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Isotopic Signatures and Outputs of Lead from Coal Fly Ash Disposal in China, India, and the United States

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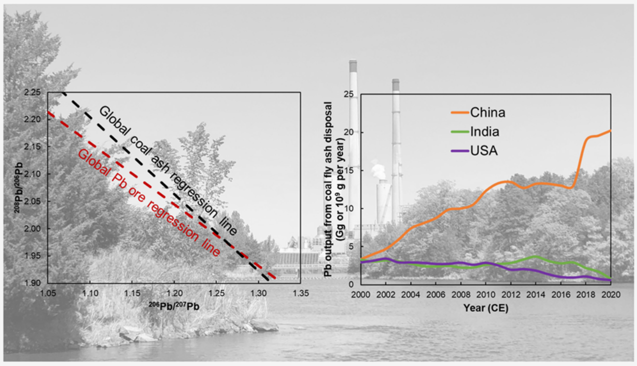

ABSTRACT: Despite extensive research and technology to reduce the atmospheric emission of Pb from burning coal for power generation, minimal attention has been paid to Pb associated with coal ash disposal in the environment. This study investigates the isotopic signatures and output rates of Pb in fly ash disposal in China, India, and the United States. Pairwise comparison between feed coal and fly ash samples collected from coal-fired power plants from each country shows that the Pb isotope composition of fly ash largely resembles that of feed coal, and its isotopic distinction allows for tracing the release of Pb from coal fly ash into the environment. Between 2000 and 2020, approx. 236, 56, and 46 Gg Pb from fly ash have been disposed in China, India, and the U.S., respectively, posing a significant environmental burden. A Bayesian Pb isotope mixing model shows that during the past 40 to 70 years, coal fly ash has contributed significantly higher Pb (∼26%) than leaded gasoline (∼7%) to Pb accumulation in the sediments of five freshwater lakes in North Carolina, U.S.A. This implies that the release of disposed coal fly ash Pb at local and regional scales can outweigh that of other anthropogenic Pb sources.

KEYWORDS: *lead (Pb) outputs, coal combustion, fly ash disposal, isotopic compositions, mixing model, environmental impacts*

1. INTRODUCTION

Lead (Pb) is a globally recognized toxic metal, and exposure to Pb can induce adverse effects on both ecological and human health. Human activities have greatly altered the biogeochemical cycle of Pb at the Earth's surface.[1,2] For instance, it was estimated that anthropogenic sources of Pb account for nearly 60% of the total natural Pb environmental releases.[3] While the human production, consumption, and release of Pb has proceeded for thousands of years (i.e., silver ore mining), combustion of leaded gasoline, along with nonferrous metal smelting, coal burning, and waste incineration has dominated the emission of anthropogenic Pb to the environment in recent history.[4−6] Among various anthropogenic sources, coal combustion plays an important role in influencing the Pb release and its biogeochemical cycling in the environment, particularly since the worldwide phasing out of leaded gasoline.[2,3] For example, coal combustion in China has contributed over 50% to the total anthropogenic Pb budget since the nationwide phase-out of leaded gasoline in 2000.[7]

Coal ash generally refers to the solid waste products generated from coal combustion for power generation, which is primarily composed of fly ash, bottom ash, boiler slag, and flue gas desulfurization products.[8] Despite the increasing recycling of coal ash for both industrial and agricultural uses in recent years,[9−12] a significant proportion has been disposed of in the environment, mainly via disposal facilities including surface impoundments and landfills. The impacts of coal ash on the environment have been demonstrated by catastrophic accidents, such as coal ash spills from the Tennessee Valley Authority (TVA) in Kingston, Tennessee in 2008,[13−17] and Duke Energy in Eden, North Carolina in 2014.[18,19] Chronic release of coal ash contaminants such as As and Se to the environment could also have adverse effects, as shown by the leaking of effluents from surface impoundments and landfills and direct discharge into aquatic ecosystems.[20−24] An increasing frequency of extreme weather events (e.g., hurricanes) and their devastating flooding aftermath increases the potential ecological and human health risks posed by the release of coal ash contaminants.[24,25]

One of the greatest environmental and human health concerns about disposed coal ash stems from its enrichment of many toxic trace elements (e.g., Hg, Pb, As, Se) during coal combustion and their potential leachability and mobiliza-

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tion.[22,25,26] Lead is one of the most noteworthy trace elements in coal and is categorized as a semivolatile element and tends to be bound to fine particulates and transported with flue gas. Lead is enriched in fly ash through condensation of volatiles from flue gas.[27−31] Modern coal-fired power plants are typically equipped with high-efficiency air pollution control devices (APCDs), such as cold-side electrostatic precipitators (ESP), fabric filters (FF), and wet flue gas desulfurization (WFGD) systems, which have markedly reduced the emission of Pb and other toxic elements to the atmosphere.[31−35] However, such a decrease in Pb emission with improved efficiency of APCDs can be expected to lead to an increase of Pb in coal fly ash waste. Considering the large portion of coal fly ash disposed of in the environment, the amount of Pb associated with it could be significant. Despite the extensive studies on the inventory of Pb emissions to the atmosphere from coal-fired power plants,[33,36−39] the output of Pb associated with coal fly ash disposal has not been fully quantified. This is of great importance because many of the coal ash disposal facilities continue to release coal ash and associated toxic metals including Pb into the environment.[21,23,24]

Variations in Pb isotopic composition (e.g., $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) can provide valuable insights into the sources and cycling of Pb in the environment.[5,40] In general, different geological reservoirs of different formation ages may have distinct Pb isotope signatures, which also depend on their initial Pb content and parent/daughter radionuclide ratios (i.e., U/Pb, Th/Pb, and U/Th ratios).[40,41] Previous studies have investigated the Pb isotopic signatures of coals of different origins,[42−46] and to a lesser extent, several studies have also reported the Pb isotope compositions of coal fly ash.[47−50] However, only a few studies have demonstrated the application of Pb isotopes to quantify the Pb contribution from coal fly ash to the environment.[50,51]

This study aims to fill the data and knowledge gap by (1) characterizing the Pb isotope signatures of coal and coal ash samples sourced from China, India, and the U.S. with the synthesis of both newly measured data in this study and the existing data in the literature; (2) providing a quantitative estimate of the Pb output associated with coal fly ash disposal in each of the three countries between 2000 and 2020; and (3) demonstrating a case study by using Pb isotopes in a Bayesian mixing model (i.e., MixSAIR) to quantify the contribution and output of Pb sourced from coal fly ash within the bottom sediments of five freshwater lakes in North Carolina, U.S.A. Collectively, this study intends to provide novel information on the present importance of coal fly ash Pb pollution to the environment in multiple countries, as well as to provide an innovative example of how to best quantify coal fly ash Pb pollution that can be applied globally.

2. MATERIALS AND METHODS

2.1. Sample Collection. Paired samples of feed coal and coal ash (i.e., fly ash and bottom ash) were collected for this study from multiple coal-fired power plants in China ($n = 14$), the U.S. ($n = 8$), and India ($n = 3$). Detailed sampling information is provided in the Supporting Information Table S1. The types of boilers, i.e., pulverized coal (PC) and circulating fluidized bed (CFB), and particulate matter control devices, i.e., electrostatic precipitator (ESP) and fabric fiber (FF), were noted where available. All sampled coal-fired power plants and/or units were in active operation during the period of sampling. Note that, in many cases, multiple fly ash and/or bottom ash samples were collected at the same power plants/units, either directly from different rows of the ESP or from different locations of the ash pile. Additionally, sediment samples were retrieved from cores of five freshwater lakes in North Carolina, U.S.A. (i.e., Hyco Lake, Mayo Lake, Belews Lake, Mountain Island Lake, and Lake Sutton; Figure S1). All of the five lakes are manmade reservoirs built between the 1960s and 1980s primarily for providing cooling water to the adjacent coal-fired power plants.[24] The pre-impoundment portion of the cores was characterized by sandy silts in lithology while the lacustrine portion was mainly clayey sediments.[24] More detailed core sampling information as well as the chronology determination of each sediment core can be found in a previous study.[24]

2.2. Pb Concentration and Isotope Analysis. Feed coal samples were first combusted in a muffle furnace at 500 °C for 4 h to remove organic matter, after which the loss on ignition (LOI, wt %) was recorded. The resultant coal ash from laboratory combustion, fly ash and bottom ash collected from coal-fired power plants, and lake sediment samples were fully digested using a mixture of concentrated hydrofluoric acid (HF), nitric acid (HNO_3), and hydrogen peroxide (H_2O_2) as reported in previous studies.[23,50] The concentration of Pb was measured on an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Fisher X-Series II) at Duke University. For the purpose of QA/QC, standard reference materials (SRM) with certified Pb concentration were digested and measured along with samples, including a bituminous coal standard (SRM 1632e), a coal fly ash standard (SRM 1633c), and a soil standard (SRM 2711a) from the National Institute of Standards and Technology (NIST). The efficiency of digestion and accuracy of measurement can be evidenced by the average recovery of Pb from repeated measurements: 99.8% ($n = 5$) for SRM 1632e, 101.3% ($n = 10$) for SRM 1633c, and 96.7% ($n = 14$) for SRM 2711a, respectively. The precision of analysis is reflected by the low coefficient of variations (<5%) from replicate runs of both samples and SRMs.

