

A record of estuarine water contamination from the Cd content of foraminiferal tests in San Francisco Bay, California

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Abstract

A five-year dissolved Cd time series from San Francisco Bay and adjacent coastal water shows that the composition of surface water towards the mouth of the estuary is determined largely by the effect of coastal upwelling. Cd concentrations inside and outside the estuary (0.2–1.0 nmol/kg) increase as Cd-rich deep water is advected to the surface near the coast during spring and summer. On average, the mean Cd concentrations inside San Francisco Bay (0.54 nmol/kg) during 1991–1995 was significantly higher than outside (0.35 nmol/kg), however. Surface samples collected throughout San Francisco Bay confirm an internal Cd source unrelated to river discharge. The Cd content of the test of a benthic foraminifer (*Elphidiella hannai*) in a dated sediment core from San Francisco Bay was measured to determine if the water column Cd enrichments in San Francisco Bay could be related to the rapid development of the watershed. The method is based on the observation that the Cd/Ca ratio of carefully cleaned tests of foraminifera is determined by the dissolved Cd content of overlying water at the time of test formation. Pre-industrial foraminiferal Cd/Ca ratios in the sediment core average 274 ± 15 nmol/mol ($n = 19$) nmol/mol. Foraminiferal Cd/Ca ratios increased to 386 ± 33 nmol/mol ($n = 19$) over the past several decades indicating a 40% increase in the mean Cd content of surface water in Central San Francisco Bay. We suggest that, in addition to Cd discharges into the estuary, indirect consequences of agricultural development in the Central Valley of California could have contributed to this increase. This new method to reconstruct estuarine contamination is not affected by some of the processes that complicate the interpretation of changes in bulk sediment metal concentrations. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A rapid increase in the number of studies of metal contamination in sediments followed the introduction of the first commercial flame atomic absorption

spectrophotometers (FAAS) in the early 1970s (Förstner and Wittman, 1981). The elevated metal concentrations measured by this technique in the upper part of numerous sediment cores have demonstrated the effect of anthropogenic discharges in rivers, estuaries, and coastal areas (e.g., Bruland et al., 1974; Förstner and Wittman, 1981; Huh et al., 1992). The introduction of FAAS also allowed the routine determination of metal concentrations in in-

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dustrial and urban waste water. In conjunction with new regulations, this has led to a steady reduction in metal discharges to the environment over the past two decades in many locations, including San Francisco Bay (Davis et al., 1990). The objective of the cooperative USGS-NOAA study that resulted in the set of papers in this volume was to determine not only when a suite of contaminants started to accumulate in the sediment of San Francisco Bay, but also if and when stricter regulations on dischargers started to have a measurable effect.

In order to determine the impact of industrialization of the watershed of San Francisco Bay, we present here the reconstruction of changes in water column concentrations in the estuary for one specific metal, Cd, as an alternative to contamination studies relying on bulk sediments. Especially in a system as perturbed as San Francisco Bay, the interpretation of sediment metal profiles can be complicated by changes in the relative contribution of sediment from various sources (Hornberger et al., 1999), post-depositional redistribution of metals (Gobeil et al., 1987; Shaw et al., 1990), and formation of insoluble sulfides that enhance metal concentrations (Jacobs et al., 1985; Lapp and Balzer, 1993).

The data presented here include a five-year time series comparing variations in dissolved Cd inside San Francisco Bay with adjacent coastal water waters and an archive of past variations retrieved from the Cd content of the calcite tests of benthic foraminifera. This work builds on past studies of the impact of human activities on metals off the California coast and inside San Francisco Bay (Bruland et al., 1974; Gordon, 1980; Flegal et al., 1991; Sañudo-Wilhelmy and Flegal, 1991; Schmidt and Reimers, 1991; Huh et al., 1992). Our approach relies on the work initiated by Boyle (1981, 1988) demonstrating that the amount of Cd substituted for Ca in the calcite lattice of certain foraminifera (expressed as their Cd/Ca ratio) living at the sediment–water interface is proportional to the dissolved Cd content of overlying water. A key to this approach is the test cleaning procedure that thoroughly removes contaminating Cd-bearing matrices such as organic matter and Fe and Mn oxides. More recently, van Geen et al. (1992) demonstrated that the Cd/Ca ratio of the benthic foraminifer *Elphidiella hannai* living in shallow coastal waters and

near the mouth of North American west coast estuaries reflects dissolved Cd concentrations in the water column integrated over the lifespan of this species. Tests of this species were analyzed in the present study.

There are several advantages to using foraminiferal Cd/Ca as a recording phase of contamination. First, foraminiferal Cd/Ca is related to the composition of the water column rather than the sediment. The information is not redundant geochemically, since the water column and sediment are not necessarily equilibrated in a simple manner in estuaries (Luoma, 1990). Estuarine waters are also continuously mixed by tidal currents and a measure of the mean dissolved metal concentration at one location is probably more representative of the estuary as a whole than the sediment composition at one location. Contamination of the water column may also reflect a relevant pathway of metal exposure for at least some organisms (e.g., phytoplankton, mussels; Wang et al., 1996). A final advantage of using foraminiferal tests is that their metal content should be insensitive to post-depositional diagenesis that could overprint the metal input history recorded in the sediment. The main limitation of using foraminifera to reconstruct past levels of water column contamination is that the method is presently not applicable to metals other than Cd. Considerable analytical hurdles may have to be overcome before this approach can be extended to other environmentally relevant metals (Boyle, 1981).

