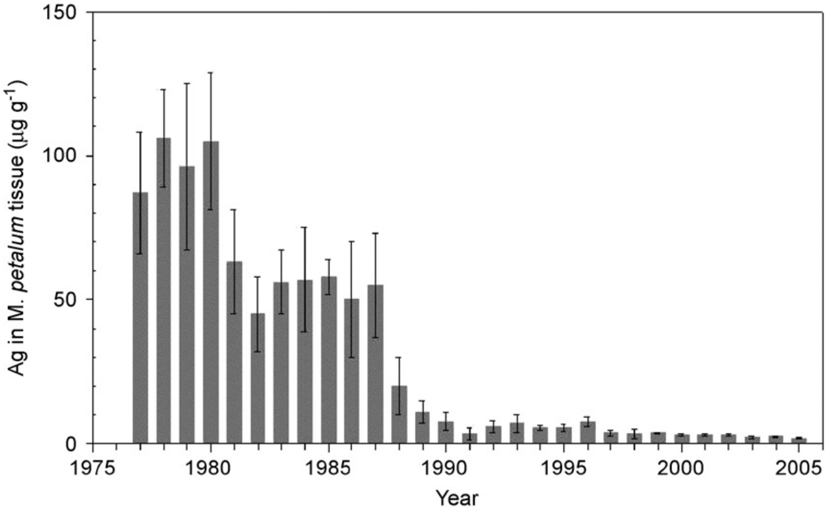

Fig. 5. Annual mean silver concentrations in *Macoma petalum* (μg g^{-1} dry wt.) from an intertidal mudflat in the southern reach of the estuarine system or South Bay (near the Palo Alto Regional Water Quality Control Plant) from 1974 to 2004. Error bars show the standard error of the mean (SEM).

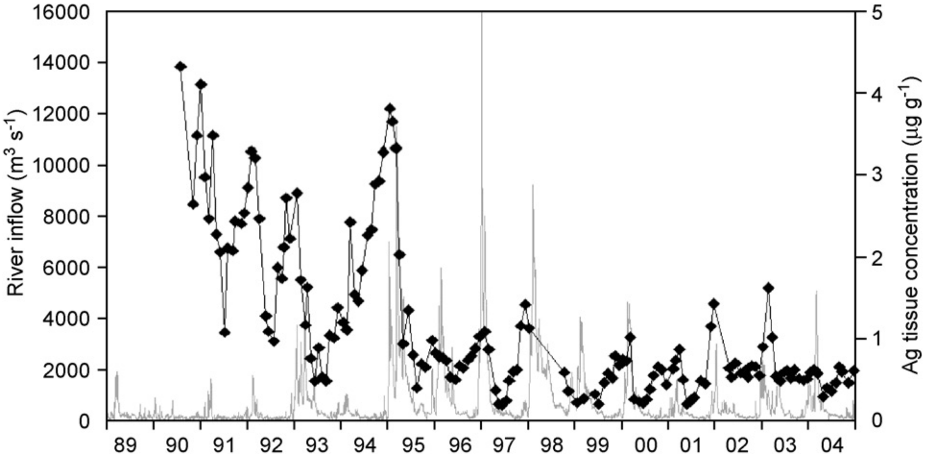

Fig. 6. Temporal variations in silver concentrations in *Corbicula amurensis* (μg g^{-1} dry wt) in the northern reach of San Francisco Bay (Carquinez Strait) relative to river inflow.

freshwater inflow from the Sacramento and San Joaquin rivers. Silver concentrations in the clams decreased when high river inflow began in the winter of every year, while their tissue concentrations steadily increased during low river inflow periods until the next episode of high river inflow. In a critically low flow year, (1994), tissue silver concentrations declined after the winter rains in 1993, then steadily increased over 18 months into 1995 to the highest levels seen in the northern reach of the Bay in that study. After 1995, there were no periods of low flow that extended beyond the typical seasonal pattern, and tissue silver concentrations did not accumulate as high as they had prior to 1995. This temporal variability suggests that the longer the period of low flow, the greater the bioaccumulation of silver in the Bay.