Aliquots of the digested solution of each sample were taken for Pb column separation and purification using hydrobromic acid (HBr) as the rinsing solution and hydrochloric acid (HCl) as the eluting solution.[50] The Pb isotope ratios (i.e., $^{208}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$, and $^{206}Pb/^{207}Pb$) were measured on a high-resolution thermal ionization mass spectrometer (TIMS, Thermo Fisher Triton) at Duke University, equipped with Faraday cups and operated in static mode. A common Pb standard SRM 981 from NIST was measured regularly over the course of analysis (2020−2022, $n = 112$), which yielded an average mass bias of 0.14% for all isotope ratios by comparing to the expected values.[52] The average analytical uncertainties (2 standard deviations, SD) are 0.0359 for $^{208}Pb/^{204}Pb$, 0.0115 for $^{207}Pb/^{204}Pb$, 0.0087 for $^{206}Pb/^{204}Pb$, 0.0010 for $^{208}Pb/^{206}Pb$, and 0.0003 for $^{206}Pb/^{207}Pb$.

2.3. Modeling Pb Concentration in Coal Fly Ash. The relative enrichment factor (REF), defined in eq 1, was used to describe the enrichment and/or depletion of trace elements in coal ash relative to the feed coal.[53,54] Correspondingly, the concentration of trace elements in coal ash can be calculated using eq 2 as follows.

$$\mathrm{REF} = ([\mathrm{TE}]_{\mathrm{ash}} \times A_{\mathrm{coal}})/[\mathrm{TE}]_{\mathrm{coal}} \quad (1)$$

$$[\mathrm{TE}]_{\mathrm{ash}} = (\mathrm{REF} \times [\mathrm{TE}]_{\mathrm{coal}})/A_{\mathrm{coal}} \quad (2)$$

where $[TE]_{ash}$ and $[TE]_{coal}$ represent the concentrations of trace elements (mg/kg) in coal ash and coal, respectively, and A_{coal} refers to the ash yield (%) of coal.

By using eq 2, we calculated the Pb concentration in coal fly ash from China, India, and the U.S., respectively. The ash yield and Pb concentration data on coals from these three countries were compiled from the U.S. Geological Survey (USGS) World Coal Quality Inventory,[55] data reported by Bi et al.,[42] and data generated in this study (Table S2). The summarized statistics of the compiled dataset are presented in Table S3. The range of REF was derived from the data on paired coal and coal ash samples analyzed in this study (Table S2) and those reported for India.[56,57] To propagate the uncertainties, Monte Carlo simulations with 100,000 iterations were run. Data distribution analysis showed that ash yield and Pb concentration were fitted with a log-normal distribution and the REF was normally distributed with the exclusion of outliers (Table S4). The results were reported as the 5th, 16th, 50th (median), 84th, and 95th percentiles and mean values (Table S4). With the modeled Pb concentration data and the annual statistics on coal fly ash in each of the three countries (i.e., production, utilization, and disposal; Figure S2), we further calculated the output of Pb with fly ash disposal.

2.4. Bayesian Isotopic Mixing Model. MixSIAR is an open-source isotopic mixing model package in R that was developed by incorporating a series of Bayesian equations.[58] Previous studies have demonstrated its utility in disentangling multiple sources in various complex ecological, geological, and environmental mixtures with the use of both stable isotopes (e.g., carbon and nitrogen)[59] and radiogenic isotopes (e.g., Pb).[51,60] Here we applied the MixSIAR model using Pb isotope ratios ($^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$) measured in the sediments of the five NC lakes, which have been shown to be widely and persistently contaminated by coal ash disposal facilities from adjacent coal-fired power plants over the past 40−70 years of coal combustion.[24] The model endmembers for this quantification include leaded gasoline,[61−63] coal fly ash derived from coals of the Appalachian Basin and Illinois Basin that have been serving as the main sources of coal for mid-eastern U.S.,[50] and local background of pre-lake sediments measured from this study (Table S5). For each endmember, the mean and standard deviation of isotope ratios were included in the calculations. The efficacy of source apportionment depends on the differences and variations of endmembers.

2.5. Statistical Analysis. All statistical calculations and analyses were performed in R (v 4.1.1).[64] Statistical significance is reported as p values (i.e., $p < 0.01$ for 99% confidence interval and $p < 0.05$ for 95% confidence interval).

3. RESULTS AND DISCUSSION

3.1. Variations of Pb Concentrations and Isotope Ratios between Coal and Coal Ash. The concentrations and isotopic compositions of Pb in feed coal and coal ash from the sampled coal-fired power plants are shown in Table S2. The feed coal samples from the U.S. coal-fired power plants analyzed in this study have the lowest ash yield (mean ± SD = 10.0 ± 2.8%), compared to those from China (27.0 ± 7.3%) and India (37.3 ± 16.6%). The mean Pb concentration measured in the Chinese feed coal samples is 13.6 ± 4.9 mg/kg, which is consistent with that of the compiled dataset (13.6 ± 8.8 mg/kg; $n = 500$; Table S3) and the values reported for average Chinese coal.[65] Likewise, the measured Pb concentrations for the feed coal samples from India (14.7 ± 5.4 mg/kg) and the U.S. (8.5 ± 2.5 mg/kg) are also within the respective ranges derived by the compiled dataset (Table S3). Thus, the feed coal samples analyzed in this study are representative of average feed coal samples from their respective countries. The Pb concentrations in coals are significantly correlated with the ash yields ($\rho = 0.62$, $p < 0.001$), which is reflective of the dominant inorganic association of Pb in coals.[66,67]

As shown in Figure 1A, the REFs of most of the analyzed fly ash samples are above the REF = 1 line. In comparison, Pb is markedly depleted in bottom ash as the REFs are generally below 1 (Figure 1A and Table S2). This characteristic partitioning of Pb between fly ash and bottom ash is largely associated with its modes of occurrence in coal, as well as the combustion conditions as discussed below.[68−70] There are

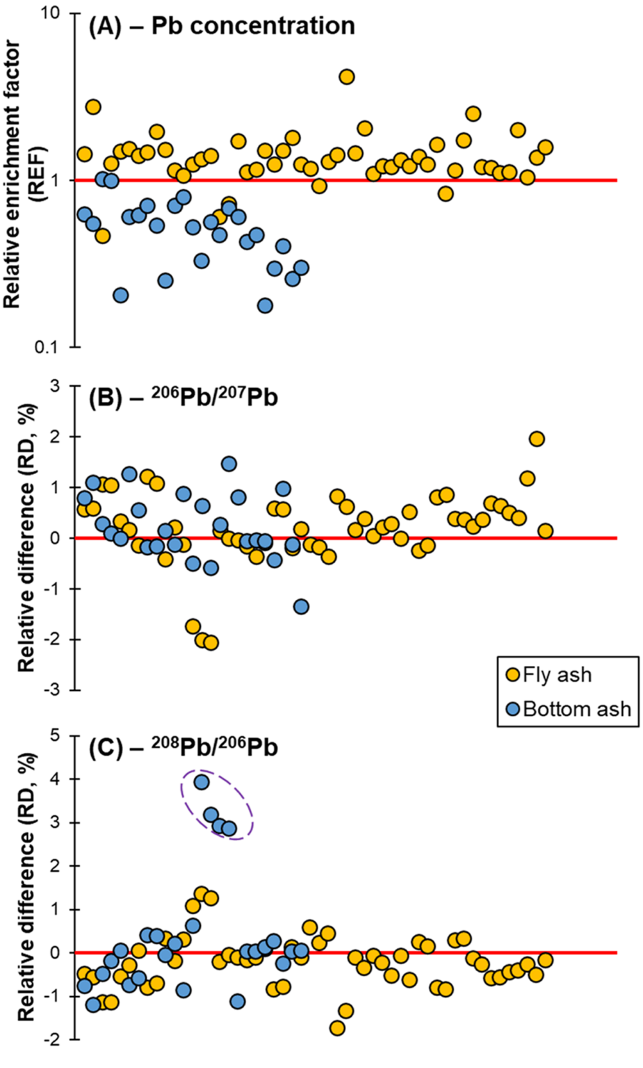

Figure 1. (A) Enrichment factor of Pb in samples of fly ash and bottom ash relative to corresponding feed coal collected from the same coal-fired power plant/unit in this study. The red solid line denotes REF = 1, meaning no enrichment nor depletion. (B, C) Relative difference (%) of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in fly ash and bottom ash compared to that in feed coal collected from the same coal-fired power plant/unit in this study. The red solid line represents RD = 0, meaning no difference. The purple ellipse highlights the Indian bottom ash samples with a notably higher $^{208}Pb/^{206}Pb$ ratio.

