

Lead Isotopes as a New Tracer for Detecting Coal Fly Ash in the Environment

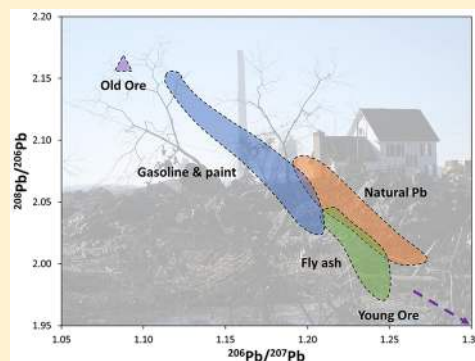
Zhen Wang,[†] Gary S. Dwyer,[†] Drew S. Coleman,[‡] and Avner Vengosh^{*,†}

[†]Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

[‡]Department of Geological Sciences, University of North Carolina, Chapel Hill, North Carolina 27599, United States

S Supporting Information

ABSTRACT: Lead (Pb) isotopes have been widely used to delineate Pb pollutants in the environment. Here, we present, for the first time, a systematic analysis of Pb isotopes in coal fly ash derived from coals from the three major coal-producing basins in the United States. Fly ash samples from Powder River Basin coals have higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (1.2271 ± 0.0086 , $n = 7$) than Appalachian Basin fly ash (1.2173 ± 0.0060 , $n = 16$), while Illinois Basin fly ash samples are much more variable (1.2270 ± 0.0140 , $n = 22$). The Pb isotopic signature of fly ash is distinguishable from that of major anthropogenic Pb sources in the United States, including leaded gasoline and paint, as well as the Pb isotope ratios of naturally occurring sediments and soils. Lead isotopic analysis of sediments from Sutton Lake in North Carolina, where other indicators have identified the occurrence of fly ash solids from unmonitored coal ash spills, shows a well-defined mixing between the Pb of unimpacted sediments and that of Appalachian Basin fly ash. This result further validates the applicability of Pb isotopes as a new tracer for detecting the occurrence of coal fly ash in the environment.



INTRODUCTION

Lead (Pb) is a globally recognized toxic pollutant that can pose risks to the environment and human health. Lead occurs in four stable isotopes, including ^{208}Pb (~52.4% of natural abundance), ^{206}Pb (~24.1%), and ^{207}Pb (~22.1%), which are three radiogenic isotopes produced by the radioactive decay chains of ^{232}Th ($t_{1/2} = 14$ billion years), ^{238}U ($t_{1/2} = 4.5$ billion years), and ^{235}U ($t_{1/2} = 0.7$ billion years), respectively, and one nonradiogenic isotope ^{204}Pb (~1.4%).^{1,2} The differences in the decay rates of nuclides within the ^{232}Th , ^{238}U , and ^{235}U decay chains, in addition to variable contents of U and Th and their ratios in rocks of different ages, result in large variations and distinctive Pb isotope ratios of terrestrial Pb reservoirs.^{1–3} Due to its relatively small mass difference between isotopes (Δmass), Pb does not undergo large isotopic fractionation during physical and chemical processes at Earth's surface conditions.^{3,4} Therefore, Pb isotopes have been widely used to determine the sources and pathways of various Pb pollutants in the environment.^{5–9}

Coal ash, also known as coal combustion residuals (CCRs), refers to the byproducts from burning coal, including fly ash, bottom ash, boiler slag, and flue gas desulfurization gypsum, among which fly ash is the most abundant. Coal ash has raised alarming environmental and human health concerns due to its elevated concentrations of hazardous elements such as As, Se, Cd, Cr, and Pb.^{10–13} In order to delineate the environmental impacts of coal ash, previous studies have explored various isotopic fingerprints (e.g., B, Sr, and Ra) as geochemical tools

to identify the presence and pathways of coal ash contamination in the environment.^{14–18} Lead isotopes in coal ash, however, have rarely been systematically documented.^{6,7,15} Although several studies have investigated the Pb isotopic compositions of coals and addressed their applications for assessing Pb pollution caused by coal combustion,^{19–23} very few have characterized the Pb isotopes of coal ash and studied its application for tracing coal ash occurrence in the environment.^{6,7,15}

In this paper, we provide, for the first time, a systematic analysis of Pb isotopes in representative coal fly ash samples derived from coals of the three major coal-producing basins in the United States, namely, the Appalachian Basin, Illinois Basin, and Powder River Basin,²⁴ which respectively accounted for 25.5%, 13.3%, and 43.2% of the total U.S. coal production in 2017.²⁵ We measured the Pb isotope ratios ($^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, and $^{206}\text{Pb}/^{207}\text{Pb}$) as well as the Pb, Th, and U concentrations of the fly ash samples. By integrating our data with existing Pb isotopic data of both naturally occurring sediments and soils and major anthropogenic sources (leaded gasoline and lead-based paint), this study aims to determine whether the Pb isotopic signature of fly ash is distinctive relative to both geogenic and

