UC Santa Cruz
UC Santa Cruz Previously Published Works

Title

Pyrogenic Remobilization of Historic Industrial Lead Depositions

Permalink

https://escholarship.org/uc/item/0tp4k026

Authors

Odigie, Kingsley O

Flegal, A. Russell

Publication Date

2011

Peer reviewed

Pyrogenic Remobilization of Historic Industrial Lead Depositions

Kingsley O. Odigie[†,*] and A. Russell Flegal[†]

[†]WIGS Laboratory, Department of Microbiology and Environmental Toxicology, University of California at Santa Cruz, 1156 High Street, Santa Cruz, California 95064, United States

ABSTRACT: Relatively high levels (4.3 to 51 μg/g) of labile lead (Pb) in ash from the 2009 Jesusita Fire in Santa Barbara County, California attest to the pyrogenic remobilization of historic industrial lead depositions in this relatively pristine area in Southern California, USA. The primarily industrial origin of that lead was evidenced by its poor correlations (simple linear regressions) with lithogenic aluminum ($r = 0.18$, $p = 0.354$, $n = 30$) and iron ($r = 0.21$, $p = 0.270$, $n = 30$) concentrations and by its associated enrichment factors (EFs): EF using aluminum as conservative element (f-Al) vs lead concentration [Pb] ($r = 0.79$, $p < 0.001$, $n = 30$), and EF using iron as conservative element (f-Fe) vs [Pb] ($r = 0.83$, $p < 0.001$, $n = 30$). The industrial origins of much of that lead were corroborated by its isotopic compositions (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb), which fell between those of natural lead in the Santa Barbara Basin and previous leaded gasoline emissions in Southern California. This apparent pyrogenic remobilization of legacy lead pollution indicates that it—and other persistent pollutants—will increase with the projected increase in the frequency and intensity of forest fires in the Southwest U.S. and elsewhere as a consequence of climate change.

■ INTRODUCTION

Historic Emissions of Industrial Lead. Massive anthropogenic emissions of lead (Pb) have greatly perturbed its natural biogeochemical cycle.[1] These industrial emissions have included exhaust from the combustion of leaded gasoline, which accounted for approximately 75% of atmospheric lead contamination in the world[1] and 90% of that contamination in California—where other sources of industrial lead emissions were relatively low—during the latter half of the previous century.[2,3] Most of the contamination from leaded gasoline emissions has been localized in urban areas, such as the Los Angeles Basin in Southern California, USA. There, during the late 1960s and early 1970s, the amount of lead used in gasoline was ~24 000 kg/day; two-thirds (~67%) of that lead (~18 000 kg/day) was aerosolized; and two-thirds (~67%) of those aerosols (~12 000 kg/day) were deposited within the basin.[4]

Atmospheric depositions of those and other industrial lead aerosols markedly increased lead concentrations of sediments in Southern California.[5,6] For example, Chow et al.[7] reported that subsequent to the introduction of leaded gasoline, lead fluxes into sediments increased from 1.0 to 2.1 μg/cm^2/year in the Santa Barbara Basin, 0.26 to 1.7 μg/cm^2/year in the San Pedro Basin and 0.24 μg/cm^2/year to 0.9 μg/cm^2/year in the Santa Monica Basin. Similarly, Harris and Davidson[8] reported that the average (mean ± SD, Standard Deviation) soil lead concentration in Southern California (Los Angeles and suburbs) increased from a 1919−1933 value of 16 ± 0.5 to 79 ± 23 μg/g between 1967 and 1970. Those temporal increases are consistent with increases in proximate, age-dated sediments in Northern California[9] and Northern Mexico[10] that have also been correlated with the use of leaded gasoline in the North American Southwest.

This massive contamination of the geosphere by industrial lead was associated with corresponding increases of lead in the biosphere: most notably in the blood lead (PbB) concentrations of humans.[11] Both occurred at the same time the threshold for sublethal lead toxicity in humans was being lowered.[12−14] Consequently, industrial uses of lead—including leaded gasoline—were reduced and/or eliminated in the U.S. and most other countries.[11]

The positive effects of those remedial actions were documented in subsequent reductions of lead contamination in the environment and in humans. The former included decreases in remote oceanic surface waters, where aeolian depositions of industrial lead were dominant;[15,16] the latter included decreases in the average PbB of children (ages 1−5 years) in the U.S. from 15 μg/dL in 1976−1980 to 3.6 μg/dL in 1988−1991, which corresponded with the phase out of leaded gasoline in the U.S.[17] Since then, PbB concentrations of children in the U.S. have continued to decrease to ~2 μg/dL.[18] Nevertheless, that current baseline level is still 2 orders of magnitude above the estimated natural PbB level (~0.016 μg/dL) in humans, and the threshold for lead toxicity in humans has yet to be established.[19]