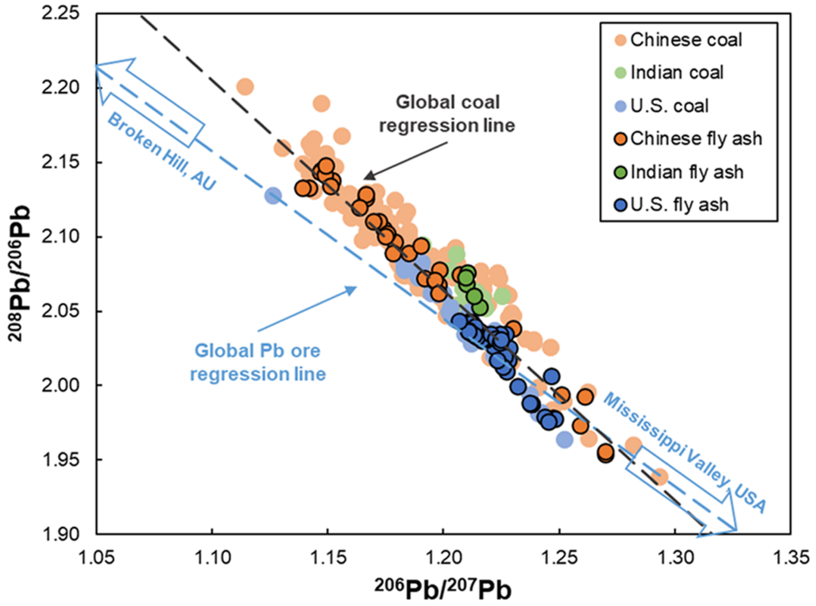

Figure 2. Plot of Pb isotope compositions of coal and coal fly ash sourced from China, India, and the U.S. The global coal regression line is based on a synthesized coal database.[42,44,45] The global Pb ore regression line is based on a previous study.[91] The two most widely used Pb ores, Broken Hill ores in Australia and Mississippi Valley Type ores in the U.S., are marked for context. The data on Indian fly ash are from this study, and data on the Chinese fly ash are from this study and a previous study,[73] and the U.S. fly ash data are from this study and a previous study.[50]

various phases of Pb present in coal, with the dominant phase as galena (PbS) and, in some cases, clausthalite (PbSe), and Pb in coal is also associated with pyrite, sulfate, carbonate, phosphate, and to a lesser extent, organic matter.[66,67,70] These dominant forms of Pb in sulfide render its volatility and transport with flue gas during high-temperature coal combustion,[68] which consequently results in its enrichment in fine particles that mostly end up in fly ash. A smaller fraction (e.g., 5−25%) of Pb, however, is also associated with (alumino)silicate minerals in coal, which are less volatile and tend to remain in the coarse residuals in bottom ash/boiler slag.[68] In addition, it has been suggested that there is no obvious difference between ESP and FF in the performance of Pb removal from flue gas, with both reaching 97−99% of the removal rate.[38,71] Therefore, the amount of Pb in fly ash represents the majority of Pb mobilized from burning coal, given that the particulate-bound Pb in flue gas could account for 77−96% of total Pb released from coal with modern-day boilers.[38,39,71] In comparison, the amount of Pb in the desulfurization gypsum is negligible.[71,72]

To demonstrate the variations of Pb isotope ratios between coal and coal ash, we calculated the relative difference (RD, %) for the Pb isotope ratios (i.e., ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb) in fly ash and bottom ash relative to those in the feed coal (Table S2). Unlike Pb elemental concentrations, the Pb isotope ratios between fly ash and bottom ash do not exhibit significant differences (p = 0.93 for ^{206}Pb/^{207}Pb and p = 0.06 for ^{208}Pb/^{206}Pb), despite a few exceptions (Figure 1B,C). Furthermore, the RDs of most of the coal ash samples fall within the ± 1% range of the RD = 0 line (Figure 1B,C). In addition, slightly higher ^{206}Pb/^{207}Pb ratios (i.e., RD > 0) and lower ^{208}Pb/^{206}Pb ratios (i.e., RD < 0) are observed in the analyzed coal ash samples (Figure 1B,C), indicating some deviation of Pb isotope signatures in coal ash relative to the feed coal. Research has suggested that Pb isotopes could undergo fractionation during coal combustion, where lighter isotopes (e.g., ^{206}Pb) tend to be more enriched in fly ash and heavier isotopes (e.g., ^{208}Pb) are likely to be enriched in bottom ash relative to feed coal.[73] However, this cannot explain the observations of higher ^{206}Pb/^{207}Pb ratios in bottom ash and lower ^{208}Pb/^{206}Pb ratios in fly ash as shown in our results (Table S2 and Figures 1B,C), as well as in the reported values by Zhu et al.[73] Instead, we argue that the variations of Pb isotope compositions of feed coal and coal ash are more likely due to the inherent heterogeneity of Pb occurrences and/or distribution of Th and U in coal,[44,50] by which different phases in coal may carry different Pb isotope signatures. The several abnormally high ^{208}Pb/^{206}Pb ratios observed in the bottom ash samples from India (Figure 1C) may be indicative of the presence of Th-rich phases in the feed coals that are not quite volatile, and therefore end up residing in bottom ash with a ^{208}Pb-enriched offset.

Nonetheless, due to the dominant presence of volatile phases of Pb in coal and preferential enrichment of Pb in fly ash, the Pb isotope composition of fly ash largely mimics that of the feed coal. As shown in Figure 2, the Pb isotope ratios of fly ash samples from China, India, and the U.S. fall within the compositional ranges of coals from each of the three countries. The Pb isotope compositions of coal/fly ash of the three countries are also significantly different from one another ($p <$ 0.05). Generally, coals from North America are characterized by higher ^{206}Pb/^{207}Pb and lower ^{208}Pb/^{206}Pb ratios than those from China and India, which is related to their differences in Th/U ratios and coal ages.[44] In addition, the isotope compositions of coal and fly ash closely follow the global coal regression line defined by the isotope compositions of coals around the world,[42,44,45] which, despite somewhat overlap, is distinct from the regression line of major Pb ore deposits that represent the major anthropogenic Pb sources, such as leaded gasoline and paint (Figure 2). This difference reinforces the potential utility of Pb isotopes for tracing coal fly ash in the environment,[50] even at a global scale.