Previous analyses of cores collected in the North Bay show that silver concentrations in sediments peaked between 1965 and 1975 and decreased since the 1980s (Hornberger et al., 1999b), and these data indicate that silver concentrations are also decreasing in the Bay's biota. However, it is interesting to note that dissolved silver concentrations have remained higher in the southern reach of the estuary than elsewhere in the Bay (Smith and Flegal, 1993; Squire et al., 2002, this report). For example, in 1990, dissolved silver concentrations were equivalent to those found in the highly contaminated San Diego Bay (Flegal and Sañudo-Wilhelmy, 1993). These relatively elevated levels of silver in Bay waters combined with the presence of historically contaminated silver concentrations in Bay sediments suggest that it is reasonable to expect that silver concentrations in *M. petalum* and *C. amurensis* in the Bay will continue to exceed regional background concentrations for a protracted period. Moreover, silver concentrations in those organisms may increase if decreasing sediment inputs to the Bay create a negative sediment budget that results in the erosion of relatively clean surface sediments and the exposure of the benthos to more contaminated subsurface sediments.

3.3. Toxicity

Although it can be difficult to determine acute toxicity, much less sublethal or chronic toxicity, in the field, the two long-term field studies of silver concentrations in the biota described above substantiate a strong cause and effect relationships between silver and its effect on reproductive activity in two different bivalves in the Bay. Hornberger et al. (2000) showed the improvement in reproductive capabilities in *M. petalum* after silver concentrations declined (Fig. 7). They found that mature gonadal tissues were not observed, during any month of the year, in more than 50% of individual clams when the concentrations of silver were elevated. Additional evidence indicates *M. petalum* was probably not reproducing successfully at Palo Alto in most years before 1989. After contamination receded in 1989, mature gonadal tissues returned. These observations, and other signs of stress in *M. petalum* during the period of high metal exposure suggest chemical disruption of reproduction by silver. Conversely, other environmental factors show no such association and, thus, are unlikely causes for that sublethal toxicity.

The study by Brown et al. (2003) demonstrated similar results between silver exposures as indicated by tissue concentrations and changes in reproductive activity at sites in the North Bay, but in a different bivalve species, *C. amurensis* (Fig. 8). Silver in the clam tissues exhibited a negative relationship with condition index. In addition, differences in silver accumulation in the tissues also correlated with changes in the reproductive activity of the clam. Reproductive activity decreased whenever tissue concentrations of silver increased above 1 μg g^{-1} in the clam tissues (Parchaso and Thompson, 2002). When silver

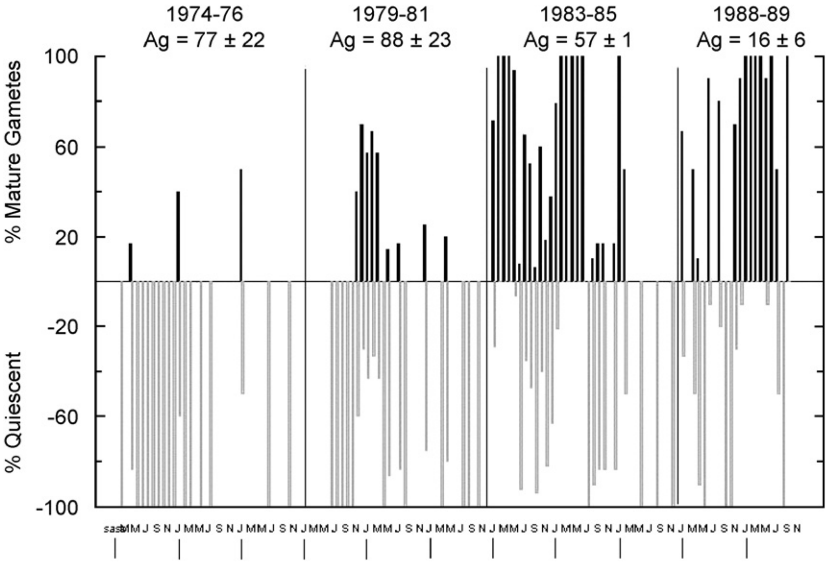

Fig. 7. Reproductive state and silver tissue concentrations in *Macoma petalum* (μg g^{-1} dry wt) at the intertidal mudflat near the Palo Alto Regional Water Quality Control Plant in the South Bay, showing the clams became more reproductively active as silver concentrations decreased in their tissues.