The legacy of historic industrial lead contamination is evident in the geosphere. For example, a decade after the elimination of leaded gasoline in California, soil lead concentrations in Pasadena (77 ± 19 μg/g) were still 6-fold greater than the preindustrial crustal lead (baseline) level of ~12.5 μg/g.[8] Likewise, it has been

Figure 1. Photograph of the 2009 Jesusita Fire burned area in Santa Barbara, California showing the relatively remote and mountainous terrain where the fire occurred (Photo by Kingsley O. Odigie).

calculated that it will take decades, if not centuries, to flush historic leaded gasoline depositions from surface sediments in California's Central Valley to San Francisco Bay.[2,3] Moreover, much of those historic depositions have been retained in terrestrial sediments, soils and vegetation in forests throughout the state where they may be remobilized by anthropogenic and natural processes—including forest fires.

Pyrogenic Remobilization of Heavy Metals. One of the potentially most important processes for the global remobilization of inorganic legacy pollutants is forest fires. While there is little information about the remobilization of lead from forest fires, there is a substantial amount of information on the pyrogenic remobilization of other pollutants, including mercury.[20] Forests are a reservoir for trace metals sequestered in sediments, soil organic matter, and vegetation, where they are relatively immobile.[21,22] The combustion of soil organic matter and vegetation releases those sequestered trace metals and increases their bioavailability.[21,23,24] Forest fires also increase soil erosion by as much as 2 orders of magnitude,[25] accelerating the transport of those mobilized trace metals to water bodies and further increasing their bioavailability.[26]

Therefore, this work was conducted to determine the amount and sources of potentially labile lead in ash from a large forest fire that occurred in Southern California in 2009. In that year, when there were several large forest fires in Southern California, we focused on ash from the Jesusita Fire in Santa Barbara because (1) emissions of industrial lead in that relatively pristine area have been primarily limited to those from leaded gasoline combustion and (2) there are data on isotopic compositions of both natural lead and leaded gasoline in the region. Consequently, we expected it would be simpler to distinguish natural and industrial sources of lead in ash from that area than in more industrial areas of Southern California (e.g., Los Angeles and San Diego).

■ MATERIALS AND METHODS

Sample Collection Sites. Samples were collected from the burned area of the May 2009 Jesusita Fire in Santa Barbara,

California (Figures 1 and 2). The fire burned about 3534 ha (8733 acres) of land.[27] Twenty-six ash samples were collected from different accessible areas around the burned perimeter (Figure 2), using trace metal clean techniques.[9] The samples were immediately double bagged in plastic containers to prevent contamination, and then stored in sealed containers at room temperature until analysis.[28]

Analytical Methods. Ash samples from the 26 sites, including two sites that were sampled in triplicate (SB11 and SB22), were processed in a trace metal clean laboratory in a filtered HEPA (Class-100) hood using established techniques.[28] All reagents were either trace metal or ultrapure ($2\times$ sub-boiling quartz distilled) grade. High purity (18.2 MΩ cm) water (Milli-Q) was used for dilutions and cleaning. Three procedural blanks and 3 samples of 2 National Institute of Standards and Technology (NIST) standard reference materials (SRMs) were processed concurrently: SRM 1547 (peach leaves) and SRM 1633b (coal fly ash).

A concentrated nitric acid digestion was used to derive a measure of the acid-leachable (labile) lead in the samples and reference materials.[29−32] Approximately 0.3 to 0.5 g of ash sample or reference material was transferred to a trace metal clean Teflon digestion vial and dried overnight at 65 °C. Ten milliliters (mL) of concentrated nitric acid (HNO_3) was then added to each sample vial and kept at room temperature for ∼18 h. Next, the solutions were heated and refluxed for ∼18 h. After the refluxed material was cooled and dried, a second 10 mL of concentrated HNO_3 was added, and the digestion process was repeated. The digests were then dried, cooled and redissolved in 10 mL of 1 M ultrapure HNO_3 for elemental and isotopic composition analyses.[33]