3.2. Estimated Annual Pb Output of Coal Fly Ash Disposal from 2000 to 2020.

The modeled Pb concen-

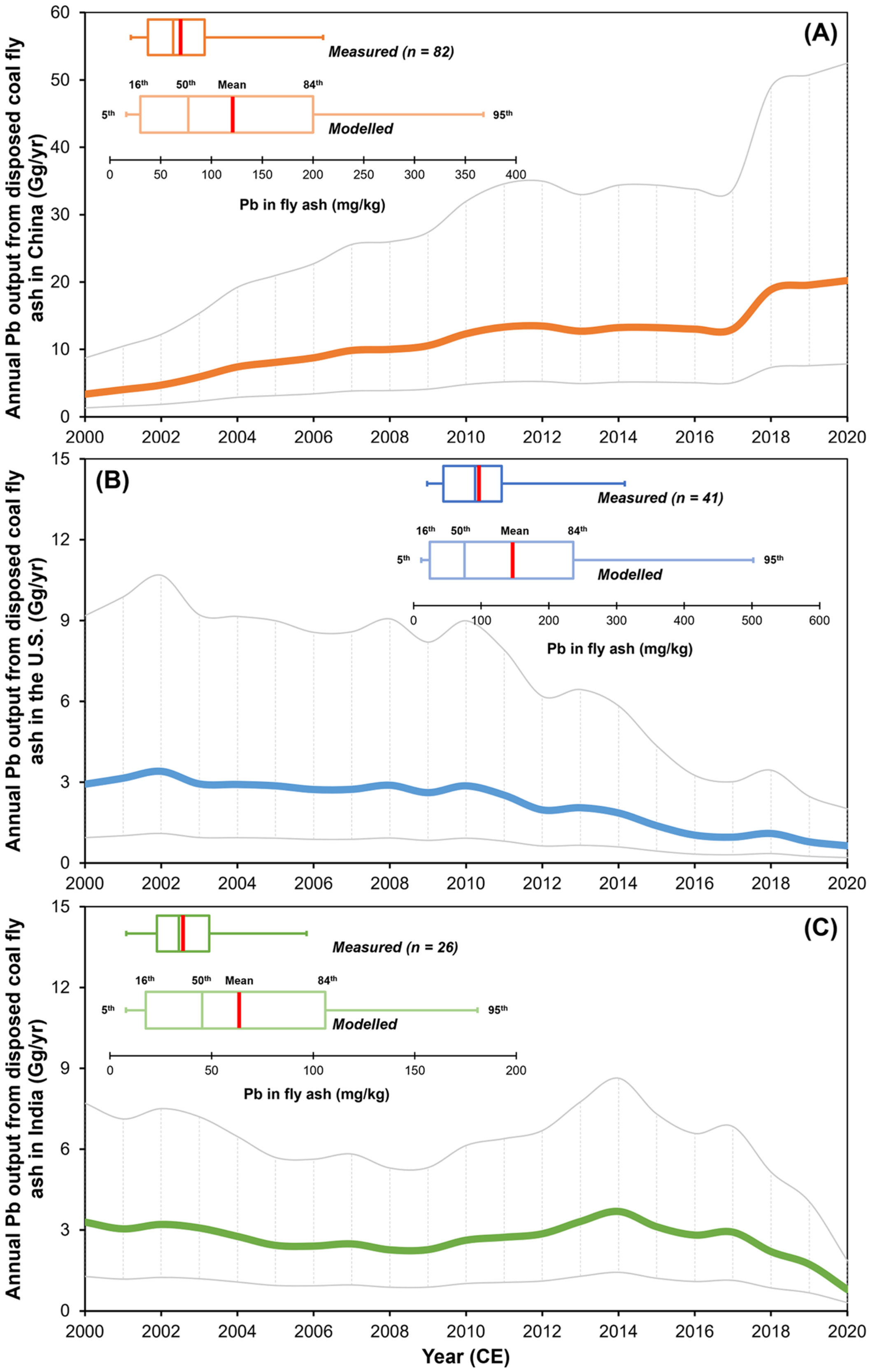

Figure 3. Estimates of annual Pb outputs (Gg/yr) from coal fly ash disposal in (A) China, (B) the U.S., and (C) India between 2000 and 2020. Thick colored lines show the median values of the estimate, and thin gray lines represent the lower and upper limits, defined by the 16th and 84th percentiles, respectively. Inset boxplots show the measured and modeled fly ash Pb concentrations (mg/kg), where red lines denote the mean values.

tration in fly ash (reported at the 5th−95th percentiles) exhibits a large variation, ranging from 11.4 to 502 mg/kg for the U.S., 16.2−368 mg/kg for China, and 7.8−181 mg/kg for India (Table S4). The fly ash Pb concentrations measured in this study and compiled from the literature from each country are systematically lower than the modeled values and yet largely encompassed by the 16th and 84th percentiles of the modeled values (Table S4 and Figure 3), indicating the predicative reliability of our model (Section 2.3). In addition, we tested if the increasing installations of high-efficiency APCDs would increase the Pb concentrations in fly ash by performing the simulations for China in three discrete years of 2000, 2010, and 2020 using a predictive model proposed by Han et al.[72] This model incorporated the variations of release rate of Pb from coal in different types of boilers, mass proportion of fly ash relative to other coal combustion residuals, and efficiencies of different APCDs among the three years. The results show that although the estimated fly ash Pb concentration in the year 2000 appears to be lower than that in 2010 and 2020 at all percentiles, the differences among the three years are not statistically significant (Table S6). Furthermore, all are close to the estimated median Pb value in this study (Table S4), further validating the reliability of the simpler model used in this study (Section 2.3). Comparatively, Hg in fly ash before and after the installation of ultralow emission control devices in China was shown to increase by 111% from 131 to 276 mg/kg.[74] Such difference between Pb and Hg can be explained by the much higher volatility of Hg than Pb, likely causing a greater fraction of gaseous Hg uncaptured by ESP and FF compared to Pb.

Based on the modeled median Pb concentration in fly ash and the annual amount of coal fly ash that was disposed of in each country (Figure S2), we calculated the annual median Pb output from coal fly ash disposal in the environment between 2000 and 2020. The 16th and 84th percentiles of Pb output represent the lower and upper limits of the estimate, respectively (Figure 3). Fly ash disposed of in China has markedly increased from ∼44 to ∼260 Mt over the past 20 years, whereas in the U.S., it has decreased from >40 Mt in the early 2000s to < 10 Mt by 2020 (Figure S2). India, in comparison, has had a relatively steady amount of fly ash disposal between 50 and 60 Mt, with a notable peak of >81 Mt in 2014 and then a significant drop to 20−30 Mt since 2019 due to an increase in the beneficial use of fly ash (Figure S2). Correspondingly, the Pb output associated with fly ash disposal in the U.S. has decreased from 3.4 (1.1−10.7, 16th−84th percentiles) Gg (i.e., 10^9 g) in the early 2000s to 0.6 (0.2−2.0) Gg in 2020, compared to the Pb output in China, which increased from 3.4 (1.3−8.8) Gg in 2000 to 20.2 (7.8−52.5) Gg in 2020. In India, the Pb output from fly ash disposal decreased from 3.3 (1.3−7.7) Gg in 2000 to 0.8 (0.3−1.9) Gg in 2020, with a peak of 3.7 (1.4−8.6) Gg in 2014 (Figure 3). Figure S3 shows the comparison between the estimated Pb output within fly ash disposal and that of atmospheric emissions from coal-fired power plants in China.[38] The estimated Pb atmospheric emission increased from 0.82 Gg in 2000 to 1.19 Gg in 2005 and 2006 and then decreased to 0.70 Gg in 2010, which is 4 to 17 times less than the contribution of Pb from fly ash disposal (Figure S3). Projected scenarios with more equipment containing advanced APCDs modeled the total Pb atmospheric emissions from coal-fired power plants in China to have decreased by over 20% to ∼0.55 Gg in 2020 relative to that in 2010.[38] Lead in fly ash disposal, on the other hand, is modeled to have increased by 64% from 2010 to 2020 (Figure 3) and is over 35 times higher than the contribution of Pb from atmospheric emissions (Figure S3).

Over the first 20 years of the 21st century, the cumulative output of disposed fly ash Pb is estimated as 236 (92−612) Gg in China, which is 4 to 4.5 times greater than that in India with an estimate of 56 (22−131) Gg, and 46 (15−145) Gg in the U.S. Given that China, India, and the U.S. account for over 70% of the total coal consumption,[75] the estimated global output of Pb associated with coal fly ash disposal from coal-fired power plants during the past two decades is about 483 (184−1269) Gg. Considering that the estimated annual Pb output associated with coal combustion in all sectors, including power, industrial, residential, and others, is 153 ± 10 Gg/yr,[3] which infers a total Pb output (∼3060 Gg) that was released to the environment over the past 20 years, our estimated global fly ash disposal Pb output accounts for ∼16% (6−41%) of the total Pb released to the environment from coal combustion. The remaining ∼84% of the total Pb includes all the other release pathways associated with coal combustion (e.g., fugitive atmospheric emissions). While we provided the estimates on a national scale for each country, the exact Pb output with fly ash disposal at the plant, or regional levels may have wide geographic variations because coal reserves and coal-fired power plants are unevenly distributed. For instance, the majority of coal-fired power plants are distributed in the northern and eastern parts of China, which in total could account for over 50% of total fly ash production.[74] Research has suggested that there might be about 13−27% of disposed fly ash being released to the Chang Jiang (CJ or Yangtze) River basin,[76] which is one of the most populated and developed regions in China. The total coal fly ash production in this region accounts for ∼36% of the national total,[76] thus resulting in the accumulation of 85 (33−220) Gg Pb in fly ash between 2000 and 2020, which is greater than the combined accumulation of both India and the U.S. Consequently, we estimate that 11 (4−29) to 23 (9−59) Gg of Pb could be released to the CJ riverine system, which would contribute to total sediment and particulate Pb discharged to the ocean.

3.3. Quantification of Released Fly Ash Pb into Lake Sediments—A North Carolina Example.

Given that many of the coal ash disposal units, i.e., coal ash ponds and landfills, are located near rivers, lakes, and reservoirs, sediments in these aquatic systems have been a major repository for the contaminants released from coal ash.[15,23,24,77−80] The bottom sediments of five freshwater lakes in North Carolina, which provide cooling water for adjacent coal-fired power plants, have been persistently contaminated by the release of coal ash and its associated toxic elements during the past 40−70 years of plant operation.[24] The concentrations of trace elements such as As, Se, Sb, Tl, Cd, and Pb in the impacted sediments of these lakes have been shown to be markedly higher than the background.[24] However, the relative contribution of Pb from coal ash as opposed to other potential Pb sources such as the legacy atmospheric deposition from leaded gasoline has not been constrained. Given that there is no significant point source of Pb to these lakes other than the adjacent coal-fired power plants,[24] by adopting a three-endmember Bayesian mixing model using MixSIAR (Section 2.4) with the Pb isotope ratios (i.e., ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{206}Pb/^{204}Pb) measured in the sediments (Table S7), we estimated the relative Pb contributions from the local sediment background, coal fly ash, and legacy leaded gasoline, respectively (Table 1 and Figure S5).

