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Legacy of anthropogenic lead in urban soils: Co-occurrence with metal(loids) and fallout radionuclides, isotopic fingerprinting, and in vitro bioaccessibility

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Elevated Pb commonly co-occurs with metal(loids) Zn, Cd, and Sb in urban soils.
- Radionuclides ¹³⁷Cs and ²¹⁰Pb reflect disturbances and contaminant mobilization.
- Legacy lead-based paint and gasoline are dominant in urban centers.
- Atmospheric deposition results in significant enrichment of Pb, Zn, Cd, and Sb.
- Over half of Pb in contaminated soils was potentially bioavailable.

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ABSTRACT

Anthropogenic lead (Pb) in soils poses risks to human health, particularly to the neuropsychological development of exposed children. Delineating the sources and potential bioavailability of soil Pb, as well as its relationship with other contaminants is critical in mitigating potential human exposure. Here, we present an integrative geochemical analysis of total elemental concentrations, radionuclides of ¹³⁷Cs and ²¹⁰Pb, Pb isotopic compositions, and in vitro bioaccessibility of Pb in surface soils sampled from different locations near Durham, North Carolina. Elevated Pb (>400 mg/kg) was commonly observed in soils from urban areas (i.e., near residential house foundation and along urban streets), which co-occurred with other potentially toxic metal(loids) such as Zn, Cd, and Sb. In contrast, soils from city parks and suburban areas had systematically lower concentrations of metal (loids) that were comparable to geological background. The activities of ¹³⁷Cs and excess ²¹⁰Pb, coupled with their correlations with Pb and co-occurring metal(loids) were used to indicate the persistence and remobilization of historical atmospherically deposited contaminants. Coupled with total Pb concentrations, the soil Pb isotopic compositions further indicated that house foundation soils had significant input of legacy lead-based paint $(mean = 1.1895 and 2.0618 for {}^{206}Pb/{}^{207}Pb and {}^{208}Pb/{}^{206}Pb, respectively)$, whereas urban streetside soils exhibiited a clear mixed origin, dominantly of legacy leaded gasoline (1.2034 and 2.0416) and atmospheric deposition (1.2004–1.2055 and 2.0484–2.0525). The in vitro bioaccessibility of Pb in contaminated urban soils furthermore revealed that more than half of Pb in the contaminated soils was potentially bioavailable, whose Pb isotope ratios were identical to that of bulk soils, demonstrating the utility of using Pb isotopes for tracking human exposure to

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anthropogenic Pb in soils and house dust. Overall, this study demonstrated a holistic assessment for comprehensively understanding anthropogenic Pb in urban soils, including its co-occurrence with other toxic contaminants, dominant sources, and potential bioavailability upon human exposure.

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1. Introduction

Human activities are increasingly impacting the elemental fluxes in the Earth's surface environment (Klee and Graedel, 2004; Sen and Peucker-Ehrenbrink, 2012). Among all elements, potentially toxic and carcinogenic metals and metalloids including Hg, Pb, As, Cd, and Cr (VI) raise serious concerns due to their adverse impacts on the ecosystem and human health (Ali et al., 2019; Mishra et al., 2019; Rahman and Singh, 2019). Soils are one of the major repositories in the environment for accumulation of these anthropogenically-sourced metal(loids) relative to respective geological background levels (Callender, 2014; Senesil et al., 1999; Wuana and Okieimen, 2011). Soils in urban environments are highly vulnerable to metal(loids) contamination, because of the potential influences by fossil fuels and widespread use in building materials exacerbated by intensifying industrialization (Imperato et al., 2003; Li et al., 2018; Manta et al., 2002; Thornton, 2009; Wong et al., 2006).

Lead is toxic to human nervous, digestive, and reproductive systems, and low levels of Pb exposure during childhood could result in neuropsychological development issues, rendering no safe threshold for human exposure (ORD US EPA, 2015a). The historic use of Pb additives in gasoline and house paint contributed to the majority of anthropogenic Pb in the urban environment, which has declined considerably since the bans took effect between 1970s and 1990s (Mielke et al., 2011, 2019; ORD US EPA, 2015a). However, legacies of these Pb sources still persist in both urban and remote soils and continue to pose longterm public health risks (Datko-Williams et al., 2014; Harlavan et al., 2021; Mielke et al., 2011). Most recent studies suggested that, even decades after the Pb ban, historical Pb stored in soils serves as a persisting source of present atmospheric Pb in the environment due to the remobilization and deposition of contaminated dust (Harlavan et al., 2021; Resongles et al., 2021). In addition to Pb, other metal(loids), including Cd, Zn, Cu, As, Mn, Ba, and Ni, likely derived from various anthropogenic activities, such as mining and metalliferous production (Das et al., 2018; Pelfrêne et al., 2012), fossil fuel combustion (Agrawal et al., 2010; George et al., 2015), waste incineration (Li et al., 2019), vehicular emission (Wang and Zhang, 2018; Wang et al., 2019a), and civil construction (Li et al., 2001; Pan et al., 2016; Turner and Lewis, 2018) could all be contributed to urban soils directly or via atmospheric deposition.

