Environmental Science & Technology
pubs.acs.org/est
Article

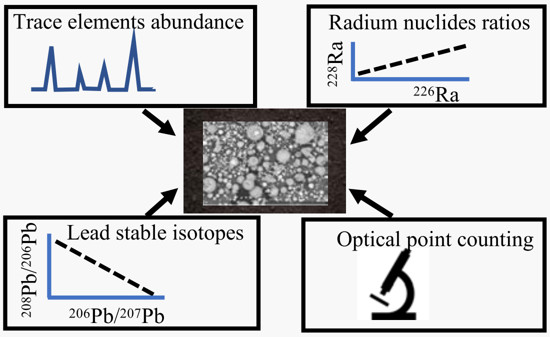
Evaluation and Integration of Geochemical Indicators for Detecting Trace Levels of Coal Fly Ash in Soils

Zhen Wang, Rachel M. Coyte, Ellen A. Cowan, Heather M. Stapleton, Gary S. Dwyer, and Avner Vengosh*

Cite This: https://doi.org/10.1021/acs.est.1c01215
Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Coal combustion residuals (CCRs), in particular, coal fly ash, are one of the major industrial solid wastes in the U.S., and due to their high concentrations of toxic elements, they could pose environmental and human health risks. Yet detecting coal fly ash in the environment is challenging given its small particle size. Here, we explore the utility and sensitivity of using geochemical indicators (trace elements, Ra nuclides, and Pb stable isotopes), combined with physical observation by optical point counting, for detecting the presence of trace levels of coal fly ash particles in surface soils near two coal-fired power plants in North Carolina and Tennessee. Through experimental work, mixing models, and field data, we show that trace elements can serve as a first-order detection tool for fly ash presence in surface soils; however, the accuracy and sensitivity of detection is limited for cases with low fly ash proportion (i.e., <10%) in the soil, which requires the integration of more robust Ra and Pb isotopic tracers. This study revealed the presence of fly ash particles in surface soils from both the recreational and residential areas, which suggests the fugitive emission of fly ash from the nearby coal-fired power plants.



KEYWORDS: *coal combustion residuals, coal fly ash, surface soils, trace elements, Pb isotopes, Ra isotopes, soil geochemistry*

INTRODUCTION

Coal combustion residuals (CCRs) generically refer to the solid waste generated from the combustion of coal in coal-fired power plants, composed of fly ash, bottom ash, boiler slag, and flue-gas desulfurization products, of which fly ash is the most abundant component.[1,2] Over the last decades, coal combustion in the U.S. has generated a large volume of CCRs that were disposed of and accumulated in surface impoundments and landfills. In 2019, approximately 80 million tons of CCRs were produced.[1] Due to its massive volume, small particle size, and high concentrations of toxic elements such as Hg, As, Se, Cd, Cr, and Pb,[2−9] CCRs, and in particular fly ash, pose significant environmental and human health risks.[3,10−17] The impacts of CCRs on the environment have been demonstrated by extreme and acute incidents, such as coal ash spills from the Kingston Fossil Plant, Tennessee in 2008,[18−22] and the Dan River Steam Station, North Carolina in 2014.[23,24] In addition, chronic release of CCRs and its contaminants to the environment can also have significant effects, as shown by the leaking of effluents from surface impoundments and landfills, and discharge of CCR effluents into the aquatic environment.[2,25,26] Furthermore, fugitive emission of fine ash particulates from coal-fired power plants and subsequent deposition and resuspension in the surrounding terrestrial environment could expose residents to the ash particles and associated contaminants.[13,17,27−30] Regardless of the mechanisms by which CCRs enter the environment, the ability to detect their occurrence is critical for delineating the environmental impacts and risks of CCRs to human health.

The geochemistry of coal fly ash is largely distinctive from those of natural rocks, soils, and sediments.[11,31−34] Hence, once it is released to the environment, the geochemistry of the impacted natural reservoir is likely to be altered, thus facilitating the use of geochemical tools to detect the possible presence of fly ash and its associated contamination in the environment. Previous studies have demonstrated the utility of a variety of geochemical tools for tracing fly ash contamination of aquatic systems. Given the high mobility of certain toxic elements from fly ash, the occurrence of soluble elements, such as As, Se, B, and Sr, combined with distinctive signatures of B and Sr isotopes, have been used to delineate its impact on groundwater, surface water, and sediment pore water.[26,34−36] For the detection of the presence of fly ash solids in the environment, various isotope systems have been used as potential tracers. Lauer et al. showed that fly ash derived from

Received: February 21, 2021
Revised: May 22, 2021
Accepted: June 30, 2021

coals of the major coal-producing basins in the U.S. has a distinctively low ^{228}Ra/^{226}Ra activity ratios (<1) relative to the common ^{228}Ra/^{226}Ra activity ratios in soils (>1), suggesting the possibility of using ^{228}Ra/^{226}Ra activity ratios to identify fly ash in the environment.[37] Wang et al. showed that the Pb isotope composition of U.S. fly ash (i.e., ^{208}Pb/^{206}Pb vs ^{206}Pb/^{207}Pb) is distinctive from those of both natural Pb in soils and major anthropogenic Pb sources (i.e., leaded gasoline and lead-based paint), making it a useful tracer of fly ash solids in the environment.[38] In addition, Sr, Hg, and Tl isotopes have also been suggested as potential tracers for delineating the occurrence of coal fly ash solids in the environment.[20,21,39−44] Furthermore, trace elements can also be indicative of the input of coal fly ash solids in the environment. Vengosh et al. identified the presence of fly ash solids in the bottom sediments of Sutton Lake near Wilmington, NC caused by multiple unmonitored coal ash spills, partially detected by high concentrations of trace elements (e.g., As, Se, Mo, Sb, and Tl) in the Sutton Lake sediments when compared with their occurrence in sediments from a background lake.[34] The presence of fly ash solids in the Sutton Lake sediments was further verified by Pb stable isotopes.[38]

While acute coal ash spills within the environment can be easily detected due to their large scales, tracing small quantities of fine fly ash particulates in soils and sediments derived from atmospheric deposition from nearby coal plants is much more challenging. Installation of high-efficiency pollution control devices in coal-fired power plants, including electrostatic precipitators and fabric filters, has significantly reduced the emission of fly ash from coal combustion by retaining the majority of ash particles.[45,46] Nonetheless, fine ash particles could still be uncaptured and accumulate in the terrestrial environment at relatively trace levels, particularly onto surface soils surrounding coal-fired power plants and coal ash disposal sites.[27,28,47,48] Previous studies have shown heavy-metal contamination in surface soils near coal-fired power plants and coal ash disposal sites;[49−65] however, no direct and definite links to coal ash source were established in these studies, reflecting the limitation of solely using chemistry data for identifying trace levels of coal fly ash in soils.

In this study, we aim to explore the utility of multiple geochemical methods, including trace elements, Ra isotopes, and Pb stable isotopes, as indicators for the presence of trace levels of coal fly ash particles in soils near coal-fired power plants and coal ash disposal sites. We evaluate the sensitivity of these methods by integrating observation and quantification of fly ash particles in soils, using point counting under polarized light microscope (PLM).[34,66−68] While some of these methods have been used individually, here, we present the first integration of geochemical methods for the purpose of tracking even trace levels of coal fly ash contamination in the environment. By integrating multiple geochemical tools and microscopic physical observation to investigate surface soil samples collected from areas adjacent to coal-fired power plants in North Carolina (NC) and Tennessee (TN), we demonstrate both their applicability and limitations for the detection of trace levels of coal fly ash presence in the environment.

■ MATERIALS AND METHODS

Sample Collection and Preparation. To examine the utility of geochemical tools for detecting coal fly ash in the environment, we collected and analyzed surface soils surrounding two operating coal-fired power plants, the Marshall Steam Station (2090 MW, began operation in 1965) near Lake Norman, NC, and the TVA Bull Run Steam Plant (865 MW, began operation in 1967) in Claxton, Anderson County, TN. To our knowledge, both the Marshall Steam Station and the Bull Run Steam Plant primarily burn coals sourced from the Appalachian (APP) Basin.