Table 1. Summary of MixSIAR Results of Mean Pb Proportions (%) and Standard Deviations (SD, %) of Three Pb Endmembers in Lake Sediments from North Carolina[24]

	local background		coal fly ash		leaded gasoline	
lake name	mean	SD	mean	SD	mean	SD
Hyco lake	68	22	27	22	5	4
Mayo lake	65	22	25	20	10	7
Belews lake	66	24	31	23	3	3
Mountain Island lake	76	18	20	18	4	3
Lake Sutton	64	23	25	20	11	8
All lakes	68	22	26	21	6	5

The mixing model indicated that the local background Pb predominantly contributed to the total Pb accumulation in the sediments (mean ± SD = 68 ± 22%), followed by coal fly ash (26 ± 21%) and leaded gasoline (6 ± 5%) in all five lakes (Table 1 and Figure S6). This is supported by the fact that most of the sediments have an isotopic cluster near the isotope compositions of the local background and coal fly ash (Figure S4). While the local background used in the mixing calculations is represented by the sediments and/or soils present prior to the impoundment of each lake, we cannot exclude the possibility that background levels may also have been influenced by anthropogenic Pb sources (e.g., gasoline and/or pesticide in agricultural uses). The coal fly ash endmember was represented by the Pb isotopes data on fly ash derived from coals of the Appalachian Basin and Illinois Basin, with the purpose of capturing the potential change of coal source over time in the studied coal-fired power plants.

The mean Pb contribution from coal fly ash ranges from 20 ± 17% in the sediment core of Mountain Island Lake to 31 ± 23% in that of Belews Lake, which is 2−9 times higher than the mean Pb contribution from leaded gasoline in the same sediment core of the corresponding lakes (Table 1). Lake Sutton, located in eastern NC, has a notably higher Pb contribution from leaded gasoline (11 ± 7%) than the lakes located in the western side of the state, i.e., Mountain Island Lake (4 ± 3%) and Belews Lake (3.4 ± 3.1%) (Figure S1 and Table 1). Furthermore, based on the Pb concentrations, average sediment density, and mean sedimentation rate (Table S7),[24] we calculated the accumulation rates of total Pb, coal fly ash Pb, and gasoline Pb in each of the five sediment cores. The mean (±1SD) total Pb accumulation rate in the five sediment cores is 152 ± 17.8 to $mg/m^2/yr$ for Mountain Island Lake (from 1960 to 2020), 199 ± 28.4 to $mg/m^2/yr$ for Hyco Lake (from 1960 to 2020), 281 ± 53.7 to $mg/m^2/yr$ for Belews Lake (from 1970 to 2020), 293 ± 46.9 to $mg/m^2/yr$ for Lake Sutton (from 1970 to 2020), and 71.4 ± 13.2 to $mg/m^2/yr$ for Mayo Lake (from 1980 to 2020), respectively. These represent higher total Pb accumulation rates than those reported in sediments deposited during the same period of time in lakes with no direct association with coal-fired power plants in Virginia (e.g., 20−170 $mg/m^2/yr$ from 1960 to 2016)[81] and Florida (e.g., 13−106 $mg/m^2/yr$ from 1960 to 2005).[82]

The mean release of coal fly ash Pb among all five lakes ranges from 17.5 ± 14.6 $mg/m^2/yr$ for Mayo Lake to 87.9 ± 68.5 $mg/m^2/yr$ for Belews Lake, which are significantly higher than the respective release of gasoline Pb (5.9 ± 5.4−32.4 ± 23.4 $mg/m^2/yr$). The maximum fly ash Pb release in the sediment cores of Hyco Lake and Belews Lake occurred between the 1970s and 1990s (Figure 4), prior to the start of landfills when coal ash was mainly stored in ponds. Releases from storage ponds are attributed to the effects of stormwater runoff/flooding and direct coal ash effluent discharge.[24] In Mountain Island Lake and Lake Sutton, where the nearby coal-fired power plants have been retired since 2013,[24] the coal ash Pb output to the sediments do not necessarily decrease with the end of using coal for power generation (Figure 4). This reinforces the conclusion that coal ash disposal facilities remain as a pollution source to the nearby aquatic systems in spite of the conversion of many thermoelectric plants from coal to natural gas.[24]

In the U.S., leaded gasoline was the dominant anthropogenic Pb source in the environment between the 1930s and 1990s, with its peak consumption during the 1970s.[83] Consequently, a peak of atmospheric Pb deposition has been observed in lakes and other natural archives in the 1970s throughout the U.S.[84−88] However, the notable peak of Pb release from the gasoline source is not visible in the sediment cores from this study (Figure 4). This expected leaded gasoline signal could have been masked by the Pb signal of fly ash. In the sediment cores of two remote lakes in northeastern U.S., the peak anthropogenic Pb release from atmospheric deposition in 1973 was estimated to be 14.7−15.2 $mg/m^2/yr$.[88] Similarly, the mean Pb deposition from precipitation in the early 1970s in New Hampshire was 20 $mg/m^2/yr$.[89] Following the phase-out of leaded gasoline since the 1990s, the release of atmospherically deposited Pb dramatically decreased by 39−52% until the early 2000s.[88] The gasoline Pb release to sediments deposited around the early 1970s in Belews Lake was 11.3−18.5 $mg/m^2/yr$, whereas the release of gasoline Pb to sediments of the same deposition period was lower in Mountain Island Lake (5.8−9.0 $mg/m^2/yr$) and Hyco Lake (3.9−5.0 $mg/m^2/yr$). In contrast, sediments of Lake Sutton in eastern NC had a greater gasoline Pb in the early 1970s (25.2−32.2 $mg/m^2/yr$). This reflects the regional variability of atmospheric Pb deposition. Higher levels of gasoline Pb in Lake Sutton persist throughout the sediment core (Figure 4), which is likely due to the continuous release and recycling of legacy Pb sources stored in the watershed soils that could have biased the calculations.[86]

4. ENVIRONMENTAL IMPLICATIONS

The relatively minor difference in the Pb isotope compositions between coal and coal ash suggests that the Pb isotope ratios of coal can be used to predict the isotope composition of fly ash, which is of particular importance given that there is far more literature data on coal than on fly ash. The isotopic signatures of Pb in coal fly ash are distinctive from those of common Pb ore deposits, and thus the legacy of gasoline and leaded paint Pb sources. This isotopic difference reinforces the potential utility of using Pb isotopes for tracing Pb associated with coal fly ash disposal in the environment.[50] Despite the growing beneficial use of fly ash in recent years, the accumulation of disposed fly ash over the two-decade span has resulted in a significant amount of solid coal ash waste. The results presented in this study suggest that the output of Pb from fly ash disposal is in fact much greater than that of the estimated output of Pb from atmospheric emissions. This large Pb output from fly ash disposal may pose a significant environmental burden, especially given that legacy fly ash disposal facilities can continue to release Pb to the environ-