Fallout radionuclides, such as ¹³⁷Cs and ²¹⁰Pb, are removed directly from the atmosphere via dry and wet deposition, and have a strong affinity for soil and sediment particles (He and Walling, 1997). The manmade radionuclide, ¹³⁷Cs ($t_{1/2} = 30.12$ years), was primarily derived from atmospheric nuclear weapons testing, whose deposition began in early 1950s and peaked in 1963 (He and Walling, 1997; Walling and He, 1999). The natural radioactive Pb isotope, ²¹⁰Pb ($t_{1/2} =$ 22.26 years), is constantly released into the atmosphere via ²²²Rn emission and decay (Mabit et al., 2014). While both ¹³⁷Cs and ²¹⁰Pb have been widely used to quantify soil and sediment erosion and mixing processes (Crusius et al., 2004; He and Walling, 1997; Mabit et al., 2008; Walling and He, 1999), to the best of our knowledge, literature on the distribution of the two fallout radionuclides and their association with metal(loids) contamination in urban soils is sparse (Vukašinović et al., 2018).

Identifying various sources of anthropogenic metal(loids) in soils by using stable isotope fingerprints is helpful for tracking and controlling their presence and mobilization in the environment (Wang et al., 2021). Lead naturally occurs in four stable isotopes, including one non-radiogenic isotope (i.e., ²⁰⁴Pb), and three radiogenic isotopes, ²⁰⁸Pb,

²⁰⁷Pb, and ²⁰⁶Pb, which are the products of ²³²Th, ²³⁵U, and ²³⁸U decay chains, respectively. The use of Pb isotopes ratios (e.g., ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb) has shown to be effective in tracing the sources of Pb and its contamination in soils (Hansmann and Köppel, 2000; Kelepertzis et al., 2016, 2020, 2021). Furthermore, compared to the total concentration, the bioavailable fraction of metals in soils, which represents the maximum amount available to human tissues and organs, is more relevant for assessing exposure risk and human health effect (Ge et al., 2000; US EPA, 2013). The in vitro bioaccessibility is a measure of the physiological solubility of the metal that may be available for adsorption into the body, which is used for predicting the in vivo bioavailability (Marschner et al., 2006; OLEM US EPA, 2015; Zia et al., 2011). While the bulk Pb isotope compositions could help to identify the contribution of various Pb sources in soils, the isotopic signatures of bioaccessible soil Pb might be more useful for specifically tracking Pb sources in the human body (Gulson, 2008; Kelepertzis et al., 2021; Li et al., 2015; Sharp and Brabander, 2017).

A recent study conducted a geospatial analysis of the hotspots of total soil Pb contamination in the city of Durham, North Carolina, for which the legacies of leaded gasoline and lead-based paint were suggested to be the major cause (Wade et al., 2021). Yet, the direct evidence for the sources of Pb contamination, as well as the bioavailability of Pb in the contaminated soils and their isotopic signatures have not been elucidated. In addition, we hypothesize that elevated soil Pb would be accompanied by the occurrence of other metals and metalloids. Further, the occurrence of fallout radionuclides ¹³⁷Cs and excess ²¹⁰Pb could be used to indicate the persistence and remobilization of atmospherically deposited metal(loids) in impacted urban soils. Therefore, by integrating the analyses of total elemental concentrations, fallout radionuclides, Pb isotopic compositions, and in vitro bioaccessibility of Pb, this study aimed to (1) evaluate the co-occurrence of Pb with other metal(loids) and fallout radionuclides; (2) characterize the isotopic compositions of soil Pb for fingerprinting its dominant sources; and (3) assess the in vitro bioaccessibility of Pb in contaminated soils, as well as the isotopic signatures of bioaccessible Pb and its potential utility for tracking anthropogenic Pb in the human body. This integrated approach provides a holistic geochemical methodology to evaluate the occurrence, sources, and potential exposure risks of Pb and other metal(loids) in an urban environment.

