New isotopic evidence for chronic lead contamination in the San Francisco Bay estuary system: Implications for the persistence of past industrial lead emissions in the biosphere

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Measurements of lead isotope compositions in unfiltered San Francisco Bay waters from 1989 to 1998 have brought new insights into the cycling of anthropogenic lead in estuaries. Isotopic compositions of lead in the shallow (<2 m) southern reach were essentially invariant (~90% derived from 1960s–1970s leaded gasoline) during the study period because of limited hydraulic flushing and the remobilization of lead from bottom sediments. In contrast, in the northern reach freshwater flushing from the San Joaquin and Sacramento rivers produced seasonal and decadal variations in lead isotope compositions. The seasonal shifts are attributed to advection of soils containing late 1980s gasoline lead into the bay during winter rains. Mass balance calculations indicate that only a small fraction (1–10%) of this leaded gasoline fallout from the late 1980s has been washed out of the San Joaquin and Sacramento rivers' drainage basin by 1995. Superimposed on this seasonal cycling was a long-term systematic shift in the component of gasoline lead expressed in the river systems, with a small (~5–10%) decrease in the amount of 1960s–1970s gasoline lead in river and North Bay waters. The retention of gasoline lead in the river systems draining into the bay as well as San Francisco Bay sediments indicates that historic gasoline deposits may remain in the combined riparian/estuarine system for decades. Such a persistence is in contraindication to recent reports of rapid (annual) decreases in lead contamination in other environments, and the link between climate and contaminant transport suggests local or global climate change will have an impact on contaminant distribution and fate.

Over the last two decades, widespread reports of reductions in environmental lead have been hailed as a major public policy victory in the United States and other industrialized nations. These reductions have been noted in a variety of environmental matrices, including urban and remote aerosols (1–4), Arctic and Antarctic snow and ice cores (5–8), Pacific and Atlantic seawater (2, 9–11), North American and European ombrotrophic bogs (12–14), European and North American rivers (15, 16), and human blood (17). Because lead in each of these reservoirs is directly or indirectly controlled by anthropogenic lead emissions, their levels of contamination will decline with source reductions. In contrast, there have been no reports of comparable declines of lead contamination in estuarine systems, where previous ^{210}Pb studies (18) indicate that contaminant lead may be retained and internally recycled.

The internal recycling of lead in an estuary is evidenced in this report, which chronicles variations in stable lead isotopic compositions (^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb) in San Francisco Bay waters and their major fluvial inputs (the Sacramento and San Joaquin rivers) over the past decade (1989–1998). Our sampling and analytical approach was adopted because spatial and temporal variations are more evident in water than in sediments (19), and because isotopic compositions are more sensitive tracers of anthropogenic inputs than are concentration measurements. However, we also use lead concentrations to produce mass balance calculations that corroborate the conclusions from our isotopic data concerning lead cycling and retention in the combined estuary and river system.

Background

The San Francisco Bay (Fig. 1) is heavily urbanized and receives drainage from a watershed encompassing 40% of the land surface area of California (20). Past industrial emissions have produced elevated trace metal concentrations in sediments and surface waters of the bay (21), and trace metal distributions are controlled by the changing hydrographic conditions from north to south. The northern reach (North Bay) is dominated by freshwater flushing from the inflow of the San Joaquin and Sacramento rivers. The southern reach (South Bay) is shallower ($<$2 m average depth) and receives limited freshwater flushing because of diversions of water due to agriculture, industry, and urbanization. Dissolved lead concentrations ($\approx$0.010–0.090 μg/kg) in surface waters throughout the Bay have remained relatively constant over the past two decades (Fig. 2), despite the marked reduction in emissions from leaded gasoline during the same period (21–23). That phase-out of leaded gasoline in California was initiated in the mid-1970s and was completed by 1992, with 99% of the total emissions occurring before 1985 (Fig. 2).