Surface soil samples were collected from recreational and residential areas near Lake Norman, NC ($n = 21$) and Claxton, Anderson County, TN ($n = 25$). Open, flat, and uncultivated natural grasslands were selected as sampling sites, where soil samples were collected from 5 cm depth below the surface using a stainless steel trowel. Each sample was a composite of three to five sub-samples collected from areas of approximately 5 m × 5 m to avoid sampling bias. Upon collection, all samples were stored and sealed in plastic bags or containers to avoid potential contamination. Maps showing the locations of coal-fired power plants and sampling sites are presented in the Supporting Information (Figure S1). As indicated by the wind rose diagrams, the majority of the sampling sites are located downwind of the coal plants, while the upwind Lake Norman State Park, northeast of the Marshall Steam Station (Figure S1a), and the upwind Haw Ridge Park, southwest of the Bull Run Steam Plant (Figure S1b), were selected for soil sampling to represent the respective local background soil according to the sampling guidelines for baseline soils by the U.S. Geological Survey (USGS).[69]

Prior to laboratory analysis, each soil sample was oven-dried at 50 °C until reaching a constant weight, plant residues and gravels were removed by hand, and the remaining soil was passed through a 2-mm sieve for homogenization. A subset of the sample by coning and quartering was ground using a ceramic mortar and pestle to pass through a 200-mesh stainless steel sieve for subsequent chemical analysis.

Laboratory and Statistical Analysis. *Trace Elements.* The concentrations of trace elements were measured on a Thermo Fisher XSeries II inductively coupled plasma mass spectrometer (ICP-MS) at Duke University. Samples were digested in a HF−HNO_3 mixture. The details of sample digestion and instrumental analysis have been documented in previous studies.[34,38,42] The efficiency of digestion and accuracy of measurement were assessed by measuring the National Institute of Standards and Technology (NIST) standard reference material (SRM) for trace elements in coal fly ash SRM 1633c as well as the U.S. Geological Survey (USGS) sedimentary rock standard SCo-1 (Cody Shale). The average percent recovery as well as relative standard deviations (RSDs) for all of the analyzed trace elements from repeated measurements of the reference materials over the course of analysis are presented in Table S1. The percent recovery for Cr in NIST 1633c is 80.4% (RSD = 5.2%, $n = 7$), lower than the average of 97.5% for all trace elements, while the percent recovery for Th in USGS SCo-1 is 80.7% (RSD = 12.2%, $n = 5$), lower than the average of 93.4% for all trace elements.

Radium Isotopes. The activities of ^{228}Ra and ^{226}Ra were determined on a Canberra DSA2000 broad-energy germanium γ detector surrounded by Pb shielding at Duke University. The sample packing and incubation followed the method reported previously.[37] Each measurement lasted for at least 86 000 s to minimize statistical counting error. Detector efficiencies were determined using a U−Th ore reference material (CCRMP DL-1a) packed and incubated in the same geometry as the samples.

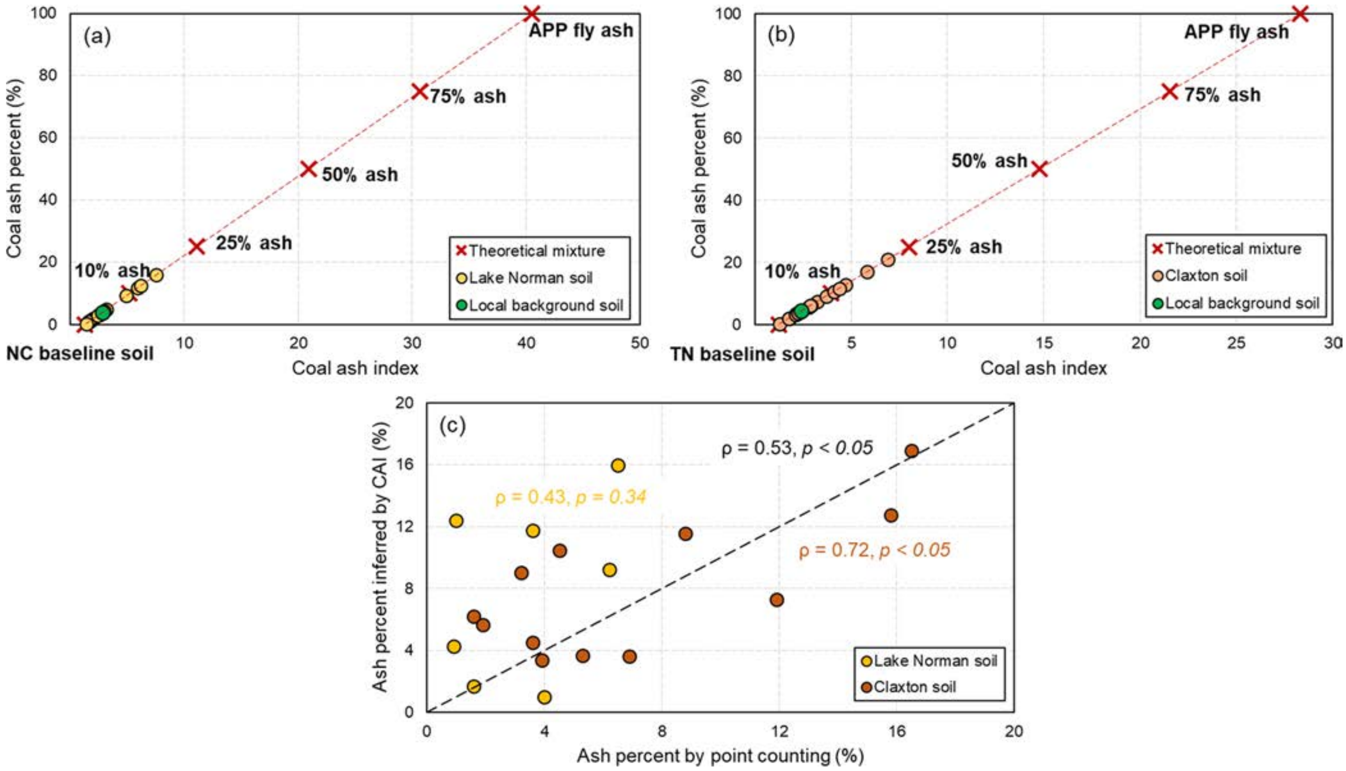


Figure 1. (a) Diagram of estimated ash percent (%) against coal ash index (CAI) of the surface soil samples from Lake Norman near the Marshall Steam Station, NC. The mixing line is defined by the theoretical mixing between the average NC baseline soil and the average APP fly ash. (b) Diagram of estimated ash percent (%) against CAI of the surface soil samples from Claxton near the Bull Run Steam Plant, TN. The mixing line is defined by the theoretical mixing between the average TN baseline soil and the average APP fly ash. The baseline soil data were compiled from the USGS database,[69] and the APP fly ash data were generated from this study. (c) Diagram of ash percent estimated by CAI against ash percent by point counting for the selected soil samples from Lake Norman and Claxton. Black dot line represents the 1:1 line.

Lead Stable Isotopes. The Pb stable isotope analysis (^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{204}Pb) was performed on a Triton thermal ionization mass spectrometer (TIMS) at Duke University, using Faraday cups and operating in static mode. The sample digestion and Pb column separation and purification have been detailed in a previous study.[38] A common Pb standard NIST SRM 981 was measured regularly over the course of analysis (n = 36) and the mass bias for all isotope ratios was determined according to the expected values.[70] The analytical uncertainties (2SD) for ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb are 0.0013 and 0.0003, respectively.

