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Decadal mercury trends in San Francisco Estuary sediments

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Abstract

Monitoring sediment quality and total mercury concentrations over the period 1993–2001 at 26 stations in San Francisco Estuary has shown the seasonal cycling of mercury sediment concentrations, as well as a significant ($P<0.05$) decrease in those concentrations at eight stations across the estuary. This decrease in sediment mercury concentrations is attributed to the transport of relatively cleaner sediment to the estuary from the Sacramento River and San Joaquin River watersheds. Despite the decreases observed in some parts of the estuary, no corresponding trend has been found in concurrent studies on sport fish and bivalves in the estuary.

Keywords: San Francisco Bay; Mercury; Sediment

1. Historical context

The history of mercury contamination and regulation in San Francisco Estuary spans more than 150 years (Table 1). In the 1970s, when mercury was recognized as an environmental health problem, it was already known that the rocks and sediments of the area were rich in mercury (D'Itri, 1972). However, it was not known at that time what the magnitude or relative contributions of natural versus anthropogenic sources were to mercury in the region. Nevertheless, mercury concentrations in some fish exceeded existing federal guidelines, and fish consumption advisories were issued by the State Department of Health for striped bass and catfish in the Sacramento-San Joaquin Delta and the San Francisco Bay area (NRC, 1978). As mercury use was reduced in the 1970s and into the 1990s due to legislation and concerns about its toxic nature, a gradual understanding of the sources of mercury to the estuary developed, including natural sources, urban runoff, atmospheric deposition, and mercury from historic gold and mercury mining (Phillips, 1987). Later studies demonstrated that the contribution of natural mineralization was relatively small, and attributed the bulk of the mercury contamination in the area to historic gold and mercury mining in the watershed (Hornberger et al., 1999; Marvin-DiPasquale et al., 2003; Conaway et al., 2004). Further, these studies showed that mercury concentrations in sediment were generally decreasing with time.

Mercury in sediment is a source of mercury to fish through bacterially-mediated mercury methylation (Compeau and Bartha, 1984; Gilmour et al., 1992) and biomagnification (Boudou and Ribeyre, 1997), and sediments have proven to be an important source of monomethylmercury (MMHg) in the San Francisco Bay-Delta (Choe et al., 2004), and in other estuary systems (Mason et al., 1999; Covelli et al., 2001; Sunderland et al., 2004; Mason et al., 2006). However, due to the many factors involved in the transformation of inorganic mercury to methylmercury (Benoit et al., 2003; Marvin-DiPasquale and Agee, 2003; Marvin-DiPasquale et al., 2003; Sunderland et al., 2006) and involved in biomagnification (Boudou and Ribeyre, 1997), the relationship between mercury in sediment and mercury in fish is complex, and

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Table 1
History of mercury contamination and regulation in San Francisco Estuary

Date	History
1852–1884	Mercury used in hydraulic mining to extract gold in the Sierra Nevada. An estimated 12 million kilograms of mercury used for gold recovery in California (Alpers et al., 2005). An estimated 4.5 million kilograms of mercury is lost to the environment in placer mining operations throughout California (Churchill, 2000)
1880	The peak of hydraulic gold mining in California (Gold Districts of California, Bulletin 193, California Division of Mines and Geology, 1970). Peak ore production at the New Almaden (Cargill et al., 1980)
1893	Caminetti Act establishes California Debris Commission to regulate hydraulic mining and keep the Sacramento and San Joaquin River watersheds free of hydraulic mining debris.
~1940–1970	Use of mercury in environmental applications, such as agriculture and anti-fouling paint. Data not compiled for California, but estimated use for USA is roughly 0.13 million kilograms per year in agriculture, and 0.04 million kilograms per year for anti-fouling paint (Nriagu, 1987).
1964	Peak mercury consumption in the USA of 2.7 million kilograms per year (Nriagu, 1987)
~1970	Mercury recognized as an environmental hazard in the United States (D'Itri, 1972). Fish advisories San Francisco Bay and Sacramento-San Joaquin Delta (NRC, 1978).
1972	Mercury banned in many pesticides and marine anti-fouling paint by the Federal Insecticide, Fungicide, and Rodenticide Act of 1972
1975	Last mine in the New Almaden Mining district closes
1986	San Francisco Bay Regional Water Board decided to incorporate the 1984 USEPA criteria for total mercury in water (25 ng/L as a 4-day average). Effluent limit for wastewater treatment plants was set at 1 μg/L
late 1980s-early 1990s	Refining and development of low-level analytical techniques for Hg measurements.(Gill and Fitzgerald, 1985; Gill and Fitzgerald, 1987; Bloom and Fitzgerald, 1988). A rapid decrease in the U.S. industrial reported consumption of mercury (from roughly 1.7 to 0.5 million kilograms per year) as legislation is enacted to end the use of mercury in batteries and as a fungicide in paint (Sznopek and Goonan, 2000). In 1991, the EPA cancels the product registration for remaining mercury-containing pesticides.
1993	RMP begins monitoring contaminants including mercury (Thompson et al., 2000; Hoenicke et al., 2003).
1997	Study in estuary sportfish shows mercury elevated ($>0.14\,mg\,g^{-1}$) in 40 of 66 samples with the highest concentrations ($1.26\,mg\,g^{-1}$) occurring in shark muscle tissues.(Fairey et al., 1997). RMP conducted its first large-scale fish tissue study for contaminants, including mercury (Davis et al., 2002).
1998	Results of the Fairey et al. (1997) study result in a new San Francisco Bay fish consumption advisory (OEHHA, 1999; Thompson et al., 2000), and place San Francisco Bay on the 1998 USEPA 303(d) list of impaired water bodies.

factors other than total mercury in sediment may be more important in describing the distribution of mercury in a system (Heyes et al., 2006). Total mercury and MMHg have been shown to covary in surface sediment (0–5 cm) in San Francisco Estuary (Conaway et al., 2003) and in other coastal and estuarine areas (Baeyens et al., 1998; Bloom et al., 1999; Mason and Lawrence, 1999; Sunderland et al., 2006). In contrast to this, Choe et al. (2004) found no correlation between total mercury and MMHg in sediments collected from open water, channel, and tributary sites in the northern reach of the estuary and Delta. Other studies in coastal areas have similarly shown a poor correlation or lack of correlation (Hammerschmidt and Fitzgerald, 2004; Heyes et al., 2004, 2006; Lambertsson and Nilsson, 2006), citing the importance of sulfur chemistry and organic matter on the distribution of MMHg. Although quantifying the relationship between sediment total mercury and MMHg is problematic, concentrations of total mercury in sediment have some impact on absolute MMHg concentrations in estuarine systems (Heyes et al., 2006), and changing inputs of mercury in systems have resulted in corresponding changes in sediment MMHg and mercury in biota (Kelly et al., 1995; Turner and Southworth, 1999). However, the effect of long-term trends in total mercury concentration in sediment on mercury in biota has not been investigated in San Francisco Estuary.

