

Stable lead isotopic analyses of historic and contemporary lead contamination of San Francisco Bay estuary

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Abstract

Variations in stable lead isotopic composition (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) in three sediment cores from the San Francisco Bay estuary document temporal changes in sources of lead during the past two centuries. Sediment, with lead from natural geologic sources, and relatively homogeneous lead isotopic compositions are overlain by sediments whose isotopic compositions indicate change in the sources of lead associated with anthropogenic modification of the estuary. The first perturbations of lead isotopic composition in the cores occur in the late 1800s concordant with the beginning of industrialization around the estuary. Large isotopic shifts, toward lower $^{206}\text{Pb}/^{207}\text{Pb}$, occur after the turn of the century in both Richardson and San Pablo Bays. A similar relationship among lead isotopic compositions and lead concentrations in both Bays suggest contamination from the same source (a lead smelter). The uppermost sediments (post 1980) of all cores also have a relatively homogenous lead isotopic composition distinct from pre-anthropogenic and recent aerosol signatures. Lead isotopic compositions of leachates from fourteen surface sediments and five marsh samples from the estuary were also analyzed. These analyses suggest that the lead isotopic signature identified in the upper horizons of the cores is spatially homogeneous among recently deposited sediments throughout the estuary. Current aerosol lead isotopic compositions [Smith, D.R., Niemeyer, S., Flegal, A.R., 1992. Lead sources to California sea otters: industrial inputs circumvent natural lead biodepletion mechanisms. *Environmental Research* 57, 163–175] are distinct from the isotopic compositions of the surface sediments, suggesting that the major source of lead is cycling of historically contaminated sediments back through the water column. Both the upper core sediments and surface sediments apparently derive their lead predominantly from sources internal to the estuary. These results support the idea that geochemical cycling of lead between sediments and water accounts for persistently elevated lead concentrations in the water column despite 10-fold reduction of external source inputs to San Francisco Bay [Flegal, A.R., Rivera-Duarte, I., Ritson, P.I., Scelfo, G., Smith, G.J., Gordon, M., Sañudo-Wilhelmy, S.A., 1996. Metal contamination in San Francisco Waters: historic perturbations, contemporary concentrations, and future considerations in San Francisco Bay. In: Hollibaugh, J.T. (Ed.), *The Ecosystem. AAAS*, pp. 173–188]. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Contamination by lead is pandemic. With multiple sources such as automobile exhaust, coal burning, and waste incineration, contamination is ubiquitous and extends from the Arctic (Boutron et al., 1991) to the Antarctic (Flegal et al., 1993). While the principal source of contaminant lead in the global budget is from atmospheric deposition, lead budgets in urbanized aquatic systems may show other large contributions from sources such as municipal and industrial discharge (Nriagu, 1986). Toxicological and clinical studies have established no lower threshold for deleterious human health effects from lead (Needleman et al., 1979; McMichael et al., 1988; Needleman et al., 1990; Bellinger et al., 1991; Bellinger et al., 1994). Thus, it is easily postulated that environmental lead contamination adversely affects important ecological resources, as well.

San Francisco Bay is a greatly modified estuary (Nichols et al., 1986) that shows significant declines of biota. Settlement of the area by Europeans began in the 1700s, while the first large population increases were associated with the 1849 discovery of gold in the Sierra Nevada. Hydraulic gold mining, which began in 1853, released tons of sediment into the tributaries of the estuary. Those mining practices were halted in 1884 but had already resulted in the deposition of meters of sediment in the upper reaches of the estuary (Hedgpeth, 1979). The increase in population, initiated by the discovery of gold, resulted in large scale urbanization and industrialization of the lands surrounding the estuary. There are now about 10 million people within the watershed of the estuary (State of California, 1993).

Early industrialization of the estuary included the Selby lead smelter located adjacent to San Pablo Bay (Fig. 1). This smelter began operation in the late 1800s and continued operating until 1970. Although contamination from throughout the smelter's operations is not well documented, it must have been a significant source of lead. This is illustrated by reports that soon after the turn of the century, as a result of processing ore, the amount of SO₂ emitted from the smelter raised health concerns in downwind communities (Holmes et al., 1915). Additionally, in the last two decades of the smelter's operation, over 40 horses died from chronic lead poisoning in adja-

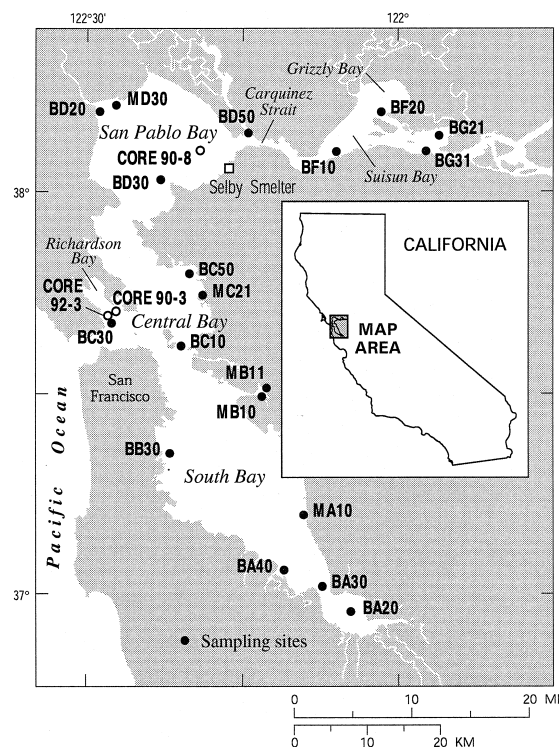


Fig. 1. A location map of the San Francisco Bay estuary showing: three sediment core sites: two in Richardson Bay (90-3 and 92-3) and one in San Pablo Bay (90-8); surface sediments delineated with a prefix B; marsh samples delineated with a prefix M; and, the Selby lead smelter.

cent pastures (Rabinowitz and Wetherill, 1972). It is possible that lead from the Selby smelter may have been a major component in some local gasolines after the introduction of leaded gasoline in 1923. There was a tetraethyl lead (TEL) plant located approximately 25 miles east of San Pablo Bay.