Optical Point Counting. The percent of coal fly ash particles present in the soil samples was determined at 500× magnification using a Leica DMLP polarizing microscope equipped with a Swift model F automated point counter at Appalachian State University. Details of sample preparation, counting procedures, and method reproducibility, as well as photomicrographs of fly ash particles in soils, are presented in the Supporting Information. To produce representative counts, each sample was thoroughly homogenized when slides were made for microscopic observation and counting. The identification of coal fly ash, which is composed of distinctive spherical particles, was based on Fisher et al.[71] and Hower.[72]

Data Compilation and Statistical Analysis. The trace element data of the surface soils (top 5 cm) collected across North Carolina (n = 83) and Tennessee (n = 66) were compiled from the USGS database,[69] which represent the baseline geochemical characteristics for the statewide surface soils (referred to as baseline soil hereafter) (Table S2). The trace element data of coal fly ash samples derived from coals of the Appalachian Basin (APP) (n = 16), Illinois Basin (ILL) (n = 22), and Powder River Basin (PRB) (n = 7) were measured on ICP-MS, which have been partially reported in previous studies (Table S2).[38,42] Monte Carlo simulation was performed for the theoretical mixing of coal fly ash and soil, by following the mixing scenarios of 10, 25, 50, and 75% of fly ash addition in soil, and each scenario was composed of 500 simulated mixtures. To confirm its reproducibility, the simulation was repeated at least 10 times for each mixing scenario until its mean values and standard deviations were calculated. Nonparametric methods were employed for statistical analysis using R,[73] including Spearman's rank correlation for investigating the correlation of two variables and Mann−Whitney test for comparing the difference between two groups.

■ RESULTS AND DISCUSSION

Evaluation of Trace Element Indicators for the Presence of Coal Fly Ash in Soils. Analysis of the trace element composition of coal fly ash samples associated with coals of the major coal basins in the U.S., including the Appalachian (APP), Illinois (ILL), and Powder River (PRB) basins[38,42] is presented in Table S2. In spite of variations in trace metal concentrations, fly ash derived from combustion of coals from the different basins in the U.S. has distinctive geochemical characteristics relative to the baseline soils of North Carolina and Tennessee[69] (Table S2; Figure S2). Similar patterns are observed for fly ash that originated from combustion of the APP and ILL coals, which have enrichment of As, Se, Mo, Sb, and Tl. In addition to these elements, PRB fly ash is also enriched in Se, Sr, and Ba relative to the baseline soils (Figure S2). Given both the Marshall Steam Station and Bull Run Steam Plant have utilized coals primarily derived from the Appalachian Basin, we used the APP fly ash data in this study (Table S2). To mimic the mechanical mixing between fly ash and soil, an archived NC surface soil sample known to have zero input from fly ash and a coal fly ash sample derived from APP coals was experimentally mixed in the laboratory, with weight percent of fly ash mixing of 10, 25, 50, and 75%. The actual measurements of trace elements in the soil−ash mixtures were compared to the theoretical calculations for the mixing combinations of the soil and fly ash (Table S3). Despite some variations, the measured values largely agree with the calculated values. The trace element concentrations of the soil−ash mixtures were then normalized to the average values of NC baseline soil, and the distribution curves of trace elements in the different mixtures are shown in Figure S3. While the distribution curves of trace elements in the original soil sample and fly ash sample are markedly different, increasing the fraction of fly ash in the soil−ash mixtures evidently causes divergence of the distribution curves from that of the pristine soil sample and resemblance to that of the fly ash sample (Figure S3).

Furthermore, mixing of fly ash and soil results in notable spikes of an assemblage of trace elements, including As, Se, Mo, Sb, and Tl in the soil−ash mixtures (Figure S3). To quantify the characteristic enrichment of the As−Se−Mo−Sb−Tl assembly in soil that resulted from mixing with fly ash, we define the coal ash index (CAI), which is the sum of the enrichment factors of each of the five characteristically enriched trace elements as normalized to their median concentrations in the background soil. To better reflect the relative contribution of fly ash as opposed to other potential contamination sources, the enrichment factors of these five elements are weighted by multiplying the percent weight of the enrichment factor of each element in fly ash (see details in Supporting Information). By calculating the CAI values, a linear relationship between CAI and estimated ash percent in the mixtures can be established. As shown in Figure S4, the relationship for the experimental mixing between CAI and ash percent largely fits with the theoretical mixing, suggesting the potential utility of CAI as an indicator for coal fly ash presence in soils, with the potential of estimating the relative input of fly ash in soils.

To demonstrate the application of the coal ash index, we calculated the CAI values using the weighted enrichment factors of the As−Se−Mo−Sb−Tl assembly for the investigated surface soil samples from Lake Norman and Claxton, respectively (Tables S4 and S5). The results are compared to the theoretical mixing relationship established between the averages of the statewide baseline soil and APP fly ash (Figure 1a,b). Most of the analyzed Lake Norman soil samples have CAI values that are similar to or lower than that of the background sample from Lake Norman State Park (corresponding to ash percent of <4%; Figure S1a). Yet a few samples (6 out of 20) yielded CAI values higher than that of the background soil, with the respective estimated fly ash percent being up to 16%, implying the possible presence of coal fly ash in these soil samples (Figure 1a; Table S4). The CAI values calculated for the Claxton surface soil samples were similarly compared to the ash percent following the theoretical mixing between the averages of the TN baseline soil and APP fly ash (Figure 1b). Compared to the Lake Norman soil samples, we find systematically higher CAI values in 21 out of the 24 soil samples from Claxton relative to the local background soil collected from the Haw Ridge Park (Figure S1b), with estimated coal ash percent up to 20% (Figure 1b; Table S5). To further assess the effectiveness of the CAI method, we employed optical point counting to physically identify and quantify fly ash within the soil samples, based on the fact that coal fly ash particles have distinctive spherical morphologies relative to typical mineral grains in soil and sediments (e.g., quartz, calcite, feldspar, and clay minerals).[66−68] The counting results confirm our hypothesis that the background soil samples from both Lake Norman and Claxton contain zero coal fly ash, even though the CAI values could suggest ∼4.0 and ∼2.1% of fly ash present, respectively (Tables S4 and S5). Besides the local background soils, seven more Lake Norman soil samples and 13 more Claxton soil samples were selected for optical point counting mostly due to their relatively high estimated ash percent by the CAI method (Tables S4 and S5). Fly ash was identified in all of the selected Lake Norman soil samples, including samples with both higher and lower CAI values than that of the background soil, although the point-counted ash percent is generally low, ranging from 0.9 to 6.5% (Table S4). Among the selected Claxton soil samples, fly ash was observed in 12 out 13, with the point-counted ash percent ranging from 1.6 to 16.5%. Sample CCS-15 was estimated to have the highest ash percent by the CAI method (∼20.9%) but had no observable fly ash under microscope (Table S5), demonstrating that solely using the CAI method may result in false detection in some cases, and the need for multiple methods to validate the observation. The estimated ash percent values by CAI for the selected soil samples were plotted against the respective percent values by point counting (Figure 1c). The estimated ash percent for the selected soil samples from Lake Norman was not significantly correlated with that from point counting ($\rho = 0.43$, $p = 0.34$), with most of the CAI-estimated ash percent higher than the point-counted ash percent (Table S4; Figure 1c). In contrast, the selected soil samples from Claxton show a much better correlation between the CAI-estimated ash percent and the point-counted ash percent ($\rho = 0.72$, $p < 0.05$) (Figure 1c). Our data indicate that detecting trace levels of fly ash presence in the soil using the coal ash index (CAI) method can be useful, yet the accuracy of this method is limited, as indicated by the inconsistency between the CAI-estimated ash percent and the point-counted ash percent, particularly for the Lake Norman soil samples.