The digests were analyzed for their lead concentration and isotopic composition with a Finnigan ELEMENT 2 high resolution—inductively coupled plasma mass spectrometer (HR ICP-MS), using established techniques that have been intercalibrated with measurements on both a Finnigan NEPTUNE multiple collector magnetic sector inductively coupled mass spectrometer[34] and a VG Sector 54-WARP thermal ionization mass spectrometer.[35]
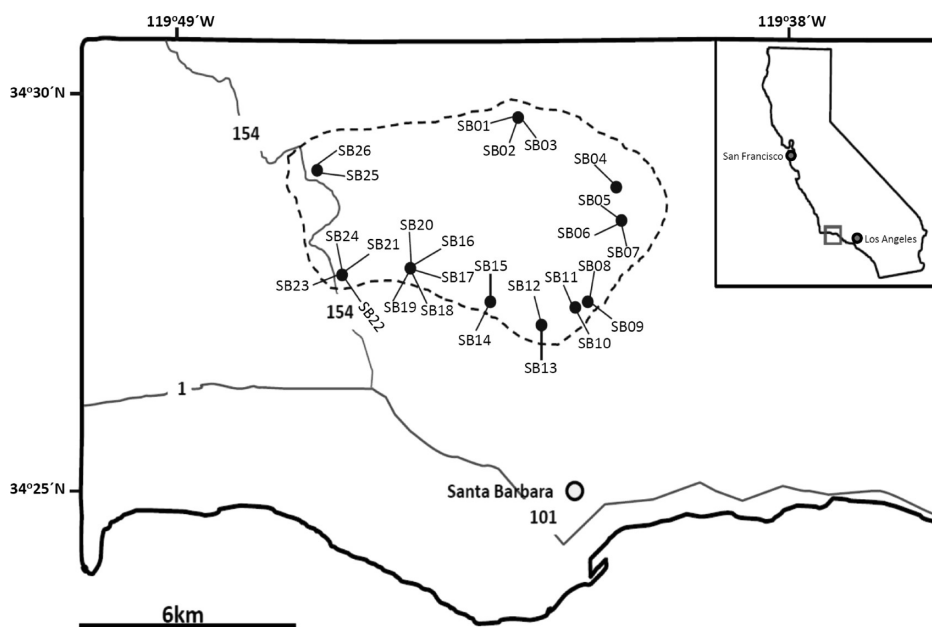
Figure 2. Map showing approximate sample collection sites within the boundary (---) of the 2009 Jesusita Fire in Southern California. Coordinates of the sites are listed in Table 1.

Bismuth (Bi) was used as an internal standard to correct for instrumental drifts, and NIST SRM 981 (common lead) was used as standard to correct for the fractionation of isotopic composition. One sample (SB01) was analyzed multiple times ($n = 7$) to assess reproducibility of the isotopic measurements. The analytical precisions (RSDs, Relative Standard Deviation) for $^{208}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, and $^{207}Pb/^{204}Pb$ were 0.22%, 0.38%, and 0.30%, respectively. Aluminum (Al) and iron (Fe) concentrations of the digests were measured with a PerkinElmer Optima 4300 DV inductively coupled plasma–optical emission mass spectrometer (ICP-OES), using established techniques, to determine the enrichment factor (EF) of lead in the ash.[36,37]

The detection limit (3 x SD of the blanks, $n = 3$) of lead concentration for this project was 0.03 ng/g of sample. Average recoveries (mean ± RSD, $n = 3$) of lead for SRM 1547 and SRM 1633b were 105 ± 2.5% and 52.1 ± 1.1% of their certified values, respectively. The RSD values for the concentrations of lead in the replicate samples ($n = 3$) of ash (SB11 and SB22) were 0.8% and 1.3%, respectively. Recoveries for aluminum and iron in SRM 1547 were 83.2% and 87.9%, respectively; those of aluminum and iron in SRM 1633b were 24.2% and 68.1%, respectively. Differences in the percent recoveries of the elements in the different SRMs were consistent with previous measurements in our laboratory, and reflect the different lability of those elements in the two matrices. The normalization to $[Fe]_{Baseline}$ is considered more appropriate for samples digested with strong acids other than hydrofluoric acid (HF) because the lead in aluminosilicates, which require an HF digestion, is extremely refractory.[36,38] That is illustrated by differences in our recoveries of aluminum (24%) and iron (68%) in coal fly ash (SRM 1633b), compared to our recoveries of aluminum (83%) and iron (88%) in peach leaves (SRM 1547) because coal fly ash (SRM 1633b) would require digestion with concentrated HF to dissolve metals bound in its aluminosilicate lattices. The peach leaves (SRM 1547), therefore, provided better estimates of recoveries of metals in our ash samples, which are predominantly derived from soil organic matter and vegetation.

RESULTS AND DISCUSSION

Lead Concentrations. Lead concentrations (μg/g dry weight) of the ash ranged from 4.3 to 51 μg/g (Table 1). As previously noted, these concentrations are conservative because they did not include a concentrated HF digestion of refractory aluminosilicates, and may also not account for all of the lead volatized by the fire. Also included in the table are the concentrations (mg/g dry weight) of labile aluminum and iron, which were used to derive the enrichment factor (EF) for lead for both of those relatively conservative, lithogenic elements. The relatively low and insignificant ($p > 0.05$) correlations (simple linear regressions) between [Pb] and [Al] ($r = 0.18$, $p = 0.354$, $n = 30$), and [Pb] and [Fe] ($r = 0.21$, $p = 0.270$, $n = 30$) indicate that lead in the ash samples was primarily from anthropogenic, rather than natural, sources. Metals of predominantly natural origin, e.g., aluminum and iron—which are difficult to contaminate because of their relatively high natural abundance, correlate better than metals enriched by anthropogenic processes.[39]