2. Methods and materials

2.1. Sample collection and preparation

A total of 99 surface soil samples (i.e., 2-3 cm of the mineral-soil surface excluding the overlying organic materials) were collected around the city of Durham, NC and analyzed in this study. They were grouped into four categories based on their sampling locations (Fig. 1): (1) soils collected near the house foundation of single-family properties (n = 31) in downtown Durham, of which 28 samples were from houses built prior to the 1978 ban on lead-based paint; (2) soils sampled from the curbside of major urban streets in Durham (n = 42); (3) soils collected from the open grassland of city parks (n = 19); and (4) soils sampled from the streetsides in suburban areas (n = 7), following the sampling protocol in Wade et al. (2021). In addition, deeper soils from the downtown area were collected (30–50 cm depth; n = 2) as local geogenic background and soils from a core (up to 22 cm deep, representing A horizon soil; n = 7) were sampled from the Korstian Division of Duke Forest at a site (35.9959°N, 79.0280°W; >4 km from the nearest highway) with a gentle slope and minimal tree canopy. The bedrock

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Fig. 1. Map of the soil sampling locations in Durham city, North Carolina, USA (35.9886°N, 78.9072°W, as shown on the inset map) for this study.

geology of the studied area is mostly Triassic sedimentary rocks composed of sandstone with interbedded siltstone, with occasional occurrences of diabase dikes (Hanna and Bradley, 2016).

All soil samples were oven-dried at 40 °C until reaching a constant weight, plant residues and gravels were removed by hand, and the remaining soil was passed through a 2-mm stainless-steel sieve for homogenization. A subset of each sample by coning and quartering was ground using ceramic mortar and pestle to pass a 200-mesh stainless-steel sieve for subsequent chemical analysis.

2.2. Total elemental concentrations

The total concentrations of Pb along with a suite of metal(loids) (i.e., Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Cd, Sb, and Ba) in all soil samples were measured on a Thermo Fisher X-Series II inductively coupled plasma mass spectrometer (ICP-MS) at Duke University. All soil samples were digested in a HF-HNO3 mixture, and the details of sample digestion and instrumental analysis are described in previous studies (Vengosh et al., 2019; Wang et al., 2019b, 2020). The efficiency of digestion and accuracy of measurement were assessed by measuring the National Institute of Standards and Technology (NIST) standard reference material (SRM) 2711a for moderately elevated trace element concentrations in Montana II soil. The average percent recovery as well as relative standard deviations for all the analyzed metal(loids) from repeated measurements of SRM 2711a (n = 8) over the course of analysis are presented in Table S1. The accuracy of analysis was reflected by the mean percent recovery >90% (ranging from 92.0% to 99.9%) for all the measured metal(loids), except for Cr with a lower recovery of 86.7%.

The precision of analysis was indicated by the coefficient of variations (i.e., RSD) of <10% (from 3.8% to 8.6%) for all the metal(loids).

2.3. Radionuclide activities

The activities of ²²⁶Ra, ²¹⁰Pb, and ¹³⁷Cs in selected soil samples were determined on a Canberra broad-energy germanium gamma detector (HPGe) at Duke University. The sample packing and incubation followed the method reported in Lauer et al. (2015). Each measurement lasted for at least 120,000 s in order to minimize the uncertainty associated with photon counting statistics. ²²⁶Ra was analyzed through the ²¹⁴Bi (609 keV) peak, ²¹⁰Pb was measured directly through its 46.5 keV peak, and ¹³⁷Cs was determined from the 662 keV peak. Excess ²¹⁰Pb activity was calculated by the difference of total ²¹⁰Pb and ²²⁶Ra under secular equilibrium conditions. Detector efficiencies for U-series radionuclides were calibrated using a certified U-Th ore reference material (Canadian Certified Reference Materials Project DL-1a) packed and incubated in the same geometry as the samples. Detector efficiency for ¹³⁷Cs was provided by a calibrated solution purchased through Eckert & Ziegler. To correct for the self-attenuation of the low-energy ²¹⁰Pb photon, the point-source transmission method described in Cutshall et al. (1983) was adopted and performed for each individual sample. The average uncertainties (2SD) for excess ²¹⁰Pb and ¹³⁷Cs are 8.40 and 1.23 Bq/kg, respectively.

2.4. Lead isotopic compositions

The Pb isotope ratios (i.e., ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁶Pb, and ²⁰⁶Pb/²⁰⁷Pb) of selected soil samples were measured on a high-

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resolution Triton thermal ionization mass spectrometer (TIMS) at Duke University, equipped with Faraday cups and operating in static mode. A common Pb standard NIST SRM 981 was measured regularly over the course of analysis (n = 31) and the mass bias for all isotope ratios was determined according to the expected values (Yuan et al., 2016). The Pb column separation and purification are detailed in Wang et al. (2019b). The long-term average analytical uncertainties (2SD) are 0.0316 for ²⁰⁸Pb/²⁰⁴Pb, 0.0079 for ²⁰⁶Pb/²⁰⁴Pb, 0.0008 for ²⁰⁸Pb/²⁰⁶Pb, and 0.0002 for ²⁰⁶Pb/²⁰⁷Pb.

