Historical trends of metals in the sediments of San Francisco Bay, California

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Abstract

Concentrations of Ag, Al, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V and Zn were determined in six sediment cores from San Francisco Bay (SFB) and one sediment core in Tomales Bay (TB), a reference estuary. SFB cores were collected from between the head of the estuary and its mouth (Grizzly Bay, GB; San Pablo Bay, SP; Central Bay, CB; Richardson Bay, RB, respectively) and ranged in length from 150 to 250 cm. Concentrations of Cr, V and Ni are greater than mean crustal content in SFB and TB sediments, and greater than found in many other coastal sediments. However, erosion of ultramafic rock formations in the watershed appears to be the predominant source. Baseline concentrations of other metals were determined from horizons deposited before sediments were influenced by human activities and by comparing concentrations to those in TB. Baseline concentrations of Cu co-varied with Al in the SFB sediments and ranged from 23.7 ± 1.2 μg/g to 41.4 ± 2.4 μg/g. Baseline concentrations of other metals were less variable: Ag, 0.09 ± 0.02 μg/g; Pb, 5.2 ± 0.7 μg/g; Hg, 0.06 ± 0.01 μg/g; Zn, 78 ± 7 μg/g. The earliest anthropogenic influence on metal concentrations appeared as Hg contamination (0.3–0.4 μg/g) in sediments deposited at SP between 1850 and 1880, apparently associated with debris from hydraulic gold mining. Maximum concentrations of Hg within the cores were 20 times baseline. Greater inventories of Hg at SP and GB than at RB verified the importance of mining in the watershed as a source. Enrichment of Ag, Pb, Cu and Zn first appeared after 1910 in the RB core, later than is observed in Europe or eastern North America. Maximum concentrations of Ag and Pb were 5–10 times baseline and Cu and Zn concentrations were less than three times baseline. Large inventories of Pb to the sediments in the GB and SP cores appeared to be the result of the proximity to a large Pb smelter. Inventories of Pb at RB are similar to those typical of atmospheric inputs, although influence from the Pb smelter is also suspected. Concentrations of Hg and Pb have decreased since the 1970s (to 0.30 μg/g and 25 μg/g, respectively) and were similar among all cores in 1990. Early Ag contamination was perhaps a byproduct of the Pb smelting process, but a modern source of Ag is also indicated, especially at RB and CB. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Human activities have accelerated cycling and increased metal deliveries to estuaries. Because many metals are toxic to aquatic life in minute quantities, changes in loadings or concentrations could have ecosystem-wide implications. It is therefore important to understand how anthropogenic activities change the concentrations of potentially toxic metals, what processes affect such change, and which activities have the greatest effects.

Most metals associate with the surfaces of particles. They are preferentially transported, deposited and eventually buried with fine grained sediments. Carefully dated cores through sediment deposits can provide chronologies of metal concentration or input in areas of net sediment deposition (e.g., Nriagu et al., 1982; Christensen and Goetz, 1987). On the west coast of North America, cores have been studied in coastal sediments of Southern California (Bertine and Goldberg, 1977; Finney and Huh, 1989; Huh, 1996) and central Puget Sound (Bloom and Crecelius, 1987). But the history of contamination in one of the largest estuaries on the West Coast, San Francisco Bay, has not been studied. In coastal ecosystems, core chronologies are typically restricted to environments where sediment resuspension and bioturbation are minimal. Many of these environments are anoxic and abiotic (Goldberg et al., 1978; Valette-Silver et al., 1993; Owens and Cornwell, 1994). Less is known about the fate of metals in the oxic, biologically rich and well mixed sediments typical of estuaries like San Francisco Bay. Here we present metal chronologies from dated cores from several locations in that Bay. Our goal is to determine how geology, dynamic hydrobiogeochemical processes and changing human activities have influenced metal concentrations in Bay sediments. We also establish the concentrations of metals that characterized Bay sediments before human activities and describe how modern sediments are responding to improvements in waste treatment.

The geology of the Bay watershed contains mineral deposits and ultramafic rocks that are naturally enriched in metals relative to the mean composition of the continental crust. Interpretation of human influences requires understanding this natural baseline of metal concentrations. A variety of specific human activities could have affected metal contamination (van Geen and Luoma, 1999). Between 1850 and 1900, most of the mercury mining in the world occurred in the watershed of San Francisco Bay (Nriagu, 1994). Hydraulic mining for gold mobilized sediments and spread Hg contamination. Activities in the Shasta mining district resulted in Cu, Cd, and Zn contamination. Between the 1930s and 1970, dams, reservoirs and canals were constructed to manage and divert the Sacramento and San Joaquin Rivers for agricultural and urban uses. Water management changed sediment transport (Peterson et al., 1993) and hydrodynamic processes that affect the fate of metals within the Bay. Modern industries first appeared on the shores of the Bay near the turn of the century, about the same time that metal usage increased in the rest of the country (Christensen and Goetz, 1987). Like elsewhere, rates of urbanization and industrialization increased after World War II. Oil refineries (sources of Ni and V) and chemical plants remain important sources of waste discharge to the Bay; but industries, like the large Selby lead smelter near San Pablo Bay, have ceased operation (Rabinowitz and Wetherill, 1972). Since 1970, extensive investments in advanced waste water treatment have occurred, that could effectively remove metals. The sum of all metal loadings to the Bay were estimated to be 993 T/yr in 1960. In 1986 they were 171 T/yr (Monroe and Kelly, 1992). Unlike coastal systems where a single large input of wastes dominate metal loadings and natural influences on sediment deposition can be readily defined (Bloom and Crecelius, 1987; Huh, 1996), a changing array of hydrobiogeochemical influences and human activities could have influenced metals in San Francisco Bay sediments. The ecosystem response is likely to be complex, and it has not been documented.

2. Methods

2.1. Sample locations

Preliminary analyses of 0.6 N HCl-extractable metals were conducted on 14 cores from a group of 273 gravity cores collected in 1990 and 1991 (Fig. 1; Table 1). Detailed analyses were conducted on six of the 14 cores and, for comparison, on one core from
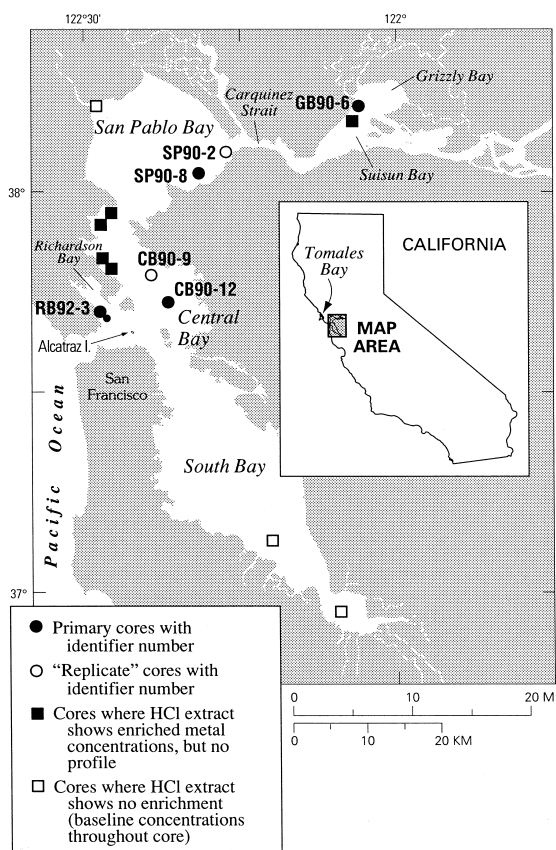
Fig. 1. Site location map.