Despite reductions in mercury use, mercury remains a persistent contaminant in the sediments of the estuary, and concentrations in some fish are still elevated (Fairey et al., 1997; Davis et al., 2002; Greenfield et al., 2005), exceeding human health screening values (OEHHA, 1999; Thompson et al., 2000). Mercury has also been measured at potentially toxic concentrations, and associated with detrimental effects in some waterbirds in the area (Hoffman et al., 1998; Hothem et al., 1998; Takekawa et al., 2002; Schwarzbach et al., 2006). In light of this, and also because of the revived concerns about the toxicological effects of mercury in the environment on human and wildlife health (NRC, 2000), there is a need to better understand and more effectively manage mercury in the estuary.

With shared financial support, direction, and participation by regulatory agencies, the regulated community, and researchers (Thompson et al., 2000; Hoenicke et al., 2003), the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) was initiated in 1993 to study and monitor the fate, distribution, and trends of contaminants in sediments, water, bivalves and fish of San Francisco Estuary. That program has been sustained and is now the longest running, consistent monitoring program for trace elements in the nation (Flegal et al., 2005). This program provides the data necessary to scientists and regulators alike for developing models of spatial and temporal trends of mercury in waters, sediments, and biota in order to understand and effectively manage mercury in the estuary. The data also show the sources, sinks and variability of mercury in the estuary that are necessary for

identifying the controlling variables for assessing long-term trends.

2. Sources, sinks, and variability of mercury in the estuary

There are multiple historic and contemporary sources of mercury to the estuary, including, in roughly decreasing magnitude: suspended sediment load from the Central Valley Watershed, the Guadalupe River (due to historic mercury mining), local urban and non-urban runoff, wastewater, and atmospheric deposition (Domagalski, 1998, 2001; Ellgas, 2001; Roth et al., 2001; SFEI, 2001; Steding and Flegal, 2002; Thomas et al., 2002; MacLeod et al., 2005; McKee et al., 2005). The majority of the contamination has been attributed to historic mining (Hornberger et al., 1999; Marvin-DiPasquale et al., 2003; Conaway et al., 2004), although the contribution of mercury from mid-to-late 20th century industrial and agricultural applications can not be ignored (Table 1). Factors distributing the mercury from these sources can be further separated into short-term (sub-annual) and long-term (decadal) effects.

Short-term variability of mercury concentrations in water and sediment in San Francisco Estuary is principally influenced by the seasonal variability in its Mediterranean-like hydrology, with relatively high freshwater discharges in the winter and spring and relatively low discharges in the summer and fall (Conomos et al., 1979, 1985; Cloern and Nichols, 1985; Kimmerer, 2002). The seasonality of these discharges are especially important for mercury because water column concentrations of mercury are dominated by particle-bound mercury (Choe et al., 2003; Conaway et al., 2003), which in turn is directly related to freshwater discharge of particulate matter to the estuary and the wind-driven resuspension and control of suspended particulate matter within the estuary (Thomson-Becker and Luoma, 1985; Schoellhamer, 1996, 2002). High-suspended sediment loads brought by winter rains also supply finer sediment to the estuary, and there is a significant positive relationship ($r^2 \geqslant 0.4$, simple linear regressions, $P < 0.05$) between mercury concentrations and the fraction of fine-grain material in the sediment (Conaway et al., 2003; Moon et al., 2005).

Long-term trends in mercury concentration in estuary sediments are dominated by sediment deposition, erosion, and mixing. Sediment core data show that mercury can be sequestered by burial, and differences in mercury concentration of buried versus surface sediments can vary by over an order of magnitude to depths of roughly one meter, representing decades of sediment deposition (Hornberger et al., 1999; Conaway et al., 2004; Flegal et al., 2005). Recent estimates of sediment transport to the estuary from the Central Valley, suggest a downward trend over the later half of the 20th century (Krone, 1996; McKee et al., 2006). Following this, although some areas of the estuary are depositional, there are other areas that are currently undergoing erosion (Krone, 1996; Jaffe et al., 1998; Cappiella et al., 1999; Watson, 2002; Foxgrover et al., 2004; Jaffe and Foxgrover, 2006), so that previously buried material with relatively higher mercury concentrations can return to the active sediment layer. The depth of sediment actively involved in mixing due to resuspension and bioturbation is poorly known for San Francisco Estuary, with estimates from less than 10 to over 30 cm in depth (Davis, 2004). Trends in surface sediment mercury concentrations may be conceptualized in some parts of the estuary as being controlled by a supply of relatively less-mercury contaminated sediment mixing in an active layer that progressively reaches lower into higher-mercury contaminated sediment.

Consequently, resolution of temporal responses in efforts to remediate mercury contamination in the estuary over the past few decades is quite complicated (Flegal et al., 2005). There are multiple historic and contemporary inputs of mercury to the estuary, and those inputs have varied spatially and temporally. There are also other pronounced short term (hours to days to months) and long term (years to decades) variations in the factors influencing the biogeochemical cycling of mercury into, within, and out of the estuary.

3. Rationale

Measurements of MMHg in sediment were added to the RMP program in 1999, and those results are discussed elsewhere along with the physical and geochemical controls of mercury speciation in water and sediment in the system, as well as a comparison of San Francisco Estuary to other estuarine systems (Conaway et al., 2003). The principal objective of this paper is to evaluate changes in mercury within San Francisco Estuary in the recent past through the examination of the trends in RMP sediment total mercury concentrations between 1993 and 2001. This decadal analysis provides a relatively synoptic view of the importance of physical, chemical, and geological controls over both short-term and decadal time variations in these mercury concentrations. Further, the analysis provides insight into the factors that will influence future mercury concentrations in estuary sediments, water and biota.