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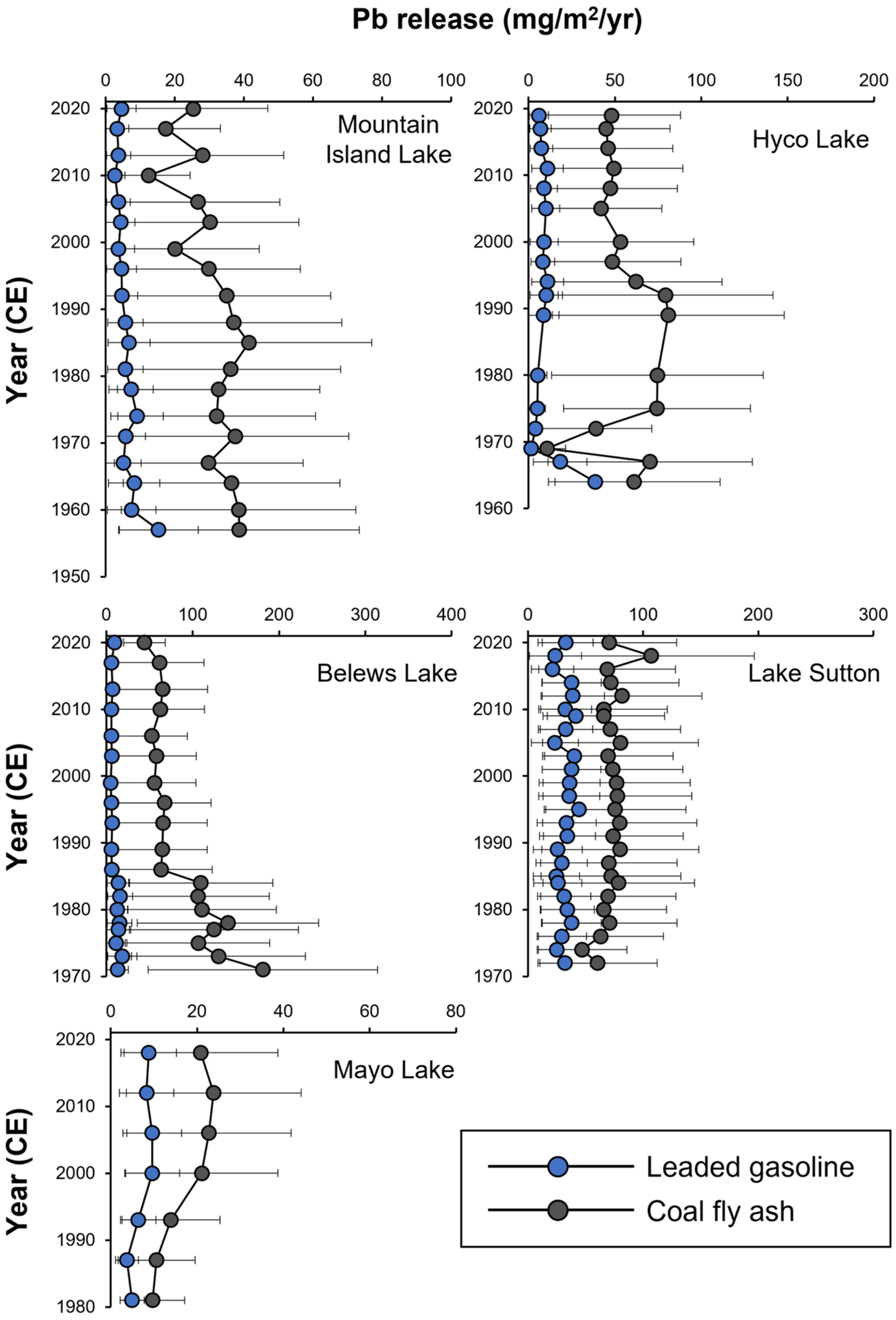

Figure 4. Downcore profiles of estimated Pb release (mg/m^2/yr) from coal fly ash and leaded gasoline deposited to the bottom sediments of five freshwater lakes across North Carolina (Figure S1). Error bars denote the uncertainty of 1 standard deviation.

ment.[24] Once released into the environment, either into the terrestrial or aquatic reservoirs (i.e., impact on soils and sediments), the relative contribution of Pb from coal fly ash can be constrained by using the Bayesian Pb isotope mixing model as demonstrated in this study. At both local and regional scales, the contributions of coal fly ash Pb to the environment could outweigh that of the once-dominant gasoline Pb.

Overall, this study represents the first attempt to provide a global perspective into the Pb isotopic fingerprints and the Pb outputs associated with the disposal of coal fly ash in the environment, focusing on China, India, and the U.S., the three largest coal consumers in the world.[75] Further research should be conducted to study the environmental fate of released fly ash Pb and its potential risks to the impacted terrestrial and aquatic ecosystems, as well as its roles in altering the biogeochemical cycles of Pb at local, regional, and global scales. In addition, while this study only focuses on Pb, the releases of co-occurring other toxic elements (e.g., Hg, As, Cd, Se, and Cr)[72,74] and organic contaminants (e.g., polycyclic aromatic hydrocarbons, PAHs)[90] associated with the fly ash disposal also warrant caution and detailed investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c03456.

> Information of sample collection (Table S1); Pb concentration and isotope ratios data of collected samples (Table S2); summary of coal data from the literature (Table S3); model parameters and results of fly ash Pb concentration (Table S4); Pb isotope ratios of endmembers for MixSIAR (Table S5); estimated Pb concentrations in fly ash from China (Table S6), and Pb concentrations and isotope ratios of lake sediments (Table S7); map of five lakes in North Carolina, USA (Figure S1); annual statistics of coal fly ash (Figure S2); comparison of Pb emissions and disposal fly ash Pb in China (Figure S3); Pb isotope plots of lake sediments and three Pb endmembers (Figure S4); boxplots of MixSIAR results (Figure S5); and downcore profiles of MixSIAR results (Figure S6) (PDF)

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Notes

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■ REFERENCES

(1) Klee, R. J.; Graedel, T. E. ELEMENTAL CYCLES: A Status Report on Human or Natural Dominance. *Ann. Rev. Environ. Resour.* **2004**, *29*, 69−107.
(2) Rauch, J. N.; Pacyna, J. M. Earth's Global Ag, Al, Cr, Cu, Fe, Ni, Pb, and Zn Cycles *Global Biogeochem. Cycles* 2009; Vol. *23, GB20012* DOI: 10.1029/2008GB003376.
(3) Sen, I. S.; Peucker-Ehrenbrink, B. Anthropogenic Disturbance of Element Cycles at the Earth's Surface. *Environ. Sci. Technol.* **2012**, *46*, 8601−8609.
(4) Pacyna, J. M.; Pacyna, E. G. An Assessment of Global and Regional Emissions of Trace Metals to the Atmosphere from Anthropogenic Sources Worldwide. *Environ. Rev.* **2001**, *9*, 269−298.
(5) Reuer, M. K.; Weiss, D. J. Anthropogenic Lead Dynamics in the Terrestrial and Marine Environment. *Philos. Trans. R. Soc., A* **2002**, *360*, 2889−2904.
(6) Shotyk, W.; Le Roux, G. Biogeochemistry and Cycling of Lead. *Met. Ions Biol. Syst.* **2005**, *43*, 239−275.
(7) Li, Q.; Cheng, H.; Zhou, T.; Lin, C.; Guo, S. The Estimated Atmospheric Lead Emissions in China, 1990−2009. *Atmos. Environ.* **2012**, *60*, 1−8.
(8) US EPA. Coal Ash (Coal Combustion Residuals, or CCR). https://www.epa.gov/coalash. (accessed March 22, 2022).
(9) Basu, M.; Pande, M.; Bhadoria, P. B. S.; Mahapatra, S. C. Potential Fly-Ash Utilization in Agriculture: A Global Review. *Prog. Nat. Sci.* **2009**, *19*, 1173−1186.
(10) Luo, Y.; Wu, Y.; Ma, S.; Zheng, S.; Zhang, Y.; Chu, P. K. Utilization of Coal Fly Ash in China: A Mini-Review on Challenges and Future Directions. *Environ. Sci. Pollut. Res.* **2021**, *28*, 18727−18740.
(11) Yao, Z. T.; Ji, X. S.; Sarker, P. K.; Tang, J. H.; Ge, L. Q.; Xia, M. S.; Xi, Y. Q. A Comprehensive Review on the Applications of Coal Fly Ash. *Earth-Sci. Rev.* **2015**, *141*, 105−121.
(12) Yousuf, A.; Manzoor, S. O.; Youssouf, M.; Malik, Z. A.; Khawaja, K. S. Fly Ash: Production and Utilization in India - An Overview. *J. Mater. Environ. Sci.* **2020**, *11*, 911−921.
(13) 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*, 6326−6333.
(14) 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*, 9272−9278.
(15) Deonarine, A.; Bartov, G.; Johnson, T. M.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Environmental Impacts of the Tennessee Valley Authority Kingston Coal Ash Spill. 2. Effect of Coal Ash on Methylmercury in Historically Contaminated River Sediments. *Environ. Sci. Technol.* **2013**, *47*, 2100−2108.
(16) Bartov, G.; Deonarine, A.; Johnson, T. M.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Environmental Impacts of the Tennessee Valley Authority Kingston Coal Ash Spill. 1. Source Apportionment Using Mercury Stable Isotopes. *Environ. Sci. Technol.* **2013**, *47*, 2092−2099.
(17) Liu, Y.-T.; Chen, T.-Y.; Mackebee, W. G.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Selenium Speciation in Coal Ash Spilled at the Tennessee Valley Authority Kingston Site. *Environ. Sci. Technol.* **2013**, *47*, 14001−14009.
(18) Lemly, A. D. Damage Cost of the Dan River Coal Ash Spill. *Environ. Pollut.* **2015**, *197*, 55−61.

(19) Yang, Y.; Colman, B. P.; Bernhardt, E. S.; Hochella, M. F. Importance of a Nanoscience Approach in the Understanding of Major Aqueous Contamination Scenarios: Case Study from a Recent Coal Ash Spill. *Environ. Sci. Technol.* **2015**, *49*, 3375−3382.