Although there have been large historical sources of lead input (smelter and leaded gasoline emissions) to the estuary, contemporary anthropogenic inputs have generally been considered to be the dominant source of contamination (Davis et al., 1991). These inputs include municipal and industrial point source discharges, surface runoff and atmospheric deposition.

In addition to direct inputs of contaminants, other factors are important in governing the cycling, distribution and concentration of lead and other trace

Table 1

Lead isotopic compositions and concentrations of core sediments from three cores in San Francisco Bay

Depth (cm)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	[Pb] $\mu\text{g/g}$
<i>(1a) (RB 90-3)</i>						
9.5	18.581	15.597	38.296	1.1913	2.0611	
19.5	18.644	15.619	38.416	1.1937	2.0609	
39.5	18.605	15.629	38.416	1.1904	2.0648	
49.5	18.565	15.627	38.416	1.1880	2.0693	
59.5	18.622	15.625	38.477	1.1918	2.0663	
69.5	18.590	15.611	38.365	1.1908	2.0638	
79.5	19.059	15.663	38.921	1.2168	2.0420	
89.5	19.137	15.703	39.015	1.2187	2.0388	
109.5	19.129	15.651	38.920	1.2222	2.0347	
119.5	19.140	15.632	38.864	1.2244	2.0305	
149.5	19.084	15.625	38.800	1.2214	2.0332	
159.5	19.125	15.617	38.821	1.2246	2.0299	
179.5	19.127	15.639	38.866	1.2230	2.0320	
189.5	19.188	15.700	39.061	1.2222	2.0356	
219.5	19.118	15.631	38.828	1.2231	2.0310	
<i>(1b) (RB 92-3)</i>						
2.5	18.526	15.593	38.279	1.1881	2.0662	20.4
21.5	18.499	15.590	38.235	1.1866	2.0669	23.2
41.5	18.418	15.591	38.189	1.1813	2.0735	29.3
56.5	18.678	15.601	38.440	1.1972	2.0580	13.3
62.5	18.190	15.567	38.100	1.1685	2.0946	29.7
66.5	18.383	15.583	38.189	1.1797	2.0774	30.3
85.5	19.042	15.643	38.834	1.2173	2.0394	8.2
99.5	19.008	15.621	38.753	1.2168	2.0433	8.7
109.5	19.095	15.629	38.829	1.2218	2.0335	7.8
119.5	19.122	15.660	38.930	1.2211	2.0359	7.8
130.5	19.107	15.642	38.878	1.2215	2.0348	7.8
139.5	19.104	15.646	38.887	1.2210	2.0356	7.9
145.5	19.106	15.642	38.855	1.2215	2.0337	
<i>(1c) (SP 90-8)</i>						
2.5	18.631	15.611	38.397	1.1934	2.0609	23.1
20.0	18.587	15.596	38.335	1.1918	2.0624	
22.5	18.590	15.600	38.330	1.1917	2.0619	18.8
29.5	18.610	15.630	38.400	1.1907	2.0634	25.2
30.0	18.607	15.631	38.402	1.1904	2.0637	
40.0	18.532	15.592	38.278	1.1886	2.0655	
50.0	18.598	15.573	38.263	1.1942	2.0573	
55.5	18.417	15.584	38.185	1.1818	2.0734	31.7
60.0	18.399	15.571	38.164	1.1816	2.0743	
69.5	18.281	15.595	38.138	1.1722	2.0862	39.1
70.0	18.275	15.549	38.009	1.1753	2.0799	
89.5	18.474	15.598	38.334	1.1844	2.0750	42.5
90.0	18.508	15.577	38.327	1.1882	2.0708	
109.5	18.690	15.610	38.480	1.1973	2.0589	19.9
110.0	18.686	15.607	38.484	1.1973	2.0595	
120.0	19.008	15.610	38.746	1.2177	2.0384	
129.5	19.050	15.620	38.810	1.2196	2.0373	13.5
130.0	19.048	15.621	38.805	1.2194	2.0372	
133.5	19.087	15.638	38.858	1.2206	2.0358	11.9
140.0	19.049	15.631	38.849	1.2187	2.0394	

Table 1 (continued)

(1a) (RB 90-3)						
Depth (cm)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	[Pb] $\mu\text{g/g}$
(1c) (SP 90-8)						
153.5	19.054	15.635	38.812	1.2187	2.0369	13.8
160.0	19.057	15.625	38.820	1.2196	2.0370	
169.5	19.086	15.632	38.843	1.2210	2.0352	12.7
189.5	19.090	15.641	38.873	1.2205	2.0363	12.3
200.0	19.094	15.625	38.865	1.2220	2.0355	
224.5	19.089	15.640	38.878	1.2205	2.0367	12.8
235.0	19.100	15.625	38.840	1.2224	2.0335	
235.5	19.113	15.634	38.870	1.2225	2.0337	

Two in Richardson Bay (1a: RB 90-3 and 1b: RB 92-3) and one in San Pablo Bay (1c: SP90-8). RB90-3 does not have corresponding lead concentration data.

elements within San Francisco Bay. Estuaries are an important sink for particle reactive contaminants carried in from the rest of the watershed due to their unique hydrodynamics and biogeochemistry (Turekian, 1977). One major factor affecting trace metal concentrations is freshwater flushing (Flegal et al., 1991; Flegal and Sañudo-Wilhelmy, 1993; Smith and Flegal, 1993). In the South Bay, where hydraulic residence time (120 days) is at least two to three times longer than in the rest of the bay, lack of flushing has been cited as a principal factor contributing to relatively high trace metal concentrations in the water column (Flegal et al., 1991; Flegal and Sañudo-Wilhelmy, 1993; Smith and Flegal, 1993). Concentrations of some metals (Cu and Ag) in this region have exceeded water quality criteria (Flegal et al., 1991).