Received: August 14, 2019

Revised: October 15, 2019

Accepted: October 16, 2019

Published: October 16, 2019

anthropogenic Pb sources and if it is useful in tracing fly ash in the environment. In order to test this potential, we analyzed sediments at different distances from coal ash ponds from Sutton Lake in North Carolina, where other indicators have shown the impact by unmonitored coal ash spills.²⁶ We also measured sediments from Lake Waccamaw in North Carolina, which is used as a reference lake and has no coal ash ponds nearby.

MATERIALS AND METHODS

Sample Collection. Coal ash analyzed in this study includes 45 fly ash samples collected from 12 U.S. coal-fired power plants between 2004 and 2013 (Table S1).¹⁸ Based on accessibility, the fly ash samples were collected from different particle collection systems, namely, mechanical, baghouse filter, and electrostatic precipitator (ESP) (Table S1). The fly ash samples originated from coals in the Appalachian Basin ($n = 16$), Illinois Basin ($n = 22$), and Powder River Basin ($n = 7$). Feed coals from the Appalachian Basin and Illinois Basin are Pennsylvanian-age bituminous coal, whereas those from the Powder River Basin are Paleocene and Late Cretaceous-age sub-bituminous coal (Table S1).²⁴ Sediment samples previously collected from Sutton Lake ($n = 7$) and Lake Waccamaw ($n = 2$) in North Carolina were also included.²⁶

Pb isotope analysis. Fly ash and sediment samples were digested in a HF-HNO₃ mixture. Following digestion, all solutions were dried down and redissolved in 11 N HCl. The Pb, Th, and U concentrations were measured on a Thermo Fisher X-Series II inductively coupled plasma mass spectrometer (ICP-MS). The accuracy was assessed by measuring a coal fly ash standard reference material (SRM) NIST 1633c. Aliquots containing approximately 100 ng of Pb were taken from digested solutions and further prepared for elemental separation using Bio-Rad anion resin AG1×8 and 1.1 N HBr solution for sample loading and matrix washing. Lead was then eluted using 6 N HCl (see details in the Supporting Information). The separation process was conducted twice to ensure complete separation of Pb from other matrix constituents. All acids used in this study were optima grade. The detailed sample digestion and Pb column separation procedures are available in the Supporting Information. The Pb isotope analysis (²⁰⁸Pb, ²⁰⁷Pb, ²⁰⁶Pb, and ²⁰⁴Pb) was performed on a Triton thermal ionization mass spectrometer (TIMS) at Duke University, using Faraday cups and operating in static mode. Separated and purified Pb was loaded with H₃PO₄-acidified silica gel onto degassed single Re filaments. To correct for instrumental mass fractionation, common Pb standard NIST SRM 981 was measured regularly over the course of analysis. The raw data of all samples were corrected for instrument mass fractionation. The mass bias was determined from replicate measurements of NIST 981 ($n = 21$) and normalization to the expected values.²⁷ The analytical uncertainties (2SD) for ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁶Pb, and ²⁰⁶Pb/²⁰⁷Pb are 0.0109, 0.0032, 0.0026, 0.0003, and 0.0001, respectively (Table S2).

RESULTS AND DISCUSSION

Characterization of Pb Isotopes in Fly Ash from the United States. The Pb isotope ratios display variations outside of analytical uncertainty (²⁰⁸Pb/²⁰⁴Pb from 38.5942 to 39.3406 ± 0.1664, ²⁰⁷Pb/²⁰⁴Pb from 15.6607 to 15.7307 ± 0.0165, ²⁰⁶Pb/²⁰⁴Pb from 18.9236 to 19.6090 ± 0.1999,

²⁰⁸Pb/²⁰⁶Pb from 1.9760 to 2.0431 ± 0.0215, and ²⁰⁶Pb/²⁰⁷Pb from 1.2079 to 1.2479 ± 0.0117) (Table S3). Specifically, the mean ²⁰⁶Pb/²⁰⁷Pb ratio for fly ash samples derived from Powder River Basin (PRB) coals is 1.2271, which is higher than that of fly ash originating from Appalachian Basin (APP) coals (1.2173) (Table S3). In contrast, fly ash samples from Illinois Basin (ILL) coals show a considerable spread of ²⁰⁶Pb/²⁰⁷Pb ratios from 1.2079 to 1.2479, which encompasses the range of all the investigated samples (Table S3, Figure 1).