In addition to the enrichment of the As−Se−Mo−Sb−Tl assembly, the APP fly ash is typically enriched in a suite of trace metals relative to the baseline soils, including Li, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Ba, Th, and U. For each of the individual trace metals, the APP fly ash is significantly higher than the NC baseline and TN baseline soils, respectively, according to the results of Mann−Whitney test ($p < 0.01$) (Figure S5). Therefore, we performed a series of hypothetical mixing calculations between the APP fly ash and the baseline soils to test the potential of using all of the trace metals as indicators for the possible presence of fly ash in soils. Given that the trace element concentrations of both the APP coal fly ash and the NC and TN baseline soils exhibit large variations (Figure S5), we performed the mixing calculations using Monte Carlo simulations to incorporate the variability in the

https://doi.org/10.1021/acs.est.1c01215

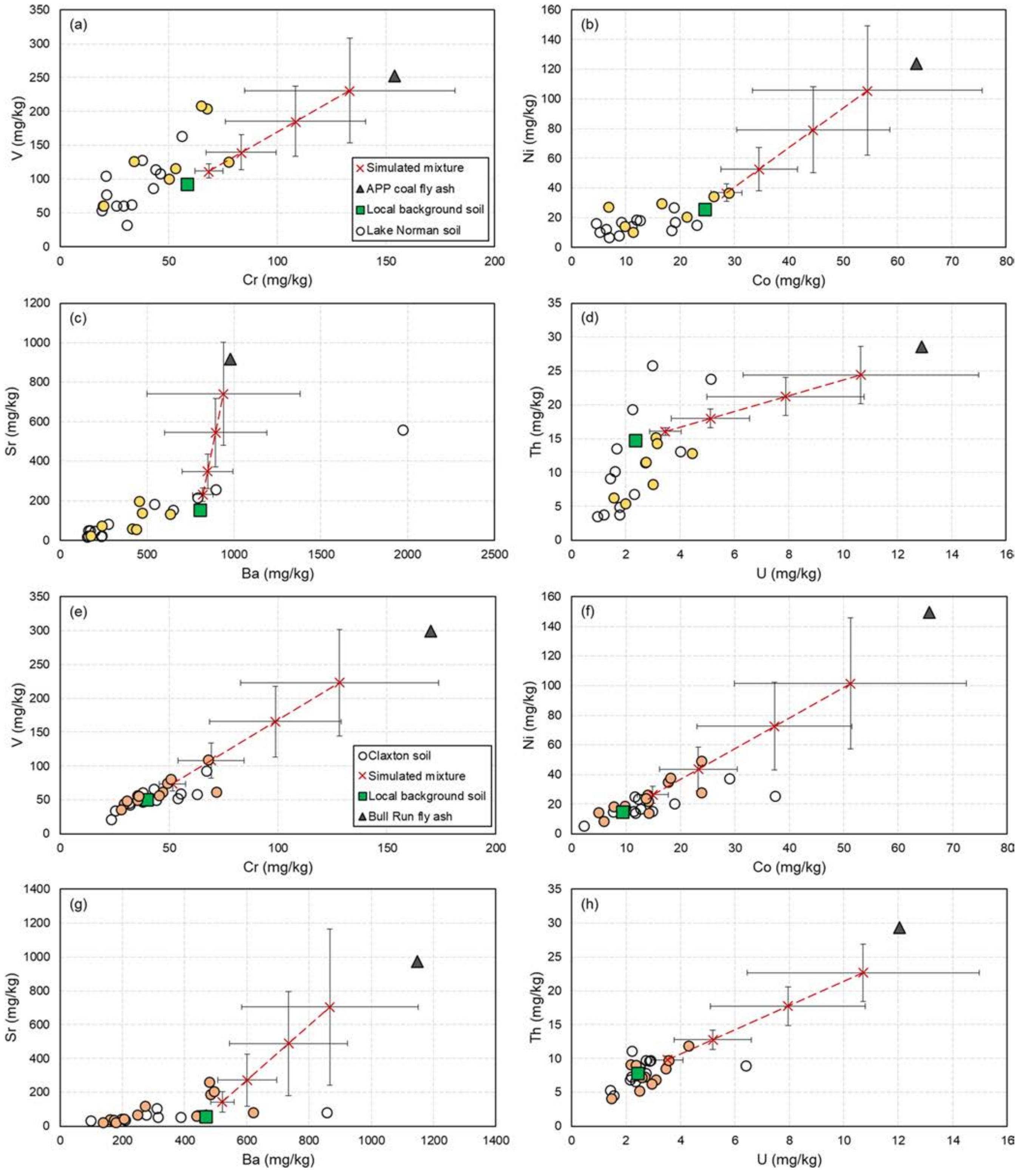


Figure 2. Biplots of trace metals for the surface soil samples collected from Lake Norman, NC and Claxton, Anderson County, TN. (a)−(d) depict the Lake Norman soil, where yellow circles represent the soil samples selected for optical point counting and physically identified to have fly ash presence under microscope, green square represents the background soil from the Lake Norman State Park, and black triangle represents the median value of APP fly ash. (e)−(h) depict the Claxton soil, where pink circles represent the soil samples selected for optical point counting and physically identified to have fly ash presence under microscope, green square represents the background soil from the Haw Ridge Park, and black triangle represents the fly ash sample from the Bull Run Steam Plant. Red mixing line is defined by Monte Carlo simulation between the APP fly ash and the respective local background soil, composed of four simulated mixtures with ash percent of 10, 25, 50, and 75%, respectively, with error bars denoting 95% confidence intervals.

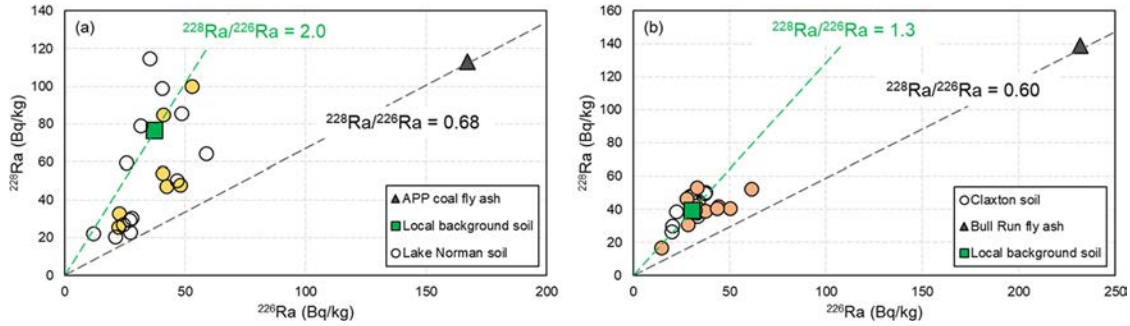


Figure 3. Diagram of ^{228}Ra vs ^{226}Ra for (a) Lake Norman, NC surface soil samples and (b) Claxton, TN surface soil samples. (a) Yellow circles represent the soil samples selected for point counting and physically identified with fly ash presence under microscope, green square represents the background soil from the Lake Norman State Park, and black triangle represents the median value of APP fly ash. The green dotted line marks the ^{228}Ra/^{226}Ra activity ratio of 2.0 for the local background soil of Lake Norman, and black dotted line marks the ^{228}Ra/^{226}Ra activity ratio of 0.68 for the median APP fly ash. (b) Pink circles represent the soil samples selected for point counting and physically identified as containing fly ash via microscopy, green square represents the background soil from the Haw Ridge Park, and black triangle represents the fly ash sample collected from the Bull Run Steam Plant. The green dotted line marks the ^{228}Ra/^{226}Ra activity ratio of 1.3 for the local background soil of Claxton, and black dotted line marks the ^{228}Ra/^{226}Ra activity ratio of 0.60 for the Bull Run fly ash sample. Error bars for the measured samples denote the average 2SD (2 × standard deviation) for ^{226}Ra (1.39 Bq/kg) and ^{228}Ra (2.76 Bq/kg), both of which do not extend past the symbol boundaries and thus are not shown.

concentration data. As with the experimental mixing, four scenarios with the weight percent of fly ash of 10, 25, 50, and 75% were applied to the mixing simulations. Under each mixing scenario, a total of 500 random mixtures were generated, and then the mean and standard deviations for each simulated mixture were calculated, which together define the simulated mixing lines as shown in Figures S5 and S6. Though the trace metal concentrations of APP coal fly ash are distinctively different from those of the NC and TN baseline soils, the results of the mixing simulation show that the simulated mixtures can span a wide range due to the large variations in the trace metal concentrations when the exact end members contributions of soil and fly ash are both unknown (Figures S5 and S6). In most cases, a low percentage of fly ash in the soil (i.e., <10%) does not yield appreciable differences relative to the majority of baseline soil, while increasing the fraction of fly ash leads to a more distinguishable soil−ash mixture from the baseline soil (Figures S5 and S6). This suggests that although trace metal concentrations have the potential to indicate fly ash presence in soils, they have limited sensitivity, particularly in detecting low levels of fly ash and in cases where the chemistry of the pristine soil end-member is not well defined.