Enrichment Factors. The predominantly industrial component of lead in the ash was further indicated by calculations of its enrichment factor (EF) relative to aluminum and iron.[36,39−41] EF is defined as follows:

$$ EF = \frac{\dfrac{[Pb]_{Sample}}{[Al]_{Sample}}}{\dfrac{[Pb]_{Baseline}}{[Al]_{Baseline}}} \text{ or } \frac{\dfrac{[Pb]_{Sample}}{[Fe]_{Sample}}}{\dfrac{[Pb]_{Baseline}}{[Fe]_{Baseline}}} $$

For our calculations, we normalized $[Pb]_{Sample}$, $[Al]_{Sample}$, and $[Fe]_{Sample}$ of our ash samples to $[Pb]_{Baseline}$, $[Al]_{Baseline}$, and $[Fe]_{Baseline}$ of Pb-210 dated preindustrial sediments deposited in a Santa Barbara Basin[5] because sediments from the study site are deposited in that basin.

The correlations ($r = 0.99$, simple linear regressions) of lead EFs calculated using aluminum (f-Al) and iron (f-Fe) for the ash samples were highly significant ($p < 0.001$), as were the

Table 1. Data from the Analyses of Ash Samples Collected from the 2009 Jesusita Fire in Southern California: Coordinates of Sample Collection Sites; Concentrations of Lead, Aluminum, And Iron; And Enrichment Factors (f-Al and f-Fe) and Isotopic Ratios of Lead

					sample collection sites and results					
	collection sites		concentration			enrichment factor		isotopic ratios		
sample ID	latitude	longitude	[Pb] (μg/g)	[Al] (mg/g)	[Fe] (mg/g)	f-Al	f-Fe	^{208}Pb/^{207}Pb	^{206}Pb/^{207}Pb	^{207}Pb/^{204}Pb
SB01	34°29′40.10″N	119°42′49.30″W	9.60	16.39	12.66	2.8	2.3	2.480	1.212	15.637
SB02	34°29′40.00″N	119°42′48.90″W	26.75	18.33	12.00	7.1	6.8	2.471	1.205	15.689
SB03	34°29′37.60″N	119°42′51.10″W	29.35	18.20	14.67	7.8	6.1	2.464	1.204	15.710
SB04	34°28′51.50″N	119°41′05.50″W	24.33	19.86	17.72	6.0	4.2	2.436	1.161	15.609
SB05	34°28′27.60″N	119°40′55.20″W	28.21	18.02	14.66	7.6	5.9	2.461	1.209	15.649
SB06	34°28′27.60″N	119°40′55.20″W	24.89	22.32	16.13	5.4	4.7	2.469	1.209	15.649
SB07	34°28′27.60″N	119°40′54.90″W	27.65	22.33	17.04	6.0	5.0	2.464	1.210	15.716
SB08	34°27′27.30″N	119°41′43.80″W	32.12	22.51	19.52	6.9	5.0	2.465	1.210	15.692
SB09	34°27′27.30″N	119°41′43.80″W	14.85	26.87	22.85	2.7	2.0	2.464	1.210	15.680
SB10	34°27′21.30″N	119°41′56.70″W	6.51	10.97	8.71	2.9	2.3	2.467	1.206	15.624
SB11A	34°27′21.50″N	119°41′57.10″W	18.66	36.01	31.11	2.5	1.8	2.481	1.207	15.576
SB11B	34°27′21.50″N	119°41′57.10″W	18.95	31.23	25.33	2.9	2.3	2.479	1.204	15.682
SB11C	34°27′21.50″N	119°41′57.10″W	18.81	25.75	20.91	3.6	2.8	2.480	1.206	15.636
SB12	34°27′12.10″N	119°42′27.40″W	13.85	9.89	8.07	6.8	5.2	2.466	1.200	15.578
SB13	34°27′12.10″N	119°42′27.40″W	10.48	7.45	5.82	6.8	5.5	2.467	1.202	15.621
SB14	34°27′30.30″N	119°43′24.30″W	12.37	23.96	19.03	2.5	2.0	2.476	1.206	15.644
SB15	34°27′30.80″N	119°43′25.00″W	14.57	14.20	11.19	5.0	4.0	2.473	1.214	15.668
SB16	34°27′55.00″N	119°44′58.20″W	48.96	7.39	7.60	32.2	19.7	2.458	1.217	15.629
SB17	34°27′55.00″N	119°44′58.20″W	36.19	15.29	13.44	11.5	8.2	2.461	1.215	15.648
SB18	34°27′56.00″N	119°44′50.90″W	17.04	14.40	13.88	5.8	3.8	2.460	1.193	15.688
SB19	34°27′56.00″N	119°44′50.90″W	9.08	27.20	23.64	1.6	1.2	2.474	1.209	15.609
SB20	34°27′55.60″N	119°44′51.00″W	4.71	12.72	10.65	1.8	1.4	2.466	1.203	15.586
SB21	34°27′50.10″N	119°46′16.70″W	4.29	5.70	5.00	3.7	2.6	2.464	1.201	15.632
SB22A	34°27′50.00″N	119°46′16.70″W	4.78	8.29	7.15	2.8	2.0	2.458	1.199	15.581
SB22B	34°27′50.00″N	119°46′16.70″W	4.68	9.26	7.46	2.5	1.9	2.455	1.197	15.637
SB22C	34°27′50.00″N	119°46′16.70″W	4.80	8.43	7.34	2.8	2.0	2.459	1.197	15.563
SB23	34°27′50.00″N	119°46′16.70″W	5.40	10.38	8.40	2.5	2.0	2.469	1.203	15.600
SB24	34°27′48.50″N	119°46′16.20″W	23.76	13.57	11.57	8.5	6.3	2.470	1.218	15.581
SB25	34°29′02.10″N	119°46′33.80″W	17.82	8.59	8.98	10.1	6.1	2.465	1.214	15.615
SB26	34°29′02.10″N	119°46′34.20″W	51.02	14.85	14.13	16.7	11.0	2.464	1.214	15.631