Previous workers (19, 24) have identified three major sources of lead to San Francisco Bay waters: (*i*) a natural component of terrestrial lead largely influenced by the weathering of granitic batholiths in the Sierra Nevada (^{206}Pb/^{207}Pb = 1.215–1.225, ^{208}Pb/^{207}Pb = 2.480–2.488) (19); (*ii*) the influx of hydraulic mine sediments washed into the bay from the Sierra Nevadan foothills during the mid- to late nineteenth century (^{206}Pb/^{207}Pb = 1.220–1.245, ^{208}Pb/^{207}Pb = 2.50–2.515) (24); and (*iii*) the recent influx of industrial lead derived almost entirely from leaded gasoline combustion (^{206}Pb/^{207}Pb = 1.14–1.23, ^{208}Pb/^{207}Pb = 2.42–2.45) (24). The preanthropogenic component has been determined directly by Ritson *et al.* (19), who measured isotopic compositions and concentrations of lead in two cores from San Francisco Bay. Ritson *et al.* (19) found that although the preindustrial core bottoms showed little variation in isotopic composition, a large increase in concentrations and a corresponding isotopic shift occurred with the onset of hydraulic

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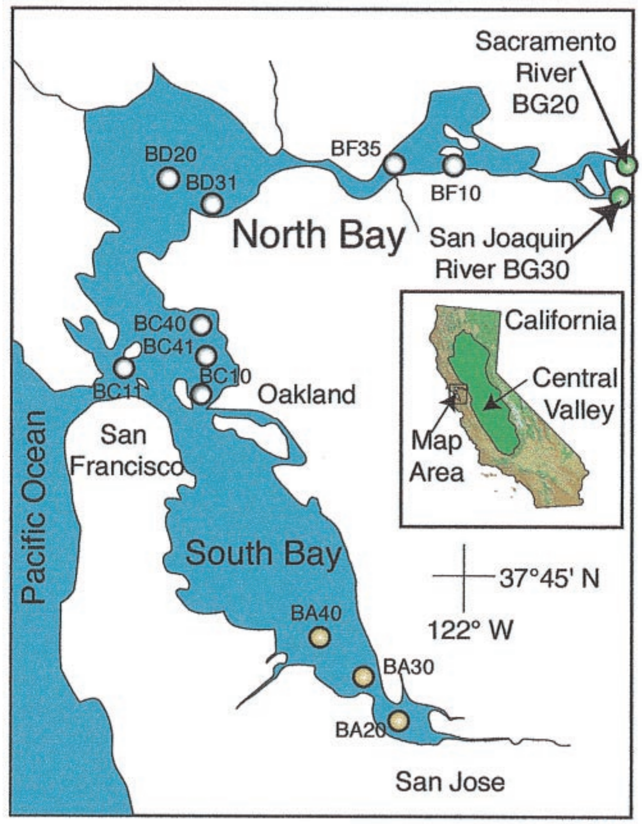

Fig. 1. Sampling sites in San Francisco Bay. The seven sites in the northern reach are shown as white circles; the three sites in the South Bay are shown as yellow circles; and the two fluvial input sites are shown as green circles. The Central Valley covers 40% of the land surface area of California and is the drainage basin of the Sacramento and San Joaquin rivers; it is shown in green on the *Inset*.

mining and industrial activity in California. Dunlap *et al.* (24) measured lead isotope compositions of waters in the Sacramento/San Joaquin river delta and concluded that approximately half of the lead in the water of those rivers was derived from past gasoline emissions and half from an end member newly identified in the rivers and dominated by hydraulic mine sediments. The variation of gasoline isotopic variation through time is a result in changes in sources of lead used in gasoline (24). This study presents data collected over a decade and thereby provides new insights into seasonal and long-term cycling of contaminant lead, identifies a new gasoline end member in river waters, and reevaluates previous conclusions about lead cycling in San Francisco Bay and its drainage basin, California's Central Valley.

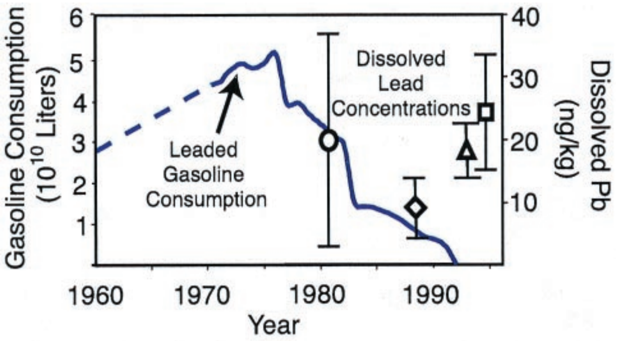

Fig. 2. Historic leaded gasoline consumption and lead concentrations in northern reach waters. The blue line charts leaded gasoline consumption in liters for the state of California from 1960 to 1992 (personal communication, J. Cogan, Energy Information Administration). Consumption is estimated for the years 1960–1970 based on the available data from 1960 and 1970. Concentrations of dissolved lead for the northern reach are given for 1979 (23), 1989, 1993, and 1995. Concentrations for each year are the average of three stations in the northern reach during the summer when the waters at each station had comparable salinities. Error bars are one standard deviation of the three station averages.