However, when the pristine background soil composition is known, the performance of the hypothetical mixing using the trace metal concentrations can be significantly improved, as demonstrated by the two study sites. Since we have no information about the chemistry of fly ash generated specifically from the Marshall Steam Station in North Carolina, we used the median value of the APP fly ash (Table S2) as a reference for the fly ash end-member for the Lake Norman case because this plant has utilized primarily APP coals. For the Claxton case in Tennessee, we used data of actual fly ash collected directly from the Bull Run Steam Plant (Table S2). Mixing calculations were performed using the Monte Carlo method under the same scenarios as described above (i.e., 10, 25, 50, and 75% of fly ash addition) between the background soils and the APP and Bull Run fly ash. The selected trace metal concentrations in all of the soil samples are plotted in Figure 2. While the soil samples from Lake Norman did not follow the mixing lines derived from the mixing simulations and the theoretical mixing proportions were not consistent with actual counting data (Figure 2a−d), soil samples from Claxton showed a better agreement between the hypothetical mixing and the actual point-counted ash percent in the soils (Figure 2e−h). We conclude that the detection of fly ash using only the trace metal concentrations in soil samples with a low percentage of fly ash has limited sensitivity, whereas soil with higher fly ash percentages (i.e., >10%) showed higher correspondence between the theoretical mixing relationships and physical observation under microscope.

Evaluation of Radium Isotope Indicators for the Presence of Coal Fly Ash in Soils. Given the limitation of the trace element indicators, we also explored the applicability of using the abundance of Ra nuclides as a tracer of coal fly ash in soils. Radium is a naturally occurring radioactive material (NORM) that is derived from the decay chains of Th and U, where ^{228}Ra ($t_{1/2}$ = 5.7 years) is the decay product of ^{232}Th and ^{226}Ra ($t_{1/2}$ = 1601 years) is a progeny nuclide of the ^{238}U decay series. As with many other trace elements, Ra is also enriched in fine coal fly ash particles following coal combustion.[37] The average ^{228}Ra/^{226}Ra ratio and the total Ra activity of the APP fly ash are 0.67 and 283 Bq/kg, respectively, which reflects the Th/U activity ratio in the parent coals.[37] In contrast, the ^{228}Ra/^{226}Ra activity and the total Ra activity in average soil are 1.2 and 70 Bq/kg, respectively.[74] Consequently, the distinction in Ra abundance and the ratios between fly ash and common soil highlight the potential utility of Ra isotopes (i.e., ^{228}Ra/^{226}Ra activity ratio) as an indicator for the presence of fly ash in soils.

In the case of Lake Norman, the ^{228}Ra/^{226}Ra activity ratio of local background soil (2.0) is notably higher than that of APP coal fly ash. The ^{228}Ra/^{226}Ra activity ratios of the Lake Norman soil samples ranged from 0.8 to 3.2 (Figure 3a; Table S4). The soil samples selected for the optical point counting that were identified with fly ash presence clearly fall within the hypothetical mixing envelope between the background soil and APP fly ash, except for one sample, which had a ^{228}Ra/^{226}Ra ratio of 2.1, slightly higher than that of background soil. In the case of Claxton, the ^{228}Ra/^{226}Ra activity ratios for all of the soil samples ranged from 0.8 to 1.7 (Table S5), which is much narrower than those for the Lake Norman soil samples. The

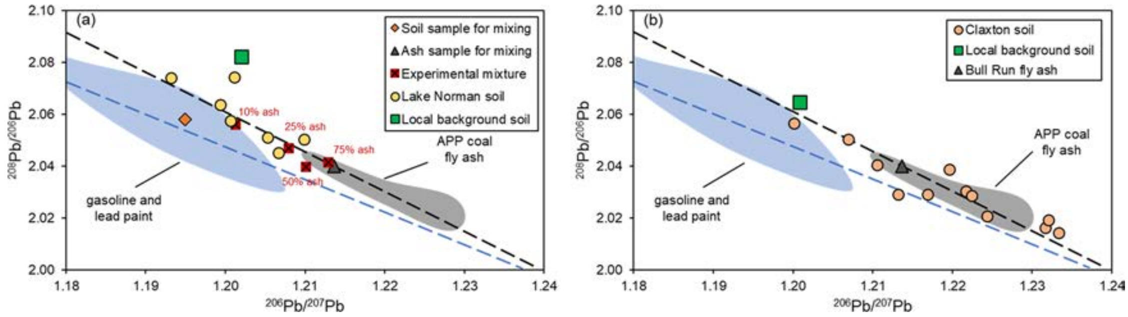


Figure 4. Diagrams of Pb isotope composition (^{208}Pb/^{206}Pb vs ^{206}Pb/^{207}Pb) of (a) selected Lake Norman, NC surface soil samples as well as soil−ash mixtures derived from the experimental mixing between an archived NC surface soil and an APP fly ash sample, and (b) selected Claxton, TN surface soil samples. Blue field represents the partial Pb isotope data compiled for leaded gasoline and lead-based paint in the U.S.[38] For context, gray field represents the Pb isotope data of the APP coal fly ash.[38] Blue dash line is the Pb regression line for gasoline and paint. Black dash line is the Pb regression line for the APP coal fly ash. Error bars that denote the analytical uncertainty 2SD (2 × standard deviation) for ^{208}Pb/^{206}Pb (0.0013) and ^{206}Pb/^{207}Pb (0.0003) do not extend past the symbol boundaries and thus are not shown.

^{228}Ra/^{226}Ra activity ratio of the local background soil of Claxton is 1.3, which is lower than that of Lake Norman background soil, and yet still distinctly higher than that of coal fly ash from Bull Run Steam Plant (^{228}Ra/^{226}Ra = 0.60; Figure 3b). Nine out of 12 samples that were identified as containing fly ash by optical point counting had ^{228}Ra/^{226}Ra ratios within the expected range between the background soil and fly ash, while the three samples with higher ^{228}Ra/^{226}Ra ratios had the lowest point-counted ash percent, 1.6, 1.9, and 3.2% (Table S5). One sample (i.e., CCS-15) had ^{228}Ra and ^{226}Ra activities close to that of the local background soil, which was consistent with the point counting results that did not indicate the presence of fly ash (Table S5). Overall, our data demonstrate the robustness of using Ra isotopes as an additional indicator for the presence of low levels of fly ash in soils, although the sensitivity of this tracer depends on the Ra activities and ^{228}Ra/^{226}Ra ratios of the background soil that could overlap with and mask the contribution of coal fly ash.

Evaluation of Lead Isotope Indicators for the Presence of Coal Fly Ash in Soils. In addition to trace elements and Ra isotopes, we further explored the applicability of Pb isotopes for detecting the occurrence of fly ash in soils. Lead naturally occurs in four stable isotopes, including one nonradiogenic isotope (i.e., ^{204}Pb), and three radiogenic isotopes: ^{208}Pb, a decay product of ^{232}Th, ^{206}Pb, a decay product of ^{238}U, and ^{207}Pb, a decay product of ^{235}U. Lead isotope ratios have been widely used for source tracing Pb contamination in the environment.[75] Typically, on a ^{208}Pb/^{206}Pb vs ^{206}Pb/^{207}Pb isotope diagram, the older Pb ore source appears to be in the upper left quadrant, while the younger Pb ore source is in the lower right quadrant.[38,76] The variations of ^{206}Pb/^{207}Pb ratios reflect the differences in the decay rates of the parent ^{238}U and ^{235}U nuclides and the differences in ^{208}Pb/^{206}Pb ratios generally reflect variations of the ratios of the parent isotopes ^{232}Th and ^{238}U.[76] The Pb isotope signature of the U.S. coal fly ash has been shown to be distinct from both natural soil and major anthropogenic Pb sources (i.e., leaded gasoline and lead-based paint), and thus it has been suggested for detecting the occurrence of coal ash in the environment.[38]

Figure 4a shows the Pb isotope compositions of the experimental mixtures composed of a NC surface soil sample and an APP fly ash sample. Evidently, the surface soil sample we used for the experiment has a Pb isotopic signature that reflects the leaded gasoline and lead-based paint isotope composition, which is distinctly different from that of the fly ash sample that is within the compositional field of APP fly ash (Figure 4a).[38] The four soil−ash mixtures, however, shift from the Pb regression line of gasoline and paint and display a clear two-end-member mixing array between the soil and fly ash samples (Table S3; Figure 4a). Despite some offsets from the mixing line, the experimental mixing results follow the expected mixing between the soil and fly ash samples and follow the Pb regression line of fly ash (Figure 4a). Therefore, we suggest that soil samples plotting along the Pb regression line of the APP fly ash likely indicate the possible presence of fly ash.