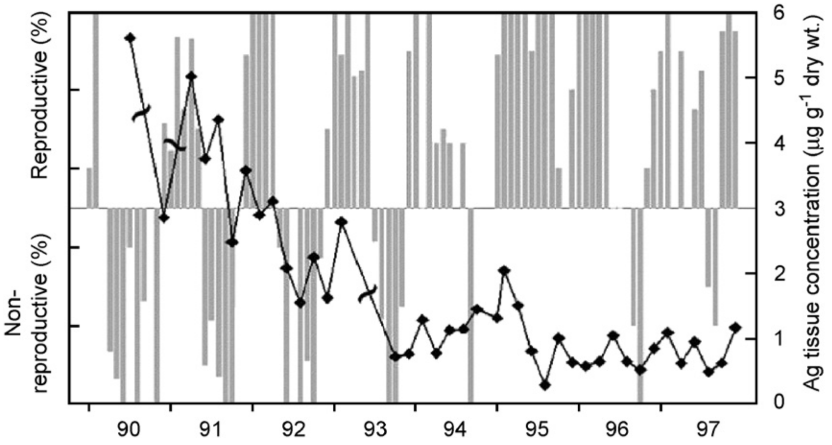

Fig. 8. Reproductive state and silver tissue concentrations in *Corbula amurensis* (μg g^{-1} dry wt) in the northern reach of the estuary (Suisun Bay), showing the clams became more reproductively active as silver concentrations decreased in their tissues.

concentrations in the tissues were highest, the clams were reproductively active only 20–60% of the year. However, when silver concentrations in the tissues of the clams were low, the clams were reproductively active 80–100% of the year. In addition, a significant ($P<0.05$) negative correlation between annual mean silver tissue concentrations and reproductive activity was observed.

The remarkable consistency in biological response in two independent and separate episodes (seen in *C. amurensis* in the North Bay and *M. petalum* in the South Bay) also strongly points to silver as a potential disrupter of reproduction in bivalves at concentrations well below those typically used in toxicity tests. Most natural confounding factors (food, salinity, temperature) were eliminated as possible causative agents of the reproductive effects in both cases. Although a lack of information on organic contaminants prevents them from being discounted as possible stressors, patterns of the toxic effects in space and time were not consistent with what is known about the spatial and temporal variations of organic contaminants in the Bay.

3.4. Water

3.4.1. Speciation

As previously indicated, the most recent RMP intercalibration of analytical methods revealed some prior measurements of silver in Bay waters may be conservatively low (Ndung'u et al., 2006). The intercalibration showed that concentrations of silver measured in Bay waters that had been acidified ($\mathrm{pH}<2$) and stored for periods of 1–2 years were still 10–70% lower than those measured in aliquots of samples after ultraviolet (UV) irradiation. The additional silver released after UV irradiation was positively correlated ($r = 0.77$, simple linear correlation) with chlorophyll-*a* concentrations, but not dissolved organic carbon (DOC) concentrations. Spatial distributions of chlorophyll-*a* and UV-released silver also paralleled along the salinity gradient in the estuary, indicative of an *in situ* biogenic source complexing silver.