Bay sediments should integrate contamination from both North and South Bay (Krone, 1979), but are probably also strongly influenced by marine processes (Conomos, 1979). Cores CB90-9 and CB90-12 were from Central Bay (Fig. 1) which is also strongly influenced by marine inputs (Conomos, 1979). In addition, these sites are approximately 6 km from the Alcatraz Island dredge spoil dumping site, where dredging waste has been deposited since 1975 (AHI and Williams Associates, 1990). Three cores from further landward in the estuary were analyzed in detail; two from San Pablo Bay (SP90-2 and SP90-8) and one from the Grizzly Bay arm of Suisun Bay (GB90-6). Together these are termed North Bay cores (Fig. 1). Water chemistry and sediment transport in these locations are influenced by inputs from the San Joaquin and Sacramento Rivers (Conomos, 1979). Salinities less than 1 can occur during the highest river flows; low flow salinities are typically 17 to 24 in northern San Pablo Bay. Previous studies have documented enriched concentrations of Cr, Ni, V, Cu and Cd in water and bivalves in Suisun and northern San Pablo Bay as a result of a variety of industrial discharges (Flegal et al., 1991; Abu-Saba and Flegel, 1995; Brown and Luoma, 1995).

2.2. Field, sample preparation and analytical procedures

All gravity cores were collected from the 'RV David Johnston' using a corer with a 363-kg weight sound. The cores were 9 cm in diameter and ranged from 0.5–2.5 m in length. The core barrel was steel, with a polybutyrate liner. In addition to the 1990–1991 sampling, a gravity core and box core were obtained from the mouth of Richardson Bay in August, 1992 (RB92-3) (Fuller et al., 1999). Comparison of isotope profiles (Fuller et al., 1999) and organic contaminant distributions (Venkatesan et al., 1999) between the box core and the surface sediments of the gravity core verified that no significant loss of surface materials or distortion of surface profiles occurred during gravity coring (Crusius and Anderson, 1991). The core from Tomales Bay was collected in 1993 using a diver-operated piston corer (Sansone et al., 1994).

After collection, the cores were X-rayed, split into a working half and an archive half and stored in a

Tomales Bay. Tomales Bay is 45 km north of San Francisco Bay and is neither industrialized nor urbanized, although there is a small, inactive mercury mine in its watershed. The six cores from San Francisco Bay included replicate cores from two major regions of the Bay. All six had bimodal depth profiles of HCl-extractable metal concentrations (higher concentrations in the near surface sediments than at depth) and were from locations of net sediment deposition, as indicated by differences in bathymetry between 1955 and 1990 (Ogden Beeman and Associates, 1992).

Core RB92-3 was collected at the mouth of Richardson Bay, a 2-km wide, wind-protected embayment near the mouth of San Francisco Bay. A ship building facility was operational during World War II within Richardson Bay; otherwise local sources of contaminants are minimal. Richardson

Table 1
List of all core locations, dates of collection and types of data collected for each core

Location/ USGS identifier	Map Number	Latitude	Longitude	Length (cm)	Collection date	Isotope dating	Digest technique	Grain size analyzed
Grizzly Bay								
SFB020190-6	∗GB90-6	38°6.06′	122°1.58′	205	1990	X	HNO$_3$	< 64 μm
SFB020190-9	–	38°5.39′	122°3.83′	76	1990	–	HCl	< 64 μm
San Pablo Bay								
SFB020790-2	SP90-2	38°2.41′	122°16.71′	190	1990	–	HNO$_3$	< 64 μm
SFB020790-8	∗SP90-8	38°2.02′	122°19.57′	240	1990	X	HNO$_3$; HF	< 64 μm; Bulk
Petaluma River								
SFB020690-12	–	38°8.44′	122°31.04′	240	1990	–	HCl	< 64 μm
Central Bay								
SFB020890-3	–	37°58.29′	122°26.86′	190	1990	–	HCl	< 64 μm
SFB020890-6	–	37°57.61′	122°27.33′	232	1990	–	HCl	< 64 μm
SFB020890-9	–	37°55.43′	122°28.39′	245	1990	–	HCl	< 64 μm
SFB020990-9	CB90-9	37°53.30′	122°23.65′	130	1990	–	HNO$_3$	< 64 μm
SFB020890-11	–	37°54.33′	122°27.60′	145	1990	–	HCl	< 64 μm
SFB020990-12	∗CB90-12	37°51.41′	122°21.54′	204	1990	X	HNO$_3$; HF	< 64 μm; Bulk
Richardson Bay								
SFB082092-3	∗RB92-3	37°51.38′	122°28.20′	150	1992	X	HNO$_3$; HF	< 64 μm; Bulk
South Bay								
10-G-25	–	37°32.67′	122°11.15′	180	1990	–	HCl	< 64 μm
SFB022190-2	–	37°29.84′	122°5.55′	173	1990	–	HCl	< 64 μm
Tomales Bay								
TB93-1	–	38°10′	122°54′	320	1993	X	HNO$_3$; HF	< 64 μm; Bulk

Primary core locations are marked with an asterisk. Metal analysis for HCl extracts include Al, Cr, Cu, Fe, Mn, Pb, V, Zn. Metal analysis for HNO$_3$ and HF digests include the same elements as the HCl extracts, with the addition of Ag and Hg. Isotope dating on cores marked with an X were dated by [137]Cs. Additional dating techniques for RB92-3 and SP90-8 included ^{210}Pb, [239]Pu, [240]Pu, [234]Th and [10]Be.

cold room (2–3°C) until sampling. Sand/silt ratio was determined on all samples. Sediment samples were wet-sieved using an acid-cleaned nylon-mesh screen into a tared 100 ml beaker to < 64 μm in ultra-clean deionized water and dried at 70°C.

The < 64 μm sediments were analyzed for metals in all cores (these are the data reported here, unless otherwise noted); bulk analyses were conducted on selected samples (see Table 1). Sieving effectively reduces the most important grain size biases that can affect comparisons (Salomons and Forstner, 1984; Luoma, 1990). Each sediment sample was homogenized using a mortar and pestle, split into 0.5 g replicate aliquots, and placed into a scintillation vial. For the weak-acid digest, two replicate 0.5 g sediment aliquots were digested at room temperature for 2 h in 0.6 N HCl. The sample was filtered with a 0.45 μm filter and analyzed by Inductively Coupled Argon Plasma Emission Spectroscopy (ICAPES). For near-total metal analyses, replicate sub-samples from each horizon and procedural blanks, were digested using the concentrated nitric acid reflux method described by Luoma and Bryan (1981). Sediment aliquots of approximately 0.5 g were placed into 22 ml scintillation vials. Ten milliliters of concentrated trace metal grade nitric acid was added to each, a reflux bulb was placed on the vial and the sample was left at room temperature overnight. Samples were then refluxed at 150°C for approximately 1 week, until clear. Reflux bulbs were

removed and the samples were evaporated to dryness. The residue was reconstituted in 0.6 N trace metal grade hydrochloric acid, then filtered through 0.45 μm filters. Decomposition with concentrated nitric acid reflux is comparable with procedures previously employed on Bay sediments (San Francisco Estuary Institute, 1994). It is indicative of metals sufficiently mobile to be of potential toxicological interest, but it has the disadvantage of not providing a complete dissolution of the sediment.