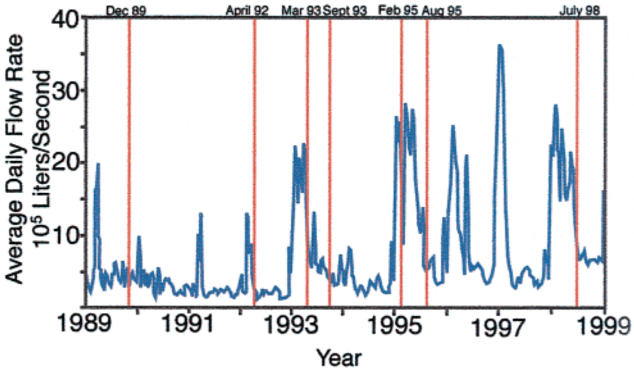

Fig. 3. Daily total discharge of the Sacramento and San Joaquin rivers from 1989 to 1999. Sampling events in this study are plotted as red lines.

Materials and Methods

Samples of unfiltered surface waters were taken from throughout the San Francisco Bay (Fig. 1) during low flow (summer) and high flow (winter) of the San Joaquin and Sacramento rivers. Samples were collected by trace metal clean techniques (25) and represent the annually variable hydraulic regimes from 1989 to 1998 (Fig. 3). Sampling sites were chosen to represent a full range of hydrographic regions within the bay: the San Joaquin and Sacramento rivers as they enter the northern reach, seven sites within the North Bay itself, and four sites in the South Bay (Fig. 1). Because isotopic equilibrium is achieved between the dissolved and filtered fractions of bay waters (24), unfiltered samples were used to simplify sample processing.

A total lead extraction from 1-liter water samples was achieved using an ammonium1-pyrrolidine dithiocarbamate/diethylammonium diethyldithiocarbamate procedure (26). Samples were analyzed for lead concentrations, and the remaining aliquot was retained for lead isotope analysis. To purify the lead, the aliquots were first heated in aqua regia (prepared from quartz-distilled acids) and hydrogen peroxide (Baker Ultrex 30%) to remove refractory organic compounds. The samples were then passed through anion exchange columns (Dowex 100), using hydrobromic acid (Seastar) to further purify the lead.

Lead isotopic compositions were analyzed by thermal ionization mass spectrometry (VG 54-WARP). Samples were corrected for mass bias, using in-run analyses of National Institute of Standards and Technology Standard Reference Material 981 (common lead standard reference material), with the per-atomic mass unit mass bias correction averaging 0.0012. Lead concentrations of the procedural blanks were less than 0.1% of sample lead mass (~200 ng Pb). Average errors (±2 standard errors of the mean) were ±0.040 for $^{206}\text{Pb}/^{204}\text{Pb}$, ±0.00060 for $^{206}\text{Pb}/^{207}\text{Pb}$, and ±0.00060 for $^{208}\text{Pb}/^{207}\text{Pb}$ for the initial (1989) analyses. The errors for the 1992, 1993, 1995, and 1998 samples were ±0.0002 for $^{206}\text{Pb}/^{204}\text{Pb}$, ±0.000045 for $^{206}\text{Pb}/^{207}\text{Pb}$, and ±0.000048 for $^{208}\text{Pb}/^{207}\text{Pb}$.

Results

Isotopic compositions of bay waters showed spatial variation from the southern to the northern reach (Table 1), in contrast

Table I. Isotopic compositions and concentrations of lead in San Francisco Bay waters from 1989 to 1998