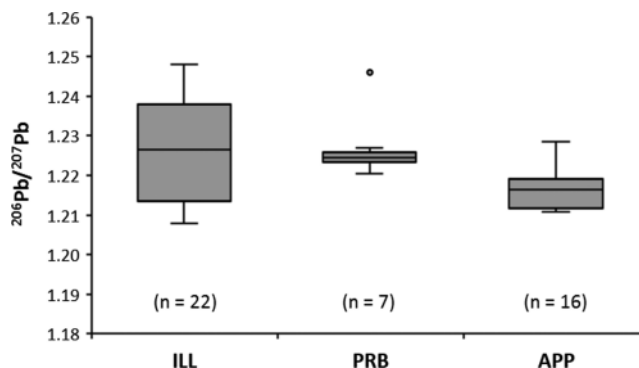


Figure 1. Boxplots of Pb isotope (²⁰⁶Pb/²⁰⁷Pb) ratios in fly ash samples derived from Illinois Basin (ILL), Powder River Basin (PRB), and Appalachian Basin (APP) coals. Summary statistics for displayed data are presented in Table S3.

Consistent with previous studies of coal,^{19,21–23} our data show that there is also no clear correlation between the ²⁰⁶Pb/²⁰⁷Pb ratios of fly ash and the respective coal age. A two-tailed *t* test indicates that the ²⁰⁶Pb/²⁰⁷Pb ratios of APP fly ash are statistically different from those of PRB fly ash and ILL fly ash ($p < 0.01$), whereas PRB and ILL fly ash samples are not statistically different from each other despite source coals of different ages (Table S1).

Lead concentrations in fly ash samples vary from 25.3 to 308.0 mg/kg. The mean Pb concentrations of Appalachian fly ash samples (88.4 ± 29.1 mg/kg) and Illinois fly ash samples (138.2 ± 56.9 mg/kg) are greater than that of Powder River Basin fly ash samples (47.3 ± 18.2 mg/kg) (Table S3). For the entire sample set of fly ash, lead concentrations show high correlations with ²¹⁰Pb activities ($r = 0.65$, $p = 0.06$) and with ²¹⁰Pb/²²⁶Ra ratios ($r = 0.81$, $p < 0.01$) that were reported for the same batch of samples,¹⁸ although the fly ash samples from the Illinois Basin display a less significant correlation between ²¹⁰Pb activities and Pb concentrations ($r = 0.24$, $p = 0.36$) by having two distinctive trends (Figure S1A–D). This confirms earlier observations on the volatilization of Pb during coal combustion, with volatilized Pb gradually condensing on finer fly ash particles at lower temperatures, resulting in a progressive enrichment of Pb and higher ²¹⁰Pb/²²⁶Ra activity ratios in fly ash.^{18,28} In contrast, across all samples, Pb stable isotope ratios are not correlated with Pb concentrations (e.g., for ²⁰⁶Pb/²⁰⁷Pb, $r = 0.24$, $p = 0.12$; Figure S2A,B) and have relatively moderate correlations with ²¹⁰Pb activities ($r = 0.31$, 0.66 , $p = 0.06$, < 0.01 ; Figure S1B,C, respectively) and ²¹⁰Pb/²²⁶Ra ratios ($r = 0.09$, 0.37 , $p < 0.01$; Figure S1E,F, respectively), largely due to higher correlations between Pb stable isotopes and ²¹⁰Pb activities for the Illinois fly ash samples ($r = 0.72$, 0.74 , $p < 0.01$; Figure S1B,C, respectively). The distinct characteristics of Illinois fly ash samples might be attributed to a greater heterogeneity of corresponding feed coal