Total decomposition was conducted on a full suite of samples from RB92-3, SP90-8 and on selected samples from CB90-12 in order to compare trends to those observed by near total decomposition (see Table 1). Around 1 ml of concentrated $HClO_4$ and 2 ml of concentrated HF were added to sub-samples of 0.2 g, with selected replicates, in a Teflon vial. The samples were placed on an aluminum heat block preset at 110°C, and taken to dryness. About 1 ml of $HCLO_4$ was added and then ultra-clean deionized water added to bring the Teflon vial to half full. Samples were returned to the hot plate for evaporation, cooled and reconstituted to 10 ml in 0.6 N HCl. The vials were capped and heated at 90°C for 1 h.

Samples for Hg analyses were reacted at 100°C in aqua regia followed by 10% nitric/dichromate reconstitution; 3% $NaBH_4$ (in 1% NaOH) was added as a reductant before analysis by cold vapor AAAS.

Concentrations of Al, Cr, Cu, Fe, Mn, Ni, V and Zn in the sediment were analyzed by ICAPES, after careful correction for peak interferences in the sediment digest matrix. Concentrations of Ag were analyzed by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) using Zeeman background correction with calibration by the method of standard additions. Lead concentrations were analyzed by flame AAS.

The ICAPES was profiled and standardized according to normal operating procedures, then a quality control (QC) standard was run every 10–15 samples to ensure consistent performance of the instrument. Procedural blanks were analyzed as an unknown, but no blank subtraction was necessary. The instrument limit of detection (LOD) and limit of quantitation (LOQ) were determined by 10 or more analyses of a standard blank (0.6 N HCl) throughout each analytical run (Keith et al., 1983). All data reported here fall above the LOQ. If readings from

replicate values of a solution were of low precision (relative standard deviation > 10%), the readings were not used.

Recoveries from standard reference materials (SRM Sediment Standard 1646 and 2709) are reported in Table 2. Because Pb analyses by ICAPES had an uncorrectable bias from Al, Pb (HNO_3 digest) was analyzed by AAS. Recoveries of Pb from SRM 2709 were low in HNO_3. As a second test of recoveries, Pb in selected horizons of core sediments were analyzed by both AAS (HNO_3 digest) and isotope dilution by mass spectrometry of totally decomposed sediments. These two methods compared within 5% in both uncontaminated and contaminated horizons, suggesting a high fraction of Pb recovery in San Francisco Bay sediment.

2.3. Dating

Analyses of ^{137}Cs, ^{210}Pb, [239,240]Pu, [234]Th, were conducted on cores RB92-3 and SP90-8 to derive chronologies (Table 1; Fuller et al., 1999). Additional analyses of [10]Be constrained early human activities on each core and ^{14}C was used to identify the oldest sediments in RB92-3 (van Geen and Luoma, 1999). Sediments in RB92-3 appeared to be continuously deposited since well before significant anthropogenic activity began in the watershed (van Geen and Luoma, 1999). The linear sedimentation rate at the surface of RB92-3 was 0.89 cm/yr and the core was vertically mixed to 33 cm depth (Fuller et al., 1999). Dates of sediment deposition were determined by numerical simulation of ^{210}Pb profiles. The dates on individual horizons are the minimum age of sediments at that depth. The deposition rate in SP90-8 averaged 4.1 cm/yr based on ^{137}Cs and [239,240]Pu activity maxima and ^{210}Pb profiles. Profiles of ^{137}Cs were also determined in three additional cores (see Table 1), in order to estimate the depth of sediment deposition since 1952 ± 2 (Table 1; method described by Fuller et al., 1999).

Jaffe et al. (1998) reconstructed depositional processes at SP90-8 by comparing five detailed bathymetry surveys conducted since 1850. A discontinuity in chemical concentrations observed at ∼ 120 cm depth in this core appears to coincide with a depositional hiatus that extended from 1880 to 1950. Both depositional history and Sr/Nd isotopic signa-

Table 2
Range of recoveries for Standard Reference Material (Estuarine Sediment Standard, SRM 1646 and San Joaquin River Sediment, SRM 2709)

		Ag	*Al	Cr	Cu	*Fe	Hg	Mn	Ni	Pb	V	Zn
SRM 2709	Certified	0.41 ± 0.03	7.5 ± 0.06	130 ± 4	34.6 ± 0.7	3.5 ± 0.1	1.40 ± 0.08	538 ± 17	88 ± 5	18.9 ± 0.5	112 ± 5	106 ± 3
HNO$_3$ ($n = 24$)	Measured	0.35 ± 0.05	3.6 ± 0.4	81 ± 4	28 ± 2	2.9 ± 0.1	1.40 ± 0.06	484 ± 23	74 ± 3	11.5 ± 0.6	79 ± 6	93 ± 4
SRM 1646	Certified	–	6.3 ± 0.2	76 ± 3	18 ± 3	3.4 ± 0.1	–	375 ± 20	32 ± 3	28.2 ± 1.8	94 ± 1	138 ± 6
HNO$_3$ ($n = 20$)	Measured	–	2.4 ± 0.4	44 ± 3	14 ± 2	2.5 ± 0.1	–	252 ± 14	25 ± 1	24.5 ± 3.4	55 ± 8	122 ± 10
HF ($n = 6$)	Measured	–	5.8 ± 0.2	65 ± 2	15.3 ± 6	3.1 ± 0.1	–	338 ± 8	28 ± 1	na	92 ± 4	135 ± 2

Al and Fe (*) are reported by percent weight. All other elements are reported in μg/g. Recoveries for near-total (HNO$_3$) and total (HF) digests are reported. Lead concentrations for the HF digest were not analyzed (see text). There are no certified values for Ag or Hg in SRM 1646.

tures suggest sediments between 150–250 cm originated from hydraulic mining activities and were deposited between 1850 and 1880 (Bouse et al., 1996; Jaffe et al., 1998). Thus, sediments deposited before 1850 lie directly beneath sediments deposited in the 1950s.

Inventories of 'excess' metal (mass per area deposited in excess of baseline) were determined in GB90-6, SP90-8 and RB92-3 by integrating contaminant metal inputs downcore. The $\mu g/cm^2$ of metal in interval a (M_a) was determined by:

$$M_a = (C_a - B) \, p_z \, \Delta z \tag{1}$$

where C_a is the metal concentration in $\mu g/g$ in interval a, B is the baseline metal concentration that occurred before anthropogenic activities began in the watershed (see later discussion), p_z is the bulk density of the sediment, and z is interval thickness in cm. Fuller et al. (1999) reported p_z for each horizon in RB92-3; an average bulk density of 1.1 g/cm^2 was used for SP90-8 and GB90-6. The integrated inventory for sediments (ϕ) was determined by:

$$\phi = \Sigma(C_{a-z} - B), \tag{2}$$

for all intervals. Intervals not sampled were assigned values by linear interpolation of the concentration (mass of metal per gram) of adjacent intervals. Long-term mean excess metal flux, ϕ, was compared among cores with different sedimentation rates. To do so, ϕ was divided by the number of years of excess metal input (e.g., normalized to the period of human disturbance) using age estimates from Fuller et al. (1999).

