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Past Leaded Gasoline Emissions as a Nonpoint Source Tracer in Riparian Systems: A Study of River Inputs to San Francisco Bay

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Variations in the isotopic composition of lead in 1995−1998 river waters flowing into San Francisco Bay trace the washout of lead deposited in the drainage basin from leaded gasoline combustion. At the confluence of the Sacramento and San Joaquin rivers where they enter the Bay, the isotopic compositions of lead in the waters define a linear trend away from the measured historical compositions of leaded gas in California. The river waters are shifted away from leaded gasoline values and toward an isotopic composition similar to Sierra Nevadan inputs which became the predominant source of sedimentation in San Francisco Bay following the onset of hydraulic gold mining in 1853. Using lead isotopic compositions of hydraulic mine sediments and average leaded gasoline as mixing end members, we calculate that more than 50% of the lead in the present river water originated from leaded gasoline combustion. The strong adsorption of lead (log K_d > 7.4) to particulates appears to limit the flushing of gasoline lead from the drainage basin, and the removal of that lead from the system may have reached an asymptotic limit. Consequently, gasoline lead isotopes should prove to be a useful nonpoint source tracer of the environmental distribution of particle-reactive anthropogenic metals in freshwater systems.

Introduction

During the 20th century, human emissions of lead to the environment have dominated its biogeochemical cycles on a global scale (*1*). For example, lead released by human activity comprises 95% of lead in the biosphere (*2*), and 90% of all lead emissions in the United States have been from the combustion of gasoline containing lead alkyl additives (*1, 3*). However, most western industrialized nations have reduced or eliminated lead additives in gasoline (*4*) due to increasing evidence of the harmful effects of lead on human health (*5*).

Since 99% of lead emissions from gasoline combustion occurred before 1985 (Figure 1), the anthropogenic lead burden in aquatic systems has substantially decreased (*3*). This is illustrated by recent measurements in the Sargasso Sea, which has experienced a 5−6-fold decrease in lead concentration, and an accompanying shift in isotopic composition, associated with the phase out of leaded gasoline

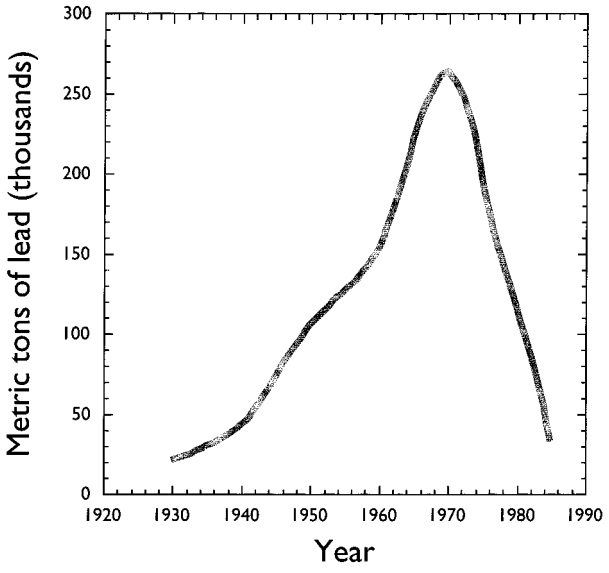

FIGURE 1. Historical consumption of lead in gasoline in the United States, after ref *3*.

in North America and western Europe over the past 2 decades (*6*). Decreases in lead concentrations in the Mediterranean by a factor of 2 from 1983 to 1992 (*7*) and in the Mississippi river by almost 2-fold between 1974 and 1983 (*8*) have also been attributed to the reduction in leaded gasoline consumption. In these studies, the pulse of high emissions in the early 1970s has been used as a temporal tracer of the biogeochemical cycling of lead.

The effect in rivers has been poorly studied, however, due to a lack of long-term monitoring data and due to the scarcity of lead isotope measurements, which are a more sensitive tracer than concentration measurements. To assess the removal of gasoline lead from river waters, we have measured the lead isotope compositions in three rivers entering into San Francisco Bay estuary (Figure 2). The river samples are compared to the preindustrial Bay sediments deposited by the Sacramento and San Joaquin rivers, surface sediment and water samples collected in 1990, historical data on the lead isotope composition of California gasoline from 1964 to 1990, and hydraulic mining sediment that entered the combined Sacramento/San Joaquin lower delta beginning in 1853.