The Pb isotope ratios (i.e., ^{208}Pb/^{206}Pb and ^{206}Pb/^{207}Pb) of the soil samples from Lake Norman and Claxton selected for point counting are presented in Tables S4 and S5 and plotted in Figure 4a,b, respectively. In the case of Lake Norman, the Pb isotope composition of the local background soil was clearly outside the compositional field and away from the regression line of the APP fly ash, consistent with the results that showed no presence of coal fly ash, as indicated by trace elements, Ra isotopes, and optical point-counting data (Figure 4a; Table S4). The Pb isotope compositions of the analyzed soil samples were different from that of the background soil and largely followed the APP fly ash regression line, except for one sample, which had the lowest counted ash percent of 0.9% (Figure 4a; Table S4). Similarly, the Pb isotope compositions of most of the analyzed soil samples from Claxton in TN that have shown evidence for fly ash presence were different from the Pb isotope composition of the local background soil, and most of these soil samples plotted along the regression line of the APP fly ash (Figure 4b; Table S5). While the analyzed soil samples from Lake Norman showed some offset from the compositional field of the APP fly ash (Figure 4a), most of the analyzed Claxton soil samples have Pb isotope compositions that overlap with the APP fly ash compositional field with notably higher ^{206}Pb/^{207}Pb and lower ^{208}Pb/^{206}Pb ratios (Figure 4b). In addition to the influence of coal fly ash, the systematically lower ^{208}Pb/^{206}Pb ratios observed in the Claxton soil samples are possibly due to a greater proportion of parent nuclide ^{238}U relative to ^{232}Th in the TN soils compared to NC soils, which is shown by the significantly higher U concentrations in the TN baseline soils (Table S2). Nonetheless, our data show that Pb isotopes can be a reliable indicator for the presence of coal fly ash in soils.

https://doi.org/10.1021/acs.est.1c01215

Integration and Implications. The results from this study show that the coal ash index (CAI), which features the enrichment of the As−Se−Mo−Sb−Tl assembly in fly ash, could provide a first-order evaluation of the possible presence of coal fly ash in soils, with the potential to estimate the ash percent. However, our data show that using the CAI as a sole indicator could result in an overestimation of the fly ash contribution, particularly when fly ash percentage in soils is low (e.g., <10%). Additionally, the ability to detect the presence of coal fly ash could be impeded by high concentrations of trace metals in the background soils and/or interference from trace metal contributions from other sources.[77,78] When the compositions of background soil and fly ash end members are unknown, the sensitivity of the trace-elements method is further decreased. We therefore posit that sole reliance on trace elements is not sufficient to detect the presence of trace levels of coal fly ash in soils. Instead, adding additional isotopic tracers such as Ra and Pb isotopes can serve as a more robust tool for detecting even trace levels of fly ash in soils. Consequently, to enhance the detectability of fly ash in soils, we suggest the integration all of these geochemical tools, which collectively can help to avoid potential detection bias and provide a better constraint on the results. The geochemical and isotopic methods provided in this study present another set of tools that can be used in concert with optical counting to detect the occurrence of coal fly ash and its associated contaminants in soils.

The presence of fly ash in soils implies two major potential pathways of human exposure: inhalation and ingestion. Due to the fine particles that are typically within the respirable range,[17] as well as the high abundances of toxic metals, fly ash poses concerning risks to human health, particularly for people working and living in communities near coal-fired power plants and coal ash disposal sites. For example, our data show that the Claxton soil samples with the highest counted ash percent (i.e., samples CCS-2, 3, 4; Table S5) were collected from a community park, which is commonly used for recreation by local residents. In spite of the relatively low concentrations of hazardous trace metals in the studied soil samples, which in most cases were below the guideline values recommended by the US EPA and other environmental agencies for hazardous trace metals in soils and dust (Figures S8 and S9), the detection of fly ash on surface soil in these communities could also indicate possible occurrence of fly ash in the nearby house dust.

Overall, in this study, we demonstrate the utility of using an integration of geochemical tools (i.e., trace elements, Ra and Pb isotopes) to detect trace levels of coal fly ash in surface soils collected from both recreational and residential areas near coal-fired power plants. Our data show evidence for the occurrence of fly ash particles, likely derived from fugitive emission from nearby coal power plants and deposition on the surrounding soils. Although we only observed relatively only low levels of heavy metals in the impacted soils, these soils could further become a source of human exposure to certain heavy metals tracked into house dust. This study focuses on developing reliable geochemical tools to identify low levels of coal fly ash in soils near coal plants, and yet future studies should investigate the time frame and mechanisms of fly ash deposition on surface soils. While fly ash emissions from coal-fired power plants in the U.S. were common before the installation of pollution control devices beginning 1970s,[79] the possibility of continued fugitive emission of fly ash particles from the Bull Run and Marshal Steam coal plants cannot be ruled out. It may be possible to determine the time frame of fly ash deposition on surface soils (i.e., legacy fly ash emissions vs recent fugitive emission) through analysis of the abundance of the ^{137}Cs radionuclide in coal fly ash-containing soils. ^{137}Cs was primarily derived from atmospheric nuclear weapons testing, which began in the early 1950s and peaked in 1963.[80] Coal fly ash co-occurring with elevated ^{137}Cs in soils from stable and undisturbed landscapes would indicate fly ash accumulation from the pre-1970s emission legacy, whereas relatively low ^{137}Cs would reflect more recent fly ash emission. Finally, while this study is focused on soils, the geochemical tools presented here can also be applied to detect the presence of coal ash solids in other environmental matrices, including house dust and aquatic sediments. Future research should expand this study and investigate the occurrence of fly ash in house dust in homes located near coal plants and the human health risks associated with chronic exposure to dust particles containing trace levels of fly ash.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c01215.

> Details of coal ash index (CAI) calculation; determination of percent ash by optical point counting; photomicrographs of fly ash particles identified in soils; maps of Lake Norman in North Carolina and Claxton in Tennessee showing sampling locations of surface soils surrounding the operating coal-fired power plants; distribution curves of trace elements in an archived surface soil from NC and an APP fly ash and their theoretical and experimental mixtures at mixing ratios of 10, 25, 50, and 75%; ash percent (%) vs coal ash index (CAI) plot of the mixing experiment using an archived NC surface soil sample and a fly ash sample derived from the Appalachian (APP) Basin coals; biplots of trace metal pairs for Monte Carlo simulated mixing between the APP fly ash and NC baseline soil (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Avner Vengosh − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States;* orcid.org/0000-0001-8928-0157; Phone: 919-681-8050; Email: vengosh@duke.edu; Fax: 919-684-5833

Authors

Zhen Wang − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States*

Rachel M. Coyte − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States;* orcid.org/0000-0001-6369-5311

Ellen A. Cowan − *Department of Geological and Environmental Sciences, Appalachian State University, Boone, North Carolina 28608, United States*

Heather M. Stapleton − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States;* orcid.org/0000-0002-9995-6517

Gary S. Dwyer − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States*

Complete contact information is available at:

https://pubs.acs.org/10.1021/acs.est.1c01215

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was funded by the National Science Foundation (EAR-1932649) and Mooresville community funding led by Susan Wind. The authors thank the local communities in Lake Norman and Claxton for their help with sample collection. The constructive comments from two anonymous reviewers that have improved the quality of this paper are greatly appreciated.