3. Results

3.1. Decomposition methods

Total decomposition and nitric acid reflux were compared in order to determine if trends were biased by the decomposition method. Concentrations of Cr, V, Fe and Al (metals often associated with mineral lattice structures) were higher in the total digests than in the concentrated nitric acid digests (Table 2). Concentrations of Cr and V in both digests were strongly correlated with Al (Fig. 2; $p < 0.001$). The differences in y-intercept of the two relationships
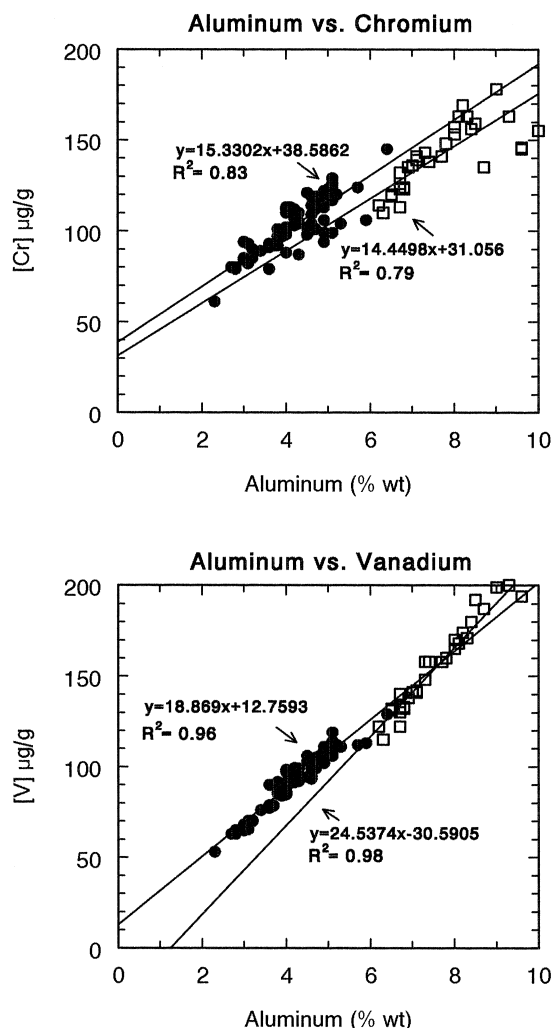

Fig. 2. Correlations between V and Cr concentrations ($\mu g/g$) and Al (% weight). Closed circles represent sediment data using the near total, concentrated nitric digestion technique (HNO_3, < 64 μm). Open squares show sediment data using the total decomposition (HF, < 64 μm).

reflected the more efficient recoveries in the total digest. The slope and the strength (R^2) of the relationships were similar between the digests. Thus, internally consistent trends among the three metals characterized both digests. Because results from the nitric acid digests were as consistent among all sediments as results from total decomposition, either approach appeared suitable for defining trends within and among cores.
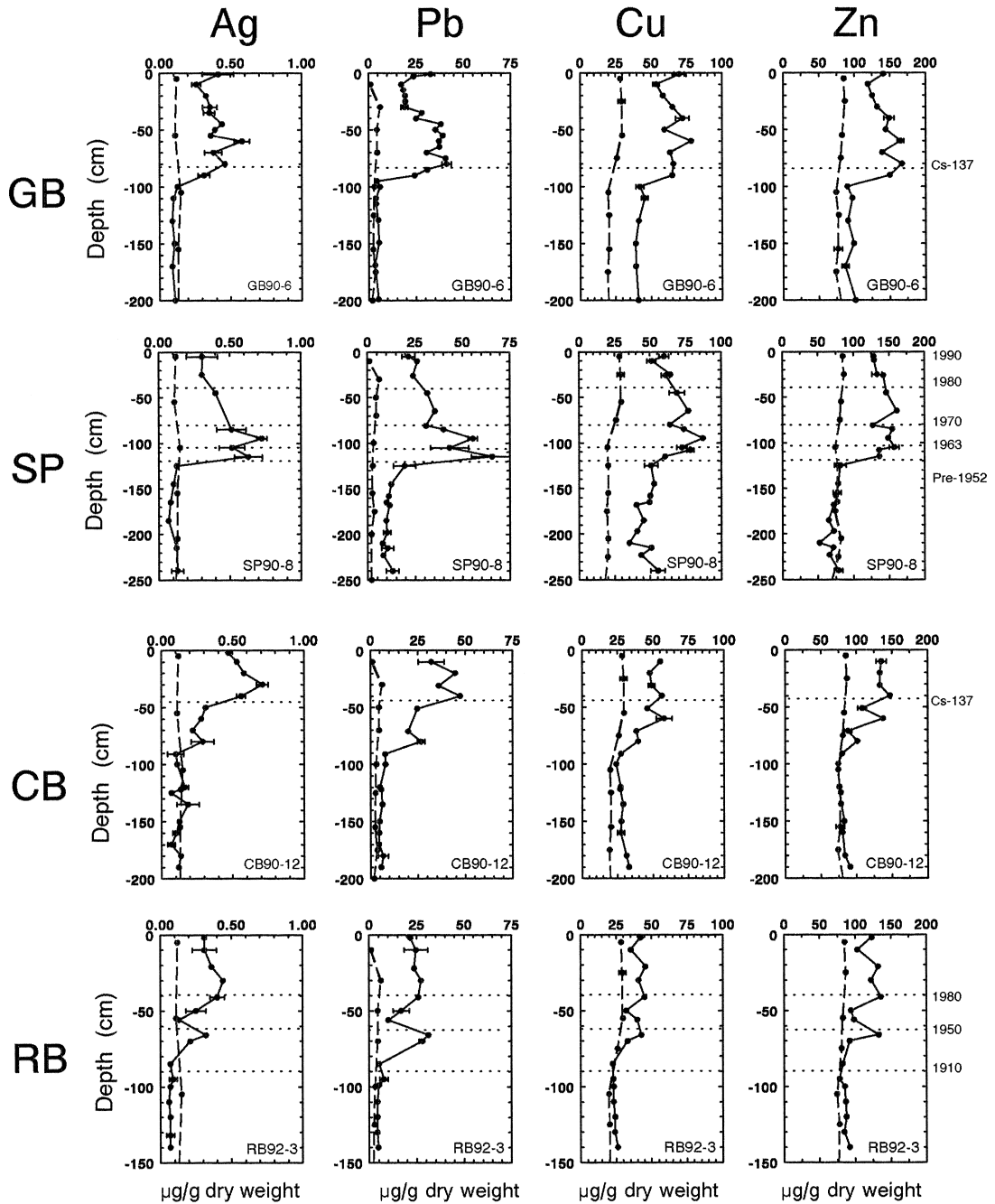
Fig. 3. Downcore trends of Ag, Pb, Cu and Zn for all primary core locations: Grizzly Bay (GB); San Pablo Bay (SP); Central Bay (CB); and Richardson Bay (RB). Horizontal dotted line represents the maximum depth of ^{137}Cs penetration or age of sediment horizon as determined by age dating model (Fuller et al., 1999). Vertical dashed line for each graph represents metal concentration in the reference estuary, Tomales Bay. All data reported in μg/g dry weight in sieved sediments ($< 64 \mu$m). Each circle represents the mean concentration (HNO_3 digest) of two samples. The error bar represents the standard deviation.

3.2. General core features

All cores showed distinct contrasts in metal composition between uncontaminated intervals and intervals deposited after chemical disturbance of the sediments by human activities. Sediments from Tomales Bay (TB93-1), which has little history of contaminant input, showed a slight surface enrichment of Cu and Zn (20–28 μg/g and 70–85 μg/g, respectively) and slightly elevated Hg concentrations (0.1–0.4 μg/g) through most of the core compared to the deepest horizons. No other significant downcore trends in metal concentrations were present (Figs. 3 and 4). Concentrations of Cu, Ag, Hg, Pb and Zn, in the deepest horizons of the San Francisco Bay cores, were comparable to concentrations in uncontaminated horizons of TB93-1 (Figs. 3 and 4). A diffuse maxima in concentrations of these metals occurred toward the surface layers of the San Francisco Bay cores. Differences were statistically significant (one-way ANOVA: $p < 0.01$) between concentrations in sediments deposited before 1910 (RB92-3) or before 1952 (GB90-6; SP90-8; CB90-12), compared to sediments deposited after 1910 (in RB92-3) or 1952 (GB90-6; SP90-8; CB90-12).