correlations ($r = 0.98$, simple linear regressions) between concentrations of those two conservative metals (aluminum and iron) in the ash ($p < 0.001$). Using the more conservative EF (f-Fe) and the classification proposed by Sutherland,[42] the normalizations conservatively indicate that of the 26 samples analyzed: 2 were not measurably contaminated (EF < 2); 14 were moderately contaminated (EF = 2−5); and 10 were significantly contaminated (EF = 5−20).

Isotopic Compositions. The industrial origins of that enrichment are indicated in Figure 3, which shows a plot of the lead isotopic ratios (^{208}Pb/^{207}Pb: ^{206}Pb/^{207}Pb) of the ash samples. Also included in the plot are the ranges of lead isotopic compositions of natural and contaminated sediments deposited in the Santa Barbara Basin,[6] as well as those reported for leaded gasoline used in California during the latter half of the previous century.[3]

The plot shows that the amount of natural lead in the ash samples is relatively small compared to that of industrial lead, based on isotopic composition of preindustrial sediments in the Santa Barbara Basin.[6,7] It also indicates that most of the lead in the

ash samples is a mixture of industrial emissions from the 1960s-1970s and the 1980s, which have been primarily attributed to the combustion of alkyl-lead in gasoline in Southern California.[6,7,43]

Temporal variations of the isotopic composition of leaded gasoline in California correspond with temporal differences in ores used to manufacture alkyl-lead in the U.S. during that period. In the 1960s, the ores were obtained primarily from Australia, Canada, Mexico, and Peru, which had ^{206}Pb/^{207}Pb ratios of about 1.037, 1.064, 1.192, and 1.200, respectively.[6] The use of lead from the Missouri deposits (^{206}Pb/^{207}Pb = 1.28 to 1.33) subsequently increased from 9% in 1962 to 82% in 1976. This change in lead sources was reflected in the lead isotopic compositions of aerosols in Southern California, where the ^{206}Pb/^{207}Pb ratio changed from ~1.15 before 1967 to ~1.20 by 1974 and to 1.23 by 1977.[44] It is, therefore, assumed that the isotopic composition of those aerosols reflects a mixture of contemporary and previous industrial lead emissions that have been resuspended, as observed in Los Angeles[8] and the San Francisco Bay area.[28]
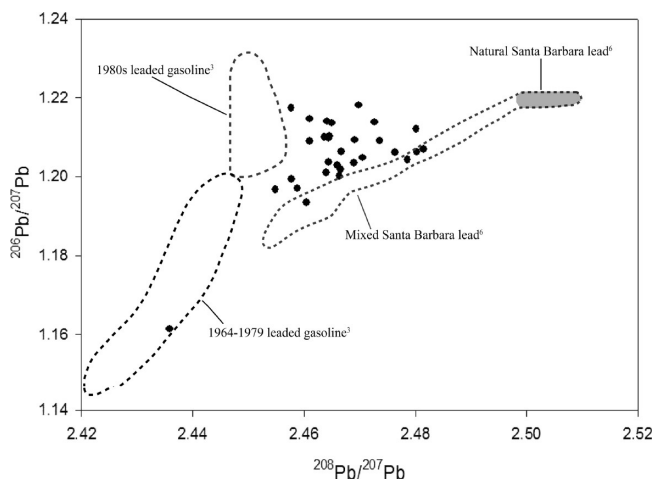
Figure 3. Lead isotopic composition (^{208}Pb/^{207}Pb: ^{206}Pb/^{207}Pb) of ash samples (●) collected from the 2009 Jesusita Fire site in Southern California. Also included in the plot are the ranges of previous reports of the isotopic composition of leaded gasoline in California[3] and Pb-210 dated sediment cores in the Santa Barbara Basin.[6]