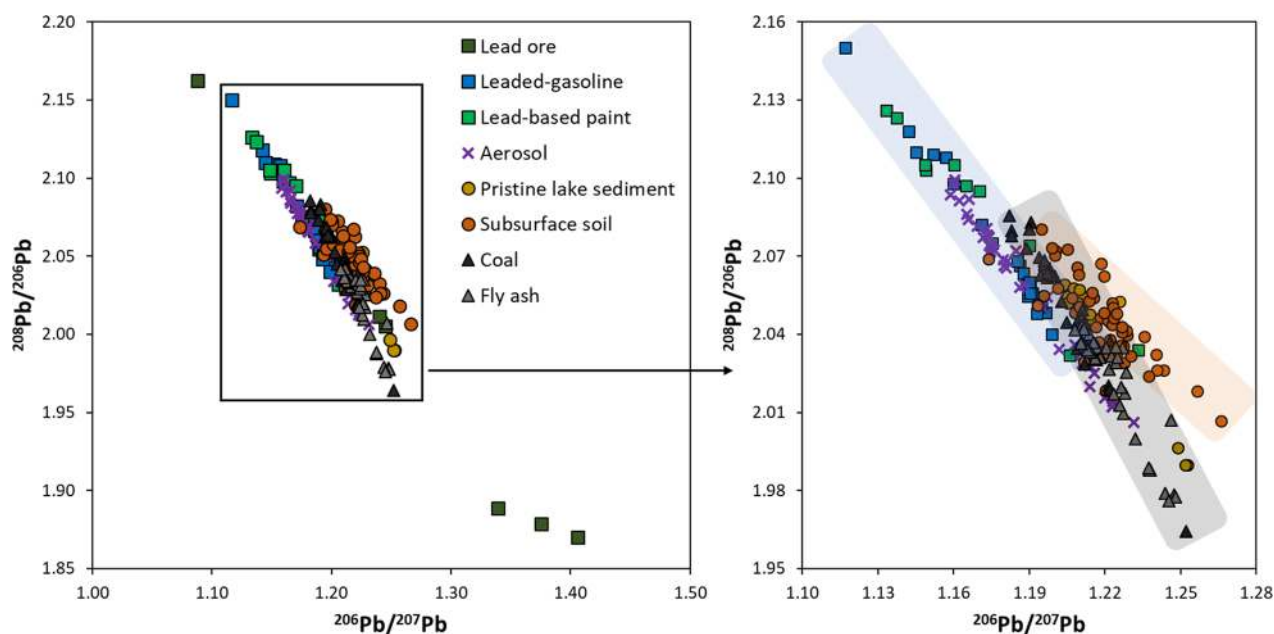


Figure 2. $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in fly ash samples investigated in this study compared to other Pb sources in the United States. The displayed data of fly ash samples are shown in Table S3. Details of the compiled data for the other Pb sources are provided in Table S4 and from refs 19,22, and 30–42. Note the three different slopes of the anthropogenic Pb (blue), coal and fly ash (gray), and natural or geogenic (orange) domains.

sources. Overall, this analysis suggests that the condensation of Pb onto fly ash during coal combustion may not cause significant Pb stable isotope fractionation, which should be further verified by measuring paired coal and coal ash samples. Furthermore, Pb stable isotopes are highly correlated with Th/U ($r = 0.62$, $p < 0.01$) and Th/Pb ratios ($r = 0.84$, $p < 0.01$) for the entire sample set, with the three basins having distinguishable trends and Illinois samples having a greater influence on the overall statistics of Th/U versus $^{208}\text{Pb}/^{206}\text{Pb}$ than the other two (Figure S2C,D). This indicates that the Pb isotopic variations of fly ash most likely correspond to the original geology of coal-forming basins. In summary, our data suggest that Pb concentrations in fly ash reflect the Pb concentrations in the original feed coals combined with the Pb enrichment in fly ash during combustion, whereas the stable Pb isotope ratios mimic the feed coal geology.

Distinction of Pb Isotope Ratios in Fly Ash Relative to Other Pb Sources in the United States. We compiled available Pb isotopic data of major anthropogenic and geogenic Pb sources in the United States (Table S4, Figure 2). These sources include lead ore deposits,^{29,30} leaded gasoline,^{31–33} lead-based paint,^{34–36} coals,^{19,22} atmospheric aerosols,^{37,38} bottom-layer lake sediments,^{39,40} and subsurface soils.⁴¹ Leaded gasoline and paint once dominated the anthropogenic sources of Pb in the environment, with Pb additives primarily originating from Pb ore bodies, which makes the isotopic ratios of this anthropogenic Pb distinct from that of natural sediment and soil Pb.^{2,40,42,43}

The Pb isotopes of ore deposits in the United States are highly variable, with $^{208}\text{Pb}/^{206}\text{Pb}$ ranging from 1.8698 to 2.1623 and $^{206}\text{Pb}/^{207}\text{Pb}$ from 1.0878 to 1.4060 (Table S4), corresponding to the geological ages of ores (from ~280 Ma to ~1300 Ma).^{29,30} The other sources all fall within the range of isotope ratios of the ores and define three separate trends (indicated with different colors in Figure 2). The ratios for leaded gasoline follow a trend (blue band in Figure 2) with

$^{208}\text{Pb}/^{206}\text{Pb}$ varying from 2.040 to 2.150 and $^{206}\text{Pb}/^{207}\text{Pb}$ from 1.117 to 1.199. The lead-based paint ratios (2.032–2.126 for $^{208}\text{Pb}/^{206}\text{Pb}$ and 1.133–1.233 for $^{206}\text{Pb}/^{207}\text{Pb}$) largely overlap this trend, but the ratios are more variable (Figure 2, Table S4).