2.5. In vitro bioaccessibility of Pb

The U.S. EPA Method 1340 (OLEM US EPA, 2015) was used to approximate the bioaccessible Pb in selected soil samples. For each sample, 1.00 (\pm 0.05) g of material was placed and then 100 (\pm 0.5) mL of extraction fluid (0.4 M glycine, pH 1.50 \pm 0.05, temperature 37 \pm 2 °C, simulated gastric fluid) was added into a 125-mL wide-mouth HDPE bottle. Extraction was conducted in a water bath at 37 \pm 2 °C and rotated at 30 \pm 2 rpm for 1 h. After extraction, ~40 mL aliquot was taken and filtered with 0.45-µm cellulose acetate disk filter and stored into a pre-acid-washed 60-mL HDPE bottle for ICP-MS analysis. For QA/QC, SRM 2711a was measured (n = 3) along with the tested soil samples, which yielded a mean bioaccessibility for Pb of 84.7% (RSD = 1.4%; Table S2), agreeing well with the recommended value of 85.7% (OLEM US EPA, 2015).

2.6. Calculations and statistical analysis

The enrichment factor (EF) was used to quantify the magnitude of potential anthropogenic contribution of metal(loids) in soils, which is defined as: $EF = \frac{|X|/(Rb)sample}{|X|/(Rb)background}$, where [X] is the concentration of a metal or metalloid, and [Rb] is the concentration of Rb, which has been routinely used as a reference element due to its relative stability in soil and its dominant lithogenic origin (Barbieri, 2016; Zoller et al., 1974). Generally, EF < 2 suggests natural weathering processes, whereas EF > 5 most likely reflects contribution from non-crustal sources (i.e., anthropogenic contamination) (Barbieri, 2016). The enrichment factors (EF) of metal(loids) for all the surface soils were calculated by normalizing to the mean total concentrations of the two deeper soil samples (30–50 cm).

Nonparametric analyses, including Spearman's rank correlation and Mann-Whitney test, were employed, where rho (ρ) represents the correlation coefficient, and statistical significance is evaluated based on p value (i.e., p < 0.01 for 99% confidence interval and 0.01 for 95% confidence interval). Principal component analysis (PCA) was conducted for the purpose of multivariate analysis. For plotting and

interpretation, the first two components (PC1 and PC2) with eigenvalues greater than 1 and explaining most of the variances were extracted. All statistical analyses were performed using R (v 4.0.2) (R Core Team, 2018).

3. Results and discussion

The results of total elemental concentrations, ²¹⁰Pb and ¹³⁷Cs radionuclide activities, Pb stable isotopic compositions, and Pb bioaccessibility and its isotope ratios of the investigated soil samples are tabulated in Supplementary Materials (Tables S3–14).

3.1. Co-occurrence of metal(loids) and fallout radionuclides

3.1.1. Total concentrations and enrichment factors

Mean total concentration (\pm standard deviation) of Pb in the house foundation soils was the highest (2281 \pm 2868 mg/kg, n = 31), significantly higher than those of the urban streetside soils (321 \pm 533 mg/kg, n = 42), the city park soils (42.1 ± 25.0 mg/kg, n = 19), and the suburban streetside soils (15.9 \pm 3.58 mg/kg, n = 7) (p < 0.01; Tables S3-6; Fig. 2). This observed Pb distribution among different soil groups is consistent with the data reported in an earlier study (Wade et al., 2021). Our results agree with the findings in other U.S. cities like Indianapolis (Filippelli et al., 2018) and Greensboro (Obeng-Gyasi et al., 2021), where soils near homes present the highest Pb concentration likely due to the direct input of exterior house paint, yet contrast to cities such as Detroit (Zahran et al., 2013a) and New Orleans (Zahran et al., 2013b), where soils close to roadways account for the highest Pb exposure risk due to the resuspension of contaminated soil. In addition to Pb, the highest total concentrations of Zn, Cu, Sb, Cd, and Ba were observed in the house foundation soils, which were significantly higher than that of the other three soil groups (p < 0.01), except for Ba (Figs. S1-2). The total concentrations of Cr and Ni in the urban streetside soils were significantly higher than that of the other soil groups (0.01 ; Figs. S2–3). No significant difference was observed among the four soil groups for Mn and Co (Fig. S2). The suburban streetside soils had significantly higher total concentrations of V and As compared to the other three soil groups (0.01 Fig. S3).