2. Methods

2.1. Water sampling and analysis

In order to monitor variations in the composition of coastal water contributing to the estuary, water samples were collected in 1991–1995 from the beach, near Pillar Point, 60 km south of the mouth of San Francisco Bay (Fig. 1). A 3-m pole was used to collect samples for Cd, salinity, and nutrients. van Geen and Luoma (1993) showed that surfzone waters near Pillar Point are not affected by the outflow from San Francisco Bay. When proper precautions are taken, dissolved Cd in California surfzone water is determined largely by circulation across the conti-

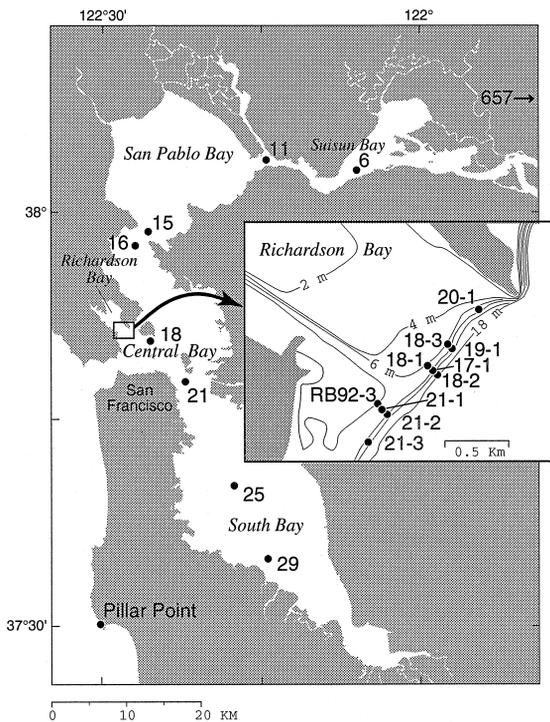


Fig. 1. Map showing the location of Pillar Point on the Pacific coast and numbered sampling stations inside San Francisco Bay. Sacramento River station 657 is outside the area of the map near the town of Rio Vista. The enlarged inset of the mouth of the Richardson Bay shows the locations of site RB92-3 and the box cores used to determine the distribution of *E. hannah* (Table 1).

mental shelf and is not affected by locally produced artifacts (van Geen and Husby, 1996). Surface water samples were also collected within the estuary on a regular basis between 1991–1993 and during the first half of 1994 and 1995. These samples were collected by pole sampling on board RV *Polaris*. Dissolved metal samples were filtered, pre-concentrated, and analyzed in the laboratory by graphite-furnace atomic absorption spectrophotometry (GFAAS) on a Perkin-Elmer Zeeman 3030 instrument under conditions described in van Geen and Boyle (1990) and modified by van Geen and Luoma (1993). The long-term reproducibility for a consistency standard of seawater that was analyzed by this method with each batch of 10 samples containing 0.44 nmol/kg Cd was ± 0.02 nmol/kg. The mean recovery was indistinguishable from 100% and the blank correction very small (0.001 ± 0.001 nmol/kg;

van Geen and Husby, 1996). This method was adapted for in-line pre-concentration of Cd followed by direct elution into the graphite furnace of a Hitachi Z8200 instrument to produce the 1994–1995 dissolved Cd data (R. Takesue and AvG, unpublished results).

Salinity was measured on samples stored in glass with a Guildline Autosol salinometer standardized with I. A. P. S. O. water. Concentrations of nutrients silicate and phosphate were measured spectrophotometrically with a QuickChem AE system (Lachat Instruments). The procedures are adaptations to flow-injection analysis of standard colorimetric methods described by Strickland and Parsons (1968). A significant interference by silicate in the determination of phosphate concentrations was corrected for (van Geen and Husby, 1996). Reproducibility for replicate injections was on the order of $\pm 5\%$. Blank corrections determined by analyzing Sargasso Sea surface water averaged 0.5 and 0.1 μM for silicate and phosphate, respectively.

2.2. Core selection

The abundance of foraminiferal tests was a key criterion used to identify a suitable core for this study. Tests of *E. hannah* had previously been found in a small embayment west of the mouth of the estuary, Richardson Bay, where sediment has been accumulating for several thousand years (Means, 1965; van Geen et al., 1992). The preferred habitat for *E. hannah* was determined by staining surface sediment (0–2 cm) with Rose Bengal from 10 box cores. The cores were collected along the outer edge of the shallow platform that defines Richardson Bay (Fig. 1). Only the protoplasm of living and recently living foraminifera is believed to be stained by this method (Corliss and Emerson, 1990). Tests were also counted in two additional intervals in two of the box cores (2–5 and 5–10 cm).