Surface-layer lake sediments and surface soils are more likely to be exposed to anthropogenic Pb inputs, whereas bottom-layer lake sediments and subsurface soils are considered to be more pristine and reflect the natural Pb (bedrock-derived).^{39–43} The Pb isotopic data of bottom-layer sediments from the Great Lakes region and the Chesapeake Bay, as well as subsurface soils from the states where APP, ILL, and PRB feed coals were mined, are referenced here as natural Pb (Table S4). With a few exceptions, the deep lake sediments and subsurface soils are generally higher in the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio than the fly ash samples for a given $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and define a different domain (orange-banded) from the gasoline and paint (Figure 2). The isotope ratios of fly ash samples in this study are slightly divergent from those of United States coals reported in previous studies, yet together they form a third trend (gray band) that is distinct from the other two trends (Figure 2). Although there is some overlap, the Pb isotope ratios of fly ash are largely distinguishable from those of anthropogenic Pb sources, as well as those of natural Pb. The aerosols display an overlap with the trend of gasoline (Figure 2), except that they have higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, specifically in aerosols from the eastern and middle United States (Table S4). This isotopic shift in aerosols may be attributed to a greater contribution from coal combustion in the eastern than western part of the United States.^{37,38}

Application of Pb Isotopes for Tracing Fly Ash in the Environment. The sediments in Sutton Lake have been shown to contain fly ash solids from unmonitored coal ash spills, whereas those of a nearby lake, Lake Waccamaw, have not been impacted, and therefore, are used as a reference.²⁶ The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of Sutton Lake

sediments vary between 1.2042 and 1.2109 and from 2.0416 to 2.0521, respectively, and are different from the Pb isotopic composition of sediments from Lake Waccamaw (mean $^{206}\text{Pb}/^{207}\text{Pb} = 1.2032$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.0528$) (Table S5). As shown in Figure 3, the Pb isotope ratios of Sutton Lake

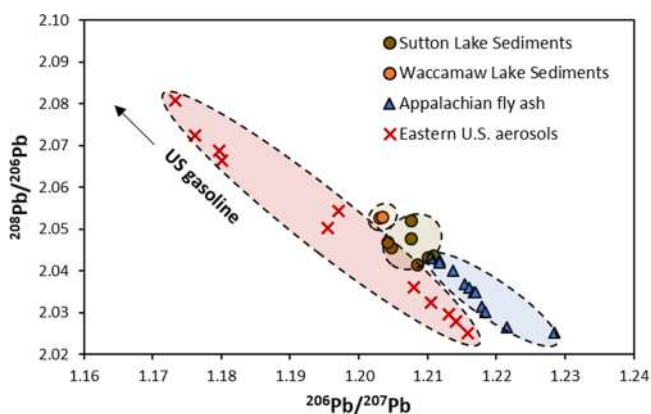


Figure 3. $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of sediments from Sutton Lake and Lake Waccamaw in North Carolina as compared to the Appalachian fly ash and the eastern United States aerosols (data from refs 38 and 39). The displayed data are shown in Table S4 and Table S5. Note that the Pb isotope ratios of the Sutton lake sediments are between the reference lake (Lake Waccamaw) and the Appalachian fly ash, suggesting a mixing between the background sediments and fly ash.

sediments clearly lie between the ratios of unimpacted Lake Waccamaw sediments and fly ash samples derived from Appalachian Basin coal, the major source of coal used in North Carolina power plants.⁴⁴ In addition, the Pb isotope ratios of aerosols from the eastern United States follow a subparallel trend to that of APP fly ash and slightly overlap the area of Sutton Lake sediments (Figure 3).

Atmospheric deposition of Pb derived from the burning of leaded gasoline and coal has been viewed as a major source of anthropogenic Pb in lake surface sediments.^{2,39,40} Although there may well be some contributions from aerosols, given the geographic proximity of Sutton Lake and Lake Waccamaw, we assume that atmospheric Pb deposition would have contributed equally to the two lakes. Further, we suggest that the Pb isotopic composition of Sutton Lake sediments resulted from a two-component mixing between the unimpacted sediments and the APP fly ash. Based on a simple binary mixing model used to estimate the contribution of anthropogenic Pb sources to the natural systems by using Pb isotopes data,^{45–48} we calculated the relative contributions of Pb from the APP fly ash to the Sutton Lake sediments (details about the model are outlined in the Supporting Information, Table S5). The relative contributions of Pb from fly ash vary from 6.7% to 54.6%, with higher percentages being observed in sediments located closer to the coal ash ponds (Table S5, Figure S3).²⁶ The isotope-based Pb contribution from the APP fly ash is also highly correlated ($r = 0.9037$, $p < 0.01$) with the percentages of fly ash particles in the sediments independently determined via physical observations (Table S5, Figure S3).²⁶

Overall, this study shows the distinctive Pb isotope signature of fly ash relative to other anthropogenic Pb sources and natural Pb in the United States and demonstrates the sensitivity of Pb isotopes for detecting, and even quantifying, the occurrence of fly ash in the environment. Future studies

should further investigate the Pb isotope ratios of paired feed coal and coal ash samples, focus on the variations of Pb isotopes in samples within and between different coal basins (i.e., the variability of Illinois Basin samples), and explore the applicability of this new proposed tracer and the magnitude of Pb pollution from current and legacy coal combustion.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.9b00512.