4. Sampling and chemical analyses

Sediment samples were collected at twenty-six sites ranging from marine to freshwater locations along the main channels of the estuary, with some additional sampling conducted at shallow water sites close to the major or important tributaries (Fig. 1). Sites were typically sampled in the winter and summer during the first seven years of the program (1993–1999), but were only sampled in the winter during 2000 and 2001. The labeling convention of station codes for sites follows an alphabetically increasing scheme, BA through BF, from south to north in the system. Each letter prefix denotes an embayment: Lower South Bay (BA), South San Francisco

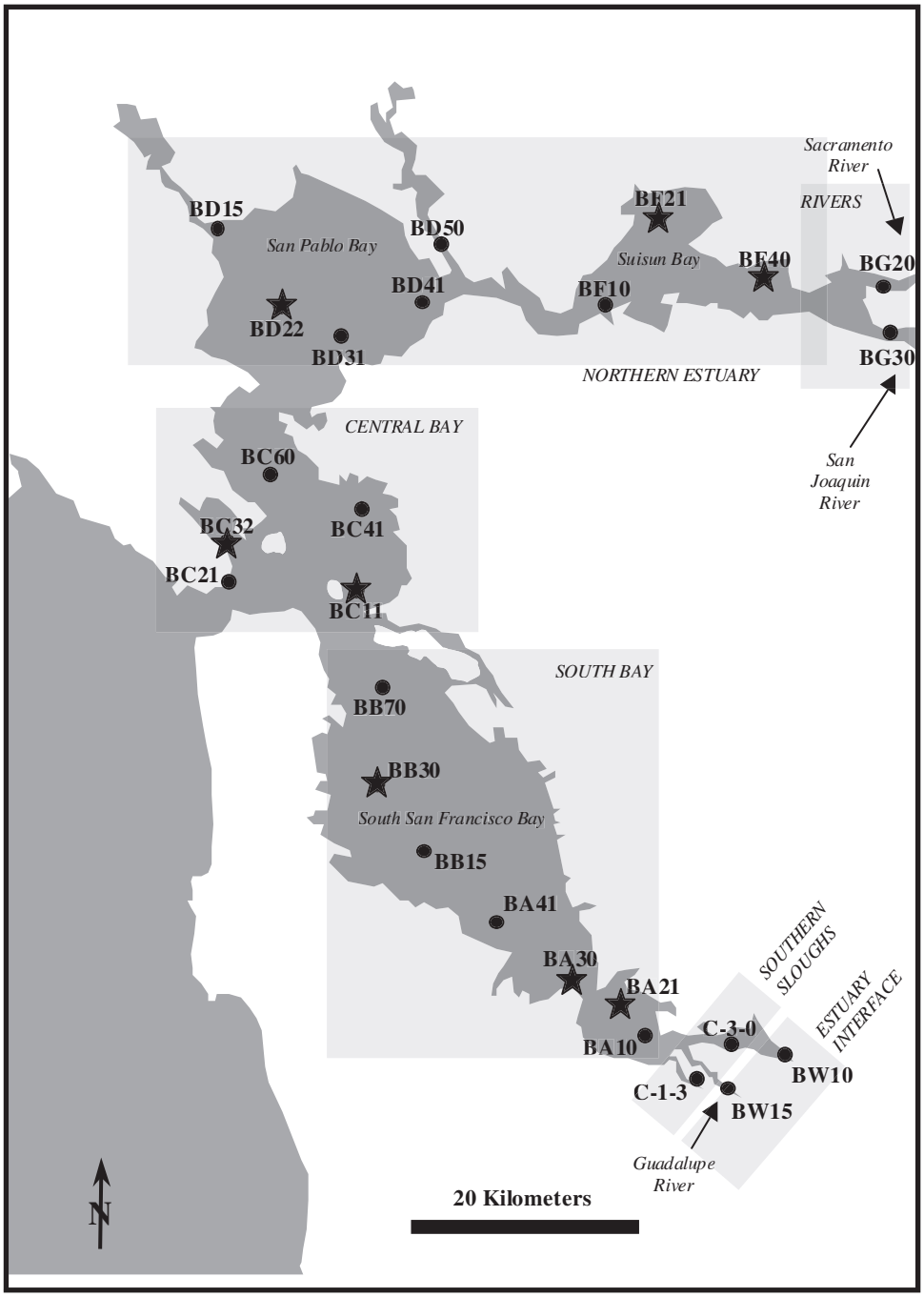

Fig. 1. Map of San Francisco Estuary showing sampling locations, which are divided among six hydrographic regions shown by shaded areas: the Estuary Interface, Southern Sloughs, South Bay, Central Bay, Northern Estuary, and Rivers. Stars represent sites showing a significant ($P<0.05$) decrease in sediment mercury concentration from 1993 to 2001.

Bay (BB), Central Bay (BC), San Pablo Bay (BD), Suisun Bay (BF), and the Sacramento and San Joaquin rivers (BG). The southern slough sites and southern tributary sites are coded as C and BW, respectively. Station names and codes are presented in Table 2.

Preparation of sampling equipment and sediment sampling was performed in a manner to minimize contamination (Gill and Fitzgerald, 1985; David et al., 2001). Duplicate grabs were taken with a Young-modified Van Veen grab at each site, and three 5-cm deep cores taken from each side of the grab for measurement of pore water chemistry. These cores were centrifuged onboard the vessel, and the supernatant used for analysis of ammonia, pH, and sulfides using standard techniques (Flegal et al., 1991). Sediment for chemical analysis was collected by compositing the top 5 cm of the two replicate grabs that were obtained using plastic scoops, and placing the sediment

Table 2
Stations, locations, and statistical parameters used in investigating temporal trends in mercury in San Francisco estuary sediment samples, 1993–2001