■ REFERENCES

(1) *American Coal Ash Association*; 2019 Coal Combustion Product (CCP) Production and Use Survey Report, 2020.

(2) 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, Vol. *2015−3037*, https://doi.org/10.3133/fs20153037, p 6.

(3) Córdoba, P.; Ochoa-Gonzalez, R.; Font, O.; Izquierdo, M.; Querol, X.; Leiva, C.; López-Antón, M. A.; Díaz-Somoano, M.; Rosa Martinez-Tarazona, M.; 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.

(4) 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.

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

(6) 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.

(7) Klein, D. H.; Andren, A. W.; Carter, J. A.; Emery, J. F.; Feldman, C.; Fulkerson, W.; Lyon, W. S.; Ogle, J. C.; Talmi, Y. Pathways of Thirty-Seven Trace Elements through Coal-Fired Power Plant. *Environ. Sci. Technol.* **1975**, *9*, 973−979.

(8) Linton, R. W.; Williams, P.; Evans, C. A. Determination of the Surface Predominance of Toxic Elements in Airborne Particles by Ion Microprobe Mass Spectrometry and Auger Electron Spectrometry. *Anal. Chem.* **1977**, *49*, 1514−1521.

(9) Smith, R. D. The Trace Element Chemistry of Coal during Combustion and the Emissions from Coal-Fired Plants. *Prog. Energy Combust. Sci.* **1980**, *6*, 53−119.

(10) Carlson, C. L.; Adriano, D. C. Environmental Impacts of Coal Combustion Residues. *J. Environ. Qual.* **1993**, *22*, 227−247.

(11) Izquierdo, M.; Querol, X. Leaching Behaviour of Elements from Coal Combustion Fly Ash: An Overview. *Int. J. Coal Geol.* **2012**, *94*, 54−66.

(12) Kosson, D. S.; van der Sloot, H. A.; Sanchez, F.; Garrabrants, A. C. An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environ. Eng. Sci.* **2002**, *19*, 159−204.

(13) Nelson, P. F.; Shah, P.; Strezov, V.; Halliburton, B.; Carras, J. N. Environmental Impacts of Coal Combustion: A Risk Approach to Assessment of Emissions. *Fuel* **2010**, *89*, 810−816.

(14) Swaine, D. J. Trace Elements in Coal and Their Dispersal during Combustion. *Fuel Process. Technol.* **1994**, *39*, 121−137.

(15) Thorneloe, S. A.; Kosson, D. S.; Sanchez, F.; Garrabrants, A. C.; Helms, G. Evaluating the Fate of Metals in Air Pollution Control Residues from Coal-Fired Power Plants. *Environ. Sci. Technol.* **2010**, *44*, 7351−7356.

(16) 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 U.S.: Boston, MA, 2003; pp13−24.

(17) Zierold, K. M.; Odoh, C. A Review on Fly Ash from Coal-Fired Power Plants: Chemical Composition, Regulations, and Health Evidence. *Rev. Environ. Health* **2020**, *35*, 401−418.

(18) 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.

(19) 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.

(20) 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.

(21) 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.

(22) 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.

(23) Dennis Lemly, A. Damage Cost of the Dan River Coal Ash Spill. *Environ. Pollut.* **2015**, *197*, 55−61.

(24) 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.

(25) 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.

(26) 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.

(27) Klein, D. H.; Russell, P. Heavy Metals. Fallout around a Power Plant. *Environ. Sci. Technol.* **1973**, *7*, 357−358.

(28) Sato, K.; Sada, K. Effects of Emissions from a Coal-Fired Power Plant on Surface Soil Trace Element Concentrations. *Atmos. Environ., Part A* **1992**, *26*, 325−331.

(29) Bhanarkar, A. D.; Gavane, A. G.; Tajne, D. S.; Tamhane, S. M.; Nema, P. Composition and Size Distribution of Particules Emissions from a Coal-Fired Power Plant in India. *Fuel* **2008**, *87*, 2095−2101.

(30) Schroeder, W. H.; Dobson, M.; Kane, D. M.; Johnson, N. D. Toxic Trace Elements Associated with Airborne Particulate Matter: A Review. *JAPCA* **1987**, *37*, 1267−1285.

(31) Wang, N.; Sun, X.; Zhao, Q.; Yang, Y.; Wang, P. Leachability and Adverse Effects of Coal Fly Ash: A Review. *J. Hazard. Mater.* **2020**, *396*, No. 122725.

(32) Alberts, J. J.; Newman, M. C.; Evans, D. W. Seasonal Variations of Trace Elements in Dissolved and Suspended Loads for Coal Ash Ponds and Pond Effluents. *Water, Air, Soil Pollut.* **1985**, *26*, 111−128.

(33) Dreesen, D. R.; Gladney, E. S.; Owens, J. W.; Perkins, B. L.; Wienke, C. L.; Wangen, L. E. Comparison of Levels of Trace Elements Extracted from Fly Ash and Levels Found in Effluent Waters from a Coal-Fired Power Plant. *Environ. Sci. Technol.* **1977**, *11*, 1017−1019.

(34) 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.

(35) 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*, 14790−14798.

(36) Davidson, G. R.; Bassett, R. L. Application of Boron Isotopes for Identifying Contaminants Such as Fly Ash Leachate in Groundwater. *Environ. Sci. Technol.* **1993**, *27*, 172−176.

(37) 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*, 11227−11233.

(38) 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*, No. 714.

(39) Hurst, R. W.; Davis, T. E. Strontium Isotopes as Tracers of Airborne Fly Ash from Coal-Fired Power Plants. *Environ. Geol.* **1981**, *3*, 363−367.

(40) Hurst, R. W.; Davis, T. E.; Elseewi, A. A. Strontium Isotopes as Tracers of Coal Combustion Residue in the Environment. *Eng. Geol.* **1991**, *30*, 59−77.

(41) Hurst, R. W.; Davis, T. E.; Elseewi, A. A. Strontium and Lead Isotopes as Monitors of Fossil Fuel Dispersion. *Trace Elements in Coal and Coal Combustion Residues*; CRC Press, 1993.

(42) Wang, Z.; Coyte, R. M.; Dwyer, G. S.; Ruhl, L. S.; Hsu-Kim, H.; Hower, J. C.; Vengosh, A. Distinction of Strontium Isotope Ratios between Water-Soluble and Bulk Coal Fly Ash from the United States. *Int. J. Coal Geol.* **2020**, *222*, No. 103464.

(43) 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.

(44) Vaněk, A.; Grösslová, Z.; Mihaljevič, M.; Trubač, J.; Ettler, V.; Teper, L.; Cabala, J.; Rohovec, J.; Zádorová, T.; Penížek, V.; Pavlů, L.; Holubík, O.; Němeček, K.; Houška, J.; Drábek, O.; Ash, C. Isotopic Tracing of Thallium Contamination in Soils Affected by Emissions from Coal-Fired Power Plants. *Environ. Sci. Technol.* **2016**, *50*, 9864−9871.

(45) 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.

(46) 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.

(47) Rodríguez Martín, J. A.; Nanos, N. Soil as an Archive of Coal-Fired Power Plant Mercury Deposition. *J. Hazard. Mater.* **2016**, *308*, 131−138.

(48) Raja, R.; Nayak, A. K.; Shukla, A. K.; Rao, K. S.; Gautam, P.; Lal, B.; Tripathi, R.; Shahid, M.; Panda, B. B.; Kumar, A.; Bhattacharyya, P.; Bardhan, G.; Gupta, S.; Patra, D. K. Impairment of Soil Health Due to Fly Ash-Fugitive Dust Deposition from Coal-Fired Thermal Power Plants. *Environ. Monit. Assess.* **2015**, *187*, No. 679.