Details on analytical techniques, five tables, and three figures. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vengosh@duke.edu.

ORCID

Avner Vengosh: 0000-0001-8928-0157

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the Nicholas School of the Environment at Duke University. The authors would like to thank Ryan Mills from UNC for helping in the Pb isotope analysis. We thank three anonymous reviewers for their thorough and constructive comments that greatly improved the quality of this paper.

■ REFERENCES

- (1) Long, L. Lead Isotopes. In *Encyclopedia of Geochemistry*; Kluwer Academic Publishers, 1999.
- (2) Komárek, M.; Ettler, V.; Chrástný, V.; Mihaljevič, M. Lead Isotopes in Environmental Sciences: A Review. *Environ. Int.* **2008**, *34* (4), 562–577.
- (3) Faure, G. *Principles of Isotope Geology*, second ed.; Wiley, 1986.
- (4) Charalampides, G.; Manoliadis, O. Sr and Pb Isotopes as Environmental Indicators in Environmental Studies. *Environ. Int.* **2002**, *28* (3), 147–151.
- (5) Veysseyre, A. M.; Bollhöfer, A. F.; Rosman, K. J. R.; Ferrari, C. P.; Boutron, C. F. Tracing the Origin of Pollution in French Alpine Snow and Aerosols Using Lead Isotopic Ratios. *Environ. Sci. Technol.* **2001**, *35* (22), 4463–4469.
- (6) Chen, J.; Tan, M.; Li, Y.; Zhang, Y.; Lu, W.; Tong, Y.; Zhang, G.; Li, Y. A Lead Isotope Record of Shanghai Atmospheric Lead Emissions in Total Suspended Particles during the Period of Phasing out of Leaded Gasoline. *Atmos. Environ.* **2005**, *39* (7), 1245–1253.
- (7) Liang, F.; Zhang, G.; Tan, M.; Yan, C.; Li, X.; Li, Y.; Li, Y.; Zhang, Y.; Shan, Z. Lead in Children's Blood Is Mainly Caused by Coal-Fired Ash after Phasing out of Leaded Gasoline in Shanghai. *Environ. Sci. Technol.* **2010**, *44* (12), 4760–4765.
- (8) Sherman, L. S.; Blum, J. D.; Dvonch, J. T.; Gratz, L. E.; Landis, M. S. The Use of Pb, Sr, and Hg Isotopes in Great Lakes Precipitation as a Tool for Pollution Source Attribution. *Sci. Total Environ.* **2015**, *502*, 362–374.
- (9) Kousehlar, M.; Widom, E. Sources of Metals in Atmospheric Particulate Matter in Tehran, Iran: Tree Bark Biomonitoring. *Appl. Geochem.* **2019**, *104*, 71–82.
- (10) Eary, L. E.; Rai, D.; Mattigod, S. V.; Ainsworth, C. C. Geochemical Factors Controlling the Mobilization of Inorganic Constituents from Fossil Fuel Combustion Residues: II. Review of the Minor Elements. *J. Env. Qual* **1990**, *19*, 202–214.