Region	Station Code	Station	P	n	adj-r^2	Durbin-Watson	
						d	Interpretation
Rivers	BG20	Sacramento River	0.778	14	0.000	2.131	Accept null
Rivers	BG30	San Joaquin River	0.275	15	0.021	1.682	Accept null
Northern Estuary	BF40	Honker Bay	0.024[a]	13	0.329	2.093	Accept null
Northern Estuary	BF21	Grizzly Bay	0.029[a]	15	0.264	1.656	Accept null
Northern Estuary	BF10	Pacheco Creek	0.210	15	0.050	2.588	Accept null
Northern Estuary	BD50	Napa River	0.365	16	0.000	2.426	Accept null
Northern Estuary	BD41	Davis Point	0.733	16	0.000	1.654	Accept null
Northern Estuary	BD31	Pinole Point	0.602	15	0.000	1.597	Accept null
Northern Estuary	BD22	San Pablo Bay	0.001[a]	16	0.559	1.857	Accept null
Northern Estuary	BD15	Petaluma River	0.064	13	0.213	2.878	Inconclusive
Central Bay	BC60	Red Rock	0.527	13	0.000	2.023	Accept null
Central Bay	BC41	Point Isabel	0.114	15	0.118	2.304	Accept null
Central Bay	BC32	Richardson Bay	0.030[a]	15	0.259	1.749	Accept null
Central Bay	BC21	Horseshoe Bay	0.153	16	0.079	1.146	Inconclusive
Central Bay	BC11	Yerba Buena Island	0.047[a]	15	0.215	2.783	Inconclusive
South Bay	BB70	Alameda	0.176	13	0.083	1.503	Accept null
South Bay	BB30	Oyster Point	0.009[a]	15	0.377	2.807	Inconclusive
South Bay	BB15	San Bruno Shoal	0.183	13	0.079	0.903	+ serial correlation
South Bay	BB15	San Bruno Shoal	0.596[b]	11	0.000	—	—
South Bay	BA41	Redwood Creek	0.090	15	0.145	2.312	Accept null
South Bay	BA30	Dumbarton Bridge	0.012[a]	16	0.326	2.779	Inconclusive
South Bay	BA21	South Bay	0.034[a]	15	0.247	2.511	Accept null
South Bay	BA10	Coyote Creek	0.223	12	0.059	2.897	Inconclusive
Southern Sloughs	C-3-0	San Jose	0.721	14	0.000	1.857	Accept null
Southern Sloughs	C-1-3	Sunnyvale	0.250	14	0.034	2.795	Inconclusive
Estuary Interface	BW10	Standish Dam	0.877	10	0.000	3.111	Inconclusive
Estuary Interface	BW15	Guadalupe River	0.444	8	0.000	2.325	Accept Null

Region	P	n	adj-r^2
Rivers	0.242	29	0.015
Northern Estuary	0.014[a]	119	0.043
Central Bay	0.009[a]	74	0.077
South Bay	0.002[a]	99	0.088
Southern Sloughs	0.412	28	0.000
Estuary Interface	0.440	18	0.000

[a]Significant decrease in mercury concentration.
[b]No trend detected after correcting for autocorrelation using the Hildreth - Lu procedure.

into acid-cleaned plastic containers that were immediately frozen.

Sediment samples for total mercury (Hg_T) analyses were processed and analyzed using trace metal clean protocols (Gill and Fitzgerald, 1985; Flegal et al., 1991; David et al., 2001). Samples were prepared by digesting sediment in boiling HNO_3/H_2SO_4, followed by 12 h oxidation with 0.2 N BrCl (Bloom and Crecelius, 1987), and analyses of Hg_T were then performed using tin chloride reduction, gold amalgamation trapping, and quantification by cold vapor atomic fluorescence spectrophotometry (Gill and Fitzgerald, 1987). The method detection limit (MDL) for Hg_T in sediments in analytical batches was less than 5 ng g^{-1} (0.02 nmol g^{-1}), and was generally less than 10% of sample values. Analyses of a polluted marine sediment certified reference material (PACS-2) from the National Research Council of Canada were within 10% of the certified value and 95% confidence interval values (3.04 ± 0.20 μg g^{-1}). The precision, relative standard deviation (RSD), of multiple analyses of certified reference materials was typically less than 10% RSD, and precision of sample analyses was less than 35% RSD.

Ancillary sediment parameters were measured using established techniques (ASTM, 1985; Chapman et al., 1986). After H_2O_2 digestion to destroy organic material, grain size analysis was performed by separating coarse and fine fractions by wet sieving, and then analyzing the fine fraction by X-ray transmission. Total inorganic carbon was determined by dissolving sediment in H_2SO_4 and measuring evolved CO_2; total carbon was determined by combusting sediment in a high-temperature oxygen atmosphere (950 °C) to oxidize all carbon to CO_2. Total organic carbon (TOC) was then determined by the difference between total carbon and total inorganic carbon measurements.

5. Statistical analyses

In examining mercury spatial distributions in sediment, 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). Comparisons between these 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 in a manner paralleling the Tukey test, with mean ranks being used instead of means (Zar, 1984). Concentrations below the method detection limit (MDL) were replaced with one half the MDL value for statistical analyses.

A method commonly used to improve the comparison of trace element and organic contaminant concentrations in sediments is to normalize them to a sediment component unaffected by anthropogenic activities, such as iron or aluminum (Luoma, 1990; Hanson et al., 1993; Daskalakis and O'Connor, 1995; Schiff and Weisberg, 1999). A significant positive relationship was observed between log-transformed mercury and iron dry weight concentrations ($adj\text{-}r^2 = 0.303$, $P<0.0005$, $n = 367$), therefore normalization was considered appropriate (Hebert and Keenleyside, 1995). Mercury and iron concentrations were $\log_{10}(X+1)$ transformed to normalize the regression residuals.

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 ($F_{25,315} = 2.74$, $P<0.0005$). Therefore, the individual station regression lines, instead of a common regression slope, were used to normalize the data (Hebert and Keenleyside, 1995). Mercury concentrations at each station were normalized for iron using linear regression analysis with iron as the independent variable and mercury the dependent variable. Residuals from this analysis represent the variation in contaminant concentration that remains after normalization. Temporal trends were then examined for each station by performing a linear regression analysis using the residuals 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, as appropriate, using the Durbin–Watson test, and corrected when found using the Hildreth–Lu procedure. A significant positive slope ($P<0.05$) indicates an increase in mercury concentrations at the station over time. Similarly, a significant negative slope indicates a decrease over time, while a lack of significance indicates no detectable change in mercury concentration.