Potential Impact of Climate Change. The present findings have broad implications because climate change is increasing the global frequency and intensity of wildfires.[45−50] For example, a recent study by Westerling et al.[47] showed a significant correlation ($r = 0.76$, $p < 0.001$, $n = 34$) between wildfire frequency and regional spring and summer temperatures in the Western U.S. They also observed that wildfires in the Western U.S. increased in frequency (∼4 times) and total area burned (∼7 times) in the mid-1980s, compared to wildfires from 1970 to 1986; this corresponded with a temperature rise of <0.9 °C. Several studies have reported similar associations between wildfires and temperature.[45,51,52] Moreover, the IPCC[48] projects that global surface temperature will increase by 1.5 to 5.8 °C by the end of the 21st century, and others have proposed there will be a corresponding increase in the frequency and intensity of wildfires during that period.[51−53] While the associated remobilization of legacy pollutants has recently been highlighted by concerns that forest fires in Russia could volatize radioactive pollutants in Chornobyl,[54,55] our preliminary study indicates forest fires are already remobilizing large amounts of lead, a much more pedestrian but pervasive pollutant and that the mobilization of lead and other refractory legacy pollutants will increase with climate change.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (831) 459-5336; Fax: (831) 459-3524; E-mail: kodigie@ucsc.edu.

■ ACKNOWLEDGMENT

■ REFERENCES

(1) Nriagu, J. O.; Pacyna, J. M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **1988**, *333* (6169), 134–139.

(2) Steding, D. J.; Dunlap, C. E.; Flegal, A. R. 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. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97* (21), 11181–11186.

(3) Dunlap, C. E.; Alpers, C. N.; Bouse, R.; Taylor, H. E.; Unruh, D. M.; Flegal, A. R. The persistence of lead from past gasoline emissions and mining drainage in a large riparian system: Evidence from lead isotopes in the Sacramento River, California. *Geochim. Cosmochim. Acta* **2008**, *72* (24), 5935–5948.

(4) Huntzicker, J. J.; Friedlander, S. K.; Davidson, C. I. Material balance for automobile-emitted lead in Los Angeles Basin. *Environ. Sci. Technol.* **1975**, *9* (5), 448–457.

(5) Bruland, K. W.; Bertine, K.; Koide, M.; Goldberg, E. D. History of metal pollution in Southern California coastal zone. *Environ. Sci. Technol.* **1974**, *8* (5), 425–432.

(6) Ng, A.; Patterson, C. C. Changes of lead and barium with time in California off-shore basin sediments. *Geochim. Cosmochim. Acta* **1982**, *46* (11), 2307–2321.

(7) Chow, T. J.; Bruland, K. W.; Bertine, K.; Soutar, A.; Koide, M.; Goldberg, E. D. Lead pollution: Records in Southern California coastal sediments. *Science* **1973**, *181* (4099), 551–552.

(8) Harris, A. R.; Davidson, C. I. The role of resuspended soil in lead flows in the California South Coast Air Basin. *Environ. Sci. Technol.* **2005**, *39* (19), 7410–7415.

(9) Ritson, P. I.; Bouse, R. M.; Flegal, A. R.; Luoma, S. N. Stable lead isotopic analyses of historic and contemporary lead contamination of San Francisco Bay estuary. *Mar. Chem.* **1999**, *64*, 71–83.

(10) Soto-Jimenez, M. F.; Hibdon, S. A.; Rankin, C. W.; Aggarawl, J.; Ruiz-Fernandez, A. C.; Paez-Osuna, F.; Flegal, A. R. Chronicling a century of lead pollution in Mexico: Stable lead isotopic composition analyses of dated sediment cores. *Environ. Sci. Technol.* **2006**, *40* (3), 764–770.

(11) National Research Council. *Measuring Lead Exposure in Infants, Children and Other Sensitive Populations*; National Academy Press: Washington, D.C., 1993.

(12) Nriagu, J. O. The rise and fall of leaded gasoline. *Sci. Total Environ.* **1990**, *92*, 13–28.

(13) Weitzman, M.; Aschengrau, A.; Bellinger, D.; Jones, R.; Hamlin, J. S.; Beiser, A. Lead-contaminated soil abatement and urban children's blood lead levels. *JAMA-J. Am. Med. Assoc.* **1993**, *269* (13), 1647–1654.

(14) Needleman, H. Lead poisoning. *Annu. Rev. Med.* **2004**, *55*, 209–222.

(15) Veron, A. J.; Church, T. M.; Flegal, A. R.; Patterson, C. C.; Erel, Y. Response of lead cycling in the surface Sargasso Sea to changes in tropospheric input. *J. Geophys. Res.* **1993**, *98* (C10), 18269–18276.

(16) Boyle, E. A.; Bergquist, B. A.; Kayser, R. A.; Mahowald, N. Iron, manganese, and lead at Hawaii Ocean Time-Series Station ALOHA: Temporal variability and an intermediate water hydrothermal plume. *Geochim. Cosmochim. Acta* **2005**, *69* (4), 933–952.