Background

San Francisco Bay comprises the largest estuarine system on the west coast of the U.S. (*9*), and it has been extensively transformed since the population growth brought on by the 1849 California Gold Rush (*10*). Large-scale human alteration of the Bay began with the influx of sediment from hydraulic gold mining of the Sierra Nevadan foothills (*10*) and has continued in the 20th century with heavy urbanization of the Bay. The physical and chemical transformation of the Bay has made it a locus for studies of the biogeochemical cycling of trace metals (*11*−*18*). At present, the lead isotopic composition of Bay surface sediments is dominated by lead retained from past human emissions (*13*).

Hydraulic mining in the Sierra Nevadan foothills led to a 10-fold increase in sediment transport in the Sacramento river from 1852 through 1914 (*19, 20*). The hydraulic mining sediment remains exposed at the surface in the northern reach of the Bay (*21*) and has been reworked into the upper

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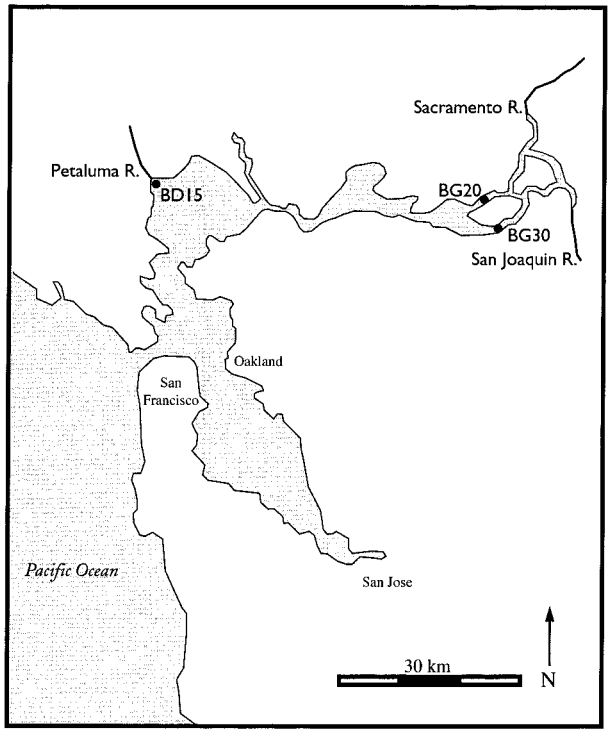

FIGURE 2. Schematic map of San Francisco Bay estuary with sampling sites from this study. Samples were collected as part of the San Francisco Bay Regional Monitoring Project.

sediment layers by periodic dredging (*22*). Similarly, the modern surface sediments of the combined Sacramento/San Jaoquin river delta are likely to contain a persistent hydraulic mining component. Due to the cumulative effects of hydraulic mining and the reclamation of land in the delta region (*10*), the mixture of natural sediments entering the Bay will be different than it was in the early 19th century. The isotopic composition of this new terrigenous input has not been previously reported.

Although the influx of hydraulic mine sediments brought the first perturbations to natural inputs of lead to the Bay, emissions of lead from human sources have generated the primary lead burden in Bay sediments and waters (*23*). By 1990 concentrations of lead in surface sediments of cores taken in the Bay were 2−28 times higher than concentrations measured in the pre-1853 core bottoms (*13*). The lead in Bay sediments has been found to be recycled into the water column by bioturbation and diagenetic remobilization (*23*). This benthic flux of lead inhibits the removal of lead from Bay water and leads to a relatively homogeneous lead isotope signature in Bay sediments and waters, particularly in the south Bay where diversion of river inputs has led to a dramatic reduction in annual flushing (*24*).

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in Bay sediments and waters from 1990 correlate to the lead compositions from gasoline emissions (Figure 3). Modern sediments and waters are distinct from the lead isotope ratios of sediment in pre-1853 core samples representing inputs before large-scale human perturbations (*13*). The isotopic composition of San Francisco Bay surface sediment from the core tops and throughout the Bay in 1990 (*13*) plots in a field (Figure 3) overlapping the range in lead isotope compositions measured in California gasoline from 1964 to 1990 (*25*−*28*). The region of overlap is significant, since it is identical to the weighted average gasoline lead isotope composition.