Understanding the geochemical cycling of trace metals in aquatic environments requires determination of input fluxes, as well as the temporal and spatial distribution of the sources of contamination. In San Francisco Bay, data characterizing sources of lead contamination have been insufficient for a complete understanding, since historic records of industrial inputs are poorly constrained, incomplete and often erroneous. Our specific objectives were to identify sources of lead to the estuary historically and contemporaneously, as well as elucidate geochemical cycling of lead within the estuary. These objectives were accomplished through lead concen-

tration and isotopic analyses of dated sediment cores and surface sediments from San Francisco Bay.

2. Methods

Cores analyzed for lead isotopic analyses were collected from three sites in San Francisco Bay, one in San Pablo Bay and two in Richardson Bay (Fig. 1). Age-dating of the San Pablo Bay core (SP90-8) and Richardson Bay core (RB92-3) is discussed in Fuller et al. (1999), and of the Richardson Bay core (RB90-3) in van Geen et al. (1999). Cores were recovered with benthic gravity corers using polybutyrate core liners. The sediment core liner was immediately removed from the barrel, capped, sealed and transported to cold storage (2–3°C) (Hornberger et al., 1999). In 1994, surface and marsh sediments (2–5 cm) were collected, from around the estuary (Fig. 1), in acid cleaned low density polyethylene jars as part of the San Francisco Bay Regional Water Quality Control Board's monitoring program (Flegal et al., 1994).

Core samples were split for isotopic analyses between the University of California, Santa Cruz (UCSC) and US Geological Survey (USGS), Menlo Park. Isotopic analyses at the UCSC used bulk 50 mg subsamples, digesting them completely with a mixture of HClO_4 , HNO_3 and HF (Ritson et al., 1994). Sieved sediment core sub-samples (< 64 μ) were analyzed for both lead isotopic compositions

and lead concentrations at the USGS. These samples (100 mg) were completely digested with a series of concentrated HF, HNO₃, and 6 N HCl dissolutions. In 6 N HCl, a 20% split was taken for lead concentration analyses. This split was dried and 50 ml of 2% HNO₃ plus 0.2 ml of internal standard were added for lead concentration analyses.

Surface sediments were leached with 0.5 N HCl. The dilute acid extraction approximates the bioavailability of some metals in sediments (Flegal et al., 1994). All core and surface sediment samples, underwent lead separation using Dowex AG-1-X8 anion exchange resin and HBr. Lead contained in the anion resin was collected with HCl.

Lead isotopic compositions were determined on either a VG sector 54-30 (UCSC) or Finnigan MAT 261 (USGS) thermal ionization mass spectrometer. Mass fractionation, determined by multiple analyses of NIST SRM 981 and 982, was 0.006/amu for the VG sector 54-30 and 0.0011/amu for the Finnigan MAT 261. The total blank for all procedures was < 1 ng of lead. Two standard deviations from the mean is better than 0.02% for the isotopic ratios ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb and better

than 0.004% for ²⁰⁶Pb/²⁰⁷Pb. Replicate samples from both labs were within analytical error of each other.

Core lead concentrations for the core sub-samples were measured on a Perkin-Elmer Sciex Elan 6000 Inductively Coupled Plasma Mass Spectrometer (ICPMS). Analytical error for lead concentration on the ICPMS is better than 1%. Lead concentrations for the surface and marsh sediments were measured with a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer equipped with an HGA-500 Heated Graphite Atomizer (Flegal et al., 1994). Analytical error for lead concentration was better than 10%.

3. Results

3.1. Sediment cores

3.1.1. Dating

The cores were dated by ²¹⁰Pb and ²³⁴Th activities (Fuller et al., 1999) and by ¹⁴C in mollusk shells (van Geen et al., 1999). Fallout isotope profiles (¹³⁷Cs and ^{239,240}Pu) were determined for comparison to the ²¹⁰Pb chronology. In RB92-3, vertical mixing