A second group of metals for which anthropogenic sources exist (Cr, V and Ni), showed little evidence of enrichment toward the surface of the cores (Fig. 5). Concentrations of Cr, V and Ni were similar throughout the length of most cores, and were similar to concentrations in Tomales Bay (Table 3). Layers of enriched Fe and Mn concentrations, as might be expected under conditions of diagenetic metal remobilization, were not evident near the surface of any cores. The coefficient of variation (CV) for mean Fe concentrations within cores was < 20%; the CV for Mn within cores was < 30% (Table 3). SP90-8 contained interbedded layers of sand and silt and RB92-3 contained variable amounts of sand (15–60%) (see Fuller et al., 1999; van Geen and Luoma, 1999 for details). The effects of variations in particle size on metal concentrations were removed after the sediments were sieved, as indicated by the absence of vertical trends in Al concentrations within the < 64 μm sediments (Fig. 5). Organic carbon concentrations were similar throughout the RB92-3 core but were higher in the upper 120 cm of SP90-8 than in deeper horizons (Pereira et al., 1999).
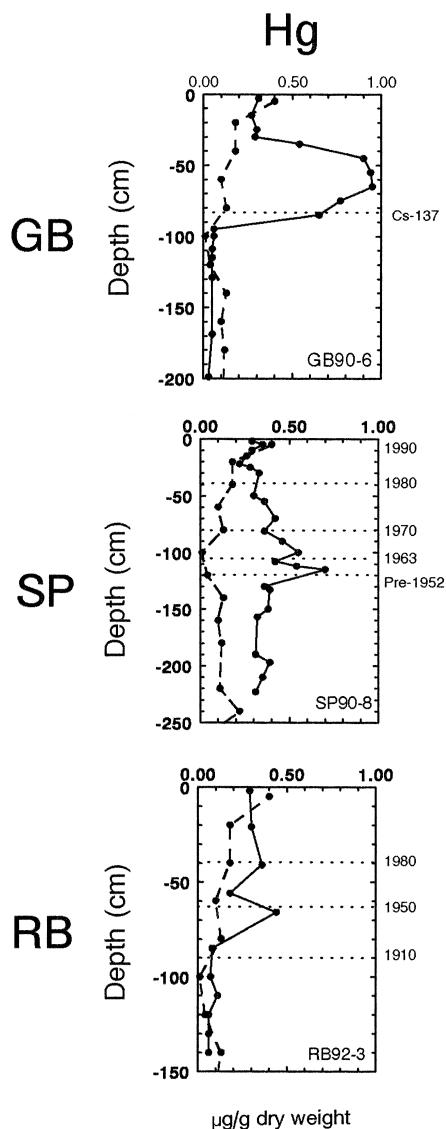

Fig. 4. Downcore trends of Hg for Grizzly Bay (GB), San Pablo Bay (SP) and Richardson Bay (RB). Horizontal dotted line represents the maximum depth of ^{137}Cs penetration or minimum age of sediment horizon as determined by age dating model (Fuller et al., 1999). Vertical dashed line for each graph represents metal concentration in the reference estuary, Tomales Bay. All data reported in μg/g dry weight in sieved sediments (< 64 μm).

3.3. Specific spatial and temporal patterns

Spatial differences in core characteristics were indicative of heterogeneous depositional processes in
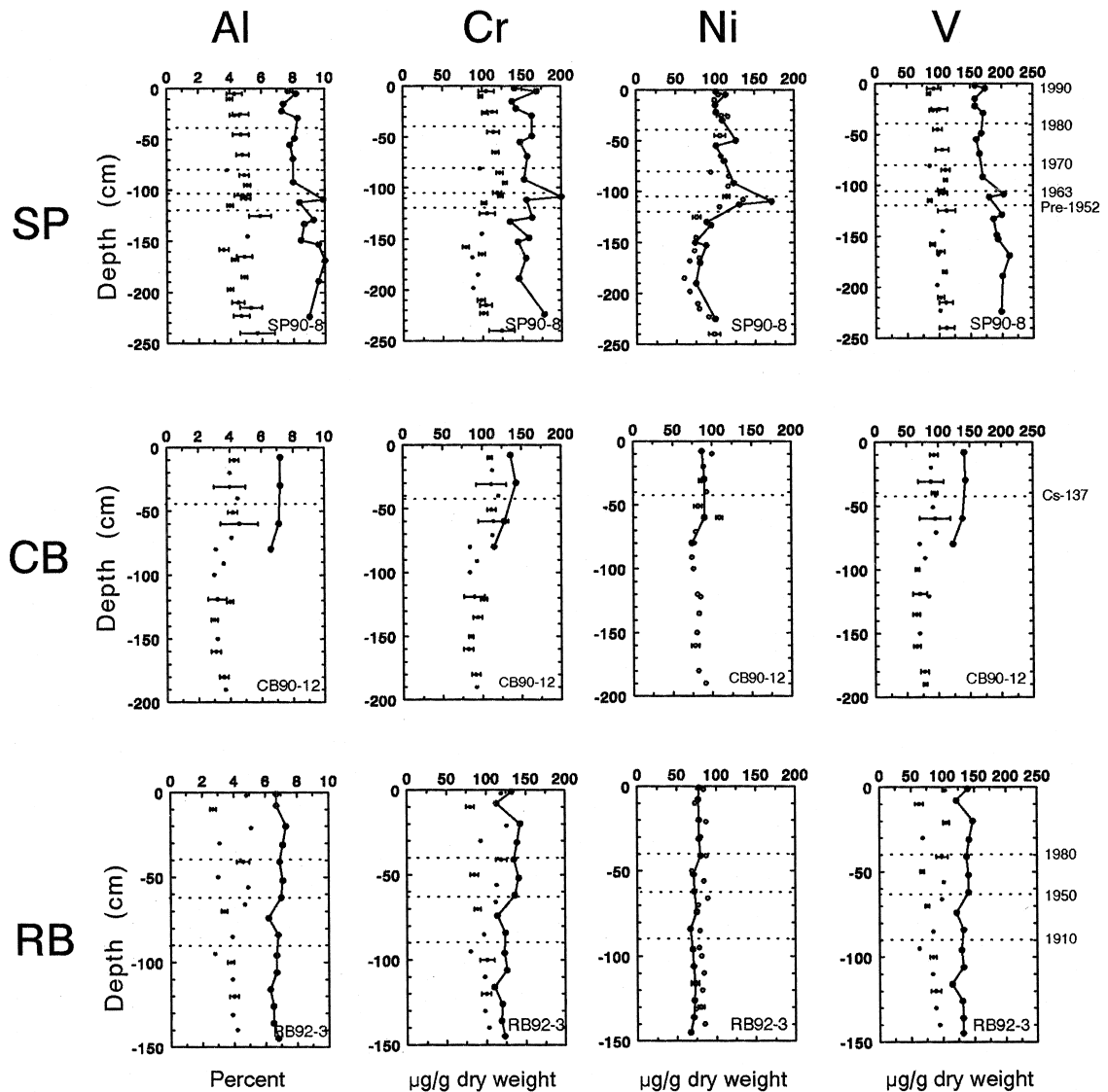
Fig. 5. Downcore trends in non-contaminant profiles for San Pablo Bay (SP); Central Bay (CB); and Richardson Bay (RB). Chromium, Ni and V are reported in $\mu g/g$ dry weight. Aluminum is reported by percent weight. All analyses conducted on sieved sediments ($< 64 \mu m$). Scatter plot represents the mean concentration (HNO_3 digest) of two samples and the error bar represents the standard deviation. Line plot represents the concentration by total decomposition (HF digest).