Abundances of stained and unstained tests determined in the upper 2 cm of the box cores are listed in Table 1. Very few tests were found northeast of the channel that cuts into Richardson Bay, with the exception of site 18-1 (Fig. 1). Surface sediment contained stained tests in three out of the four sites southwest of the channel. The number of stained

Table 1
Abundance of the foraminifer *E. hannai* in Richardson Bay sediment

Station	Water depth (m)	Depth in core (cm)	Number of tests (core diameter of 9 cm)	
			Unstained	Stained
17-1	12	0–2	1	0
18-1	7	0–2	8	7
		2–5	22	1
		5–10	83	1
18-2	18	0–2	0	0
18-3	8	0–2	0	1
19-1	10	0–2	0	0
20-1	7	0–2	1	0
RB92-3	7	0–2	125	15
		2–5	104	5
		5–10	360	5
21-1	10	0–2	22	1
21-2	15	0–2	48	5
21-3	13	0–2	12	0

tests at the site with the largest number of foraminifera, core SFB082092-3 abbreviated hereafter as RB92-3, decreased downcore from 7.5/cm core at 0–2 cm depth (for a core diameter of 9 cm) to 1.7/cm and 1.0/cm at 2–5 cm and 5–10 cm, respectively. Sediment mixing at this site is constrained by a ^{234}Th activity profile measured in another subcore from the same box core (Fuller et al., 1999). Unsupported activity of ^{234}Th was detected in both the 0–2 cm and the 2–5 cm intervals, but not the 5–10 cm interval. This indicates that some sediment at 2–5 cm depth was in contact with the water column about one half-life of ^{234}Th (24 days) before the time the core was collected. Assuming that the degradation rate of the stainable constituents is comparable or larger than the half-life of ^{234}Th , the relative distributions of stained foraminifera and unsupported ^{234}Th is generally consistent with a presumed epifaunal habitat for *E. hannai*. This is a pre-requisite for obtaining a record of chemical variations in bottom water by this approach rather than in pore water (McCorkle et al., 1990). The site of core RB92-3 was selected for downcore analysis.

2.3. Test cleaning and analysis

Each foraminiferal Cd/Ca determination for *E. hannai* requires 10–20 tests cleaned of Cd-rich organic matter with hydrogen peroxide. Fe and Mn

oxide coatings are removed with a reducing hydrazine solution. Reagent concentration and cleaning times have been reduced relative to the revised procedure of Boyle and Keigwin (1985/1986) because tests of *E. hannai* appear to dissolve more rapidly than deep ocean benthic foraminifera. Further modifications were based on changes in the reproducibility of Cd/Ca determinations analyses with various permutations of the cleaning steps for a large batch of tests collected from nearby Tomales Bay, California. The revised procedure used for this study is described by Lynch-Stieglitz et al. (1996). The reproducibility of Cd/Ca determinations for a consistency standard similar in composition to that of a solution of dissolved foraminifera was $\pm 5\%$.

2.4. Sediment Cd determinations

The Cd content of the same hydrofluoric acid sediment extracts used by Hornberger et al. (1999) for other metal determinations was measured by GFAAS with calibration by standard additions.

3. Results

Variations in salinity and Cd concentrations at Pillar Point and in Central Bay at Station 18 during 1991–1995 are shown in Fig. 2. Cd concentrations varied within a range of 0.2–1.0 nmol/kg inside and outside the estuary over this period (Table 2). Com-