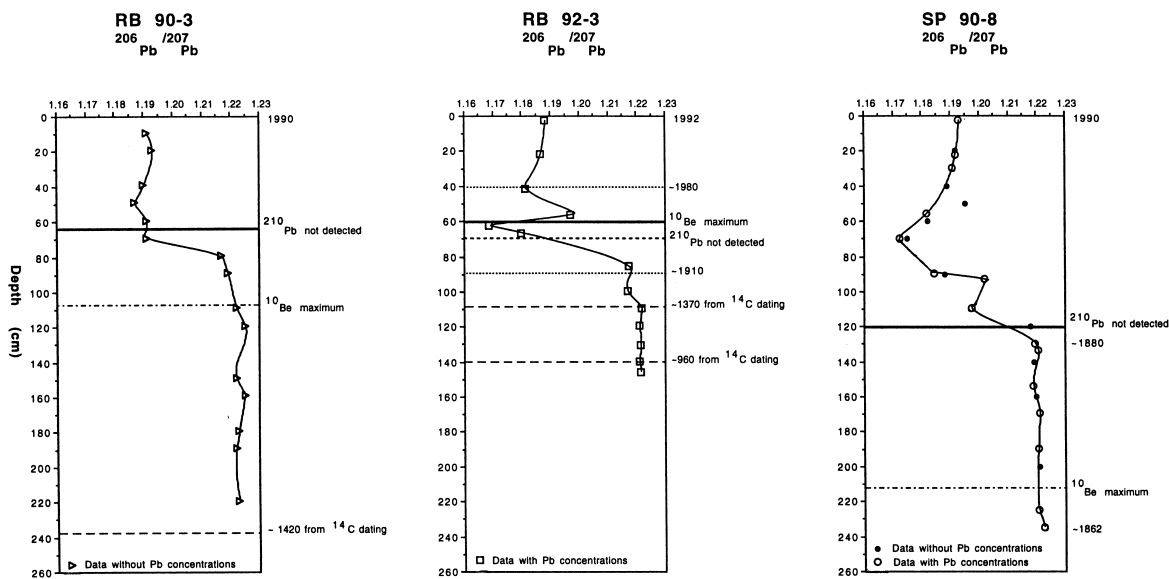


Fig. 2. Lead isotopic composition (²⁰⁶Pb/²⁰⁷Pb) of the Richardson Bay and San Pablo Bay cores plotted against depth in centimeters. Heavy solid line across graphs indicates the disappearance of ¹³⁷Cs. ²¹⁰Pb also disappears at the same depth in cores RB90-3 and SP90-8, but not in RB 92-3. On core RB92-3, the dates ~ 1910 and ~ 1980 are from a mixing model in Fuller et al. (1999). On core SP90-8, the dates ~ 1880 and ~ 1862 are from historic comparative bathymetry (Jaffe et al., 1998). The ¹⁰Be maximum and ¹⁴C dates on mollusk shells are from van Geen et al. (1999).

of surface sediments was indicated by the nearly constant excess ^{210}Pb in the upper 25 cm. The chronology of RB92-3 was developed by assigning a minimum age of deposition corresponding to the earliest date a contaminant could have been deposited (Fuller et al., 1999). The period of human influence (after the 1849 gold rush) was constrained by the appearance of ^{10}Be , an indicator that erosion had accelerated in the watershed. The earliest dates in RB92-3 were developed from the AMS ^{14}C data

on shells. Profiles of ^{210}Pb , ^{137}Cs , and $^{239,240}\text{Pu}$ in SP90-8 indicate considerably higher, albeit sporadic, sedimentation over the past several decades (Fuller et al., 1999). A hiatus in this core, suggested by the radionuclides and other properties, is consistent with historical changes in bathymetry (Jaffe et al., 1983), indicating a period of erosion around the turn of the century. Comparative bathymetry, the characteristics of the sediments (similarity to hydraulic mining debris), and ^{10}Be , in core SP90-8 suggest that the core