Station	Unfiltered lead concentration (μg/kg)	Filtered lead concentration (μg/kg)	^{206}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb
December 1989					
BA20	3.28	0.0370	18.415	1.1830	2.4488
BA30	2.40	0.0360	18.445	1.1833	2.4482
BA40	1.07	0.0259	18.428	1.1845	2.4484
BA40	1.07	0.0259	18.440	1.1852	2.4486
BC10	0.44	0.0174	18.486	1.1840	2.4521
BC11	0.83	0.0111	18.471	1.1842	2.4501
BD31	1.48	0.0169	18.491	1.1859	2.4513
BF35	0.58	0.0244	18.466	1.1867	2.4493
BG20	0.73	0.0362	18.375	1.1837	2.4443
April 1992					
BA30	0.60	0.0342	18.432	1.1857	2.4471
BA40	0.30	0.0302	18.421	1.1851	2.4468
BC10	0.10	0.0192	18.418	1.1814	2.4473
BC40	0.10	0.0152	18.353	1.1810	2.4449
BF10	1.30	0.0108	18.451	1.1870	2.4506
BG10	1.00	0.0409	18.568	1.1925	2.4546
BG20	0.90	0.0162	18.533	1.1932	2.4537
March 1993					
BA20	0.62	0.0874	18.571	1.1925	2.4509
BA40	0.33	0.0275	18.473	1.1854	2.4484
BC40	0.47	0.0132	18.427	1.1857	2.4486
BD20	0.33	0.0213	18.563	1.1937	2.4546
BF10	2.34	0.2120	18.731	1.2029	2.4618
BG20	0.92	0.0409	18.739	1.2034	2.4619
BG30	0.91	0.2890	18.722	1.2020	2.4608
September 1993					
BA20	0.41	0.0247	18.461	1.1852	2.4499
BA40	0.45	0.0059	18.370	1.1833	2.4453
BC41	0.89	0.0106	18.432	1.1816	2.4487
BD20	0.27	0.0123	18.460	1.1867	2.4501
BF10	1.17	0.0088	18.482	1.1887	2.4521
BG20	0.69	0.0662	18.697	1.1953	2.4611
BG30	1.07	0.0476	18.556	1.1909	2.4538
February 1995					
BA20	0.39	0.0884	18.526	1.1896	2.4484
BA40	0.35	0.0287	18.441	1.1860	2.4471
BC41	0.17	0.0178	18.500	1.1914	2.4521
BD20	0.35	0.0022	18.644	1.1984	2.4583
BF10	1.01	0.0095	18.663	1.1993	2.4592
BG20	0.62	0.0753	18.738	1.2049	2.4621
BG20	0.62	0.0753	18.739	1.2045	2.4622
BG30	0.54	0.0109	18.687	1.2017	2.4597
August 1995					
BA30	2.12	0.0463	18.453	1.1865	2.4479
BA40	0.75	0.0211	18.442	1.1856	2.4475
BC41	0.18	0.0100	18.416	1.1843	2.4473
BD20	0.60	0.0079	18.541	1.1869	2.4560
BF10	0.53	0.0056	18.562	1.1921	2.4547
BG20	0.50	0.0054	—	1.1971	2.4667
BG30	0.63	0.0115	—	1.1896	2.4561
July 1998					
BG20	0.50	0.1130	18.740	1.1992	2.4654
BG30	0.32	0.0990	18.754	1.1996	2.4658

Samples are given in order from the south (Fig. 1, BA) to the north (Fig. 1, BC, BD, BF, and BG).

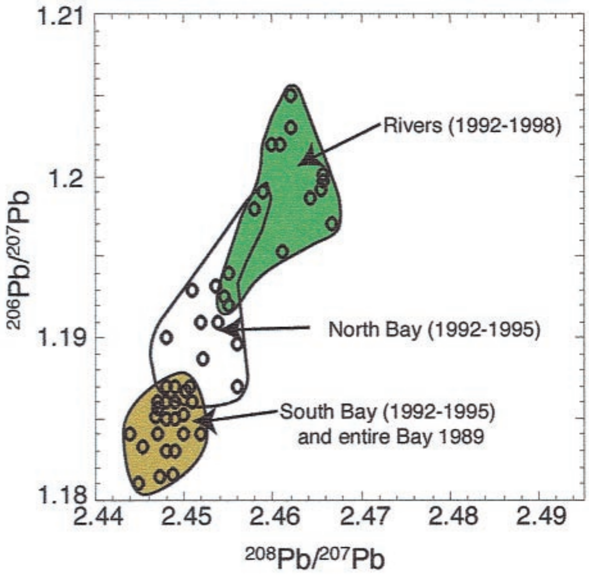

Fig. 4. Lead isotopic compositions of bay waters from 1989 to 1998. Fields are drawn around waters from the northern reach (white), South Bay (yellow), and rivers (green). Lead isotopic compositions in all waters sampled in 1989 fall within a field occupied by South Bay samples during the entire study period (see text for discussion).

to the homogeneity found in previous measurements (22) of isotopic compositions in bay sediments (Fig. 4). In December 1989, waters from the northern and southern reaches had similar isotopic compositions (^{206}Pb/^{207}Pb from 1.180 to 1.186 and ^{208}Pb/^{207}Pb from 2.443 to 2.452), and the compositions were consistent with those of surface sediment (22). However, in subsequent years there was a significant shift in ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in the waters of the northern reach as well as at the common delta of the Sacramento and San Joaquin rivers. The river waters had ^{206}Pb/^{207}Pb ratios from 1.196 to 1.120 and ^{208}Pb/^{207}Pb ratios from 2.462 to 2.467 at the end of the study, which represented the maximum shift from the lowest 1989 values.