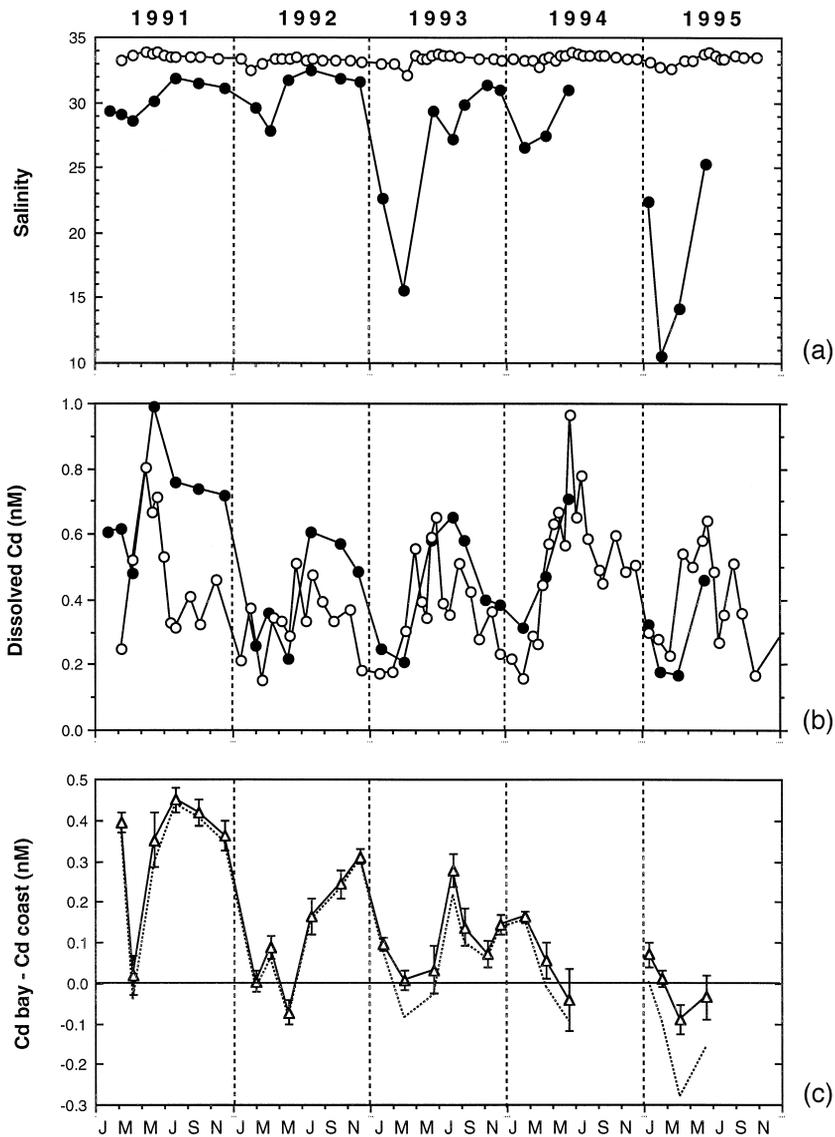


Fig. 2. Comparison of variations in (a) salinity and (b) dissolved Cd at Pillar Point on the Pacific coast (open circles) and station 18 in San Francisco Bay (filled circles). The difference between dissolved Cd measured at station 18 and dissolved Cd interpolated between the two samplings closest dates at Pillar Point is shown by the dashed line in panel (c). The solid line shows the difference between dissolved Cd inside and outside San Francisco Bay after the effect of dilution by low-Cd river water has been subtracted from the salinity difference between Central Bay and the mean salinity at Pillar Point. Error bars were estimated by assuming a 5% uncertainty in dissolved Cd in Central Bay and at Pillar Point and by propagating these errors.

parison of the two time series suggests that fluctuations in the composition of Central Bay water reflect at least in part seasonal variations in the composition of coastal water. These variations are driven by strong northwesterly winds during spring and sum-

mer causing upwelling of Cd-enriched deep water along the coast (van Geen et al., 1992; van Geen and Husby, 1996). Cd was shown to be enriched in subsurface water of the North Pacific by some of the first reliable trace metal studies in the ocean (Boyle

Table 2
Variations in surface water composition at Station 18 in San Francisco Bay

Date	Salinity	Phosphate (μM)	Silicate (μM)	Cadmium (nmol/kg)
02-06-91	29.360	2.00	51.0	0.606
03-11-91	29.010	3.50	54.0	0.618
04-11-91	28.610	2.40	61.6	0.479
06-05-91	30.110	3.70	70.5	0.992
08-01-91	31.870	2.60	42.4	0.760
10-01-91	31.517	2.90	41.1	0.737
12-10-91	31.112	3.80	50.6	0.715
03-04-92	29.587	0.52	39.8	0.256
04-07-92	27.834	1.99	49.6	0.358
05-27-92	31.770	1.42	23.2	0.219
07-28-92	32.478	2.24	31.2	0.605
10-14-92	31.822	2.72	39.1	0.573
12-02-92	31.529	2.71	35.7	0.487
02-24-93	22.584	2.32	90.2	0.248
04-01-93	15.562	1.32	129.9	0.206
06-16-93	29.300	1.94	45.9	0.581
08-10-93	27.143	2.66	62.7	0.649
09-10-93	29.861			0.579
11-08-93	31.358			0.398
12-07-93	30.974			0.386
02-16-94	26.519			0.315
04-19-94	27.487			0.471
06-15-94	31.001			0.708
01-18-95	22.337			0.323
02-08-95	10.562			0.178
04-04-95	14.174	1.15	140.6	0.169
06-15-95	25.266	1.79	68.0	0.462

et al., 1976; Martin et al., 1976; Bruland et al., 1978; Bruland, 1980). Fig. 2 also shows that there were periods of persistent enrichment in dissolved Cd inside San Francisco Bay relative to nearby coastal

waters, typically during late summer and fall. In an attempt to quantify the enrichment of surface water in Central Bay, Cd concentrations in coastal water corresponding to sampling cruises inside the estuary

Table 3
Variations in surface water cadmium at several stations in San Francisco Bay

Station	Salinity	Cd (nmol/kg)	Salinity	Cd (nmol/kg)	Salinity	Cd (nmol/kg)
	June 5, 1991		October 1, 1991		April 1, 1993	
29	29.242	1.210	32.144	1.061	18.826	0.226
25	29.751	1.059	32.272	1.294	18.802	0.244
21	30.676	0.980	31.403	0.718	10.790	0.210
16	28.337	0.945	30.607	0.747	5.101	0.252
15	25.892		28.654	0.865	4.226	0.213
11	17.705	0.861	20.218	1.019	2.647	
6	6.849	0.361	11.478	0.608	0.070	0.042
657	0.098	0.132	0.104	0.154	0.077	0.074