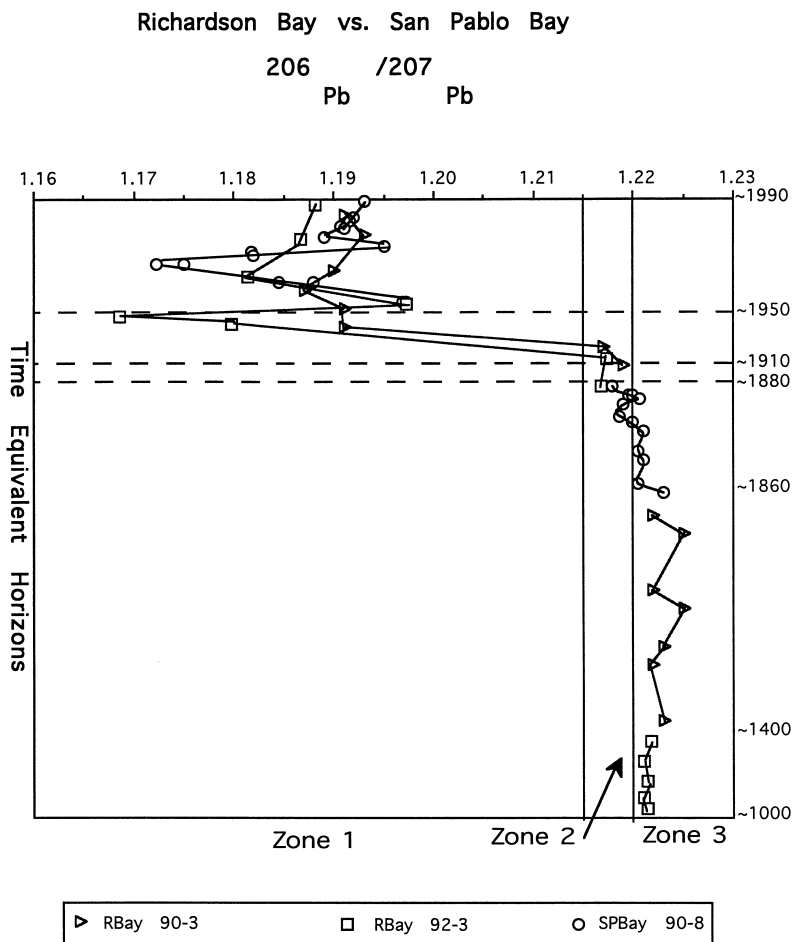


Fig. 3. A plot of the lead isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) of the San Pablo Bay core 90-8 and Richardson Bay cores 90-3 and 92-3 in time equivalent horizons. The zones are differentiated by isotopic composition and represent changing sources of lead. Zone 3 = natural background, Zone 2 = slight shift in Pb isotopic composition in late 1800s, Zone 1 = horizons highly contaminated with lead. The dates are interpreted in other papers on these cores. The dates shown are: ~1990, for the year cores were collected; ~1950, for the first appearance of ^{137}Cs (Fuller et al., 1999); ~1910 is from a mixing model for Richardson Bay core 92-3 based on a combination of radioisotopes ^{137}Cs , ^{210}Pb , ^{234}Th , $^{239,240}\text{Pu}$ (Fuller et al., 1999); ~1880 and ~1862 are from a comparative bathymetry study in San Pablo Bay (Jaffe et al., 1998); and, ~1400 and ~1000 are from ^{14}C dates on a mollusk shells (van Geen et al., 1999).

Table 2

Lead isotopic compositions and concentrations of leachates from surface sediments and marsh samples (top to 3–5 cm)

Station	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	[Pb] $\mu\text{g/g}$
BA20	18.48	15.61	38.25	1.183	2.070	26.9
BG21	19.37	16.32	40.02	1.188	2.066	9.6
BB30	18.37	15.57	38.05	1.181	2.071	32.5
BC10	18.13	15.55	37.84	1.166	2.087	34.2
BD50	18.45	15.60	38.23	1.183	2.072	31.0
BA30	18.47	15.58	38.15	1.185	2.065	23.8
BF10	18.45	15.59	38.22	1.183	2.072	22.7
BD20	18.50	15.61	38.27	1.185	2.069	24.3
BC30	18.48	15.62	38.20	1.183	2.067	34.0
BA40	18.47	15.59	38.18	1.185	2.067	21.4
BC50	18.42	15.60	38.15	1.181	2.071	31.5
BD30	18.53	15.62	38.28	1.186	2.066	19.9
BG31	18.49	15.59	38.21	1.186	2.067	11.7
BF20	18.33	15.58	38.18	1.176	2.083	24.9
MA10	18.64	15.73	38.53	1.185	2.067	15.5
MB10	18.33	15.59	38.00	1.176	2.073	97.3
MB11	18.57	15.63	38.20	1.189	2.057	127.6
MC21	18.60	15.60	38.14	1.192	2.051	168.9
MD30	18.45	15.59	38.19	1.183	2.070	26.8

Surface sediment samples have a prefix B and marsh samples have a prefix M.

segment deposited between 120 and 240 cm was deposited between ~ 1860 and 1880.

3.1.2. Pb isotopic compositions

Similar lead isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.22$) were found in the deepest sections of all the cores, but in core SP90-8 the Pb concentrations are one and a half times higher. The deepest section of SP90-8 represents the period of hydraulic mining debris input, and the deepest sections in both Richardson Bay cores represent sediments not disturbed by human activities (Table 1, Figs. 2 and 3 (Zone 3)). Up core, in the late 1800s, lead concentrations slightly increase in RB92-3 and SP90-8 and lead isotopic compositions in all cores shift to slightly lower $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.218$ (Table 1, and Fig. 3 (Zone 2)). After the turn of the century, the cores begin large, rapid isotopic excursions, congruent with lead concentration increases (Table 1, Figs. 2 and 3 (Zone 1)). The top section of all cores show a relatively homogeneous isotopic composition from approximately 50 cm to the surface ($^{207}\text{Pb}/^{206}\text{Pb} \approx 1.19$) (Figs. 2 and 3).

3.2. Surface Sediments

The $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratios of the surface sediment leachates ranged from ~ 1.167 to 1.188 and the lead concentrations ranged from 10–34 $\mu\text{g/g}$ (Table 2). The isotopic range and lead concentrations of surface sediment leachates are similar to those of core sediments deposited since approximately 1940 (Tables 1 and 2; Fig. 3 (Zone 1)). The $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic compositions of the marsh sediment leachates ranged from 1.176 to 1.192, while concentrations ranged from 16–169 $\mu\text{g/g}$ (Table 2). The marsh sediment leachates extend to higher $^{206}\text{Pb}/^{207}\text{Pb}$ values and lead concentrations than the surface sediment leachates.

4. Discussion

4.1. Sediment cores: historical changes

Sediment in the deepest horizons of the Richardson and San Pablo Bay cores lie below the penetration of excess ^{210}Pb (Fuller et al., 1999). Richardson

Bay sediments below 110 cm (Zone 3) predate anthropogenic perturbations to the region (van Geen et al., 1999); San Pablo Bay sediments below 120 cm appear to be from the late 1800s (Fuller et al., 1999; Jaffe et al., 1983). The similarity in isotopic composition of these deep intervals suggest that the particulate supply was predominantly from the same source, most probably a result of erosion of natural geologic sources creating fluvial material coming through the delta. This fluvial sediment source is supported by contemporary data showing incoming fluvial sediment eclipses (> 75%) all other sources of particulate material to the estuary (Krone, 1979). The isotopic compositions of the deep intervals are within the range of granitic Sierra Nevada material ($^{206}\text{Pb}/^{207}\text{Pb} = 1.215\text{--}1.224$, Erel et al., 1991) and are the same as terrigenously derived continental shelf sediments ($^{206}\text{Pb}/^{207}\text{Pb} = 1.208\text{--}1.226$) found outside the mouth of the estuary (Church, 1976). Based on these lines of evidence, the sediments appear to represent a natural background lead isotopic compositions.