The total elemental concentrations for all the surface soil samples were compared to the risk-based regional screening levels (RSL) for metal(loids) and/or their compounds in residential soil as recommended by the U.S. EPA (Table S8) (ORD US EPA, 2015b). The enrichment factors (EF) of measured metal(loids) for all the surface soil samples are shown in Tables S9–12. In addition to the low total elemental concentrations, the deeper soil samples had non-detectable excess ²¹⁰Pb and ¹³⁷Cs activities and a distinctive geogenic Pb isotope composition that we discuss later (Tables S7; Fig. 5c). For Pb, over half of the



Fig. 2. Boxplots of total concentrations and enrichment factors of Pb in the surface soil samples of different groups: house foundation, urban streetside, city park, and suburban streetside. The red dashed line marks the regional screening level (RSL) 400 mg/kg of Pb for residential soil by the U.S. EPA. The red solid line represents the enrichment factor of 5 and the brown solid line marks the enrichment factor of 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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house foundation soils exceeded the RSL (i.e., 400 mg/kg), about a guarter of the urban streetside soil samples were above this threshold, while none of the city park and suburban streetside soils had Pb levels above this threshold (Fig. 2; Tables S3-6). Consistently, the relative enrichment (i.e., EF values; see Methods and materials section) of Pb for most of the foundation soils were above 5 (median = 77), which was also observed in over half of the urban streetside soil samples (median = 8.9), in contrast to the city park soils (median = 1.8) and suburban streetside soils (median = 0.9) mostly with EF values < 2 (Fig. 2; Tables S9-12). Similar to Pb, this trend was also observed for other metals including Ba, Sb, Cd, Zn, and Cu (Figs. S1-2; Tables S9-12). Zinc, in particular, was above the EF of 5 in all four soil groups (Fig. S1), with EF of Zn in the house foundation soils (median = 266) significantly higher than that of the urban streetside soils (median = 26), city park soils (median = 11), and suburban streetside soils (median = 12) (p < 0.01; Tables S9–12), indicating ubiquitous anthropogenic contamination in surface soils across the city, although the total concentrations of Zn did not exceed the RSL of 2300 mg/kg for the majority of soils (only ~7% exceedance). It should be noted that the exceedances of RSL and EF values of metal(loids) are not necessarily consistent, likely due to the lack of consideration of local geological variations in the establishment of RSLs (Boente et al., 2020). For example, the EF values of As, Cr, V, Co, and Rb largely fell below 2 or within the range of 2 and 5, indicating their dominant lithogenic origin, although their absolute concentrations were above the respective RSL values in many of the soil samples (Figs. S2–3). Overall, while with a relatively small sample size, our data shows that soils from urban areas were generally much higher in Pb and Zn, and to a less extent, in Cu, Sb, and Cd, than soils from suburban areas. This coincides with the trend of urbanization for many cities in the U.S., where old downtown areas have much higher anthropogenic legacies than the newly developing areas outside downtown, as shown by a previous study with a much larger sample size in Indianapolis, Indiana (Filippelli et al., 2018).

3.1.2. Correlations of Pb with metal(loids)

We observed strong positive correlations between the total concentrations of Pb and other metal(loids) in the house foundation soils, including Ba, Sb, Cd, Zn, Mn (p < 0.01), and As (p = 0.05) (Table 1; Fig. S4), weak positive correlations with Co, Cu, Ni, and Cr, and weak negative correlations between Pb and Rb, Al, Fe, and V (Table 1). Similarly, the total concentrations of Pb in the urban streetside soils and city park soils were positively correlated with Sb, Cd, Zn, and Cu (p < 0.01), marginally with Mn for the city park soils ($\rho = 0.48$, p = 0.04; Table 1; Figs. S5–6), while no significant correlations were observed between Pb and other metal(loids) (i.e., As, Ni, Co, Cr, V, Rb, Fe, and Al) in both soil groups (Table 1). In comparison, the Pb concentrations in the suburban streetside soils exhibited positive correlations

Table 1

Spearman's correlation coefficient (ρ) between Pb and other metal(loids) in the surface soil samples of different groups.

| Metal (loids) | House foundation | Urban streetside | City park | Suburban streetside |
|------------------|---------------------|---------------------|--------------|------------------------|
| Ва | 0.72** | 0.06 | 0.28 | 0.82* |
| Sb | 0.72** | 0.57** | 0.85** | 0.71 |
| Cd | 0.91** | 0.80** | 0.62** | -0.87 |
| Rb | -0.36^{*} | -0.05 | 0.13 | 0.71 |
| As | 0.35* | 0.19 | 0.32 | 0.64 |
| Zn | 0.90** | 0.80** | 0.66** | -0.11 |
| Cu | 0.29 | 0.57** | 0.59** | 0.79* |
| Ni | 0.17 | 0.29 | 0.33 | -0.11 |
| Со | 0.32 | 0.01 | 0.42 | -0.25 |
| Cr | 0.11 | 0.29 | 0.45 | 0.04 |
| V | -0.19 | -0.06 | 0.27 | 0.79* |
| Mn | 0.46** | -0.02 | 0.48* | -0.46 |
| Fe | -0.23 | 0.00 | 0.27 | 0.82* |
| Al | -0.26 | -0.03 | 0.02 | 0.82* |