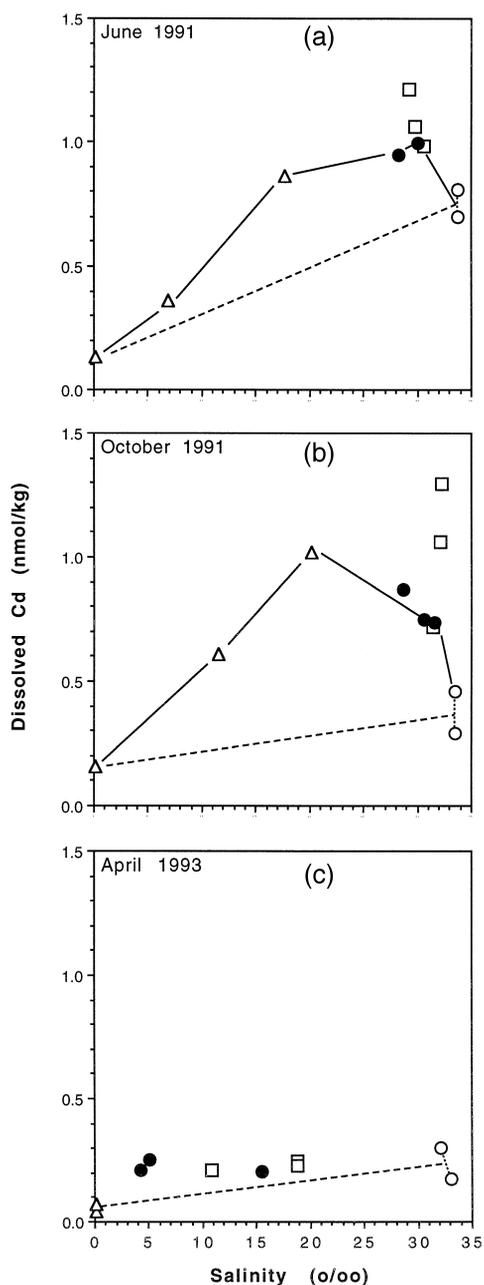


Fig. 3. Mixing relation for Cd along a surface transect through the northern reaches of San Francisco Bay in (a) June 1991, (b) October 1991, and (c) February 1993 (solid line). The relation corresponding to conservative of Sacramento River water and coastal water is indicated by a dashed line. Central Bay and southern San Pablo Bay stations 15, 16, 18 are indicated by closed circles, and North Bay and Sacramento River stations 11, 6, and 657 by triangles. South Bay stations 21, 25, 29 are shown by squares for comparison. See Fig. 1 for station locations.

were estimated by interpolating between sampling occasions at Pillar Point closest to the time of sampling in Central Bay (Fig. 2). Central Bay waters were particularly enriched in Cd relative to coastal water during the second half of 1991, and to a lesser extent during the second half of 1992. San Francisco Bay was not sampled year-round in 1994 and 1995. The mean Cd concentration in Central Bay during the three years of uninterrupted sampling was 0.54 nmol/kg (mean salinity of 29.1). The mean Cd concentration in coastal water over the same period was 0.35 nmol/kg (mean salinity of 33.3), calcu-

Table 4
Downcore foraminiferal Cd/Ca data at 37°51.3'N, 122°28.3'W

Box core		Gravity core	
Depth (cm)	Cd/Ca (nmol/mol)	Depth (cm)	Cd/Ca (nmol/mol)
1.0	340	18.5	359
	411	28.5	470
	346		391
	359		365
3.5	354		397
	7.5	38.5	355
12.5	396		353
	426	48.5	359
	386		325
	422		367
17.5	362		390
	384		333
	405		392
	22.5	396	58.5
27.5	422		277
	391	68.5	299
	410		286
	375		298
	387		258
	32.5	377	
37.5	488	78.5	296
	3		294
	500	88.5	256
	354		259
460		108.5	262
			282
			270
			265
		128.5	261
		138.5	270
		148.5	275
			258
			275
			279

lated by averaging over monthly intervals to avoid a bias towards spring and summer when sampling was more frequent (van Geen and Husby, 1996).

Salinity–Cd mixing relations within San Francisco Bay help to identify the main end-members contributing to the estuary (Table 3). The data selected for Fig. 3 are representative of the wide range of conditions encountered during the sampling period. The Sacramento and San Joaquin rivers constitute the main fresh water source to the estuary and contain little dissolved Cd (0.07–0.15 nmol/kg). Coastal water contains up to an order of magnitude more dissolved Cd than river water and this explains part of the increase in concentration from the northern reaches of the estuary to Central San Francisco Bay (Fig. 3a). Significant deviations from the conservative mixing relation between river and coastal water in San Pablo Bay, and more so in South Bay, however, clearly indicate a source of Cd to the water column within the estuary other than upwelling (Flegal et al., 1991; Shiller, 1996). The highest Cd concentrations in San Francisco Bay were observed in October 1991 (Fig. 3b). At the time, Cd levels

outside the estuary had decreased from 0.8 to 0.3 nmol/kg due to the seasonal reduction in coastal upwelling (Fig. 3b). In contrast, some of the lowest Cd concentrations of the time series were recorded throughout the estuary in April 1993 when a six-year drought in California was broken by higher than average precipitation. Increased run-off caused a large drop in salinity throughout the Bay and Cd enrichments relative to conservative mixing between river and coastal water were small, even in South Bay (Fig. 3c).