the Bay. Among the 14 cores initially screened, some cores were contaminated throughout (1–2 m depth); while metal concentrations in the entire length of others were similar to the lowest concentrations found in the Bay sediments, suggesting these were areas of little net sediment deposition (Fig. 1). Among the six cores analyzed in detail, GB90-6, SP90-2 and

SP90-8 had higher concentrations of Al, Cr, V, Fe and Mn than did the cores from the more seaward locations (CB and RB cores) (Table 3; Fig. 5). This could reflect particle sorting, or a declining abundance of clays from landward to seaward in the Bay, although local areas of fine particle deposition probably also occur. In CB90-12 and CB90-9, concentra-

Table 3

Mean concentrations of Al, Cr, Fe, Mn, Ni and V in bulk sediments (total decomposition) and < 64 μm sieved sediments (nitric acid refluxed) from San Francisco and Tomales Bay cores

	Al (%)	Cr (μg/g)	Fe (%)	Mn (μg/g)	Ni (μg/g)	V (μg/g)
Total decomposition (bulk sediments)						
GB90-6	na	na	na	na	na	na
SP90-8	8.2 ± 0.9	143 ± 13	4.5 ± 0.4	639 ± 114	103 ± 15	170 ± 19
CB90-12	7.1 ± 0.3	131 ± 12	3.9 ± 0.2	377 ± 28	85.3 ± 7.6	136 ± 9
RB92-3	6.4 ± 0.3	113 ± 8	3.5 ± 0.2	378 ± 32	73.3 ± 4.1	117 ± 7
TB93-1	6.5 ± 0.4	150 ± 8	3.7 ± 0.3	324 ± 21	116 ± 11	74.4 ± 4.4
Nitric acid digest (sieved sediments)						
GB90-6	4.7 ± 0.6	112 ± 12	4.3 ± 0.9	573 ± 179	105 ± 11	104 ± 10
SP90-2 *	5.7 ± 1.2	121 ± 17	4.4 ± 0.5	528 ± 126	102 ± 16	119 ± 17
SP90-8	4.7 ± 0.6	105 ± 13	4.0 ± 0.4	501 ± 156	94.1 ± 20	101 ± 9
CB90-9 *	4.0 ± 0.5	104 ± 11	3.8 ± 0.5	315 ± 30	86.2 ± 7.2	87.2 ± 9.6
CB90-12	3.7 ± 0.5	100 ± 13	3.7 ± 0.6	291 ± 18	85.0 ± 9.1	80.8 ± 11
RB92-3	3.9 ± 0.7	101 ± 14	3.7 ± 0.3	305 ± 22	81.2 ± 5.3	86.0 ± 14.6
TB93-1	3.5 ± 0.3	123 ± 7	3.4 ± 0.2	305 ± 17	116 ± 11	74.4 ± 4.4

Replicate cores are marked with an asterisk. Total decomposition analysis was not conducted on core GB90-6.

tions of Al, Cr, Ni and V were all enriched in horizons toward the surface (Fig. 5), in contrast to profiles of these metals from other regions.

Baseline concentrations of Ag, Cu, Hg, Pb and Zn were estimated from comparisons with Tomales Bay sediments and from the deepest horizons of RB92-3 and GB90-6. Concentrations of Cu in the deep horizons of all cores ranged from 16 to 55 μg/g and decreased from GB90-6 to RB92-3. Among these data, Cu was strongly correlated with Al ($R^2 = 0.80$; Fig. 6). Thus, baseline Cu was determined by comparison with Al concentration in each horizon and contamination was distinguished as positive residuals from the relationship of Cu and Al (Fig. 6). Baseline concentrations of Ag, Pb and Hg were more uniform. Ag baseline concentrations were 0.09 ± 0.02 μg/g; baseline Pb was 5.2 ± 0.7 μg/g; and baseline Hg 0.06 ± 0.01 μg/g (Figs. 3 and 4). Concentrations of Pb and Hg were slightly enriched in the deep horizons (> 115 cm, 10.4 ± 1.7 μg/g, and 0.35 ± 0.03 μg/g, respectively) of SP90-8 and SP90-2, but these sediments were deposited after 1850. Concentrations of Zn were also high in the deepest layers of GB90-6 (> 100 cm, 94 ± 6 μg/g), but averaged 78 ± 7 in the deepest layers of other cores, including TB93-1.

The earliest detectable anthropogenic contamination in San Francisco Bay was the elevation of Hg concentrations to 0.3–0.4 μg/g in sediments de-

posited between 1850 and 1880 in SP90-8 (Fig. 4). Elevated Hg concentrations were not observed at RB92-3 until horizons deposited between 1910 and 1925. Increases in concentrations of Cu, Pb and Zn in RB92-3 were also not evident before 1910. Concentrations of Cu and Zn in Richardson Bay sediments have not declined substantially since the 1940s
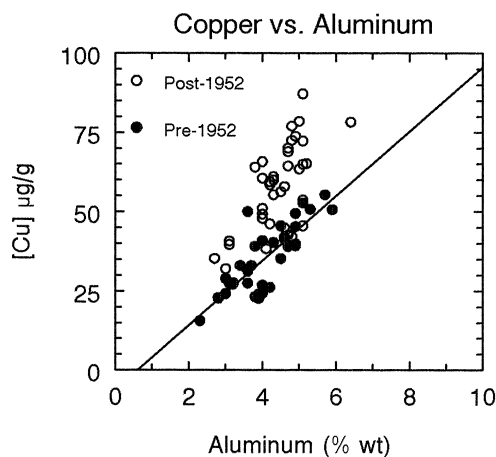

Fig. 6. Correlation between Al (% weight) and Cu (μg/g) concentrations for near total (HNO₃) digests in sediments deposited before 1952 (baseline). Closed circles represent concentrations below the ¹³⁷Cs boundary ($R^2 = 0.80$). Open circles represent concentrations in horizons that contain ¹³⁷Cs and have been deposited since 1952.
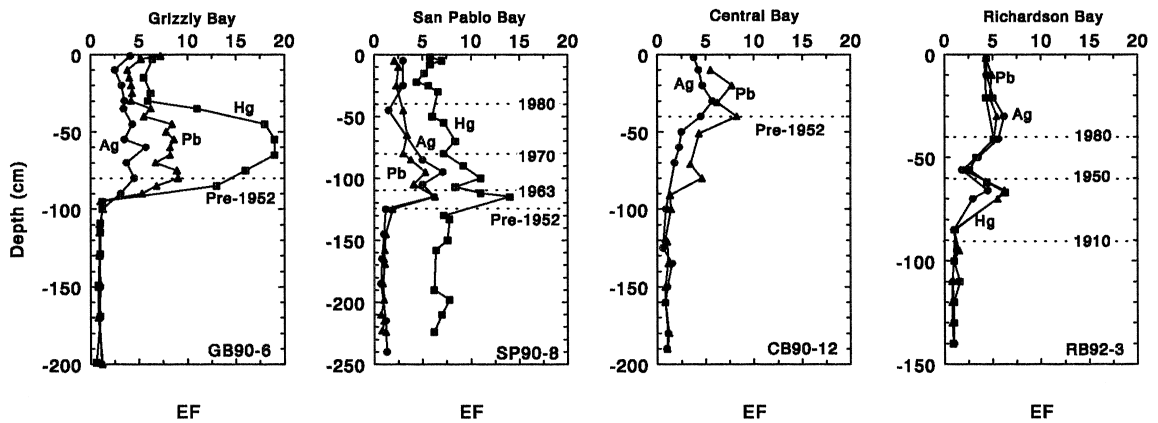
Fig. 7. Metal concentrations plotted as a function of enrichment factors in Ag (closed circle), Hg (closed square) and Pb (closed triangle). Enrichment factors (EF) are calculated by dividing the concentration in horizon 'i' by the mean baseline concentration. Horizontal dotted line represents the maximum depth of ^{137}Cs penetration or minimum age of sediment horizon as determined by age dating model (Fuller et al., 1999).