(49) Çayır, A.; Belivermiş, M.; Kılıç, Ö.; Coşkun, M.; Coşkun, M. Heavy Metal and Radionuclide Levels in Soil around Afsin-Elbistan Coal-Fired Thermal Power Plants, Turkey. *Environ. Earth Sci.* **2012**, *67*, 1183−1190.

(50) Cicek, A.; Koparal, A. S. Accumulation of Sulfur and Heavy Metals in Soil and Tree Leaves Sampled from the Surroundings of Tunçbilek Thermal Power Plant. *Chemosphere* **2004**, *57*, 1031−1036.

(51) Ćujić, M.; Dragović, S.; Đorđević, M.; Dragović, R.; Gajić, B. Environmental Assessment of Heavy Metals around the Largest Coal Fired Power Plant in Serbia. *CATENA* **2016**, *139*, 44−52.

(52) Dragović, S.; Ćujić, M.; Slavković-Beškoski, L.; Gajić, B.; Bajat, B.; Kilibarda, M.; Onjia, A. Trace Element Distribution in Surface Soils from a Coal Burning Power Production Area: A Case Study from the Largest Power Plant Site in Serbia. *CATENA* **2013**, *104*, 288−296.

(53) George, J.; Masto, R. E.; Ram, L. C.; Das, T. B.; Rout, T. K.; Mohan, M. Human Exposure Risks for Metals in Soil Near a Coal-Fired Power-Generating Plant. *Arch. Environ. Contam. Toxicol.* **2015**, *68*, 451−461.

(54) Glöbel, B.; Andres, C. Investigations on Fly-Ash and Soil Samples in the Environment of a Coal-Fired Power Plant. *Sci. Total Environ.* **1985**, *45*, 63−67.

(55) Huang, X.; Hu, J.; Qin, F.; Quan, W.; Cao, R.; Fan, M.; Wu, X. Heavy Metal Pollution and Ecological Assessment around the Jinsha Coal-Fired Power Plant (China). *Int. J. Environ. Res. Public Health* **2017**, *14*, No. 1589.

(56) Keegan, T. J.; Farago, M. E.; Thornton, I.; Hong, B.; Colvile, R. N.; Pesch, B.; Jakubis, P.; Nieuwenhuijsen, M. J. Dispersion of As and Selected Heavy Metals around a Coal-Burning Power Station in Central Slovakia. *Sci. Total Environ.* **2006**, *358*, 61−71.

(57) Lu, X.; Liu, W.; Zhao, C.; Chen, C. Environmental Assessment of Heavy Metal and Natural Radioactivity in Soil around a Coal-Fired Power Plant in China. *J. Radioanal. Nucl. Chem.* **2013**, *295*, 1845−1854.

(58) Mandal, A.; Sengupta, D. An Assessment of Soil Contamination Due to Heavy Metals around a Coal-Fired Thermal Power Plant in India. *Environ. Geol.* **2006**, *51*, 409−420.

(59) Nanos, N.; Grigoratos, T.; Rodríguez Martín, J. A.; Samara, C. Scale-Dependent Correlations between Soil Heavy Metals and As around Four Coal-Fired Power Plants of Northern Greece. *Stoch. Environ. Res. Risk Assess.* **2015**, *29*, 1531−1543.

(60) Okedeyi, O. O.; Dube, S.; Awofolu, O. R.; Nindi, M. M. Assessing the Enrichment of Heavy Metals in Surface Soil and Plant (*Digitaria eriantha*) around Coal-Fired Power Plants in South Africa. *Environ. Sci. Pollut. Res.* **2014**, *21*, 4686−4696.

(61) Praharaj, T.; Tripathy, S.; Powell, M. A.; Hart, B. R. Geochemical Studies to Delineate Topsoil Contamination around an Ash Pond of a Coal-Based Thermal Power Plant in India. *Environ. Geol.* **2003**, *45*, 86−97.

(62) Rodriguez-Iruretagoiena, A.; Fdez-Ortiz de Vallejuelo, S.; Gredilla, A.; Ramos, C. G.; Oliveira, M. L. S.; Arana, G.; de Diego, A.; Madariaga, J. M.; Silva, L. F. O. Fate of Hazardous Elements in Agricultural Soils Surrounding a Coal Power Plant Complex from Santa Catarina (Brazil). *Sci. Total Environ.* **2015**, *508*, 374−382.

(63) Tang, Q.; Liu, G.; Zhou, C.; Zhang, H.; Sun, R. Distribution of Environmentally Sensitive Elements in Residential Soils near a Coal-Fired Power Plant: Potential Risks to Ecology and Children's Health. *Chemosphere* **2013**, *93*, 2473−2479.

(64) Wangen, L. E.; Williams, M. D. Elemental Deposition Downwind of a Coal-Fired Power Plant. *Water, Air, Soil Pollut.* **1978**, *10*, 33−44.

(65) Zhang, Y.; Wu, D.; Wang, C.; Fu, X.; Wu, G. Impact of Coal Power Generation on the Characteristics and Risk of Heavy Metal Pollution in Nearby Soil. *Ecosystem Health Sustainability* **2020**, *6*, No. 1787092.

(66) 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.

(67) Cowan, E. A.; Seramur, K. C.; Hageman, S. J. Magnetic Susceptibility Measurements to Detect Coal Fly Ash from the Kingston Tennessee Spill in Watts Bar Reservoir. *Environ. Pollut.* **2013**, *174*, 179−188.

(68) Cowan, E. A.; Epperson, E. E.; Seramur, K. C.; Brachfeld, S. A.; Hageman, S. J. Magnetic Susceptibility as a Proxy for Coal Ash Pollution within Riverbed Sediments in a Watershed with Complex Geology (Southeastern USA). *Environ. Earth Sci.* **2017**, *76*, No. 657.

(69) Smith, D. B.; Cannon, W. F.; Woodruff, L. G.; Solano, F.; Kilburn, J. E.; Fey, D. L. Geochemical and Mineralogical Data for Soils of the Conterminous United States: U.S. Geological Survey Data Series, 801, 19 p, 2013; https://pubs.usgs.gov/ds/801/.

(70) 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.

(71) Fisher, G. L.; Prentice, B. A.; Silberman, D.; Ondov, J. M.; Biermann, A. H.; Ragaini, R. C.; McFarland, A. R. Physical and

Morphological Studies of Size-Classified Coal Fly Ash. *Environ. Sci. Technol.* **1978**, *12*, 447−451.

(72) Hower, J. C. Petrographic Examination of Coal-Combustion Fly Ash. *Int. J. Coal Geol.* **2012**, *92*, 90−97.

(73) Team, R. C. *R: A Language and Environment for Statistical Computing*, Vienna, Austria, 2018.

(74) International Atomic Energy Agency. *The Environmental Behaviour of Radium*; International Atomic Energy Agency: Vienna, 2014.

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

(76) Graney, J. R.; Landis, M. S. Coupling Meteorology, Metal Concentrations, and Pb Isotopes for Source Attribution in Archived Precipitation Samples. *Sci. Total Environ.* **2013**, *448*, 141−150.

(77) Steinnes, E.; Friedland, A. J. Metal Contamination of Natural Surface Soils from Long-Range Atmospheric Transport: Existing and Missing Knowledge. *Environ. Rev.* **2011**, *14*, 169−186.

(78) Environmental Pollution. In *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*, 3rd ed.; Alloway, B. J., Ed.; Springer: Netherlands, 2013; https://doi.org/10.1007/978-94-007-4470-7.

(79) Grimley, D. A.; Lynn, A. S.; Brown, C. W.; Blair, N. E. Magnetic Fly Ash as a Chronological Marker in Post-Settlement Alluvial and Lacustrine Sediment: Examples from North Carolina and Illinois. *Minerals* **2021**, *11*, No. 476.

(80) He, Q.; Walling, D. E. The Distribution of Fallout 137Cs and 210Pb in Undisturbed and Cultivated Soils. *Appl. Radiat. Isot.* **1997**, *48*, 677−690.