During the first half of each year, there was little Cd enrichment to speak of in Central Bay (Fig. 3c). This was not simply due to dilution by river water depleted in Cd. For a mean coastal salinity of 33.3 and a mean river salinity of 0.09, the fraction of river water contributing to Central Bay on each sampling occasion was calculated. The difference between Central Bay and coastal water Cd concentrations was then corrected for dilution by assuming conservative mixing of river water containing 0.12 nmol/kg Cd. Comparison of these results with uncorrected enrichments in Central Bay shows that winter reductions in

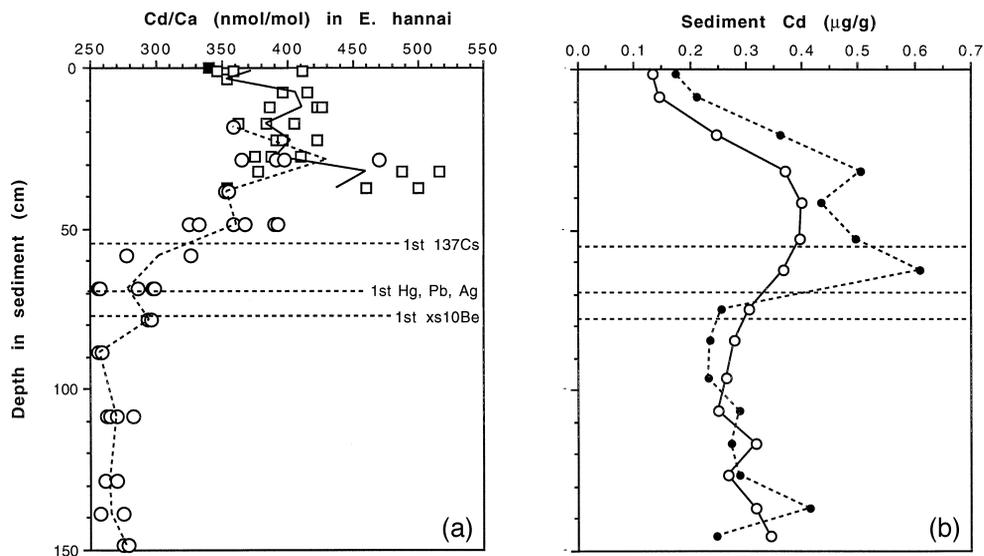


Fig. 4. Downcore records of foraminiferal Cd/Ca and sediment Cd in Richardson Bay core RB92-3. Cd/Ca ratios indicated by open circles indicate individual measurements in the gravity core. Samples indicated by open squares were taken from the box core. Closed square indicated Cd/Ca determination on one sample of Rose Bengal stained tests. Sediment Cd concentration indicated by open circles were measured on bulk sediment dissolved in hydrofluoric acid. Closed circles show determinations on $< 63 \mu\text{m}$ fraction separated by sieving. Horizontal dashed lines indicate sediment horizons in core RB92-3 of (1) the first appearance of a ^{10}Be anomaly dated to the turn of the century (van Geen et al., 1999), (2) the first indication of Hg, Pb, and Ag contamination in the sediment (Hornberger et al., 1999), and (3) the first detectable ^{137}Cs dated to the early 1950s (Fuller et al., 1999).

Cd concentrations can be explained by dilution with run-off only during the unusually wet year of 1995 (Fig. 2c). The implication is that other factors reduce the degree of Cd enrichment in Central Bay during late winter and spring.

The interpretation of the foraminiferal record relies on the proportionality between the Cd/Ca ratio of properly cleaned tests and the dissolved Cd content of water overlying the sediment when the tests were formed (Boyle, 1988; van Geen et al., 1992). In the 0–30 cm interval of the box core, Cd/Ca ratios average 386 ± 33 nmol/mol ($n = 19$), including one determination for a set of Rose Bengal-stained tests from the upper 2 cm of the box core (Table 4). The age model of Fuller et al. (1999) for core RB92-3 indicates that sediment, and therefore presumably foraminifera, deposited as recently as 1985 is mixed throughout the upper 30 cm of the core. Cd/Ca ratios in the 65–150 cm interval of the gravity core average 274 ± 15 nmol/mol ($n = 19$) and are more reproducible (Fig. 4a). This interval contains sediment deposited between as recently as the 1940s and as long ago as 1000 AD because the sedimentation rate was about an order of magnitude lower at this site before industrialization of the region (Fuller et al., 1999; van Geen et al., 1999). The record clearly shows that dissolved Cd concentrations in Central San Francisco Bay have not always been as high as they are today. Foraminiferal Cd/Ca ratios, and therefore mean dissolved Cd in Central Bay, nearly doubled between the early 1950s and the 1970s (Fuller et al., 1999). Although reproducibility of Cd/Ca determinations at the subsurface maximum corresponding to the 1970s is not good, the mean trend in the box core suggests a decline in dissolved Cd concentrations in Central Bay over the past decade (Fig. 4a).