(20) Deonarine, A.; Kolker, A.; Doughten, M. W. *Trace Elements in Coal Ash; Fact Sheet; USGS Numbered Series 2015−3037*; U.S. Geological Survey: Reston, VA.

(21) Harkness, J. S.; Sulkin, B.; Vengosh, A. Evidence for Coal Ash Ponds Leaking in the Southeastern United States. *Environ. Sci. Technol.* **2016**, *50*, 6583−6592.

(22) 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*, 12226−12233.

(23) 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.

(24) Wang, Z.; Cowan, E. A.; Seramur, K. C.; Dwyer, G. S.; Wilson, J. C.; Karcher, R.; Brachfeld, S.; Vengosh, A. Legacy of Coal Combustion: Widespread Contamination of Lake Sediments and Implications for Chronic Risks to Aquatic Ecosystems. *Environ. Sci. Technol.* **2022**, *56*, 14723−14733.

(25) Deonarine, A.; Schwartz, G. E.; Ruhl, L. S. Environmental Impacts of Coal Combustion Residuals: Current Understanding and Future Perspectives. *Environ. Sci. Technol.* **2023**, *57*, 1855−1869.

(26) Twardowska, I.; Szczepanska, J.; Stefaniak, S. Occurrence and Mobilization Potential of Trace Elements from Disposed Coal Combustion Fly Ash. In *Chemistry of Trace Elements in Fly Ash*; Sajwan, K. S.; Alva, A. K.; Keefer, R. F., Eds.; Springer US: Boston, MA, 2003; pp 13−24.

(27) Córdoba, P.; Ochoa-Gonzalez, R.; Font, O.; Izquierdo, M.; Querol, X.; Leiva, C.; López-Antón, M. A.; Díaz-Somoano, M.; Martinez-Tarazona, M. R.; Fernandez, C.; Tomás, A. Partitioning of Trace Inorganic Elements in a Coal-Fired Power Plant Equipped with a Wet Flue Gas Desulphurisation System. *Fuel* **2012**, *92*, 145−157.

(28) Querol, X.; Juan, R.; Lopez-Soler, A.; Fernandez-Turiel, J.; Ruiz, C. R. Mobility of Trace Elements from Coal and Combustion Wastes. *Fuel* **1996**, *75*, 821−838.

(29) 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*, 331−343.

(30) Swanson, S. M.; Engle, M. A.; Ruppert, L. F.; Affolter, R. H.; Jones, K. B. Partitioning of Selected Trace Elements in Coal Combustion Products from Two Coal-Burning Power Plants in the United States. *Int. J. Coal Geol.* **2013**, *113*, 116−126.

(31) Xu, M.; Yan, R.; Zheng, C.; Qiao, Y.; Han, J.; Sheng, C. Status of Trace Element Emission in a Coal Combustion Process: A Review. *Fuel Process. Technol.* **2004**, *85*, 215−237.

(32) Bai, X.; Tian, H.; Zhu, C.; Luo, L.; Hao, Y.; Liu, S.; Guo, Z.; Lv, Y.; Chen, D.; Chu, B.; Wang, S.; Hao, J. Present Knowledge and Future Perspectives of Atmospheric Emission Inventories of Toxic Trace Elements: A Critical Review. *Environ. Sci. Technol.* **2023**, *57*, 1551−1567.

(33) Li, X.; Bi, X.; Li, Z.; Zhang, L.; Li, S.; Chen, J.; Feng, X.; Fu, X. Atmospheric Lead Emissions from Coal-Fired Power Plants with Different Boilers and APCDs in Guizhou, Southwest China. *Energy Fuels* **2019**, *33*, 10561−10569.

(34) Meij, R.; te Winkel, B. H. Trace Elements in World Steam Coal and Their Behaviour in Dutch Coal-Fired Power Stations: A Review. *Int. J. Coal Geol.* **2009**, *77*, 289−293.

(35) Wu, R.; Liu, F.; Tong, D.; Zheng, Y.; Lei, Y.; Hong, C.; Li, M.; Liu, J.; Zheng, B.; Bo, Y.; Chen, X.; Li, X.; Zhang, Q. Air Quality and Health Benefits of China's Emission Control Policies on Coal-Fired Power Plants during 2005−2020. *Environ. Res. Lett.* **2019**, *14*, No. 094016.

(36) Chen, J.; Zhang, B.; Zhang, S.; Zeng, J.; Chen, P.; Liu, W.; Wang, X. A Complete Atmospheric Emission Inventory of F, As, Se, Cd, Sb, Hg, Pb, and U from Coal-Fired Power Plants in Anhui Province, Eastern China. *Environ. Geochem. Health* **2021**, *43*, 1817−1837.

(37) Pacyna, J. M.; Pacyna, E. G.; Aas, W. Changes of Emissions and Atmospheric Deposition of Mercury, Lead, and Cadmium. *Atmos. Environ.* **2009**, *43*, 117−127.

(38) Tian, H.; Liu, K.; Zhou, J.; Lu, L.; Hao, J.; Qiu, P.; Gao, J.; Zhu, C.; Wang, K.; Hua, S. Atmospheric Emission Inventory of Hazardous Trace Elements from China's Coal-Fired Power Plants—Temporal Trends and Spatial Variation Characteristics. *Environ. Sci. Technol.* **2014**, *48*, 3575−3582.

(39) Tian, H.; Cheng, K.; Wang, Y.; Zhao, D.; Lu, L.; Jia, W.; Hao, J. Temporal and Spatial Variation Characteristics of Atmospheric Emissions of Cd, Cr, and Pb from Coal in China. *Atmos. Environ.* **2012**, *50*, 157−163.

(40) Komárek, M.; Ettler, V.; Chrastný, V.; Mihaljevič, M. Lead Isotopes in Environmental Sciences: A Review. *Environ. Int.* **2008**, *34*, 562−577.

(41) Weis, D. Lead Isotopes. In *Encyclopedia of Geochemistry*; White, W. M., Ed.; Encyclopedia of Earth Sciences Series; Springer: Cham., 2018; pp 813−818.

(42) 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*, 13502−13508.

(43) Chow, T. J.; Earl, J. L. Lead Isotopes in North American Coals. *Science* **1972**, *176*, 510−511.

(44) 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*, 1078−1085.

(45) 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*, 28−36.

(46) 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*, 257−272.

(47) 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*, 1245−1253.

(48) Hurst, R. W.; Davis, T. E.; Elseewi, A. A.; Page, A. L. Strontium and Lead Isotopes as Monitors of Fossil Fuel Dispersion. In *Trace Elements in Coal and Coal Combustion Residues*; Taylor & Francis Group, 1993 Chapter 5, pp 99−118.

(49) 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*, 4760−4765.

(50) Wang, Z.; Dwyer, G. S.; Coleman, D. S.; Vengosh, A. Lead Isotopes as a New Tracer for Detecting Coal Fly Ash in the Environment. *Environ. Sci. Technol. Lett.* **2019**, *6*, 714−719.

(51) Dietrich, M.; Krekeler, M. P. S.; Kousehlar, M.; Widom, E. Quantification of Pb Pollution Sources in Complex Urban Environments through a Multi-Source Isotope Mixing Model Based on Pb Isotopes in Lichens and Road Sediment. *Environ. Pollut.* **2021**, *288*, No. 117815.

(52) 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*, 74−78.

(53) Meij, R. Trace Element Behavior in Coal-Fired Power Plants. *Fuel Process. Technol.* **1994**, *39*, 199−217.

(54) Meij, R.; Van Der Kooij, J.; Van Der Sluys, J. L. G.; Siepman, F. G. C.; Van Der Sloot, H. A.*Characteristics of Emitted Fly Ash and Trace*

Elements from Utility Boilers Fired with Pulverized Coal, KEMA scientific and technical reports, 19841-8.

(55) Palmer, C. A.; Oman, C. L.; Park, A. J.; Luppens, J. A. *The U.S. Geological Survey Coal Quality (COALQUAL)*, Database Version 3.0: U.S. Geological Survey Data Series 975, 43 p, 2015. (accessed June 7, 2022).

(56) Bhangare, R. C.; Ajmal, P. Y.; Sahu, S. K.; Pandit, G. G.; Puranik, V. D. Distribution of Trace Elements in Coal and Combustion Residues from Five Thermal Power Plants in India. *Int. J. Coal Geol.* **2011**, *86*, 349−356.

(57) Saha, D.; Chatterjee, D.; Chakravarty, S.; Roychowdhury, T. Investigation of Environmental-Concern Trace Elements in Coal and Their Combustion Residues from Thermal Power Plants in Eastern India. *Nat. Resour. Res.* **2019**, *28*, 1505−1520.