6. Results and discussion

6.1. Spatial and temporal trends of mercury in surface sediments

Spatially, the six hydrographic regions of the estuary showed significantly different mercury concentrations in surface sediments ($H = 56.71$, df = 5, $P<0.0005$; Table 2). Ranking by median mercury concentration was: Estuary Interface ($0.35\,\mu g\,g^{-1}$) > South Bay ($0.28\,\mu g\,g^{-1}$) and Northern Estuary ($0.28\,\mu g\,g^{-1}$) > Southern Sloughs ($0.24\,\mu g\,g^{-1}$) > Central Bay ($0.22\,\mu g\,g^{-1}$) > Rivers ($0.10\,\mu g\,g^{-1}$). Non-parametric multiple comparisons showed the Estuary Interface, South Bay, Northern Estuary, and Southern Sloughs sediments were significantly higher ($P<0.05$) in mercury than sediments from the Central Bay, and Rivers regions. Significant differences in mercury concentrations were also found among the individual stations ($H = 197.36$, df = 25, $P<0.0005$): BW15 (median $0.60\,\mu g\,g^{-1}$), BD50 ($0.34\,\mu g\,g^{-1}$), BA30 ($0.33\,\mu g\,g^{-1}$), BA21 ($0.32\,\mu g\,g^{-1}$), and BD22 ($0.32\,\mu g\,g^{-1}$) were observed to be significantly higher in mercury than BC21 ($0.14\,\mu g\,g^{-1}$), BD41 ($0.08\,\mu g\,g^{-1}$), BF10 ($0.07\,\mu g\,g^{-1}$), BG20 ($0.05\,\mu g\,g^{-1}$), and BC60 ($0.03\,\mu g\,g^{-1}$). This spatial distribution reflects the relatively lower mercury concentration sediments of the Central Valley and the accumulation of contaminated sediment from historic mining in the wide, shallow bays of the southern and northern reaches of the estuary.

The analyses indicate that mercury concentrations in sediment have decreased at some locations in the estuary over the period 1993–2001. Significant decreases ($P<0.05$) in sediment mercury concentrations were observed at stations BA21, BA31, BB30, BC11, BC32, BD22, BF21, and BF40 (Table 2, Figs. 1 and 2). Based on linear regression analysis, grand mean-adjusted mercury concentrations were estimated to have decreased 22% in the Northern Estuary from 0.27 to $0.21\,\mu g\,g^{-1}$ between 1993 and 2001. Likewise, concentrations have declined from 0.30 to $0.25\,\mu g\,g^{-1}$ (a 17% decrease) in the Central Bay and 32% in the South Bay from 0.25 to $0.17\,\mu g\,g^{-1}$ during that period. After normalization, no significant regional ($H = 0.32$, df = 5, $P = 0.997$), seasonal ($H = 0.00$, df = 1, $P = 0.985$) or station ($H = 2.95$, df = 25, $P = 1.000$) differences were found in grand mean-adjusted mercury concentrations.

An examination of sediment quality characteristics shows that mean concentrations of iron and aluminum are related and appear to follow seasonal cycles associated with freshwater flow into the estuary (Fig. 3). Iron and aluminum concentrations tend to covary (show a similar pattern) through the sampling period, although aluminum has a wider range of concentrations. Mean values of iron and aluminum appear to be higher in years with increased freshwater input. Presumably, the fraction of iron and aluminum increase as the fraction of silica ($\%SiO_2$, the largest oxide fraction of sediment) in the sediment decreases. This temporal variation suggests that years of

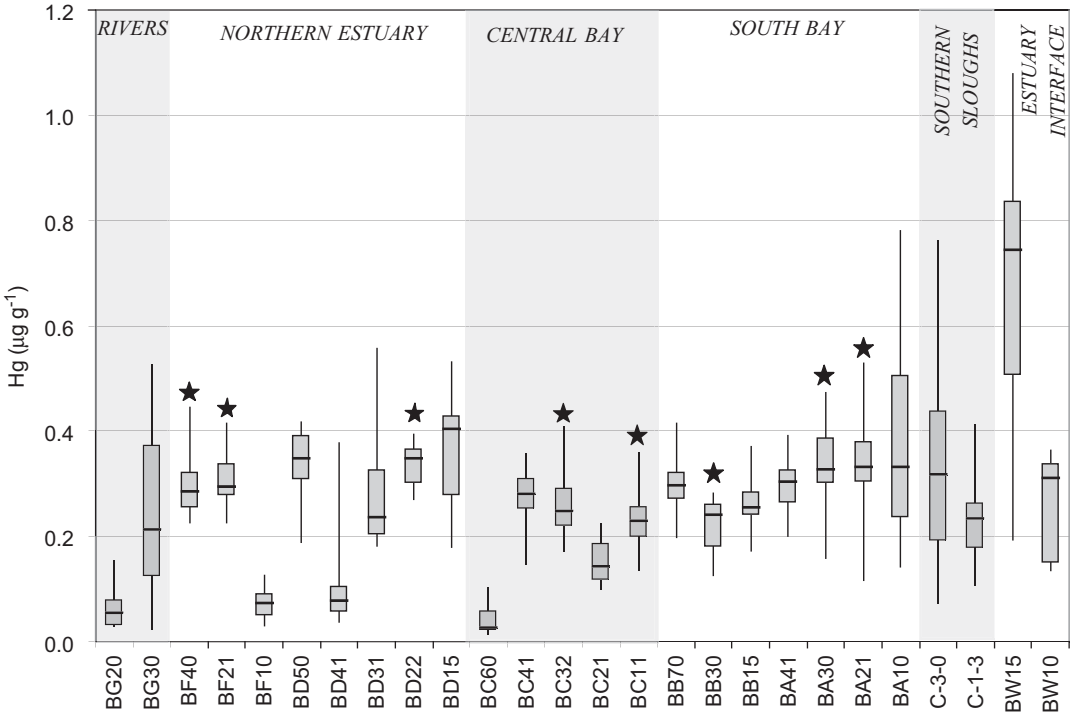

Fig. 2. Box and whisker plot of mercury concentrations in micrograms per gram ($\mu g\,g^{-1}$ dry weight) in San Francisco Estuary, 1993–2001, at stations shown on Fig. 1. Sites are divided among six hydrographic regions shown by shaded areas: the Estuary Interface, Southern Sloughs, South Bay, Central Bay, Northern Estuary, and Rivers. Box ends represent the 1st and 3rd quartiles, and whiskers extend to maximum/minimum values. Median concentrations are displayed inside boxes. Stars represent sites showing a significant ($P<0.05$) downward trend in concentration.

high discharge transport relatively silica-poor sediments, with relatively low mercury concentration, to the relatively silica-rich estuary sediments. This proposed pulse of new geologic material to the estuary may partly explain the observed decreases in mercury concentrations in estuary sediments.