The downcore profile of foraminiferal Cd/Ca bears little resemblance to changes in the Cd content of the sediment (Fig. 4b). Cd concentrations in the bulk sediment and in the < 62 μm fraction of sediment are higher deep in the core (0.3–0.4 $\mu\text{g/g}$) and decrease towards the surface (0.1–0.2 $\mu\text{g/g}$). Above 70 cm depth, Cd appears enriched in the sieved sediment fraction relative to the bulk sediment. The data suggest that downcore trends in sediment Cd and foraminiferal Cd/Ca ratios may not have the same origin.

4. Discussion

Distribution coefficients $K_d = (\text{Cd}/\text{Ca})_{\text{test}}/(\text{Cd}/\text{Ca})_{\text{water}}$ for Cd in the test of *E. hannai* inside and outside the estuary can be calculated independently from the data presented here. A K_d of 6.3 ± 0.4 is calculated from the mean composition of coastal water during 1991–1993 (Cd $0.35 \cdot 10^{-9}$ mol/kg, Ca $9.7 \cdot 10^{-3}$ mol/kg) and the composition of tests collected in rocky tidal pools at Pillar Point in 1991 and 1992 (Cd/Ca 228 ± 13 nmol/mol, $n = 25$; van Geen et al., 1992). This distribution coefficient is indistinguishable from a K_d of 6.1 ± 0.5 for Richardson Bay calculated for tests in the upper 30 cm of the box core and the mean composition of Central Bay water in 1991–1993 (Cd $0.54 \cdot 10^{-9}$ mol/kg, Ca $8.5 \cdot 10^{-3}$ mol/kg). The lower mean salinity, and therefore lower Ca concentration, in Central Bay relative to coastal water was taken into account for this calculation. The very close agreement between distribution coefficients in and outside the bay confirms that differences in salinity and sediment type between the two environments have little effect on the relation between water column and test composition. The average K_d of 6.2 for *E. hannai* calculated here is higher than the K_d value of 5.3 calculated by van Geen et al. (1992) on the basis of a higher mean coastal Cd concentration for the coastal series through September 1991.

The mean Cd/Ca ratio in the lower portion of core RB92-3 (274 ± 14 , $n = 19$) is indistinguishable from a value of 278 ± 22 ($n = 75$) reported previously for tests between 100 and 250 cm depth in a core about 1 km northeast of the site (van Geen et al., 1992). Reproducibility from one core to the other suggests that the composition of Central Bay water can be calculated from these results with some confidence. Such a calculation must take into account the lower mean salinity in Central Bay prior to water diversion for agriculture in the Central Valley (salinity ~ 27 ; Peterson et al., 1989), although the salinity dependence of Cd incorporation in the test *E. hannai* could be determined by factors in addition to the Cd/Ca ratio of bay water (e.g., organic or chloride Cd complexation). The resulting estimated mean Cd concentration of Central Bay water prior to 1950 is $0.35 \cdot 10^{-9}$ mol/kg (Ca $7.9 \cdot 10^{-3}$ mol/kg), assuming a K_d of 6.2. This is only slightly higher than the Cd

concentration of 0.30 nmol/kg predicted for the pre-industrial Central Bay assuming conservative mixing with river water (Cd 0.12 nmol/kg) and coastal water, and similar upwelling conditions as in 1991–1993 (Cd 0.35 nmol/kg). Thus, the composition of the foraminifera suggests that until about 1950, Central Bay and coastal water-dissolved Cd levels were very similar. A similar calculation based on Cd/Ca ratios ranging between 350–500 nmol/mol indicates that average dissolved Cd concentrations in Central Bay ranged between 0.4–0.6 nmol/kg since the 1950s. The data do not rule out the possibility that mean dissolved Cd concentrations in Central Bay could have been considerably higher than today during this period because the Richardson Bay record is highly filtered by sediment mixing (Fuller et al., 1999).

While the foraminiferal record shows that Cd concentrations in the water column of San Francisco Bay increased relatively recently, it is more difficult to identify the origin of the enrichment. Some clues are provided by the geochemical behavior of Cd in other estuaries. The desorption of Cd from river-borne particles in the low salinity range results in enrichments in the dissolved phase in both pristine and impacted estuaries (Boyle et al., 1982; Edmond et al., 1985; Elbaz-Poulichet and Martin, 1987; Shiller and Boyle, 1991). In San Francisco Bay, however, the largest Cd enrichments relative to conservative mixing are found near Carquinez Strait and in South Bay where salinities are relatively high (Fig. 3). This was also shown previously by Flegal et al. (1991). Because Cd desorption typically occurs at salinities < 10, this suggests that river-borne particles are a relatively small source of Cd to the water column in San Francisco Bay. Dissolved Cd concentrations in the Sacramento River during recent surveys (Table 3) were comparable to the relatively pristine Amazon and Lena rivers (Boyle et al., 1982; Martin et al., 1993). Thus, the data indicate that Cd enrichments in San Francisco Bay have their origin within the estuary.