These recent observations contrast with those based on previous measurements of silver speciation in the Bay (Miller and Bruland, 1995). The latter, by GFAAS following a competitive equilibrium/solvent extraction, indicated there was not any significant silver-organic complexation in the Bay and the chemical speciation of silver in the Bay was dominated by inorganic chloride complexation. The recent observations also contrast with those of Yang and Sturgeon (2002) in analyses of silver in NRCC certified reference material (CRM) for estuarine water (SLEW-3) that was collected from the Bay. These differences may be due (1) UV radiation release of organo-silver complexes, which is unlikely because of the predominance of inorganic $\mathrm{AgCl}_n^{(n-1)}$-complexes in acidified (pH <2) chloride media (Adams and Kramer, 1999; Miller and Bruland, 1995); (2) UV radiation destruction of anionic organic species competing with $\mathrm{AgCl}_n^{(n-1)}$-species for resin adsorption sites, which is more plausible because of the presence of a diverse array of DOM (humic acids, fulvic acids, glycollic acid, peptides, amino acids, lipids and polysaccharides in estuarine waters (Buffle, 1988) and the presence of relatively large amounts of industrial chelating ligands (ethylenediaminetetraacetic acid, nitrilotriacetate, phosphonates, citric acid, tartaric acid, and surfactants) in the Bay (Bedsworth and Sedlak, 1999); and (3) UV radiation release of $\mathrm{AgCl}_n^{(n-1)}$-species associated with colloids and flocculates formed by acidification of organic-rich estuarine waters, which is most plausible based on previous reports of colloidal flocculation and precipitation of acidified estuarine waters (Sholkovitz, 1976; Sholkovitz and Copland, 1981; Kramer et al., 1994) and the predominance (75–85%) of total dissolved silver in San Francisco Bay (Sañudo-Wilhelmy et al., 1996), and Galveston Bay (Wen et al., 1997).

Consequently, the following comparisons of changes in silver concentrations in the Bay over the past two decades are qualified by the newly recognized presence of an undefined interferent in silver analyses of Bay waters. Future comparisons with samples collected after 2004, when the Ndung'u et al. (2006) methodology was adapted for the RMP, will need to address the impact of that poorly defined interferent on spatial and temporal variations of silver concentrations in the Bay. Specifically, comparisons of data reported prior to 2005 with data reported since then will tend to underestimate hypothesized ongoing decreases in total dissolved silver concentrations in Bay waters associated with decreases in industrial silver inputs and the diagenetic remobilization of industrial silver from previous industrial inputs to the Bay (Flegal et al., 1996a).

3.4.2. Concentration

With the preceding qualification, total dissolved silver concentrations in Bay surface waters have ranged from <1 to 244 pM over the past two decades (1989–2005). The highest of those concentrations was found in the South Bay during the very first summer collection in August 1989 (Flegal and Sañudo-Wilhelmy, 1993; Smith and Flegal, 1993). While relatively high silver concentrations have persisted in the South Bay during summer collections since then, that first, highest value has never been equaled, much less surpassed.

Moreover, the once considered exceptionally high silver concentrations (244 pM) measured in surface waters of the Bay, compared to those of both its freshwater (~6 pM) and sea water (1 pM) end members, are lower than those in other embayments. These include silver concentrations in Long Island Sound (270 pM), Hudson River (260 pM), and San Diego Bay (307 pM). Moreover, the lower silver concentrations measured in the Bay ($\leqslant 5$ pM) are comparable to or lower than those measured in Long island Sound (Buck et al., 2005), the Peconic Bay (Breuer et al., 1999), Great South Bay (Clark, 2000), San Diego Bay (Flegal and Sañudo-Wilhelmy, 1993), Hudson River system (Sañudo-Wilhelmy and Gill, 1999), and Texas estuaries

(Benoit et al., 1994; Wen et al., 1997). Even the highest silver concentrations (4000 pM) in pore waters in the Bay (Rivera-Duarte and Flegal, 1997b) are less than half of those (9000 pM) in pore waters of the Mystic River (Lyons and Fitzgerald, 1983). Consequently, new data for other estuarine systems have again shown that silver concentrations in the Bay are — rather than exceptional — pedestrian.