(17) Pirkle, J. L.; Brody, D. J.; Gunter, E. W.; Kramer, R. A.; Paschal, D. C.; Flegal, K. M.; Matte, T. D. The decline in blood lead levels in the United States—The National Health and Nutrition Examination Surveys (NHANES). *JAMA-J. Am. Med. Assoc.* **1994**, *272* (4), 284–291.

(18) Dixon, S. L.; Gaitens, J. M.; Jacobs, D. E.; Strauss, W.; Nagaraja, J.; Pivetz, T.; Wilson, J. W.; Ashley, P. J. Exposure of US children to residential dust lead, 1999−2004: II. The contribution of lead-contaminated dust to children's blood lead levels. *Environ. Health Perspect.* **2009**, *117* (3), 468–474.

(19) Flegal, A. R.; Smith, D. R. Lead levels in preindustrial humans. *N. Engl. J. Med.* **1992**, *326* (19), 1293–1294.

(20) Witt, E. L.; Kolka, R. K.; Nater, E. A.; Wickman, T. R. Forest fire effects on mercury deposition in the boreal forest. *Environ. Sci. Technol.* **2009**, *43* (6), 1776–1782.

(21) Biswas, A.; Blum, J. D.; Klaue, B.; Keeler, G. J. Release of mercury from Rocky Mountain forest fires. *Global Biogeochem. Cycles* **2007**, *21*, GB1002.

(22) Obrist, D.; Moosmuller, H.; Schurmann, R.; Chen, L. W. A.; Kreidenweis, S. M. Particulate-phase and gaseous elemental mercury emissions during biomass combustion: Controlling factors and correlation with particulate matter emissions. *Environ. Sci. Technol.* **2008**, *42* (3), 721–727.

(23) Badora, A.; Furrer, G.; Grunwald, A.; Schulin, R. Immobilization of zinc and cadmium in polluted soils by polynuclear Al-13 and Al-montmorillonite. *J. Soil Contam.* **1998**, *7* (5), 573–588.

(24) Erel, Y.; Veron, A.; Halicz, L. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. *Geochim. Cosmochim. Acta* **1997**, *61* (21), 4495–4505.

(25) Rulli, M. C.; Rosso, R. Hydrologic response of upland catchments to wildfires. *Adv. Water Resour.* **2007**, *30* (10), 2072–2086.

(26) Meyer, G. A.; Wells, S. G.; Balling, R. C.; Jull, A. J. T. Response of alluvial systems to fire and climate change in Yellowstone National Park. *Nature* **1992**, *357* (6374), 147–150.

(27) California Department of Forestry and Fire (Cal Fire). Jesusita Fire, 2009; http://cdfdata.fire.ca.gov/incident/.

(28) Flegal, A. R.; Gallon, C.; Hibdon, S.; Kuspa, Z. E.; Laporte, L. F. Declining-but persistent-atmospheric contamination in Central California from the resuspension of historic leaded gasoline emissions as recorded in the lace lichen (*Ramalina menziesii* Taylor) from 1892 to 2006. *Environ. Sci. Technol.* **2010**, *44* (14), 5613–5618.

(29) Teutsch, N.; Erel, Y.; Halicz, L.; Banin, A. Distribution of natural and anthropogenic lead in Mediterranean soils. *Geochim. Cosmochim. Acta* **2001**, *65* (17), 2853–2864.

(30) Kober, B.; Wessels, M.; Bollhofer, A.; Mangini, A. Pb isotopes in sediments of Lake Constance, Central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere. *Geochim. Cosmochim. Acta* **1999**, *63* (9), 1293–1303.

(31) Schaider, L. A.; Senn, D. B.; Brabander, D. J.; McCarthy, K. D.; Shine, J. P. Characterization of zinc, lead, and cadmium in mine waste: Implications for transport, exposure, and bioavailability. *Environ. Sci. Technol.* **2007**, *41* (11), 4164–4171.

(32) Emmanuel, S.; Erel, Y. Implications from concentrations and isotopic data for Pb partitioning processes in soils. *Geochim. Cosmochim. Acta* **2002**, *66* (14), 2517–2527.

(33) Steinmann, M.; Stille, P. Rare earth element behavior and Pb, Sr, Nd isotope systematics in a heavy metal contaminated soil. *Appl. Geochem.* **1997**, *12* (5), 607–623.

(34) Gallon, C.; Aggarwal, J.; Flegal, A. R. Comparison of mass discrimination correction methods and sample introduction systems for the determination of lead isotopic composition using a multicollector inductively coupled plasma mass spectrometer. *Anal. Chem.* **2008**, *80* (22), 8355–8363.