The isotopic composition of lead in California (and U.S.) gasoline has changed through time, as has the concentration of lead in gasoline and the resulting lead flux into the air. The

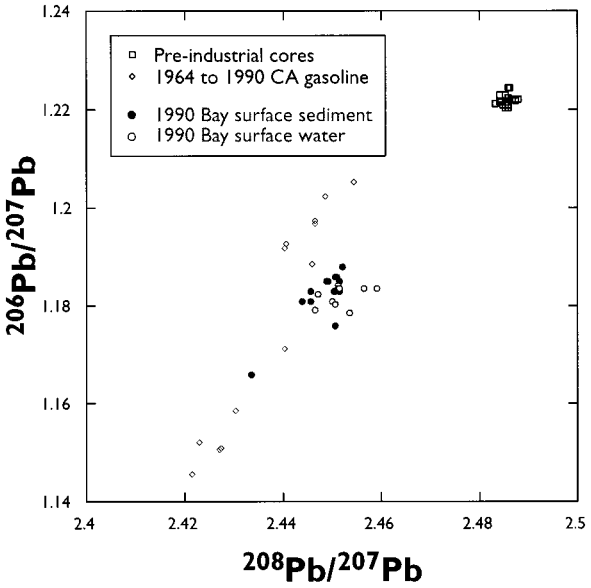

FIGURE 3. Comparison of preindustrial Bay sediment, California gasoline from 1964 to 1990 and surface sediment and water from 1990. The sediment and water data are from ref *13*. The gasoline data are yearly averages calculated from data in refs *25*−*28*.

yearly variation in the lead concentration of California gasoline can be used to weight the yearly composition of lead isotopes in gasoline in order to calculate the expected isotopic composition of a reservoir that has accumulated lead from gasoline emission. The weighted average $^{206}Pb/^{207}Pb$ of California gasoline from 1964 to 1990 is 1.18. The modern Bay waters and sediments intersect the field of gasoline lead over the $^{206}Pb/^{207}Pb$ range of 1.180−1.186. The gasoline lead sufficiently accounts for the lead isotope ratio of modern contaminated sediments throughout the San Francisco Bay, although a smelter operating in the north Bay may have had a localized influence on waters and sediments within a small area of the northern Bay (*13*). The past smelter emissions will not influence the recent lead content of the rivers considered in this study since the river waters were collected 25 km upstream from the old smelter site and, as discussed below, are not in chemical communication with the Bay sediments or waters that may retain smelter lead.

Since the San Francisco Bay can be viewed as a receiving basin for gasoline lead emissions, a comparison of the Bay's present and historical lead isotope composition with its dominant riparian inputs should provide insight into the washout of past gasoline emissions from the rivers. The Sacramento and San Joaquin rivers are the primary sediment inputs to the San Francisco Bay, with a combined watershed covering 40% of the land area of the state (*20*). The dynamics of lead removal from these rivers, therefore, represents large-scale, regional processes.

Sampling and Analysis

Samples were taken at the mouths of the Sacramento and San Joaquin rivers (the major sediment sources to the Bay) and at the mouth of the Petaluma river (a minor input) (Figure 2). We collected filtered ($<0.45\mu$) and unfiltered water at all sites using trace metal clean techniques (*2*). Samples of the San Joaquin and Sacramento rivers were taken in August 1995, February 1996, April 1996, and August 1996 on our 2 yearly sampling cruises during the typically dry summers and wet winters. An additional sample was taken in July 1998 to assess whether any significant shifts lead isotopic composition occurred after 1996. The Petaluma river was not sampled in February 1996 or July 1998.

TABLE 1. Lead Isotopic Compositions of River Waters and Hydraulic Mining Sediment Analyzed in This Study[a]

ICPMS Data

river	date	$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$	
Sacramento [BG 20]	Aug-95	1.1971	(3)	2.4667	(57)
	Feb-96	1.1999	(29)	2.4723	(9)
	Apr-96	1.1971	(39)	2.4652	(28)
	Aug-96	1.1918	(14)	2.4592	(68)
San Joaquin [BG30]	Aug-95	1.1896	(88)	2.4561	(50)
	Feb-96	1.2011	(59)	2.4696	(26)
	Apr-96	1.1953	(16)	2.4597	(14)
	Aug-96	1.1911	(29)	2.4590	(19)
Petaluma [BD15]	Aug-95	1.1835	(4)	2.4466	(0)
	Feb-96				
	Apr-96	1.1834	(73)	2.4599	(21)
	Aug-96	1.1853	(52)	2.4507	(11)

TIMS Data

river	date	$^{206}Pb/^{207}Pb$		$^{208}Pb/^{207}Pb$		$^{206}Pb/^{204}Pb$		$^{207}Pb/^{204}Pb$		$^{208}Pb/^{204}Pb$	
Sacramento											
filtered	Jul-98	1.19861	(2)	2.46427	(4)	18.7400	(19)	15.6345	(16)	38.5289	(39)
unfiltered	Jul-98	1.19919	(2)	2.46539	(4)	18.7416	(15)	15.6285	(13)	38.5303	(31)
San Joaquin											
filtered	Jul-98	1.20008	(2)	2.46569	(5)	18.7638	(30)	15.6349	(22)	38.5518	(54)
unfiltered	Jul-98	1.19963	(2)	2.46567	(4)	18.7538	(23)	15.6331	(16)	38.5467	(46)
Malakoff #1		1.24165	(5)	2.51612	(10)	19.4840	(4)	15.6920	(3)	39.4830	(8)
Malakoff #2		1.22502	(5)	2.50134	(10)	19.1960	(4)	15.6700	(3)	39.1960	(8)

[a] Errors on river water isotope measurements are shown as ±2 SE in the final two decimal places. Errors on Malakoff Diggins sediment are given as ±2 SD on the mean from counting statistics.