and Pb concentrations have declined little, although variability occurs among horizons. In contrast, maximum concentrations of Ag, Cu, Hg, Pb, and Zn in SP90-8, SP90-2 and GB90-6 occurred in the subsurface, and concentrations have declined in recent decades, but not to the levels that occurred before 1850.

Using the baseline concentrations described above, enrichment factors (EF) (Alexander et al., 1993; Valette-Silver, 1993) were calculated for all horizons in each core from:

$$EF = C_i / C_r \tag{3}$$

where C_i was the concentration in horizon i and C_r was the baseline value. Although enrichment factors for metals were highly variable baywide, there were

similarities within a given geographic region. EFs for Hg and Pb in the subsurface peak in GB90-6 were the highest in the Bay (20 and 10 times baseline, respectively). EFs for Hg and Pb were also high in SP90-8 (15 and 7 time baseline, respectively) and decreases in enrichment factors after 1970 characterized both GB90-6 and SP90-8 (Fig. 7). Lead enrichment in CB90-12 and RB92-3 were lower than values observed in the North Bay cores, (a range from 5–10 times baseline), as was Hg, (five times higher in RB92-3; Hg not measured in CB90-12) (Fig. 7). Silver enrichment throughout the bay ranged from 2–7 times higher than baseline, with decreasing enrichment occurring since the 1970s (Fig. 7). Copper and Zn enrichment averaged 2–3 times higher than baseline concentrations at all sites (data not shown).

Table 4
Deposition rate of metal accumulation in three cores collected in San Francisco Bay

	Grizzly Bay (GB90-6) $\mu g/(cm^2\ yr)$	San Pablo Bay (SP90-8) $\mu g/(cm^2\ yr)$	Richardson Bay (RB92-3) $\mu g/(cm^2\ yr)$
Ag	0.74	1.2	0.28
Cu	61.9	92.5	16.6
Hg	1.49	1.1	0.2
Pb	65.9	75.2	17.8
Zn	128	168	61.1

See Section 2 for description of inventory calculations.

Deposition rates of Ag, Cu, Pb and Zn were greatest in SP90-8 (Table 4). The highest rate of Hg deposition occurred at GB90-6. A gradient in metal deposition rates was evident from landward to seaward (GB90-6 to RB92-3) among the cores, with the lowest rates occurring at the mouth of the estuary (Table 4).

4. Discussion

Anthropogenic inputs of metals between 1850 and the present are the simplest explanation for the profiles of Ag, Cu, Hg, Pb and Zn in cores from depositional areas in San Francisco Bay. The strongly mixed sediment column documented at RB92-3 (Fuller et al., 1999), did not obscure the anthropogenic enrichment. Alternative causes of enrichment (Crusius and Anderson, 1991; Farmer, 1991) cannot explain the metal profiles or the differences between San Francisco Bay and Tomales Bay. Comparison with box cores indicate that gravity core profiles were not affected by compression or loss of the near surface sediment during coring (Fuller et al., 1999). Sieving appeared to eliminate most particle size effects. Concentrations of Fe and Mn did not follow patterns indicative of diagenetic redistribution of metals (Ridgway and Price, 1987; Farmer, 1991; Valette-Silver, 1993). Metal loss from sediments when they resided at the oxidized surface (Westerlund et al., 1986) cannot be discounted, but it was not sufficient to eliminate the metal profiles.

Most of the metal contamination associated with industrialization appeared later in San Francisco Bay sediments than in Europe or eastern North America (Christensen and Goetz, 1987; Bricker, 1993). The most enriched concentrations of metals occurred with the onset of rapid industrial growth after World War II, as is typical of industrialized ecosystems (Valette-Silver, 1993). A 'recovery phase' of declining metal concentrations began in the late 1970s at least at some locations for some metals. Like elsewhere, metal concentrations have not declined to baseline values (Valette-Silver, 1993; Huh, 1996; Callendar and Van Metre, 1997). Differences in enrichment factors, proximity to input and differences in local mixing/sedimentation regimes contribute to differences in recovery rates among locations.

Copper and Zn are only moderately enriched in San Francisco Bay sediments. EFs for these metals are less than observed near the head of Narragansett Bay, where contamination is extreme (Bricker, 1996), but are similar to Southern California coastal waters (Finney and Huh, 1989) and an industrialized estuary in Texas (Ravichandran et al., 1995).

EFs for Hg are high in San Francisco Bay. Rasmussen (1994) argued that the contribution of anthropogenic inputs to Hg concentrations in aquatic environments are difficult to determine because natural concentrations vary from 0.01–0.3 μg/g. However, baseline concentrations of Hg (0.06 $\pm$ 0.01 μg/g) are not highly variable in San Francisco Bay, despite some of the richest geologic deposits of Hg in the world in the watershed (Nriagu, 1994). Mining contaminated Bay sediments with Hg, perhaps as early as 1850. Mercury was extracted from mines in the Bay watershed, at an average rate of 1290 ton/yr, between 1850 and 1900 (Nriagu, 1994). Most of this Hg was used to amalgamate and extract gold in the hydraulic mining processes employed in the Sierra Nevada between 1852 and 1884. Historic accounts (Nriagu, 1994) estimate that 25–30% of the Hg used in gold mining was lost in waste water or to soils. The hydraulic mining also released 1.2×10^9 m^3 of sediment, much of which was deposited in San Francisco Bay (Gilbert, 1917). If 40,000 ton of Hg were used in gold mining and 25% was left associated with sediments, then as much as 10,000 ton of Hg could have been transported to the Bay with hydraulic mining sediments. The highest concentration of Hg in the Bay sediments (0.95 μg/g in GB90-6) was deposited after most hydraulic mining inputs to the Bay had ceased (but mercury mines were still operative). Maximum Hg levels buried in Bay sediments are below the extreme contamination associated with industrial activities (Smith and Loring, 1981), but are five times the geometric mean concentration in US coastal sediments (Daskalakis and O'Connor, 1995) and exceed the level (0.7 μg/g) predicted to cause adverse biological effects in benthic fauna (Long et al., 1995). Spatial trends in peak Hg concentrations and inventories in sediments point to a historic source in the watershed (the mines); however, concentrations in surface sediments

were relatively uniform among the different cores in 1990 (0.3–0.4 μg/g). Thus, inputs from the head of the estuary may not be as dominant as they once were (Fuller et al., 1999).