Statistical significance is noted as **p < 0.01 and *0.01 .

with Ba ($\rho = 0.82$, p = 0.03), Cu and V ($\rho = 0.79$, p = 0.05), Fe and Al ($\rho = 0.82$, p = 0.03), and Rb ($\rho = 0.71$, p = 0.09) (Table 1; Fig. S7).

Given their general origins, Pb, Sb, Cd, As, Zn, and Cu in soils are often grouped as anthropogenically-sourced metal(loids), Al, Fe, and Rb are generally associated with lithogenic sources, whereas metals such as V, Cr, Co, Ni, Ba, and Mn are likely to be of both lithogenic and anthropogenic origins (Barbieri, 2016; Zhang, 2006). Positive correlations are likely suggestive of co-occurrences of metal(loids) with shared sources and/or similar mobility (Gunawardana et al., 2015), which could also be tested by the principal component analysis (PCA). The PCA analyses for the house foundation, urban streetside, and city park soil groups, show that Pb was commonly associated with Cd, Sb, and Zn with higher loadings on PC1 that explained the largest variance, whereas V, Cr, Ni, and Co had more resemblance to Al and Fe with higher loadings on PC2 (Fig. S8). Therefore, in all the three soil groups, PC1 likely represents the anthropogenic source, whereas PC2 reflects the geogenic source. In contrast, Pb, as well as Al, Fe, and Rb, in the suburban streetside soils had higher loadings on PC1, suggesting a geogenic origin, whereas Co, Ni, Cr, Zn, Mn, and Cd had higher loadings on PC2, likely indicating their anthropogenic origins (Fig. S8). Based on the combined results of metal(loids) correlations with Pb and the PCA analyses, we suggest that Pb in the urban soils (i.e., house foundations, urban streetside soil, and city park soils) is co-occurring with Cd, Sb, Cu, Zn, Ba, and Mn, all of which were primarily derived from anthropogenic sources. Metals like Pb, Cd, Zn, and Ba that were highly correlated in the house foundation soils are likely to be derived by the contamination of lead-based paint (Mielke et al., 2001; Turner and Lewis, 2018). In addition, the significant enrichment of Zn in the house foundation soils could also be caused by the Zn addition in the galvanized roofing materials, and thus roof runoff containing large amount of Zn could further result in the accumulation in the soils near foundations (Chang et al., 2004; Filippelli et al., 2018). Finally, metal(loids) like V, Mn, Sb, and Cu that were found in the urban streetside and city park soils are more likely to be derived from vehicular and/or industrial emissions (Li et al., 2019; Resongles et al., 2021; Wang and Zhang, 2018; Wang et al., 2019a).

3.1.3. Correlations of fallout radionuclides with Pb

Previous studies have used ¹³⁷Cs variations in soil and lake sediments to detect atmospheric deposition during the 1950s and 1960s (i.e., the beginning and peak of atmospheric nuclear testing) for evaluating accumulated versus eroded soils (He and Walling, 1997; Mabit et al., 2008). Yet little is known about the distribution of ¹³⁷Cs and excess ²¹⁰Pb and their relationships with Pb and other metal(loids) contamination in urban soils. Selected soil samples from the house foundation and urban streetside groups that have elevated Pb concentrations were measured for fallout radionuclides ¹³⁷Cs and excess ²¹⁰Pb. Our data showed significantly higher ¹³⁷Cs activities in the house foundation soils compared to those in the urban streetside soils (p < 0.01), whereas no significant difference was observed between the two soil groups for the excess ²¹⁰Pb activities (p = 0.65; Fig. S9). In addition, the ¹³⁷Cs activities were found to be highly correlated to total Pb concentrations in the house foundation soils ($\rho = 0.70$, p < 0.01) and urban streetside soils ($\rho = 0.57$, p = 0.012), as shown in Fig. 3. In addition to Pb, metal(loids) such as Zn, Cd, Sb, Ba, Mn, and Cu were also correlated with ¹³⁷Cs activity in the house foundation soils (Fig. S10).