The samples from both the San Joaquin and Sacramento river mouths were of freshwater. As rivers enter an estuary, they override a wedge of dense, saline estuary water that is in chemical communication with bottom sediments. In the San Joaquin and Sacramento river waters the salinity was less than 2, indicating no mixing with brackish estuarine waters. However, mixing was apparent in the Petaluma river water, where sample salinity ranged from 3 to 21.

In addition to the rivers, two mine tailings samples were taken at the Malakoff Diggins. In 1884, the Malakoff Diggins was the largest hydraulic gold mining operation in California as well as the world. Tailings from this mine and other smaller operations in the Sierra Nevadan foothills were washed into tributaries of the Sacramento and accumulated in the Sacramento/San Joaquin delta (*19, 20*).

Lead isotopic compositions of the samples were measured by thermal ionization mass spectrometry (TIMS, used for 1998 river waters and Malakoff Diggins) and by high resolution inductively couple plasma mass spectrometry (ICPMS, used for 1995−1996 river waters) after processing in trace metal clean laboratories under class 100 air. In preparation for TIMS analysis, a 250 mL volume of each water sample from July 1998 was dried and then purified using Teflon microcolumns loaded with AG 50 resin. The samples were analyzed using a VG Sector 54-Warp thermal ionization mass spectrometer (TIMS) as in previous studies (*29*−*31*). Sediment samples from the Malakoff Diggins hydraulic mine site were analyzed by TIMS following the procedure described by Ritson et al. (*13*). The 1995−1996 waters were analyzed for isotopic composition using a Finnegan ELEMENT ICP-MS after lead extraction using an APDC/DDDC solvent procedure (*32*). Procedural blanks (≤50 pg) for this solvent procedure were 1000 times lower than sample concentrations.

For both TIMS and ICPMS, a fractionation correction was derived for each instrument from in-run analyses of NIST SRM 981. Errors on the ICPMS analyses in Table 1 are calculated as 1 SD from the mean of two analyses made on a single aliquot of each sample. The errors given are consistent with, though slightly higher than, our reproduced NBS 981 isotope ratios on this instrument. Errors on TIMS measurements are given as two times the standard error from counting statistics.

Isotopic Variation in River Waters. No isotopic fractionation is evident between unfiltered and filtered aliquots of river water. This is shown by the almost complete overlap in isotopic composition between filtered and unfiltered samples measured in the 1998 river waters (Table 1). Such isotopic equilibrium is consistent with ^{210}Pb studies which indicate that isotopic equilibrium is quickly established between the surfaces of suspended particulates and the lead in the filtered fraction of river water (*33*). Therefore, we will refer only to the unfiltered samples in plots, tables, and discussion.

The San Joaquin and Sacramento river mouth waters are isotopically distinct from San Francisco Bay surface waters and sediments sampled in 1990, while the Petaluma river waters are not. Waters from the shallow Petaluma river mouth are mixed with Bay waters and incorporate a component of diagenetically altered Bay sediment pore water (*34*). The Cr/Al in waters from the Petaluma river mouth are anomalous and attributed to the mixing of Bay sediment pore water with river water as the river enters the Bay (*34*). Bay sediment pore water is not detected in the Cr/Al of the surface water in the much deeper San Joaquin and Sacramento river mouths (*34*). Physical mixing with Bay waters is suggested by the salinity of the Petaluma river water as well. Of the three rivers analyzed it is the only one with salinity above the minimum detection limit. The Petaluma river, therefore, is receiving its lead isotope composition from the sediment and water of the Bay and is excluded from further discussion. The San Joaquin and Sacramento rivers are considered below to represent the current freshwater inputs to the Bay.