In Richardson Bay surface sediment, Cd concentrations are not significantly different from the average of composition of the Earth's crust ($\sim 0.1 \mu\text{g/g}$; Taylor and McLennan, 1985). This contrasts with other metals such as Hg, Pb, and Ag showing anthropogenic enrichments over background concentrations

that start at ~ 70 cm depth and extend to the surface in the same core (Fig. 4; Hornberger et al., 1999). Extreme levels of Cd enrichment have been reported in the vicinity of a few point sources, however (Luoma and Phillips, 1988). One reason anthropogenic Cd inputs may be less consistently recorded in sediments is a significantly lower particle reactivity than, for instance Cu, Zn, and Pb, demonstrated by laboratory manipulations of slurries of sediment and pure metal oxides (Leckie et al., 1980; as quoted in Salomons and Förstner, 1984). The sediment Cd record is also more difficult to interpret in terms of anthropogenic discharges because of post-depositional redistribution. Three-fold higher Cd concentrations in sediment deposited well before significant disturbance of the estuary (van Geen et al., 1999) than at the surface, for instance, are probably a diagenetic feature characteristic of mildly reducing conditions (Gobeil et al., 1987; van Geen et al., 1995). Although this is hard to establish with certainty, it may be that the subsurface maximum in sediment Cd concentrations between 60 and 30 cm depth is a reflection of anthropogenic inputs caused by mining activities, industrialization, and urban runoff (Hornberger et al., 1999). The release of ~ 53 kg of fluorescent Zn-Cd-sulfide particles to the air over the San Francisco Bay area in 1950 and 1967 as part of the US Army's chemical warfare tests (NRC, 1997) is unlikely to have contributed significantly. Mean Cd would have increased by no more than 0.014 nmol/kg throughout the estuary, even if all the Cd reportedly released had dissolved instantaneously in the water column.

The lack of a simple relation between water column and sediment contamination suggests that processes other than direct input may have affected dissolved Cd in San Francisco Bay. Changes in water management, driven by the growth of modern agriculture, have resulted in long-term reductions in river inflows to the estuary, increases in nutrient inputs, and an increase in the mean residence time of water in the estuary (Nichols et al., 1986). One potential mechanism that could have led to increased dissolved Cd levels is analogous to the process of nutrient trapping observed in certain estuaries (Redfield et al., 1963). Cd is enriched in oceanic plankton matter (Knauer and Martin, 1981; Collier and Edmond, 1984). Luoma et al. (1998) recently showed

that phytoplankton strip a significant amount of dissolved Cd from the water column during the spring blooms characteristic of South Bay. Regeneration of Cd-enriched plankton matter could therefore conceivably enrich the overlying water column later in the year and produce seasonal patterns such as those in Central Bay (Fig. 2), as well as gradients within the bay (Fig. 3a,b). Lower river flow, the resulting increase in residence time of water in the estuary, and increased nutrient inputs could therefore all have accentuated trapping in the estuary of Cd from either natural or anthropogenic sources.

The water column time series shows some evidence of this trapping process. For example, the residual Cd enrichment inside Central Bay and the maximum concentrations in local coastal waters were both higher in 1991 relative to 1992, during years with similar flow regimes (see similar salinities in Fig. 2a). In this case, greater Cd inputs from upwelling may have contributed to the greater late-year trapping of Cd contamination in the Bay. In 1993, Cd contamination in Central Bay was reduced compared to the earlier years, despite higher concentrations in coastal waters. River flow was substantially higher in 1993 than in the earlier years, which may have reduced the efficiency of Cd trapping in the estuary. By analogy, reductions in river flow over the past several decades may also have increased Cd trapping in the estuary. Water column contamination recorded by the foraminiferal tests could therefore have been the combined result of changes in Cd input as well as other processes.

5. Conclusion

The Cd content of foraminifera is a new tool to reconstruct the history of water column contamination in an estuary. This approach complements bulk sediment metal analysis because (1) it is not affected by sediment diagenesis, (2) the dissolved metal pool can be more directly related to bioaccumulation in certain organisms, and (3) the water column is a better integrator of contamination throughout the estuary.

Surface water collected inside and outside San Francisco Bay during 1991–1995 shows that dissolved Cd levels in Central Bay are controlled by two sources: (1) upwelling of Cd-enriched water

outside the estuary, and (2) an internal Cd source that is not riverine. The foraminiferal Cd/Ca record indicates that this second source did not become prominent until the 1950s, at least two decades after discharges of Hg, Pb, and Ag modified the composition of bulk sediment in the estuary. The seasonality and year-to-year variability of present-day Cd contamination suggest that water column concentrations are sensitive to river inflow and may increase in response to reduced inflow. Thus, the combined evidence from the foraminiferal record and the surface water time series suggests that reduction of river inflows since the 1950s could have increased dissolved Cd levels, at least in Central Bay.

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