Concentrations of Pb buried in San Francisco Bay sediments are not among the highest found in US coastal sediments (Daskalakis and O'Connor, 1995), Southern California (Finney and Huh, 1989), other industrialized estuaries (Rozan et al., 1994; Bricker, 1996), or urban reservoirs (Callendar and Van Metre, 1997). Callendar and Van Metre (1997) suggest that atmospheric Pb deposition in urban areas was 14.5 μg/(cm^2 yr) for the years 1965–1975, with declining rates thereafter. This is similar to the long-term average rate of deposition in Richardson Bay (17.8 μg/(cm^2 yr)). On the other hand, long-term inventories of Pb in San Pablo and Grizzly Bay (75.2 and 65.9 μg/(cm^2 yr), respectively) exceed those found in all but the most polluted of the above circumstances. Thus, the high sedimentation rates in North San Francisco Bay may have diluted substantial local Pb inputs. The isotopic signature of Pb in SP90-8, clearly shows a signal consistent with large inputs from the Selby Pb smelter (Ritson et al., 1999). Documented Pb releases from the smelter were ~ 16 T/yr of Pb between 1900 and 1970 (Rabinowitz and Wetherill, 1972), compared to Pb releases of 18 T/yr from the 50 known industrial and municipal discharges in 1990 (Gunther et al., 1987). Isotope signatures also suggest the effects of the smelter could have been highly influential over a broad area of San Francisco Bay (Ritson et al., 1999). Widespread recovery from Pb contamination is reported in sediments from systems dominated by atmospheric inputs (Smith and Flegal, 1995; Callendar and Van Metre, 1997). In San Francisco Bay, it is possible that recovery will be delayed if smelter Pb is still being redistributed in the estuary.

Silver is a modern contaminant of interest because of its association with sewage discharges. Silver contamination has been reported from South Bay since the 1970s (Thomson et al., 1984; Luoma and Phillips, 1988; Smith and Flegal, 1995). The highest Ag concentrations in San Francisco Bay cores are similar to the highest concentrations found in central Puget Sound, but are less than the highest Ag concentrations found in some other coastal systems (Daskalakis and O'Connor, 1995; Bricker, 1996;

Huh, 1996). Trends in Ag concentrations closely follow trends in Pb concentrations in the North Bay cores, raising the possibility that Ag co-occurs with Pb in smelter wastes. Silver concentrations among all cores show a nearly 1:1 relationship with Pb, especially in sediments deposited before 1952, while the Pb smelter was still active (Fig. 8). After 1952, Ag concentrations are greater than would be expected from the Ag/Pb relationship in sediments deposited when the Pb smelter was most influential in San Pablo Bay (Fig. 8; see also Ritson et al., 1999). The relatively recent maxima in Ag concentrations in the Central and Richardson Bay sediments thus may reflect a modern increase in Ag inputs, followed by some recovery (Fig. 3). A similar, recent peak in Ag concentrations, compared to other metals, was also observed in Puget Sound (Bloom and Crecelius, 1987). Thus, a second source of Ag, perhaps the South Bay source, may have enriched Central and Richardson Bay sediments within the last two decades, as other metal concentrations were stabilized or declining.

Interpretation of metal concentrations in estuarine sediments must consider the geology of the watershed (Gobiel et al., 1995). Erosion from the watershed is most likely the dominant sources of Cr, V and Ni in San Francisco Bay. Concentrations of these metals, especially Ni, are high throughout the
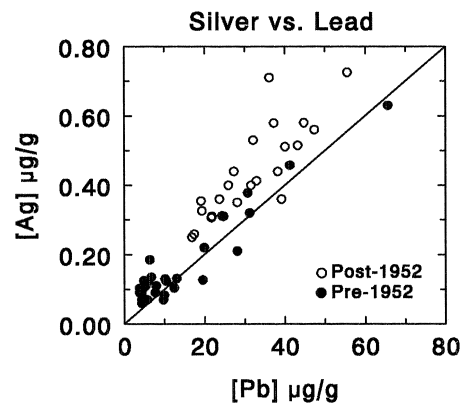

Fig. 8. Relationship between Ag and Pb concentrations (HNO$_3$, < 64 μm) at all depths from Grizzly Bay, San Pablo Bay, Central Bay and Richardson Bay. Open symbols are sediment horizons deposited after 1952; closed symbols are sediments deposited before 1952. The line is a 1:1 linear relationship between Ag and Pb.

length of all cores, compared to many other coastal ecosystems (Campbell and Loring, 1980; Katz and Kaplan, 1981). For example, 42 μg/g was designated as the 'high' concentration of Ni (geometric mean plus one standard deviation) in US Coastal sediments (Daskalakis and O'Connor, 1995). Nickel concentrations in the Gulf of Mexico coast do not exceed 50 μg/g, with the highest concentrations occurring with Al concentrations of 8–10% (Summers et al., 1996). Nickel concentrations in our cores ranged from 70–200 μg/g, and exceeded Gulf Coast Ni concentrations by a factor of 2 or more at similar Al concentrations. Greywackes and ultramafic rocks, such as serpentine, are predominant in the Franciscan Formation that surrounds the Bay. Ultramafics can contain as much as 2000 μg/g Ni and Cr, and greywackes > 150 μg/g V (Taylor and McLennan, 1985). Inputs of Cr, Ni and V from oil refineries and a steel mill in San Pablo and Suisun Bays (Gunther et al., 1987; Luoma et al., 1990; Brown and Luoma, 1995; Abu-Saba and Flegel, 1995) do not appear to affect sediment concentrations of these metals. Perhaps the oxidation states of locally discharged Cr and V is not conducive to adsorption to particle surfaces (Abu-Saba and Flegel, 1995); or the high natural baseline might confound detection of industrial influences.

Spatial heterogeneity of depositional processes is an important characteristic of San Francisco Bay sediments (Krone, 1979; Fuller, 1982; Ogden Beeman and Associates, 1992; Jaffe et al., 1998). Because of this extreme heterogeneity, large-scale mass metal deposition and retention are not easily extrapolated from core data, as has been done in other systems (Bricker, 1996). Comparative bathymetry (Ogden Beeman and Associates, 1992; Jaffe et al., 1998) and screening analyses to explore patterns of pollutant concentrations are necessary to find cores that contain continuous, reliable chronologies. Superimposed upon local and regional variability in deposition, land-to-sea gradients may occur in concentrations of Al, Cu, Cr, Ni, and V, and in deposition rates, most notably, of Hg, at least in depositional areas of San Francisco Bay. Enriched riverine or terrigenous sources of metals can be mixed with and diluted by marine sediments in estuaries (e.g., Uncles et al., 1988; Bricker, 1996). Strong diurnal winds, moderately strong tides, seasonally high river inflows and gravitational circulation would aid mixing and perhaps particle sorting in a shallow estuary like San Francisco Bay (Conomos, 1979). Mixing can also be affected by human activities. A shift in the contribution of sediment sources, rather than industrial pollution, may be the best explanation for the enrichment of Cr and V toward the surface of Central Bay cores because concentrations of Al changed coincidentally with Cr and V in those cores (Fig. 5). Krone (1996) concluded that the upper or landward bays are not trapping sediment as effectively as they were before 1950, and consequently greater amounts of sediment are being transported toward the Golden Gate. This suggests that more fine-grained sediments may be depositing in Central Bay than in the past. Causes of these changes could include a smaller Bay volume in the upper Bays (Krone, 1996), a change in residence times in the estuary induced by freshwater diversion (D. Schoellhamer, USGS, personal communication), or incorporation into the Central Bay of dredge spoils from the finer grained sediments of North Bay.

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