The table does not include silver concentrations of oceanic subsurface waters, which exhibit nutrient-like profiles (Ranville and Flegal, 2005). Nor does it include those of fresh waters, which vary from 10^0 to 10^7 pM (Benoit, 1994, 1995; Flegal et al., 1996b; Sañudo-Wilhelmy and Gill, 1999; Buck et al., 2005). The anomalously high values in freshwater are often associated with hot springs, acid mine drainage, and receiving waters of municipal and industrial wastes, including treated photo-processing wastes with silver concentrations as high as 27 mg g^{-1} (Eisler, 1996). In contrast, silver concentrations in the Sacramento River and San Joaquin River (~6 pM) at the head the San Francisco Bay estuary are among the lowest reported for any freshwater system (Flegal et al., 1996b). This includes those for nine other rivers that were collected and measured with comparable trace metal clean techniques and found to have silver concentrations ranging up to 90 pM (Benoit, 1994, 1995; Sañudo-Wilhelmy and Gill, 1999; Buck et al., 2005). Consequently, while silver concentrations of fresh waters flowing into the Bay were initially found to be high compared to silver concentrations in oceanic surface waters, subsequent measurements of silver in other freshwater systems have shown that silver concentrations in those riverine inputs to the Bay are now among the lowest measured in any freshwater system.

3.4.3. Spatial variation of silver in Bay waters

Pronounced spatial variation in silver concentrations in Bay waters have been previously detailed, with anomalously high concentrations being found in the South Bay during low flow periods (Smith and Flegal, 1993; Squire et al., 2002). Similar distributions, with less elevated levels in the South Bay, have been observed in subsequent (post-1999) collections. Consequently, the declines in silver concentrations in that region are consistent with those observed in sediments and biota.

3.4.4. Temporal variation of silver in Bay waters

Temporal variations of total (unfiltered) and total dissolved (<0.45 μm) silver concentrations in the Bay were reanalyzed with the time series model developed by Squire et al. (2002). The models, again, were based on associations between the RMP sites, using cluster analysis (average linkage method) that uses variance contained in the original data set to categorize variables by their similarity. The spatial boundaries employed in the new time series models define stations 6–11 as the South Bay and stations 17–23 and SPB001W to SPB0012W to the North Bay.

As previously noted, the models were enabled by the inter-annual consistency of the analyses, based on systematic comparisons of sampling and pretreatment methodologies, numerous intercalibrations of GFAAS and HR ICP-MS measurements, and the reproducibility of concurrent analyses of standard reference materials from each sampling period (Ndung'u et al., 2006). Cluster analyses were used to classify variables in different regions of the Bay based on their similarities, because of heterogeneities in the Bay's physical transport processes and metal inputs. Primary factors controlling silver concentrations were then identified, and incorporated into the following equation:

$$xj(t_k) = a_0 \prod_{i=1}^{n} \exp(a_i f_{ij}(t_k))] \exp(\mathrm{bt}_k)$$

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 (= 2 or 4) 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 primary geochemical factors controlling silver concentrations in water, based on those analyses were determined to be (1) salinity, total suspended solids (TSS), chlorophyll, and time for dissolved (<0.45 μm) silver in the North Bay and South Bay; (2) salinity and TSS for total silver in the North Bay; and (3) salinity, TSS, chlorophyll, and river discharge for total (unfiltered) silver in the South Bay. These models were checked for errors and confirmed using a bootstrapping approach.

Not surprisingly, the extended models showed continuing declines of both total and dissolved silver in the southern reach or South Bay between 1989 and 2005 (Fig. 9), corroborating previous models of those declines from 1989 to 1999 (Squire et al., 2002). All of those modeled declines of silver in water in the southern reach were also consistent with the >2-fold decrease in industrial silver loadings to the area (Squire et al., 2002) and corresponding temporal declines of silver in sediments and biota within the region, during that period. The modeled declines, most notably, occurred in spite of increases in the seasonal mean flux of total and dissolved silver after their minima in 1997. Consequently, the decontamination of silver in the South Bay appears to be an on-going and effective process — i.e., silver is not being depleted in some phase(s) by being sequestered in another phase(s) within the South Bay.