Temporal variations in lead isotope compositions differed for water in the northern and southern reaches. Samples in the southern reach showed no temporal variation, with ^{206}Pb/^{207}Pb ratios ranging from 1.181 to 1.188 and ^{208}Pb/^{207}Pb ratios ranging from 2.442 to 2.452 throughout the entire period (Fig. 4), although no South Bay samples were measured in the final year of the study in 1998. In contrast, the northern reach samples showed temporal variation both seasonally and over the 9 years of monitoring (Fig. 5). Seasonal variation was seen in the winter/summer sampling pairs from 1993 and 1995, in which the isotopic compositions of summertime samples were higher in ^{208}Pb/^{207}Pb and lower in ^{206}Pb/^{207}Pb than the corresponding wintertime samples. Superimposed on the seasonal shift is a progressive increase through time in the ^{206}Pb/^{207}Pb measured in North Bay waters during high flow (winter) periods of the San Joaquin and Sacramento rivers. There is also a progression in isotopic values of waters during low flow, with a systematic increase in ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb during the study (Fig. 5).

Discussion

The results of the isotopic analysis of San Francisco Bay waters collected during one decade of monitoring refine the previously developed perceptions about cycling of lead in the bay. Those perceptions, based on a limited number of preliminary measurements, held that the isotopic composition was spatially homo-

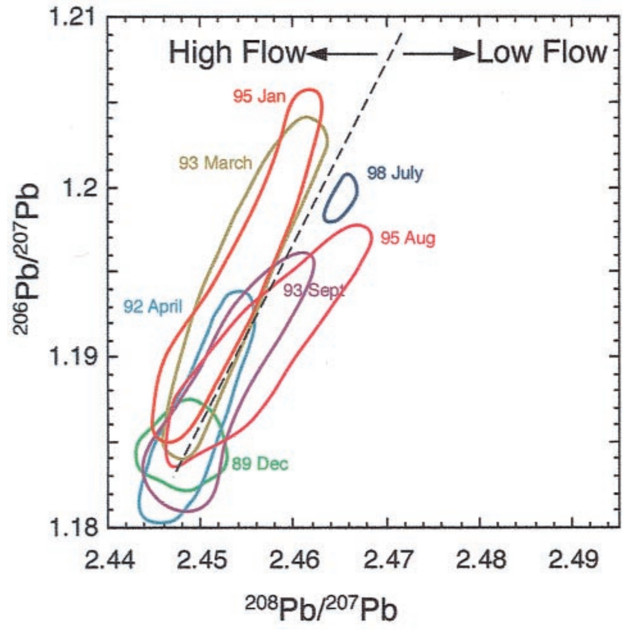

Fig. 5. Seasonal shifts in lead isotope compositions in bay waters compared with the generalized flow rate of the Sacramento and San Joaquin rivers. A field is drawn around the isotopic compositions of waters sampled in each collection period. The highest $^{206}Pb/^{207}Pb$ values recorded in each collection period are found in river waters, whereas the lowest $^{206}Pb/^{207}Pb$ values are found in South Bay water samples (compare Fig. 4).

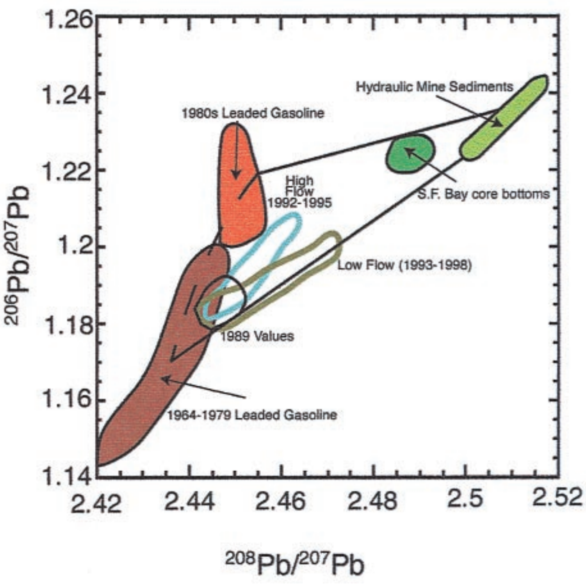

Fig. 6. Lead isotopic compositions of San Francisco Bay waters and potential lead sources. Bay waters are shown as fields that encompass the waters collected during low flow (brown outline) and high flow (blue outline). A third field (black outline) surrounds all San Francisco Bay waters collected in 1989 and waters in the South Bay throughout the study period. Possible sources of lead to the bay include 1960s–1970s leaded gasoline (dark red), 1980s leaded gasoline (light red) (2, 34–44), preindustrial bay sediment as recorded in the bottoms of sediment cores (19), and a component representing hydraulic mine sediments (24).