In general, the distribution of grain size follows a similar seasonal pattern (Fig. 3), with a higher fraction of fine-grained material present in the winter season. High-suspended loads brought by winter rains supply finer sediment in winter, and there is a winnowing to coarser sediment in the summer through the process of wind-driven resuspension and erosion of finer-grained material (Thomson-Becker and Luoma, 1985; Moon et al., 2005). This seasonal pattern of greater percent fines in winter does not always hold, however. In the southern reach (South Bay, Estuary Interface, and Southern Sloughs regions), percent fines are driven by Southern Sloughs and Estuary Interface values, resulting in apparent summer highs in percent fines (Fig. 2). This probably reflects a build-up of fine-grained sediment in the channels there over the relatively low-flow period. This effect is also seen at BF10 in the Northern Estuary. Changes in grain-size are perhaps better illustrated by the changes in sediment mercury concentrations (Fig. 4) shown for individual stations, which are generally correlated with percent fines ($<63\,\mu m$).

Following general sediment characteristics, mercury concentrations at individual stations also show a seasonal cycling (Fig. 4), with a typical elevation in mercury concentrations in winter relative to summer, consistent with observations in other long term data sets of mercury in the estuary (Moon et al., 2005). This seasonal cycling is attributed to the hydrogeological processes affecting grain-size distributions described above. Overall, no significant seasonal difference was found in sediment mercury concentrations between the wet and dry sampling periods when concentrations were normalized to the fraction of iron ($H = 3.08$, $df = 1$, $P = 0.079$). The cycle is generally apparent in the Rivers and Northern Estuary stations (BD31, BG20, BF21, BG30, and BD15), although the 1993–1994 years and 1998–2001 years show exceptions (due to low sampling density in the latter case). It is less apparent in the South Bay, but can still be observed in the Lower South Bay (BA10, BA 21) and on the eastern side of the South Bay region (BB15, BB30). Some sites, however, show an opposite trend (BF10, BF40, and Southern Sloughs stations). The trend of higher sediment mercury values in the summer is typically found at stations situated where there is an opening to a larger channel, and is attributable to a build-up of a delta of fine-grained sediment over the relatively low-flow summer period.

Sediment cores in the estuary have generally shown decreasing sediment mercury concentrations over the past century (Hornberger et al., 1999; Conaway et al., 2004) suggesting the change between 1993 and 2001 is due to sediment mixing as relatively less-mercury contaminated sediment is transported to the estuary. Suspended sediment transport to the Delta is dominated by the Sacramento

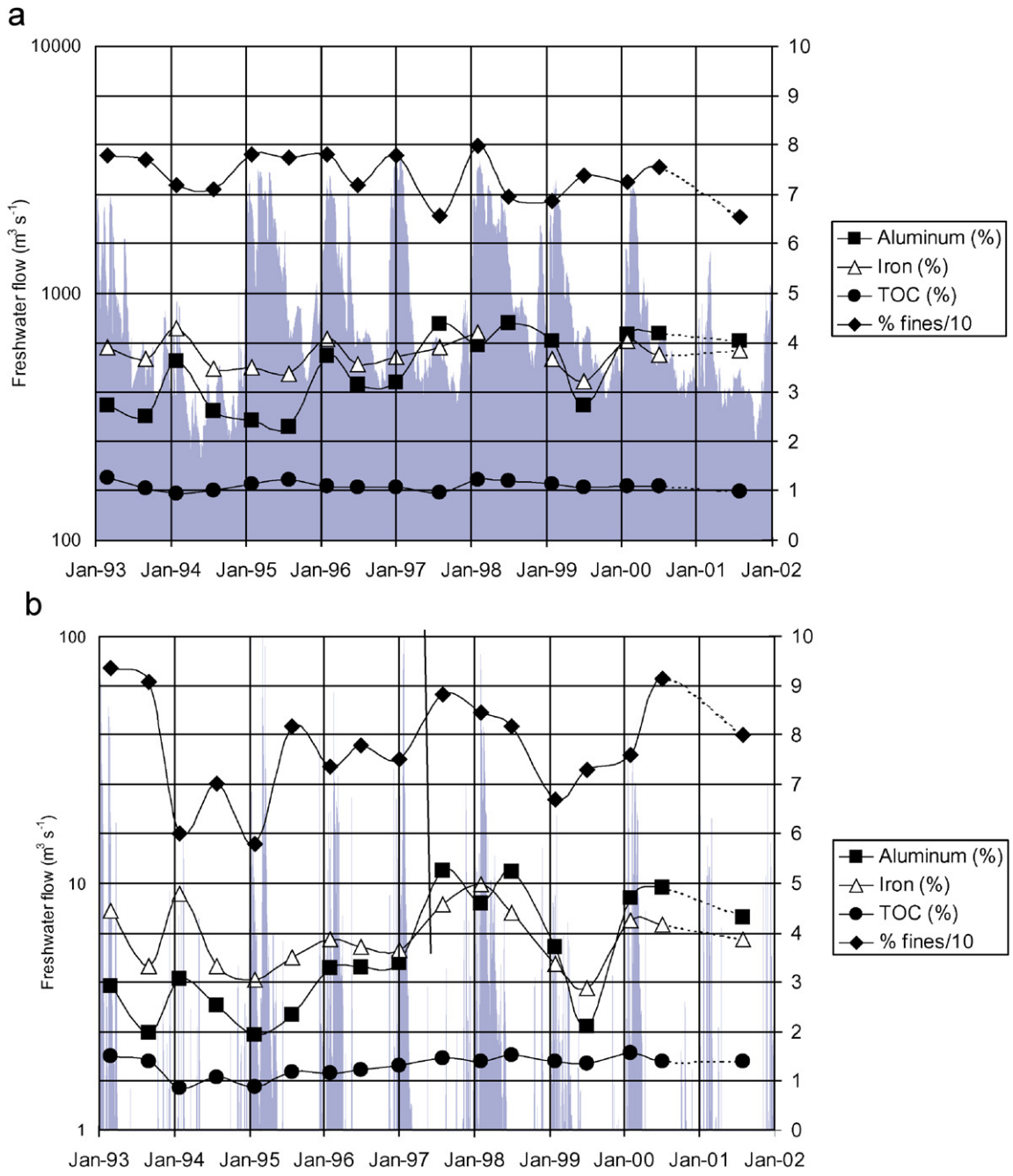

Fig. 3. Mean concentrations of iron, aluminum, and total organic carbon (TOC) in percent (%) for sediments in San Francisco Estuary, 1993–2001. Percent fine grain material shown divided by 10 for scale purposes. Discharge from tributaries shown in cubic meters per second ($m^3 s^{-1}$) on a logarithmic scale. Figures show values from (a) northern reach with the freshwater flow as input from the Sacramento–San Joaquin Delta measured as the sum of discharge measured at Freeport and Vernalis, and (b) the southern reach with freshwater flow measured from the Guadalupe River. Discharge data from the USGS (2005) and California Data Exchange Center 2005.