In contrast, but also not surprisingly, the extended models did not show similar declines of either total or dissolved silver in the northern reach or North Bay between 1989 and 2005 — rather they showed increases (Fig. 10). The absence of temporal declines of silver in surface waters in the North Bay was consistent with

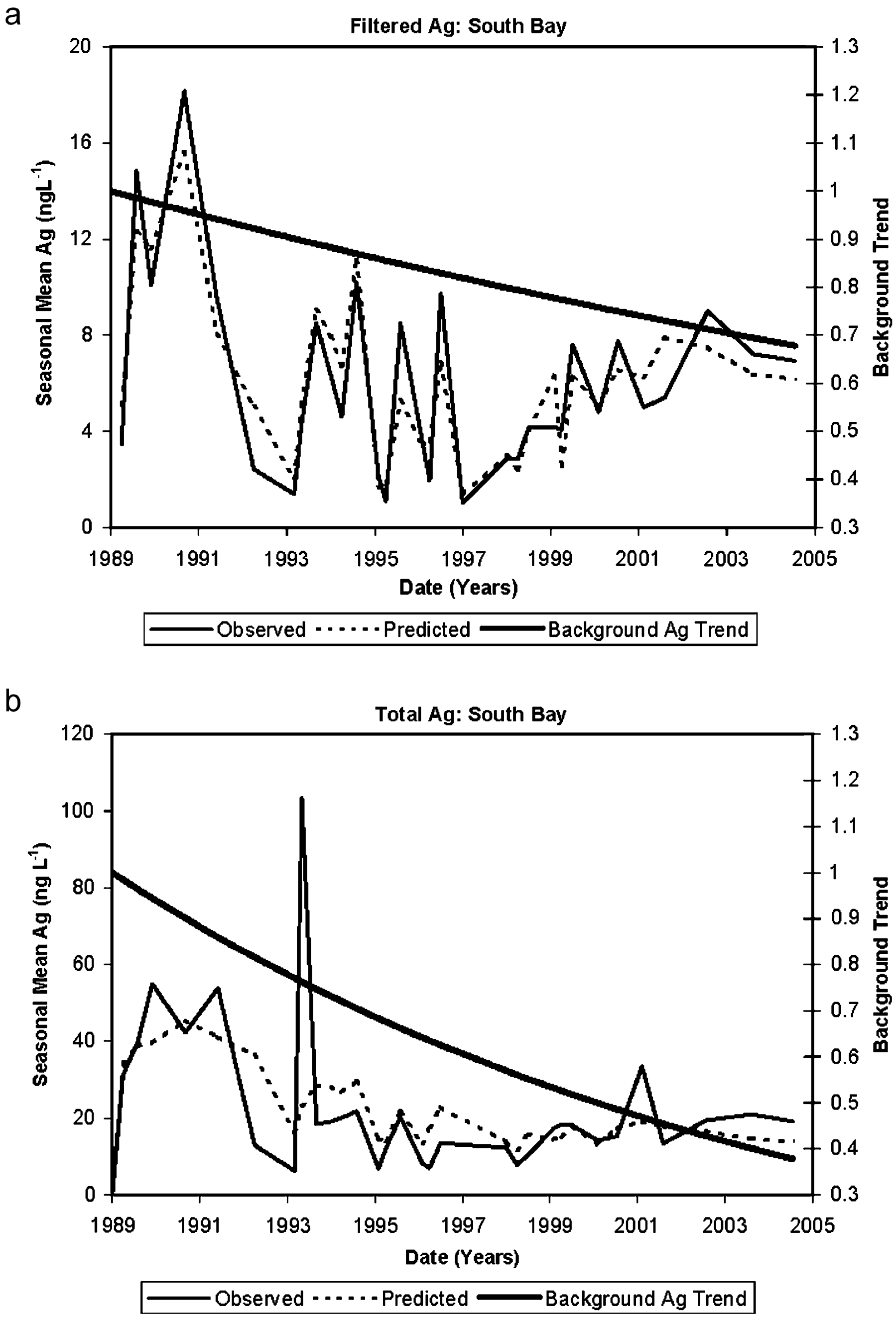

Fig. 9. Temporal variation in observed and projected (a) filtered (0.45 μm) and (b) total (unfiltered) silver concentrations in the southern reach of the estuarine system or South Bay (1989–2005).

previous models of temporal changes of those concentrations in that area (Squire et al., 2002). Moreover, the apparent increase in both total and dissolved silver in surface waters of that region corresponded with spatial measurements of silver in biota within that region, which indicated an internal source of silver contamination within the North Bay. Again, that source may be an unrecognized contemporary source of contamination and/or the diagenetic remobilization of historically contaminated sediments due to the erosion of cleaner surface sediments (Table 3).