geneous, relatively invariant through time, and dominated by the large amount of industrial lead generated during the height of leaded gasoline emissions during the 1970s. When those initial measurements are coupled with these new data, it is apparent that the cycling is much more dynamic, which is reflected in the shifting isotopic compositions. Yet, the removal of lead from both San Francisco Bay and its drainage basin still appears to be remarkably slow compared with other types of environments.

Spatial Variability. Previous benthic flux measurements and mass balance calculations indicate that surface waters in both reaches of the bay (northern and southern) receive a large proportion of their lead via remobilization of lead from benthic sediments (27). During low-flow periods, the net benthic flux (through both diffusion and resuspension of sediments) of lead in the estuary is estimated to be 1.2–37.2 kg day^{-1}, which is approximately 1–3 orders of magnitude greater than the low-flow fluvial flux of dissolved lead (0.4 kg day^{-1}) into the estuary (27). The readsorption of lead from the water column onto sediments has brought about a homogenized lead isotope composition in bay sediments that is identical to the average composition of leaded gasoline emitted in the 1960s and 1970s (19, 24).

In the southern reach the benthic flux of lead dominates the lead budget in the water column, because stream diversions resulting from urbanization on the perimeter of the southern reach have limited hydraulic flushing. The southern reach is also shallower than the northern reach, allowing for less dilution of lead from sediments into the water column. The two factors combine to maintain an elevated lead concentration in the southern reach (21, 27) compared with the north. Moreover, the isotopic composition of the lead was invariant over the course of this study and was primarily (90 ± 2%) composed of 1960s–1970s gasoline lead, based on isotope dilution calculations. That constancy verifies earlier conclusions regarding benthic control on lead in the water column and the dominance of 1960s–1970s emissions now retained in sediments within the southern reach.

In contrast to the southern reach, the northern reach has experienced both seasonal and long-term shifts in lead isotopic composition (Figs. 4 and 5). The North Bay regularly receives freshwater flushing from the Sacramento and San Joaquin rivers during wintertime high flow, and the isotopic composition of the river water appears to be different from that of the bay's bottom sediments and to have shifted over the decade of the study.

Seasonal Variability. The seasonal shift in the isotopic composition of lead in the North Bay during high-flow periods (Fig. 6) is attributed to the distinct composition of lead washed into the river system by surface runoff in the drainage basin. During low flow, lead isotope compositions fall on a mixing line between a time-averaged composition of 1960s–1970s gasoline lead and lead from the hydraulic mining sediment that persists in the river mouth and bed load (Fig. 6). During high flow a third component appears in the river system, and it is attributed to the advection into the rivers of soils containing a lead isotope composition dominated by that of 1980s leaded gasoline. This gasoline lead accumulated in drainage basin soils during the California drought from 1986 to 1992 and was therefore strongly expressed in the lead isotope composition of surface runoff during the mid- to late 1990s. The 1980s gasoline lead advected from soils mixes rapidly with lead from the bed load containing a composite 1960s–1970s gasoline lead and lead from hydraulic mining sediments. During high flow, therefore, the lead in the North Bay and river mouths is controlled by a ternary mixture (Fig. 6). Conversely, the reduced contribution of basin soils during low flow (typically late spring until early fall) results in a lead isotope composition in waters that is controlled by bimodal mixing of 1960s–1970s gasoline lead (in both bay and river bed load sediments) and hydraulic mine sediments (in the rivers' delta and bed loads) (Fig. 6). Such controls on lead sources are consistent with the work of others (28–30) who concluded that the residence time of lead in soils is on the order of 17–80 years and that industrial lead in soils is primarily introduced into streams during periods of high surface runoff. This delayed transport of contaminant lead aerosols is also predicted by the delayed transport of ^{210}Pb aerosols deposited in terrestrial systems (18).