(58) Stock, B. C.; Jackson, A.; Ward, E.; Venkiteswaran, J. Brianstock/MixSIAR 3.1.9 Zenodo 2018 https://zenodo.org/record/1209993.

(59) Stock, B. C.; Jackson, A. L.; Ward, E. J.; Parnell, A. C.; Phillips, D. L.; Semmens, B. X. Analyzing Mixing Systems Using a New Generation of Bayesian Tracer Mixing Models. *PeerJ* **2018**, *6*, No. e5096.

(60) Longman, J.; Veres, D.; Ersek, V.; Phillips, D. L.; Chauvel, C.; Tamas, C. G. Quantitative Assessment of Pb Sources in Isotopic Mixtures Using a Bayesian Mixing Model. *Sci. Rep.* **2018**, *8*, No. 6154.

(61) Chow, T. J.; Johnstone, M. S. Lead Isotopes in Gasoline and Aerosols of Los Angeles Basin, California. *Science* **1965**, *147*, 502−503.

(62) 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*, 1211−1215.

(63) 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*, 11257−11268.

(64) R Core Team. R: A Language and Environment for Statistical Computing. 2021.

(65) Dai, S.; Ren, D.; Chou, C.-L.; Finkelman, R. B.; Seredin, V. V.; Zhou, Y. Geochemistry of Trace Elements in Chinese Coals: A Review of Abundances, Genetic Types, Impacts on Human Health, and Industrial Utilization. *Int. J. Coal Geol.* **2012**, *94*, 3−21.

(66) Finkelman, R. B. Modes of Occurrence of Potentially Hazardous Elements in Coal: Levels of Confidence. *Fuel Process. Technol.* **1994**, *39*, 21−34.

(67) Finkelman, R. B.; Palmer, C. A.; Wang, P. Quantification of the Modes of Occurrence of 42 Elements in Coal. *Int. J. Coal Geol.* **2018**, *185*, 138−160.

(68) Bartoňová, L.; Raclavská, H.; Čech, B.; Kucbel, M. Behavior of Pb During Coal Combustion: An Overview. *Sustainability* **2019**, *11*, No. 6061.

(69) Wang, Y.; Hu, H.; Wang, X.; Liu, H.; Dong, L.; Luo, G.; Zhao, Y.; Yao, H. A Critical Review on Lead Migration, Transformation and Emission Control in Chinese Coal-fired Power Plants. *J. Environ. Sci.* **2023**, *124*, 397−413.

(70) Dai, S.; Finkelman, R. B.; French, D.; Hower, J. C.; Graham, I. T.; Zhao, F. Modes of Occurrence of Elements in Coal: A Critical Evaluation. *Earth-Sci. Rev.* **2021**, *222*, No. 103815.

(71) Deng, S.; Shi, Y.; Liu, Y.; Zhang, C.; Wang, X.; Cao, Q.; Li, S.; Zhang, F. Emission Characteristics of Cd, Pb and Mn from Coal Combustion: Field Study at Coal-Fired Power Plants in China. *Fuel Process. Technol.* **2014**, *126*, 469−475.

(72) Han, D.; Xu, L.; Wu, Q.; Wang, S.; Duan, L.; Wen, M.; Li, Z.; Tang, Y.; Li, G.; Liu, K. Potential Environmental Risk of Trace Elements in Fly Ash and Gypsum from Ultra−Low Emission Coal−Fired Power Plants in China. *Sci. Total Environ.* **2021**, *798*, No. 149116.

(73) Zhu, Z.; Li, Z.; Wang, S.; Bi, X. Magnetic Mineral Constraint on Lead Isotope Variations of Coal Fly Ash and Its Implications for Source Discrimination. *Sci. Total Environ.* **2020**, *713*, No. 136320.

(74) Chen, Q.; Chen, L.; Li, J.; Guo, Y.; Wang, Y.; Wei, W.; Liu, C.; Wu, J.; Tou, F.; Wang, X.; Yang, Y. Increasing Mercury Risk of Fly Ash Generated from Coal-Fired Power Plants in China. *J. Hazard. Mater.* **2022**, *429*, No. 128296.

(75) BP. Coal − Statistical Review of World Energy 2021 https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2021-coal.pdf.

(76) Li, G. K.; Fischer, W. W.; Lamb, M. P.; West, A. J.; Zhang, T.; Galy, V.; Wang, X. T.; Li, S.; Qiu, H.; Li, G.; Zhao, L.; Chen, J.; Ji, J. Coal Fly Ash Is a Major Carbon Flux in the Chang Jiang (Yangtze River) Basin. *Proc. Natl. Acad. Sci. U.S.A.* **2021**, *118*, No. e1921544118.

(77) Cowan, E. A.; Gaspari, D. P.; Brachfeld, S. A.; Seramur, K. C. Characterization of Coal Ash Released in the TVA Kingston Spill to Facilitate Detection of Ash in River Systems Using Magnetic Methods. *Fuel* **2015**, *159*, 308−314.

(78) Donahue, W. F.; Allen, E. W.; Schindler, D. W. Impacts of Coal-Fired Power Plants on Trace Metals and Polycyclic Aromatic Hydrocarbons (PAHs) in Lake Sediments in Central Alberta, Canada. *J. Paleolimnol.* **2006**, *35*, 111−128.

(79) Hatcher, C. O.; Ogawa, R. E.; Poe, T. P.; French, J. R. P. Trace Elements in Lake Sediment, Macrozoobenthos, and Fish Near a Coal Ash Disposal Basin. *J. Freshwater Ecol.* **1992**, *7*, 257−269.

(80) Lalonde, B. A.; Ernst, W.; Comeau, F. Trace Metal Concentrations in Sediments and Fish in the Vicinity of Ash Lagoon Discharges from Coal-Combustion Plants in New Brunswick and Nova Scotia, Canada. *Arch. Environ. Contam. Toxicol.* **2011**, *61*, 472−481.

(81) Balascio, N. L.; Kaste, J. M.; Meyer, M. G.; Renshaw, M.; Smith, K.; Chambers, R. M. A High-Resolution Mill Pond Record from Eastern Virginia (USA) Reveals the Impact of Past Landscape Changes and Regional Pollution History. *Anthropocene* **2019**, *25*, No. 100190.

(82) Escobar, J.; Whitmore, T. J.; Kamenov, G. D.; Riedinger-Whitmore, M. A. Isotope Record of Anthropogenic Lead Pollution in Lake Sediments of Florida, USA. *J. Paleolimnol.* **2013**, *49*, 237−252.

(83) Nriagu, J. O. The Rise and Fall of Leaded Gasoline. *Sci. Total Environ.* **1990**, *92*, 13−28.

(84) 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*, 1715−1728.

(85) Kamenov, G. D.; Brenner, M.; Tucker, J. L. Anthropogenic versus Natural Control on Trace Element and Sr−Nd−Pb Isotope Stratigraphy in Peat Sediments of Southeast Florida (USA), ∼1500 AD to Present. *Geochim. Cosmochim. Acta* **2009**, *73*, 3549−3567.

(86) Mahler, B. J.; Van Metre, P. C.; Callender, E. Trends in Metals in Urban and Reference Lake Sediments across the United States, 1970 to 2001. *Environ. Toxicol. Chem.* **2006**, *25*, 1698−1709.

(87) Ritson, P. I.; Esser, B. K.; Niemeyer, S.; Flegal, A. R. Lead Isotopic Determination of Historical Sources of Lead to Lake Erie, North America. *Geochim. Cosmochim. Acta* **1994**, *58*, 3297−3305.

(88) Sarkar, S.; Ahmed, T.; Swami, K.; Judd, C. D.; Bari, A.; Dutkiewicz, V. A.; Husain, L. History of Atmospheric Deposition of Trace Elements in Lake Sediments, 1880 to 2007. *J. Geophys. Res.: Atmos.* **2015**, *120*, 5658−5669.

(89) Schlesinger, W. H.; Reiners, W. A.; Knopman, D. S. Heavy Metal Concentrations and Deposition in Bulk Precipitation in Montane Ecosystems of New Hampshire, USA. *Environ. Pollut.* **1974**, *6*, 39−47.

(90) Buha-Marković, J. Z.; Marinković, A. D.; Nemoda, S. Đ.; Savić, J. Z. Distribution of PAHs in Coal Ashes from the Thermal Power Plant and Fluidized Bed Combustion System; Estimation of Environmental Risk of Ash Disposal. *Environ. Pollut.* **2020**, *266*, No. 115282.

(91) Sangster, D. F.; Outridge, P. M.; Davis, W. J. Stable Lead Isotope Characteristics of Lead Ore Deposits of Environmental Significance. *Environ. Rev.* **2000**, *8*, 115−147.