- (11) Querol, X.; Fernández-Turiel, J.; López-Soler, A. Trace Elements in Coal and Their Behaviour during Combustion in a Large Power Station. *Fuel* **1995**, *74* (3), 331–343.
- (12) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Deonarine, A.; Bergin, M.; Kravchenko, J. Survey of the Potential Environmental and Health Impacts in the Immediate Aftermath of the Coal Ash Spill in Kingston, Tennessee. *Environ. Sci. Technol.* **2009**, *43* (16), 6326–6333.
- (13) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Deonarine, A. Environmental Impacts of the Coal Ash Spill in Kingston, Tennessee: An 18-Month Survey. *Environ. Sci. Technol.* **2010**, *44* (24), 9272–9278.
- (14) Hurst, R. W.; Davis, T. E.; Elseewi, A. A. Strontium Isotopes as Tracers of Coal Combustion Residue in the Environment. *Eng. Geol.* **1991**, *30* (1), 59–77.
- (15) Hurst, R. W.; Davis, T. E.; Elseewi, A. A. Strontium and Lead Isotopes as Monitors of Fossil Fuel Dispersion. In *Trace Elements in Coal and Coal Combustion Residues*; Keefer, R. F.; Sajwan, K. S., Eds.; CRC Press, 1993, Chapter 5.
- (16) Ruhl, L. S.; Dwyer, G. S.; Hsu-Kim, H.; Hower, J. C.; Vengosh, A. Boron and Strontium Isotopic Characterization of Coal Combustion Residuals: Validation of New Environmental Tracers. *Environ. Sci. Technol.* **2014**, *48* (24), 14790–14798.
- (17) Brandt, J. E.; Lauer, N. E.; Vengosh, A.; Bernhardt, E. S.; Di Giulio, R. T. Strontium Isotope Ratios in Fish Otoliths as Biogenic Tracers of Coal Combustion Residual Inputs to Freshwater Ecosystems. *Environ. Sci. Technol. Lett.* **2018**, *5* (12), 718–723.
- (18) Lauer, N. E.; Hower, J. C.; Hsu-Kim, H.; Taggart, R. K.; Vengosh, A. Naturally Occurring Radioactive Materials in Coals and Coal Combustion Residuals in the United States. *Environ. Sci. Technol.* **2015**, *49* (18), 11227–11233.
- (19) Chow, T. J.; Earl, J. L. Lead Isotopes in North American Coals. *Science* **1972**, *176* (4034), 510–511.
- (20) Farmer, J. G.; Eades, L. J.; Graham, M. C. The Lead Content and Isotopic Composition of British Coals and Their Implications for Past and Present Releases of Lead to the UK Environment. *Environ. Geochem. Health* **1999**, *21* (3), 257–272.
- (21) Díaz-Somoano, M.; Suárez-Ruiz, I.; Alonso, J. I. G.; Ruiz Encinar, J.; López-Antón, M. A.; Martínez-Tarazona, M. R. Lead Isotope Ratios in Spanish Coals of Different Characteristics and Origin. *Int. J. Coal Geol.* **2007**, *71* (1), 28–36.
- (22) Díaz-Somoano, M.; Kylander, M. E.; López-Antón, M. A.; Suárez-Ruiz, I.; Martínez-Tarazona, M. R.; Ferrat, M.; Kober, B.; Weiss, D. J. Stable Lead Isotope Compositions In Selected Coals From Around The World And Implications For Present Day Aerosol Source Tracing. *Environ. Sci. Technol.* **2009**, *43* (4), 1078–1085.
- (23) Bi, X.-Y.; Li, Z.-G.; Wang, S.-X.; Zhang, L.; Xu, R.; Liu, J.-L.; Yang, H.-M.; Guo, M.-Z. Lead Isotopic Compositions of Selected Coals, Pb/Zn Ores and Fuels in China and the Application for Source Tracing. *Environ. Sci. Technol.* **2017**, *51* (22), 13502–13508.
- (24) East, J. A. *Coal Fields of the Conterminous United States - National Coal Resource Assessment Updated Version*; Open-File Report; USGS Numbered Series 2012-1205; U.S. Geological Survey: Reston, VA, 2013.
- (25) *Annual Coal Report 2017*; U.S. Energy Information Administration: Washington, DC, 2018; p 83.
- (26) Vengosh, A.; Cowan, E. A.; Coyte, R. M.; Kondash, A. J.; Wang, Z.; Brandt, J. E.; Dwyer, G. S. Evidence for Unmonitored Coal Ash Spills in Sutton Lake, North Carolina: Implications for Contamination of Lake Ecosystems. *Sci. Total Environ.* **2019**, *686*, 1090–1103.
- (27) Yuan, H.; Yuan, W.; Cheng, C.; Liang, P.; Liu, X.; Dai, M.; Bao, Z.; Zong, C.; Chen, K.; Lai, S. Evaluation of Lead Isotope Compositions of NIST NBS 981 Measured by Thermal Ionization Mass Spectrometer and Multiple-Collector Inductively Coupled Plasma Mass Spectrometer. *Solid Earth Sci.* **2016**, *1* (2), 74–78.