Although Pb isotopic compositions of the deepest horizons in the SP90-8 (> 170 cm) and Richardson Bay cores (> 110 cm) are similar, the deep horizons in the SP90-8 core are higher in Pb concentration (Table 1, Fig. 4). This Pb concentration change is attributed to a shift in the sediment source, but with a similar range of isotopic compositions. For several reasons, this change is thought to be the result of hydraulic mining activities in the drainage basin. Both the Pb isotopic compositions and Pb concentrations of two large abandoned hydraulic gold-mines in the Sierras (Bouse et al., 1997) are similar to those in the deepest horizons of the San Pablo Bay core (Fig. 4). Moreover, the estimated dates of deposition are consistent with sediment inputs from hydraulic mining.

Moving up the sediment column, there is a small but noticeable shift in the lead isotopic compositions and slight increase in Pb concentrations of the sediments at the depth intervals 120–160 cm in San Pablo Bay and ~ 80–90 cm in Richardson Bay 90-3 (Table 1, Figs. 2 and 3 (Zone 2)). This shift occurs

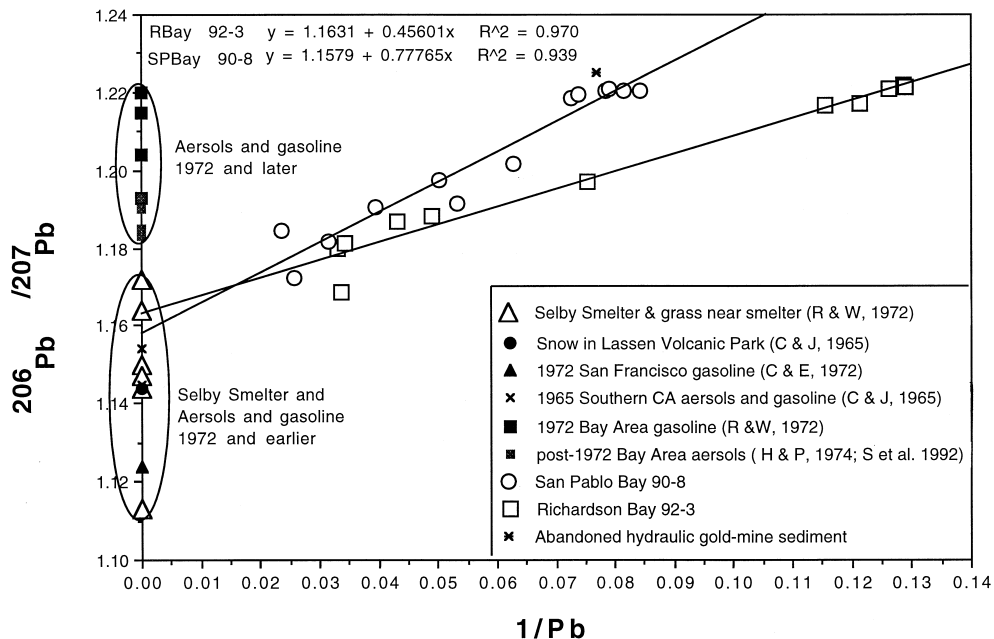


Fig. 4. A plot of lead isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}$) vs. concentration ($1/\text{Pb}$) for core sediments in RB92-3 and SP90-8. Mixing lines suggest a common end member contaminant for both Bays that is lower in $^{206}\text{Pb}/^{207}\text{Pb}$ than recent (post-1972) aerosols. C & J = Chow and Johnstone, 1965; C & E = Chow and Earl, 1972; R & W = Rabinowitz and Wetherill, 1972; H & P = Hirao and Patterson, 1974; and S et al. = Smith et al., 1992. Abandoned hydraulic gold-mines = You Bet Pit and Malakoff Diggings.

in sediment deposited in the late 1800s and early 1900s and coincides with the early operation of the Selby Pb smelter. These same depth intervals also show initiation of other anthropogenic contamination by increased PAHs (Pereira et al., 1999). The timing and proximity of the Selby smelter suggest that it may have been responsible for this shift in Pb isotopic composition and concentration. This horizon predates another possible large lead source, leaded gasoline, whose widespread use didn't begin until after 1923 (Chow and Johnstone, 1965).

The next interval in the cores has large isotopic shifts to lower $^{206}\text{Pb}/^{207}\text{Pb}$ values (Figs. 2 and 3, Zone 1). The horizons with the lowest $^{206}\text{Pb}/^{207}\text{Pb}$ have corresponding higher lead concentrations (Fig. 4). Common intercepts for mixing lines on a $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $1/\text{Pb}$ diagram suggest that both SP90-8 and RB92-3 have a similar unradiogenic end member, with $^{206}\text{Pb}/^{207}\text{Pb}$ between approximately 1.14 and 1.17. This range of end member isotopic compositions is consistent with those of the stack emission, ore, and refined metal from the Selby smelter near the time of its closing ($^{206}\text{Pb}/^{207}\text{Pb} = 1.11\text{--}1.17$) (Rabinowitz and Wetherill, 1972) (Fig. 4). While discharge data and lead isotopic compositions are not available for much of the smelter's operation, the magnitude of the contamination in this core interval is consistent with the fact that the smelter processed enough ore and released enough SO_2 that health concerns arose in downwind communities shortly after the turn of the century (Holmes et al., 1915).