4. Summary

In summary, San Francisco Bay is no longer the poster child for silver contamination. Active efforts to reduce industrial silver discharges to the Bay have been effective, as evidenced by the systematic declines of silver concentrations in the sediments, biota, and water within the most contaminated region of the Bay, its southern reach, over the past three decades. Within that time frame, measurements of silver in other estuarine systems and embayments have revealed higher levels

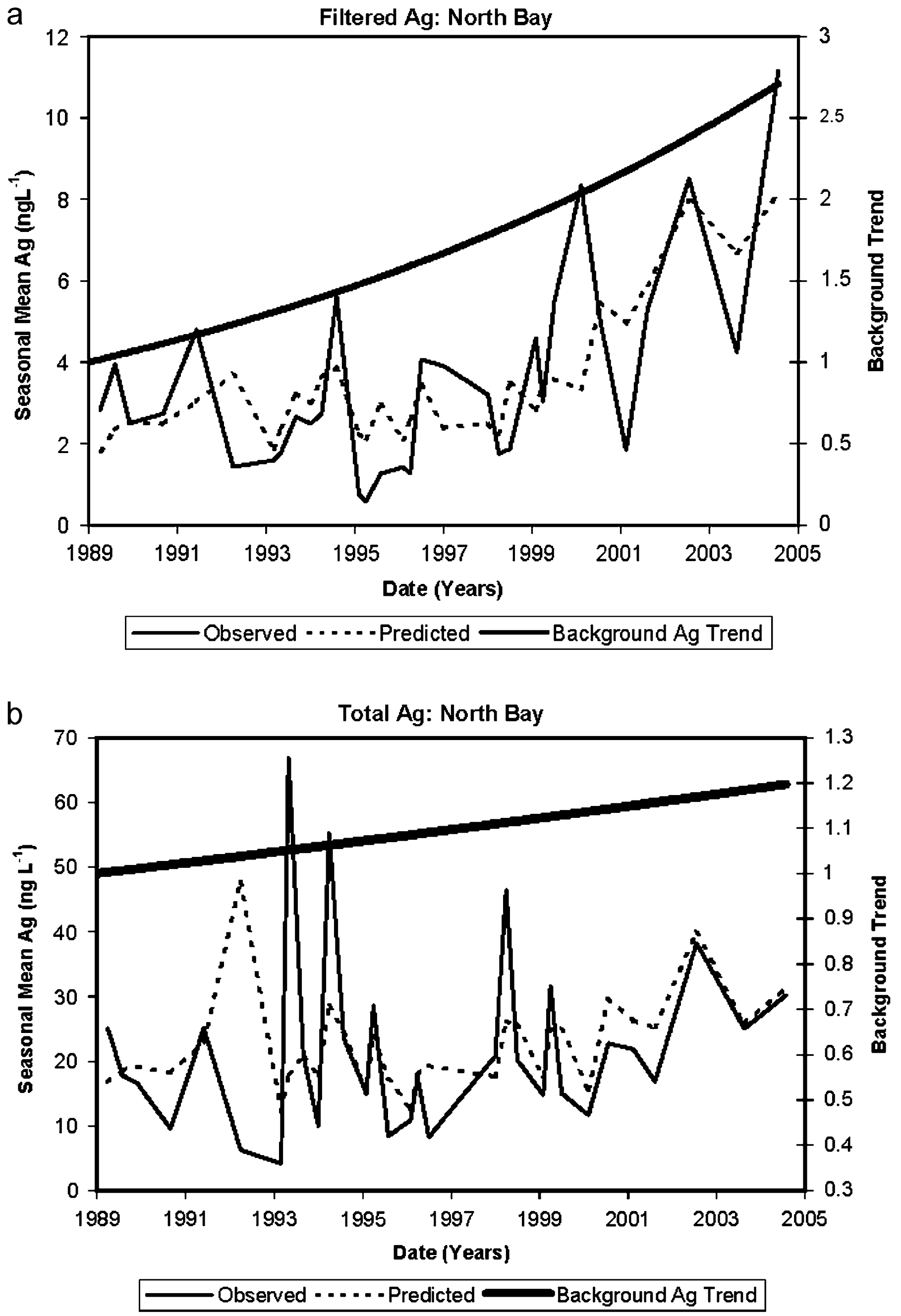

Fig. 10. Temporal variation in observed and projected (a) filtered (0.45 μm) and (b) total (unfiltered) silver concentrations in the northern reach of the estuarine system or North Bay (1989–2005).

of silver contamination in their waters, sediments, and biota.

Those declines evidence both the efficacy of regulatory controls on industrial silver discharges to the Bay initiated over three decades ago and the value of systematic measurements of silver contamination in sediments, biota, and water during the last two to three decades. Without those sustained monitoring programs, neither the validity of the regulatory controls nor the relative health of the Bay would be known.

However, those monitoring programs have demonstrated that silver contamination is still a legitimate concern for the health of the Bay. In spite of reduced concentrations of silver in water, sediments, and biota, the most recent toxicity studies indicate that the element is still adversely impacting invertebrate benthos in the Bay. Moreover, time series analyses indicate that silver concentrations may be increasing in the Bay, as its sediment budget becomes negative and historically contaminated sediments with higher levels of industrial silver are being exposed to surface waters and infauna by erosion.

Consequently, the demonstrated value of systematic, long-term monitoring and complementary research of silver, as well as other contaminants, in the Bay is readily