- (28) Zielinski, R. A.; Budahn, J. R. Radionuclides in Fly Ash and Bottom Ash: Improved Characterization Based on Radiography and Low Energy Gamma-Ray Spectrometry. *Fuel* **1998**, *77* (4), 259–267.
- (29) Sangster, D. F.; Outridge, P. M.; Davis, W. J. Stable Lead Isotope Characteristics of Lead Ore Deposits of Environmental Significance. *Environ. Rev.* **2000**, *8* (2), 115–147.
- (30) Leach, D. L.; Bradley, D. C.; Huston, D.; Pisarevsky, S. A.; Taylor, R. D.; Gardoll, S. J. Sediment-Hosted Lead-Zinc Deposits in Earth History. *Econ. Geol. Bull. Soc. Econ. Geol.* **2010**, *105* (3), 593–625.
- (31) Chow, T. J.; Johnstone, M. S. Lead Isotopes in Gasoline and Aerosols of Los Angeles Basin, California. *Science* **1965**, *147* (3657), 502–503.
- (32) Sherrell, R. M.; Boyle, E. A.; Hamelin, B. Isotopic Equilibration between Dissolved and Suspended Particulate Lead in the Atlantic Ocean: Evidence from ²¹⁰Pb and Stable Pb Isotopes. *J. Geophys. Res.* **1992**, *97* (C7), 11257–11268.
- (33) Dunlap, C. E.; Bouse, R.; Flegal, A. R. Past Leaded Gasoline Emissions as a Nonpoint Source Tracer in Riparian Systems: A Study of River Inputs to San Francisco Bay. *Environ. Sci. Technol.* **2000**, *34* (7), 1211–1215.
- (34) Rabinowitz, M. B. Stable Isotope Mass Spectrometry in Childhood Lead Poisoning. *Biol. Trace Elem. Res.* **1987**, *12* (1), 223–229.
- (35) Viczian, M.; Laszity, A.; Barnes, R. M. Poisoning by Inductively Coupled Plasma Mass Spectrometry. Verification and Case Studies. *J. Anal. At. Spectrom.* **1990**, *5*, 8.
- (36) Jaeger, R. J.; Weiss, A. L.; Manton, W. I. Isotopic Ratio Analysis in Residential Lead-Based Paint and Associated Surficial Dust. *J. Toxicol., Clin. Toxicol.* **1998**, *36* (7), 691–703.
- (37) Bollhöfer, A.; Rosman, K. J. R. Isotopic Source Signatures for Atmospheric Lead: The Northern Hemisphere. *Geochim. Cosmochim. Acta* **2001**, *65* (11), 1727–1740.
- (38) Bollhöfer, A.; Rosman, K. J. R. The Temporal Stability in Lead Isotopic Signatures at Selected Sites in the Southern and Northern Hemispheres. *Geochim. Cosmochim. Acta* **2002**, *66* (8), 1375–1386.
- (39) Graney, J. R.; Halliday, A. N.; Keeler, G. J.; Nriagu, J. O.; Robbins, J. A.; Norton, S. A. Isotopic Record of Lead Pollution in Lake Sediments from the Northeastern United States. *Geochim. Cosmochim. Acta* **1995**, *59* (9), 1715–1728.
- (40) Marcantonio, F.; Zimmerman, A.; Xu, Y.; Canuel, E. A Pb Isotope Record of Mid-Atlantic US Atmospheric Pb Emissions in Chesapeake Bay Sediments. *Mar. Chem.* **2002**, *77* (2), 123–132.
- (41) Reimann, C.; Smith, D. B.; Woodruff, L. G.; Flem, B. Pb-Concentrations and Pb-Isotope Ratios in Soils Collected along an East–West Transect across the United States. *Appl. Geochem.* **2011**, *26* (9), 1623–1631.
- (42) 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.
- (43) 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.
- (44) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Schwartz, G.; Romanski, A.; Smith, S. D. The Impact of Coal Combustion Residue Effluent on Water Resources: A North Carolina Example. *Environ. Sci. Technol.* **2012**, *46* (21), 12226–12233.
- (45) Monna, F.; Lancelot, J.; Croudace, I. W.; Cundy, A. B.; Lewis, J. T. Pb Isotopic Composition of Airborne Particulate Material from France and the Southern United Kingdom: Implications for Pb Pollution Sources in Urban Areas. *Environ. Sci. Technol.* **1997**, *31* (8), 2277–2286.
- (46) Emmanuel, S.; Erel, Y. Implications from Concentrations and Isotopic Data for Pb Partitioning Processes in Soils. *Geochim. Cosmochim. Acta* **2002**, *66* (14), 2517–2527.
- (47) Ettler, V.; Mihaljevič, M.; Komárek, M. ICP-MS Measurements of Lead Isotopic Ratios in Soils Heavily Contaminated by Lead Smelting: Tracing the Sources of Pollution. *Anal. Bioanal. Chem.* **2004**, *378* (2), 311–317.
- (48) Hou, X.; Parent, M.; Savard, M. M.; Tassé, N.; Bégin, C.; Marion, J. Lead Concentrations and Isotope Ratios in the

Exchangeable Fraction: Tracing Soil Contamination near a Copper Smelter. *Geochem.: Explor., Environ., Anal.* **2006**, *6* (2–3), 229–236.