From the 1930s to the 1980s, US industrial aerosols were dominated by lead from gasoline combustion. Aerosol isotopic compositions have changed temporally as a result of different ore sources employed in TEL production (Rabinowitz and Wetherill, 1972; Shirahata et al., 1980; Ritson et al., 1994). Most San Francisco Bay area gasolines and aerosols from 1972 and later have lead isotopic compositions higher in $^{206}\text{Pb}/^{207}\text{Pb}$ (Rabinowitz and Wetherill, 1972; Hirao and Patterson, 1974; Smith et al., 1992) than those prior to 1972 (Chow and Johnstone, 1965; Chow and Earl, 1972; Rabinowitz and Wetherill, 1972) (Fig. 4). The one exception is a 1972 San Francisco gasoline that has a $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.12$. Although we cannot rule out 1972 and earlier gasoline as a contaminant in some horizons, clearly, in

sediments deposited before 1923, direct smelter input is the most likely source of lead. The magnitude of contamination and the close proximity of the Selby smelter to SP90-8 also make direct smelter input the most likely source of lead contamination until 1970 when the smelter closed. Even near the end of its operations, the smelter was still a large source of lead contamination (Rabinowitz and Wetherill, 1972). Spatial trends in lead concentration also indicate a large source of lead in the vicinity of San Pablo Bay (Hornberger et al., 1999). An excursion in RB92-3 to very low $^{206}\text{Pb}/^{207}\text{Pb}$ prior to ~ 1950 suggest that at least periodically pulses of concentrated contaminant reached Richardson Bay.

To determine the isotopic composition of contaminant lead in Zone 1 sediments (sediments deposited after ~ 1940), background corrections were made using an average natural background lead concentration of 7.8 ug/g and the isotopic compositions $^{206}\text{Pb}/^{204}\text{Pb} = 19.107$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.644$, and $^{206}\text{Pb}/^{207}\text{Pb} = 1.222$. For example, the equation used to calculate the contaminant $^{206}\text{Pb}/^{207}\text{Pb}$ is:

$$\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{contaminant}} = \frac{\left[\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{sample}} - x \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}} \right)_{\text{natural}} \right]}{1 - x}$$

where x is calculated by

$$x = \frac{7.8 \text{ } \mu\text{g/g}}{[\text{Pb}]_{\text{sample}}}$$

The calculated $^{206}\text{Pb}/^{207}\text{Pb}$ values for the lead contamination indicate that modern atmospheric deposition alone cannot explain lead contamination in the upper core sediments in San Francisco Bay. If modern aerosols were the major source of contamination, then, the contaminated core sediment field should fall between the modern aerosol field and the natural background field instead of between the modern aerosol field and the historic aerosol and smelter field (Fig. 5). After 1923, we cannot say if lead from the smelter or lead from local gasoline contributed most of the lead in San Francisco Bay, but we can

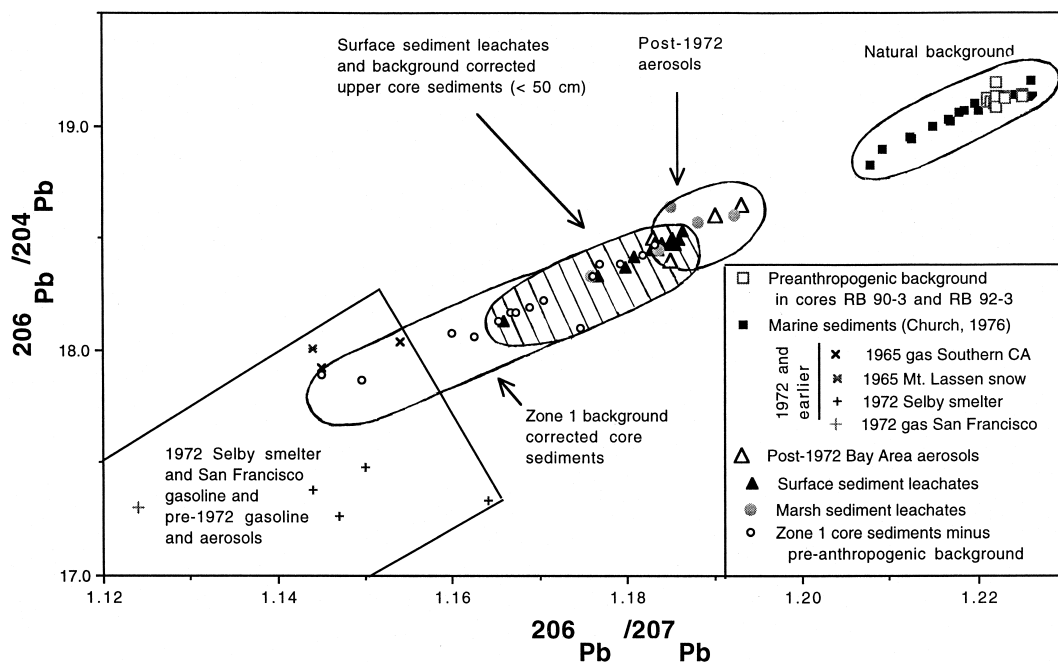


Fig. 5. A $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot of the lead isotopic composition of leachates from surface sediments and marsh sediments, background corrected Zone 1 core sediments, and natural background values compared to recent Bay area aerosols [San Francisco air filter (Hirao and Patterson, 1974), Oakland aerosols in 1989 (Smith et al., 1992)], and older gasolines and aerosols. Background corrected Zone 1 core sediments suggest a historic (pre-1972) source of lead dominates lead contamination in the Bay and not recent (post-1972) aerosols. If modern aerosols were the dominant source of lead contamination, then the background corrected Zone 1 core sediment field should fall between modern aerosols and natural background, but it does not. Some surface sediment leachates and background corrected core sediments (< 50 cm from the surface) (striped field) overlap the recent aerosol field but most are less radiogenic indicating that contemporary atmospheric deposition is not the dominant source of lead to surface sediments in the estuary. Marsh sediment leachates suggest that lead in some marshes may be dominated by recent aerosols while others marshes may receive contaminated sediment from the Bay.

say that a historic source appears to dominate the lead isotopic signature in recent core sediments. And, although no single lead source could be identified in these upper core sediments, it is apparent from their similar Pb isotopic compositions and concentrations that all cores received lead from the same sources and in relatively the same proportions.