Long-Term Variability. Superimposed on the seasonal shifts in lead isotopes in the North Bay is a long-term shift controlled by the reworking of sediments rather than changes in surface runoff. The long-term shift can be seen in comparisons between the beginning and ending points of the study (Fig. 5), which were similar in flow rate despite being sampled during different seasons (Fig. 3). The similarity is due to drought conditions from 1986 to 1992 that caused the normally high discharge during winter, December 1989, to be similar to summer low flow in August 1998. By 1993, the drought had ended, and with the exception of 1994, the seasonal cycle of high freshwater inputs to the bay during the winter resumed (Fig. 3).

As a result of the resumption of high discharge rates during the winter, the proportion of lead derived from different sediment types shifted during the study period. The shift toward higher ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb through time is accounted for by the increased contribution of sediment from past hydraulic mining of the Sierra Nevadan foothills (Fig. 6). Hydraulic mining became the predominant source of sedimentation in the bay during the California Gold Rush 150 years ago, and it was widely distributed into the Sacramento River and the common delta region of the Sacramento and San Joaquin rivers (19). With successive years of winter high flow after 1992 there has been an increase in the proportion of hydraulic mine lead in both the rivers and the northern reach. The effect can be most clearly seen in the progression of wintertime lead isotope ratios toward higher values during low-flow periods when the added influence of surface runoff is not present.

The presence of the lead signature of hydraulic mining sediment throughout the bay is controlled by the hydrographic segmentation of bay waters from north to south and by the amount of river discharge into the North Bay. The contribution of the Gold Rush lead is greatest near the mouth of the Sacramento and San Joaquin rivers and is negligible in the central and southern reaches of the estuary, which are farthest from that source. Moreover, the hydraulic mining lead signature was not present in the bay during the prolonged drought (1986–1993) in California, during which time the isotopic composition of lead in all reaches of the bay closely mirrored that of 1960s–1970s leaded gasoline emissions (Fig. 6). These findings reflect the dominance of the internal recycling and remobilization of lead in San Francisco Bay: in the absence of seasonal freshwater flushing, lead that is remobilized from bay bottom sediments dominates the isotopic signature of surface waters and is the dominant source of lead in the bay. This remobilization of lead from bottom sediments is a combination of advective fluxes of lead from sediments through bioturbation and turbulent resuspension and a flux of lead from pore waters as a result of the benthic remobilization of lead through diagenesis (27).

In the northern reach the long-term increase in lead contributed by hydraulic mining can be quantified by mixing calculations (Fig. 5). In 1989, waters from the river mouths, North Bay, and South Bay all plotted in the same range (Fig. 5), with a ~90% component associated with the isotopic composition of leaded gasoline in the 1960s–1970s. Since that time, the dilution of North Bay sediments by Sacramento and San Joaquin river sediments with a mixed leaded gasoline/hydraulic mine signature (24) has resulted in the reduction of the proportion of 1960s–1970s lead in the North Bay from ~90% in 1989 to 80–85% in 1995. This rate of change indicates that the residence time of lead in the North Bay may be on the order of decades, which is consistent with previous estimates (21, 31).

Mass Balance Calculations. To better constrain the movement of anthropogenic lead from the San Joaquin and Sacramento river system in the San Francisco Bay estuary, mass balance calculations for the high flow periods of 1993 and 1995 were made in a manner similar to the recent work of Lankey *et al.* (32). Total lead emitted to the San Joaquin and Sacramento river basins was estimated using statistics from the Energy Information Administration (personal communication, J. Cogan, Energy Information Administration) on leaded gasoline consumption (3.9×10^{10} liters) during the California drought of 1986–1992. The consumption for California was then scaled by the percentage of California's population that lived within the two river basins (7% in the Sacramento Basin and 4.5% in the San Joaquin Basin). Gasoline lead concentrations were based on an average of 0.4 g/liter (33), a conservatively low estimate, which yields 9×10^5 kg of lead emitted within the Sacramento Basin and 6×10^5 kg of lead emitted within the San Joaquin Basin for the period 1986–1992. This estimate of lead emissions was combined with estimates of total lead delivered to the bay during high flow (December–April), based on U.S. Geological Survey river flow data and lead concentration measurements made by our laboratory at the University of California, Santa Cruz. Lead delivered to the bay in 1993 is calculated to have been 12,000 kg and 850 kg for the Sacramento and San Joaquin rivers, respectively, and in 1995 it was 11,000 kg and 1,700 kg, respectively.