These results are consistent with the hypothesis that the two fallout radionuclides, in particular ¹³⁷Cs, can be used to indicate the persistence and remobilization of atmospherically deposited metal(loids) in urban soils. The variations between the two soil groups likely reflect the degree of mechanical and/or biological disturbances and soil erosion that is greater in the urban streetside soils than in the house foundation soils, likely resulted from the more significant pedogenic processes occurred in the urban streetside soils (Wade et al., 2021). While elevated ¹³⁷Cs activities reflect past atmospheric deposition (i.e., early 1960s),

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Fig. 3. Bivariate plots of ¹³⁷Cs vs. excess ²¹⁰Pb, ¹³⁷Cs versus total Pb concentration, and excess ²¹⁰Pb versus total Pb concentration in the house foundation and urban streetside soil samples. Error bars represent 2SD counting uncertainty for radionuclides.

the activities of excess ²¹⁰Pb in soils would reflect continuous atmospheric flux given its natural origin from ²²²Rn emission and decay. Consequently, while the high correlation between ¹³⁷Cs and Pb in the house foundation soils is directly linked to the historical Pb and other metal (loids) contamination, the weaker correlation between the excess ²¹⁰Pb activities and total Pb concentrations in the house foundation soils ($\rho = 0.54$, p = 0.012) and the non-significant one in the urban streetside soils ($\rho = 0.09$, p = 0.72; Fig. 3) is attributed to continuous deposition of ²¹⁰Pb over time. Overall, the co-occurrence of fallout radionuclides with Pb and other metal(loids) in the soils near house foundations is likely due to: (1) long-term accumulation and preservation of radionuclides along with metal(loids) originated from historical contamination of residual lead-based paint in the house foundation soils as hypothesized by Wade et al. (2021); and/or (2) input of atmospherically deposited metal(loids) and radionuclides in roof runoff that resulted in the accumulation in soils near house foundations (Chang et al., 2004; Dockal and Dockal, 1989).

3.2. Isotopic fingerprints of anthropogenic Pb sources

3.2.1. Atmospheric deposition

The geochemical signatures of atmospheric deposition were characterized by studying the undisturbed forest soils located away from the city to eliminate the possible influence of other anthropogenic sources (Fig. 1). The activities of both fallout radionuclides ¹³⁷Cs and excess 210 Pb ranged from the top 2 cm (16.2 \pm 0.6 and 84.3 \pm 4.5 Bq/kg, respectively) to the bottom 3 cm (0.70 ± 0.3 and 0.73 ± 1.3 Bg/kg, respectively) in the Duke Forest soil core (A horizon, total 22 cm; Table S13), showing a sharp decrease from the surface to the depth of 15 cm and remaining relatively constant to the core bottom (Fig. 4a-b). Similarly, the total Pb concentration showed a decrease from 39.6 mg/kg at the top 2 cm to 7.1 mg/kg at the bottom 3 cm, with the upper portion (~15 cm) significantly higher than the lower section (p < 0.01; Table S13; Fig. 4c). In addition to Pb, the total concentrations of other metal(loids), including Mn, Fe, V, Cr, Co, As, Cd, Sb, and Ba, decreased with depth (Table S13; Fig. S11). Furthermore, the ²⁰⁶Pb/²⁰⁷Pb ratios exhibited a marked depth-dependence, in which higher ²⁰⁶Pb/²⁰⁷Pb ratios (i.e., more radiogenic) were observed in the surficial layers (Fig. 4d). Collectively, the results were consistent with previous studies on remote and undisturbed soils, indicating that atmospheric deposition was the major source of accumulation of Pb as well as other metal (loids), which could penetrate the soil to depths between 10 and 20 cm (He and Walling, 1997; Kaste et al., 2003; Puchelt et al., 1993). In contrast, the profiles of Ni, Cu, and Zn with depth were similar to that of Al, suggesting that natural mineral weathering outpaced atmospheric deposition for these metals, while Rb was relatively constant over depth (Fig. S11; Table S13).

Given the profiles of both radionuclides and metal(loids), one would suggest that soil at depth > 20 cm likely represents the geogenic background. However, in spite of the notable depth-dependent change

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Fig. 4. Downward profiles of geochemical signatures of the Duke Forest soil core (A horizon). (a) Profile of excess ²¹⁰Pb activity. (b) Profile of ¹³⁷Cs activity. (c) Profiles of total Pb concentration. (d) Profile of ²⁰⁶Pb/²⁰⁷Pb ratio.