Discussion

The 1995−1998 San Joaquin and Sacramento river waters have lead isotope compositions that are distinct from past gasoline lead isotope compositions and define a linear trend toward higher lead isotope values (Figure 4). The simple linear

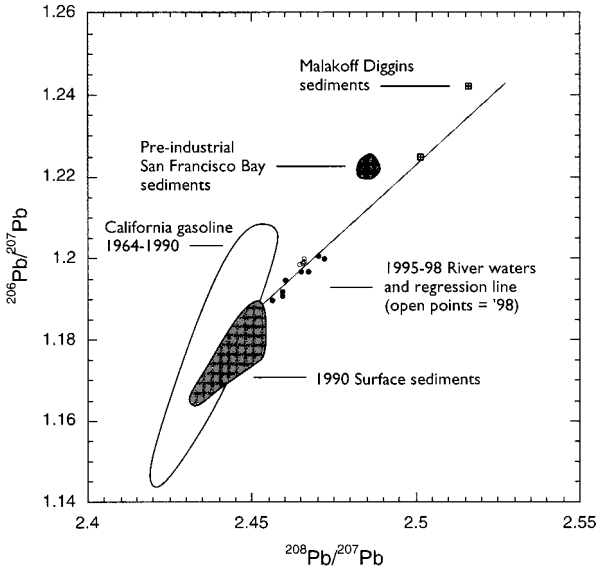

FIGURE 4. Comparison between 1995 and 1998 river and hydraulic mining data (this study) and previous lead isotope data for San Francisco Bay (see Figure 3 caption). The hydraulic mining data plotted are from sediments at the Malakoff Diggins, one of the largest hydraulic mine operations.

regression through the river water data points in Figure 4 is highly significant ($R^2 = 0.98$). This trend suggests that river waters contain a lead component distinct from the component of anthropogenic contamination in the Bay. We interpret this second component to be the present day natural background lead composition. As previously noted, the current natural background composition is not identical to the preindustrial background.

Hydraulic mining sediment has caused a redistribution of the terrigenous lead signature into the Sacramento and San Joaquin rivers. Water, alpine pond sediment, and silicate rocks from the Sierra Nevada all have $^{206}Pb/^{207}Pb$ as high or higher than the preindustrial Bay core samples. The $^{208}Pb/^{207}Pb$ of the natural Sierra Nevadan inputs, however, cover a range, from 2.43 to 2.57, skewed toward values higher than in the pre-mining core bottoms (*35*−*37*). Although the sediment inputs to the river basin have been reworked, the new mixture of natural components must maintain an isotopic signature consistent with the source region. For the sake of discussion, therefore, we propose that the new natural background lead isotope ratio has a $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in the range of hydraulic mining sediment (e.g. the Malakoff Diggins, the largest hydraulic mine site in California, and the world, at the time). Based upon this proposed modern background composition, the river waters have not yet returned to a natural lead isotope composition, and more than 50% of the lead in the rivers is persistent from past leaded gasoline emissions.

The recovery of the rivers from gasoline lead contamination is limited by the high conditional partition coefficients (K_d) for lead in suspended sediments. Under natural pH, the log K_d for lead may be greater than 7.4 (*38*). Since 97.5% of the lead in natural waters can be found in the suspended particulates (size fraction > 0.2 μm), the lead in the Sacramento and San Joaquin rivers will be stored as particle adsorbed lead in the bed load. In order for the rivers to remove 50 years of gasoline lead accumulated in the drainage basin they must transport the contaminated bed load to the Bay. Since the river will suspend and redeposit its bed load during transport, this is a relatively slow process. The isotopic composition of lead in samples taken in 1998 has not shifted toward a more natural value than samples taken in 1995 or 1996, indicating no appreciable gasoline lead removal occurred during the three intervening years. The influence of gasoline lead in the rivers is likely to remain for decades to centuries.

Since 1985 the input of lead from gasoline exhaust has been 2 orders of magnitude lower than during the period of high leaded gasoline emissions in the 1970s. Although 99% of gasoline lead was deposited at least 10 years before our samples were taken, the lead in the Sacramento and San Joaquin rivers retains a strong component of gasoline lead. This river lead is on a well defined mixing line consistent with an anthropogenic end member that is the average lead isotope composition of historic gasoline emissions. The other end member is a natural background composition that is distinct from the preindustrial Bay sediment background. The change is likely to be due to the greater contribution from Sierra Nevadan foothills sediments released into the Sacramento and San Joaquin drainage basins by hydraulic mining.

The recovery of the river waters from gasoline lead contamination is not complete. Lead is particle reactive, and lead bound to particles in the watershed as well as the bed load of the river will limit the ability of the system to flush. Even in the most actively flushed surface environments, the presence of human lead pollution seems likely to persist. The leaded gasoline signature, therefore, is a promising tracer of nonpoint source distributions of particle-reactive anthropogenic metals for decades.

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