River, with the Sacramento River (including the Yolo Bypass) contributing 60–80% of the total suspended sediment load (Arthur and Ball, 1979; Krone, 1979; Wright and Schoellhamer, 2005; McKee et al., 2006). In addition, the Sacramento River provides 85% and the San Joaquin 11% of the annual freshwater flow into the Delta (Kimmerer, 2002). Riverbed/benthic sediments in the Sacramento River system have mercury concentrations typically less than $0.15\,\mu g\,g^{-1}$ (Domagalski, 2001), and are relatively cleaner than those in the estuary, which are typically between 0.2 and $0.4\,\mu g\,g^{-1}$ (Fig. 4). Although the source of the sediments to the southern reach is uncertain (though thought to be dominated by local rivers), large flood events can carry sediments from the northern to the southern reach (Ruhl et al., 2001; Watson, 2002). The nine-year sampling period covers a transition from a period of

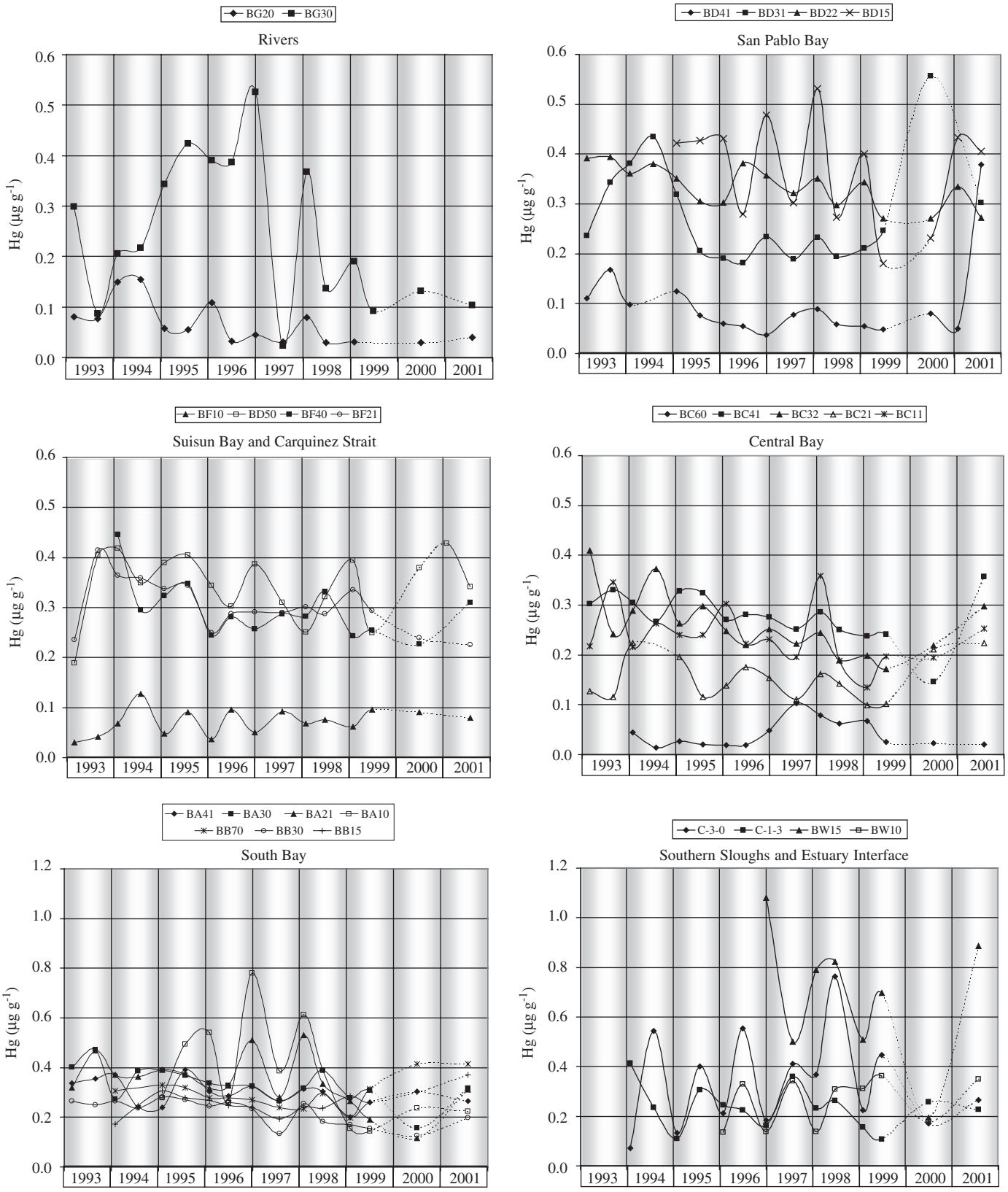

Fig. 4. Concentrations of mercury in micrograms per gram ($\mu g\,g^{-1}$ dry weight) in sediment at stations in San Francisco Estuary, 1993–2001. Rainy season for each year, which lasts roughly from November to March, is shown with a gray background. Smoothed lines highlighting temporal trends at stations are dashed when sampling density is less than twice annually. Note the different concentration scales on stations in the southern reach (South Bay, Southern Sloughs, and Estuary Interface).

drought (1987–1992) to wet conditions—two of the wettest years since the 1960s (1995 and 1998) and a flood year in 1997 (Kimmerer, 2002). Accompanying this transition from drought to wet years, there appears to be a broad increase in the relative percent of iron and aluminum in the sediment of both the northern and southern reach of the estuary (Fig. 3), beginning in about 1995 and continuing through 1999. This shift in lithology represents a pulse of allochthonous material entering the estuary as a result of the heightened runoff in the mid-1990 period. Therefore, it is possible that the decrease in sediment mercury concentrations documented in this paper can be attributed to a series of relatively high precipitation years with relatively high fluvial inputs contributing a pulse of relatively less mercury-contaminated sediment into the estuary.

6.2. Implications and comparison to water data

Although site specific sediment data do not match well with water data (Conaway et al., 2003), we expect regional changes in sediment concentrations to be reflected in water concentrations. This expectation is based on the log distribution for mercury between particulate and dissolved phases ($\log K_d$) that ranges from about 10^4 to 10^7, showing that the bulk of the mercury in the water column is associated with the particulate phase (Choe et al., 2003; Conaway et al., 2003). Total water column concentrations are, therefore, driven by physical factors affecting sediment, such as wind and water driven resuspension. However, it has been shown that the K_d typically increases with increasing organic content of the particles (i.e. the % fines), so that in wet years there should actually be a higher dissolved mercury concentration than in years of lower flow, even if the loading of particulate Hg is lower in the dryer years.