(35) Rankin, C. W.; Nriagu, J. O.; Aggarwal, J. K.; Arowolo, T. A.; Adebayo, K.; Flegal, A. R. Lead contamination in cocoa and cocoa products: Isotopic evidence of global contamination. *Environ. Health Perspect.* **2005**, *113* (10), 1344–1348.

(36) Schiff, K. C.; Weisberg, S. B. Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. *Mar. Environ. Res.* **1999**, *48* (2), 161–176.

(37) Andrews, S.; Sutherland, R. A. Cu, Pb and Zn contamination in Nuuanu watershed, Oahu, Hawaii. *Sci. Total Environ.* **2004**, *324*, 173–182.

(38) Hornberger, M. I.; Luoma, S. N.; van Geen, A.; Fuller, C.; Anima, R. Historical trends of metals in the sediments of San Francisco Bay, California. *Mar. Chem.* **1999**, *64*, 39–55.

(39) Daskalakis, K. D.; Oconnor, T. P. Normalization and elemental sediment contamination in the Coastal United States. *Environ. Sci. Technol.* **1995**, *29* (2), 470–477.

(40) Schropp, S. J.; Lewis, F. G.; Windom, H. L.; Ryan, J. D.; Calder, F. D.; Burney, L. C. Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. *Estuaries* **1990**, *13* (3), 227–235.

(41) Ettler, V.; Mihaljevic, M.; Sebek, O.; Molek, M.; Grygar, T.; Zeman, J. Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Pribram, Czech Republic. *Environ. Pollut.* **2006**, *142* (3), 409–417.

(42) Sutherland, R. A. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol.* **2000**, *39* (6), 611–627.

(43) Chow, T. J.; Johnston, M. S. Lead isotopes in gasoline and aerosols of Los Angeles Basin, California. *Science* **1965**, *147* (3657), 502–503.

(44) Shirahata, H.; Elias, R. W.; Patterson, C. C.; Koide, M. Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. *Geochim. Cosmochim. Acta* **1980**, *44* (2), 149–162.

(45) Gillett, N. P.; Weaver, A. J.; Zwiers, F. W.; Flannigan, M. D. Detecting the effect of climate change on Canadian forest fires. *Geophys. Res. Lett.* **2004**, *31*, L18211.

(46) Kim, Y.; Hatsushika, H.; Muskett, R. R.; Yamazaki, K. Possible effect of boreal wildfire soot on Arctic sea ice and Alaska glaciers. *Atmos. Environ.* **2005**, *39* (19), 3513–3520.

(47) Westerling, A. L.; Hidalgo, H. G.; Cayan, D. R.; Swetnam, T. W. Warming and earlier spring increase Western US forest wildfire activity. *Science* **2006**, *313* (5789), 940–943.

(48) IPCC. *Climate Change 2007: The Physical Science Basis*; Cambridge University Press: New York, 2007.

(49) Wang, Y. H.; Flannigan, M.; Anderson, K. Correlations between forest fires in British Columbia, Canada, and sea surface temperature of the Pacific Ocean. *Ecol. Model.* **2010**, *221* (1), 122–129.

(50) Marlon, J. R.; Bartlein, P. J.; Walsh, M. K.; Harrison, S. P.; Brown, K. J.; Edwards, M. E.; Higuera, P. E.; Power, M. J.; Anderson, R. S.; Briles, C.; Brunelle, A.; Carcaillet, C.; Daniels, M.; Hu, F. S.; Lavoie, M.; Long, C.; Minckley, T.; Richard, P. J. H.; Scott, A. C.; Shafer, D. S.; Tinner, W.; Umbanhowar, C. E.; Whitlock, C. Wildfire responses to abrupt climate change in North America. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106* (8), 2519–2524.

(51) McKenzie, D.; Gedalof, Z.; Peterson, D. L.; Mote, P. Climatic change, wildfire, and conservation. *Conserv. Biol.* **2004**, *18* (4), 890–902.

(52) Schuur, E. A. G.; Bockheim, J.; Canadell, J. G.; Euskirchen, E.; Field, C. B.; Goryachkin, S. V.; Hagemann, S.; Kuhry, P.; Lafleur, P. M.; Lee, H.; Mazhitova, G.; Nelson, F. E.; Rinke, A.; Romanovsky, V. E.; Shiklomanov, N.; Tarnocai, C.; Venevsky, S.; Vogel, J. G.; Zimov, S. A. Vulnerability of permafrost carbon to climate change: Implications for the global carbon cycle. *Bioscience* **2008**, *58* (8), 701–714.

(53) Flannigan, M. D.; Logan, K. A.; Amiro, B. D.; Skinner, W. R.; Stocks, B. J. Future area burned in Canada. *Clim. Change* **2005**, *72*, 1–16.

(54) Gilbert, N. Russia counts environmental cost of wildfires. *Nature* **2010**, DOI:10.1038/news.2010.404.

(55) Charles, D. Russia's forest fires ignite concerns about Chornobyl's legacy. *Science* **2010**, *329* (5993), 738–739.