The seasonal shift in isotopic composition of North Bay waters during high flow (Fig. 5) was used to estimate the proportion of the total lead delivered to the bay that had an isotopic composition of late 1980s leaded gasoline. To account for the isotopic variability of late 1980s leaded gasoline (Fig. 6), a range of isotopic values (^{206}Pb/^{207}Pb = 1.21–1.23) for the gasoline end-member was used. Pairs of analyses taken from individual sampling stations during each high/low flow event were used to calculate the magnitude of the isotopic shift during high flow, with the low-flow values defining the other riverine end-member (a mix of 1960s–1970s leaded gasoline and hydraulic mine sediments). This model yields a range of values of the proportion of total lead (25–50%) that was derived from late 1980s leaded gasoline combustion and was delivered to the bay during high flow in 1993 and 1995.

The results of these calculations indicate that only 1–10% of the total lead emitted to the Sacramento and San Joaquin river basins during the late 1980s and early 1990s had been delivered to the bay by 1995. This finding is consistent with the long residence time of lead in surface soils (28–30) and indicates that there is still a large (>90%) proportion of 1980s lead emissions in the river basins.

In addition to this reservoir of 1980s leaded gasoline emissions, there is a substantial reservoir of 1960s–1970s leaded gasoline emissions within the Sacramento and San Joaquin basins. The magnitude of emissions from 1960 through the 1970s is much greater (3×10^7 kg) than the emissions in the late 1980s. This disparity accounts for the continued presence of 1960s–1970s emissions in river waters entering the bay (24).

However, the reservoirs are relatively isolated, as evidenced by the shifts in isotopic compositions during high flow. The 1980s gasoline lead must be located mostly in a reservoir that is readily mobilized by surface runoff (i.e., surface soils). The 1960s–1970s leaded gasoline, in contrast, is located deeper in soils and in the bed loads of the river systems. This stratigraphic isolation is consistent with studies on the downward migration of atmospherically deposited lead in soils with time (28–30), with the separation of reservoirs being a consequence of the drought during the late 1980s when the 1980s lead was deposited in surface soils. Over decades, surface runoff and transport will homogenize these two reservoirs, resulting in a decay in the seasonal signal as detailed in this study. Progress towards this homogenization has led to a mixture of 1960s–1970s lead in river sediments, with an emphasis on the larger mass of lead from the 1960s and 1970s.

Conclusions

The results of this study provide insight into the cycling of metals in a complex aquatic environment. In the southern reach of San Francisco Bay, elevated concentrations of trace metals persist despite recent efforts to eliminate emissions of those metals. This persistence of metals is seen in the continued cycling of lead into the water column of the South Bay, where the maximum flux of lead occurred during the peak of leaded gasoline consumption in the mid-1970s, and that lead is still predominant in surface sediments and overlying waters more than two decades later. Moreover, 1960s–1970s gasoline lead continues to be a well-expressed mixing component in the northern reach of the estuary, despite continuous flushing by freshwater discharges from the Sacramento and San Joaquin rivers. Again, this persistence of industrial lead attests to its relatively long (decadal) residence time in the bay and reflects the sensitivity of the bay to pollution in California.

The cycling of lead and other particle reactive contaminants within San Francisco Bay is dominated by a complex interplay between benthic remobilization, freshwater inputs, and the segmentation of hydrographic regimes within the bay. Because transport of particle-reactive pollutants through the Sacramento and San Joaquin rivers has been demonstrated to be a slow process, inputs of uncontaminated sediments to the Bay will only occur after the rivers themselves are flushed of their contaminated bedloads. In the case of lead, this flushing has not been achieved, despite the more than 20 years that have passed since the first efforts to phase out leaded gasoline (24). The delayed transport of particle reactive contaminants in the Sacramento and San Joaquin rivers is further demonstrated by the influence of the small (1–10%) portion of the total lead emitted in the late 1980s that has entered the bay during high surface runoff events in the 1990s. Therefore, in addition to the over two-decade-old reservoir of 1960s–1970s gasoline lead, a large reservoir of late 1980s gasoline lead still resides in the river basins, waiting to be advected into the bay during winter runoff. This late 1980s gasoline has also served to trace nonpoint source fluxes from the rivers' drainage basin. When these inputs diminish, there will still be elevated lead levels within the bay as a result of the internal diagenic recycling of lead. The ability of winter storms to influence the redistribution of lead bound in soils and sediments of the San Francisco Bay estuary and its riparian sources suggests that on a global scale local climate change has the potential to alter the regional distributions of particle-bound contaminants.

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