4.2. Surface sediments

Lead isotopic compositions of surface sediments leachates and marsh sediment leachates from around the estuary, are similar to those of the background corrected uppermost core sediments (< 50 cm) and suggest similar widespread contamination throughout the Bay (Fig. 5). Lead isotopic compositions of the surface sediment leachates and background corrected uppermost core sediments form a relatively homoge-

neous field (Fig. 5) that overlaps the field of recent Bay area aerosols (Smith et al., 1992); however, it clearly extends to lower $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ indicating that a contaminant is involved that has less radiogenic values than contemporary aerosols (Fig. 5). This indicates that the anthropogenic lead contribution to the spatially widespread surface sediments cannot be solely explained by recent atmospheric deposition. Furthermore, the surface sediment leachates and the background corrected upper 50 cm of core sediments have a similar lead isotopic range indicating that a similar contaminant source can explain lead contamination in surface sediments throughout the Bay.

Three of the five marsh leachate samples overlap with the field of modern aerosol isotopic compositions measured by Smith et al. (1992), while the other two samples are comparable with surface sedi-

ment leachates (Fig. 5). This indicates that contemporary atmospheric deposition may be the primary source of lead contamination in some marsh locations while others sites are receiving contaminated sediment from within the estuary.

The range of contemporary lead fluxes is poorly constrained, and historical data is almost completely lacking. Davis et al. (1991) estimate the total anthropogenic flux of lead to the estuary to be 73–636 tons/year which includes urban runoff (30–250 tons/year), rural runoff (31–360 tons/year), municipal and industrial discharge (11–16 tons/year), atmospheric deposition (6–21 tons/year), and dredging (1–10 tons/year). Although no isotopic composition studies exist for rural and urban runoff, it is assumed that these lead sources reflect accumulated atmospheric deposition, and therefore reflects atmospheric deposition isotopically.

Atmospheric deposition and waste water discharge are the largest external sources to aquatic systems with surrounding urbanized areas (Nriagu, 1986; Flegal and Sañudo-Wilhelmy, 1993). Clearly, recent aerosol isotopic compositions are not the only source of lead contamination in recent Bay sediments. Also, no point source associated with waste water could be identified on the basis of lead isotopic composition. The South Bay receives the largest quantity of municipal effluent in the estuary ($1400 \times 10^6 \text{ Ld}^{-1}$; Davis et al., 1991) and despite the ability to distinguish waste water discharge with lead isotopic composition (Ritson et al., 1994; Sañudo-Wilhelmy and Flegal, 1994), no point source was identified.

The relatively homogeneous lead isotopic compositions in the surface sediments could result from either the substantial internal pool of recycling lead or a large external source of lead to San Francisco Bay. There are several lines of evidence suggesting that biologically accessible lead (e.g., lead in contact with the biosphere) in the estuary is primarily a result of redistribution of lead from the internal pool of historically contaminated sediments. First, the isotopic composition of surface sediments is distinct from those of recent aerosols, but the same as that of total lead in the water column (Flegal et al., 1994). Second, the similarity between sediment and water supports calculations which indicate that diagenic remobilization of lead from benthic sediments may

be within an order of magnitude of the total anthropogenic inputs to the estuary (Rivera-Duarte and Flegal, 1994). Finally, the Bay is generally shallow and well-mixed by winds, tidal currents, and seasonally strong river inflows (Conomos, 1979). These physical forces interconnect the embayments and can redistribute either contaminated sediment or benthic fluxes throughout the estuary.

5. Conclusions

The isotopic composition of the Richardson and San Pablo Bay cores record distinct historical intervals of lead contamination. The isotopic composition of the three cores suggest a similar source of lead contamination in the different regions of the estuary. Contamination in San Pablo Bay by the Selby lead smelter is supported by that core's isotopic composition, high lead concentration, and proximity to the smelter. Common intercepts of the mixing lines of SP90-8 and RB92-3 at isotopic compositions similar to output from the Selby smelter suggest that this industry is a major source of Pb contamination in Richardson Bay also. The isotopic compositions of the upper sediments in all cores and surface sediments around the Bay are relatively homogeneous but do not suggest a modern aerosol source. Based upon the isotopic signature, most of the lead in the estuary now appears to be coming from historically contaminated sediments and is cycling back into the water column.

Despite contaminant source reduction in the estuary due to municipal effluent controls, the closing of the lead smelter, and, the elimination of lead additives to gasoline, no significant lowering of concentrations in overlying waters has been observed (Flegal et al., 1994). Other aquatic systems have shown persistent contamination despite elimination of external sources (Flegal and Sañudo-Wilhelmy, 1993; Ritson et al., 1994). This is thought to be due to cycling of contaminants between historically deposited sediments and overlying waters (Flegal and Sañudo-Wilhelmy, 1993; Rivera-Duarte and Flegal, 1994; Ritson et al., 1994). Water quality regulations should take into account contaminant inputs associated with remobilization of historic contamination from sediment in order to understand and improve water quality in the estuary.

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