Table 3
Silver concentrations in bivalves (μg g^{-1} dry wt) in San Francisco Bay and elsewhere

Species	Location	Ag (μg g^{-1} dry wt)			Dates of data	References
		Min	Max	Mean		
C. amurensis	North SFB	0.130	8.05	0.957	1990–2004	a
M. petalum	South SFB	0.485	208	32.171	1977–2004	b
C. fluminea	Transplanted to SFB	0.030	0.59	0.192	1993–2003	c
C. fluminea	Residents in SFB/Delta	0.120	1.096	0.286	2003–2004	d
C. gigas	Transplanted to SFB	0.230	36.7	5.243	1993–2002	c
M. californianus	Transplanted to SFB	0.020	46.38	0.749	1993–2003	c
D. polymorpha	Great Lakes area	0.008	0.671	0.07	1992–1999	e
C. rhizophorae	Puerto Rico	0.200	5.300	1.288	1992–1998	e
C. sinuosa	Florida Keys	0.050	1.400	0.847	1991–1998	e
C. virginica	East Coast	0.150	51.700	3.729	1986–1999	e
C. virginica	Gulf of Mexico	0.035	31.700	2.806	1986–1999	e
M. edulis	East Coast	0.024	5.155	0.345	1986–1999	e
M. edulis	West Coast	0.001	0.913	0.113	1986–1999	e
M. edulis	Gulf of Mexico	0.002	0.078	0.029	1986–1999	e
M. californianus	West Coast	0.005	33.760	1.406	1986–1999	e
O. sandvicensis	Hawaii	1.530	23.710	12.54	1986–1998	e

References: (a) Brown et al. (2003), (b) Moon et al. (2005), (c) RMP, (d) Brown, unpublished data, (e) NOAA National Status and Trends Program.

apparent. The former are needed to chronicle changes in the environment, which are being exacerbated by urbanization and industrialization of the Bay's watershed and by global climate change. The latter are needed to chronicle subtle changes in the health of the Bay, which are being further exacerbated by the invasion of alien species and the discharge of synergistic contaminants. Only with those complementary monitoring and research studies will it be possible to distinguish natural and anthropogenic perturbations of the system and to quantify impacts of different processes on the biogeochemical cycle of silver and other potential toxicants in San Francisco Bay and elsewhere.

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