6.3. Implications and comparison to fish and bivalves

Linking observations made in changes of mercury in sediment to biota is an essential part of understanding the biogeochemistry of mercury in the estuary. Consequently, we compared the trends observed in our data with concurrent, interannual and long-term studies of mercury in biota.

Long-term studies of bivalves in the estuary have been conducted by the RMP (Gunther et al., 1999), and by the US Geological Survey (David et al., 2002; Moon et al., 2005). The RMP study was conducted between 1993 and 1996 monitoring the concentration of mercury and other contaminants at locations throughout the estuary using transplanted bivalve species (*Mytilus californianus*, *Crassostrea gigas*, and *Corbicula fluminea*) suspended in the water column with moored buoys. Median accumulation factors (AFs) for mercury, calculated as the ratio of the mercury concentration in bivalves after deployment to the pre-deployment concentration, were 1.1, 0.9, and 1.3, respectively, for the species listed, leading Gunther et al. (1999) to conclude that bivalve transplants are not an effective bioaccumulation monitoring tool for mercury in the estuary.

In contrast, a study by the US Geological Survey showed a decrease in mercury concentrations measured in the tissue of resident bivalve *Macoma petalum* at a tidal mudflat location in South San Francisco Bay, with 1994–1996 (0.22–0.53 $\mu g\,g^{-1}$) values generally higher than 1997–2001 values (0.15–0.36 $\mu g\,g^{-1}$), and relatively lower concentrations persisting through 2004 (David et al., 2002; Moon et al., 2005). However, the study shows no evidence of a concurrent decrease in mercury concentrations in surface sediments (1–2 cm) at that site.

Greenfield et al. (2005) present the results of an RMP study on seasonal, interannual, and long-term variation of contaminants, including mercury, in sport fish collected from sites throughout San Francisco Estuary in 1994, 1997, and 2000. Four of the species sampled in the study, shiner surfperch (*Cymmatogaster aggregata*), white croaker (*Genyonemus lineatus*), striped bass (*Morone saxatilis*), and leopard shark (*Triiakis semifasciata*), had sufficient sample size to conduct analysis of variance (ANOVA) for determining significant interannual differences in mercury concentration, length, and lipid content of each species. Of these, mercury concentrations in striped bass in the estuary were significantly higher ($P<0.02$, $r^2=0.47$, ANOVA) in 1997 than they were in 1994 and 2000, even after correction for fish length. Explanations for this interannual variation included variation in movement patterns, diets, and populations sampled, or alternatively the high freshwater discharge winter of 1997 causing an increase of bioavailable mercury in the estuary and Sacramento–San Joaquin Delta (Greenfield et al., 2005). The latter explanation is consistent with a roughly ten-fold increase in MMHg in unfiltered water observed in the flood season of 1997 in the Sacramento River (Domagalski, 2001). However, variation observed on this seasonal/interannual time scale did not translate to a long-term trend: between 1970 and 2000, Greenfield et al. (2005) found no evidence of a trend in length-corrected striped bass mercury concentrations ($P>0.2$, Spearman rank correlation coefficient analysis). In addition, it should be noted that although there is an interannual difference in striped bass mercury concentration, there are apparently insufficient data to show differences by site, either by station or hydrographic region (Davis et al., 2002; Greenfield et al., 2005). Although given the seasonal migration and variable movement patterns of striped bass in the estuary this should not be surprising, but it does complicate comparison to our results.

From the available long term and interannual data on mercury concentrations in fish and bivalves (Gunther et al., 1999; David et al., 2002; Greenfield et al., 2005; Moon et al., 2005), it appears that the decreases we observed in 1993–2001 sediment mercury concentrations at some locations cannot be related to biota. This disconnect could be because the species studied are not ideal to show a sediment-biota relationship: the bivalve studies do not

show a clear relationship between mercury in sediment and mercury is clam tissue, and striped bass appear to be a poor choice for monitoring changes in local sediment mercury concentrations. Alternatively, this disconnect could exist because the dominant physical processes in the estuary (e.g., freshwater input) influence total mercury and MMHg in different ways. If Greenfield et al.'s (2005) hypothesis that interannual variations in bass mercury concentration is caused by high freshwater discharge resulting in an increase of bioavailable mercury in the estuary and Sacramento–San Joaquin Delta proves correct, then it may be concluded that floods like the one in January 1997 *increase* MMHg in water and biota while at the same time transporting relatively cleaner sediment into the system causing a *decrease* in total mercury in sediment at some locations. This suggests that the effect of small changes in sediment Hg concentration on MMHg in biota is overwhelmed by the effect of the variable input of bioavailable mercury (or fresh organic matter) in freshwater entering the estuary. To test this hypothesis, it will be necessary to monitor changing concentrations of total mercury in sediment (due to erosion/deposition) and concurrently sediment methylmercury production. This must be coupled with monitoring of mercury species in the water column as well as tissue monitoring of species that are representative of mercury bioconcentration in the estuary.

7. Summary and conclusion

Monitoring sediment quality and mercury concentrations have shown the seasonal cycling of mercury sediment concentrations, as well as a significant decrease in those concentrations from 1993 to 2001 in some parts of the San Francisco Estuary. The decrease in sediment mercury concentrations is attributed to the transport of relatively lower-mercury sediment to the estuary from the Sacramento River and San Joaquin River watersheds. Despite the prediction that a decrease in mercury in the sediment should result in a decrease in mercury in biota, no corresponding trend was observed in studies of long-term concentrations of mercury in fish and bivalves. This apparent decoupling might be related to a number of factors: (1) the change in sediment was not in a predominantly bioavailable fraction, (2) the absolute change in MMHg due to change in total mercury in sediment was obscured by other factors, such as freshwater inputs changing the amount of bioavailable mercury in the water column, (3) the biomonitors used in the studies described above do not effectively measure local changes in sediment mercury concentration, or (4) sediment locations and depths interval sampled are not representative of the total mercury in the system available for possible methylation and incorporation into the food web. Future monitoring of mercury concentrations in San Francisco Estuary must address these possibilities in order to effectively understand and manage mercury in this system.

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