(Fig. 4d), the Pb isotope ratios of all the soil samples from the core were within the isotopic range of the Piedmont A horizon soils reported from Virginia (Reimann et al., 2011), as well as that of the eastern U.S. aerosols (Bollhöfer and Rosman, 2001, 2002) and followed the regression line of the U.S. Pb ores, which have contributed to the major anthropogenic Pb in the U.S. (Fig. 5c). C horizon soils (i.e., deeper than 80-100 cm), generally reflecting the geogenic source, have been shown to have higher ²⁰⁶Pb/²⁰⁷Pb ratios than the A horizon soils (Reimann et al., 2011), which is contrary to the observed decreasing trend that we showed in the Duke Forest soil core (Fig. 4d). This implies the presence of anthropogenic contributions of Pb and other metal (loids) throughout the A horizon soil core, even though the absolute concentrations were low and comparable to the geological background. This is consistent with previous studies that have suggested anthropogenic Pb is widespread in A horizon soils across the U.S. (Reimann et al., 2011; Woodruff et al., 2015). Furthermore, the observed isotopic changes in the Duke Forest soil core (Fig. 4d) likely reflect the temporal changes in the source of lead ores used in gasoline in the U.S. Idaho ore deposits with less radiogenic Pb (i.e., 206 Pb/ 207 Pb = ~1.06) was mostly used in gasoline until the 1960s (Hurst et al., 1996), after which the use of more radiogenic Pb from Mississippi Valley Type (MVT) deposits (i.e., 206 Pb/ 207 Pb = ~1.40) in gasoline increased until 1980s (Hurst et al., 1996; Kamenov et al., 2009). However, since deeper soils were not collected at the same coring site, we would not exclude the possibility that the less radiogenic ratios in the lower portion are the mixing result of the anthropogenic source and less radiogenic geogenic source. Overall, we posit that atmospheric deposition of anthropogenic Pb is notable even in a remote area like Duke Forest and was accompanied by the synchronous enrichment of other metal(loids). The magnitude of atmospheric deposition and accumulation of anthropogenic metal(loids) increased over time, with variations of the Pb isotope ratios in the soil that could reflect the changes of different Pb ores used in the U.S. over time (Hurst et al., 1996; Kamenov et al., 2009).

3.2.2. Legacies of lead-based paint and leaded gasoline in the urban environment

The house foundation soils displayed a wide range of Pb isotope ratios (i.e., 37.6732–39.5828 for 208 Pb/ 204 Pb, 17.8597–19.9615 for 206 Pb/ 204 Pb, 1.1435–1.2663 for 206 Pb/ 207 Pb, and 1.9829–2.1095 for 208 Pb/ 206 Pb, respectively; Table S3). The urban streetside soils had a similar yet narrower range, varying from 37.7764–38.8727 for 208 Pb/ 204 Pb, 17.9485–19.4647 for 206 Pb/ 204 Pb, 1.1522 to 1.2374 for

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Fig. 5. (a) Boxplot of ²⁰⁸Pb/²⁰⁶Pb ratios of all groups of soil samples. (b) Boxplot of ²⁰⁶Pb/²⁰⁷Pb ratios of all groups of soil samples. (c) Lead isotope plot (²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb) of all the soil samples analyzed in this study, with Pb isotope compositions of major potential Pb sources from literature used for context, including leaded gasoline (Chow and Johnstone, 1965; Dunlap et al., 2000; Sherrell et al., 1992), lead-based paint (Jaeger et al., 1998; Rabinowitz, 1987; Viczian et al., 1990), eastern U.S. aerosols (Bollhöfer and Rosman, 2001, 2002), and Appalachian coal fly ash (Wang et al., 2019b). Red dash line indicates the regression line of the U.S. Pb ores. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

²⁰⁶Pb/²⁰⁷Pb, and 1.9971 to 2.1048 for ²⁰⁸Pb/²⁰⁶Pb (Table S4). While the inclusion of ²⁰⁴Pb in plotting Pb isotope data could infer multiple sources that may not be easily revealed without ²⁰⁴Pb (i.e., via ²⁰⁸Pb/²⁰⁶Pb vs ²⁰⁶Pb/²⁰⁷Pb diagram) (Ellam, 2010), the ²⁰⁸Pb/²⁰⁴Pb vs ²⁰⁶Pb/²⁰⁴Pb diagram shown in Fig. S12a did not exhibit significant differences from Fig. 5c, thus much of the discussions will be focused on the ²⁰⁸Pb/²⁰⁶Pb versus ²⁰⁶Pb/²⁰⁷Pb diagram (Fig. 5c). The Pb isotope ratios of the house foundation soils were significantly different from that of the urban streetside soils (p = 0.014 for ²⁰⁶Pb/²⁰⁷Pb and p < 0.01 for ²⁰⁸Pb/²⁰⁶Pb; Fig. 5a–b). Both ranges encompassed that for the city park soils with ²⁰⁶Pb/²⁰⁷Pb from 1.1822 to 1.2184 and ²⁰⁸Pb/²⁰⁶Pb from 2.0150 to 2.0706 (Table S5; Fig. 5a–b), and for the suburban streetside soils, whose Pb isotope ratios ranged from 1.1912–1.2138 and 2.0402–2.0597 for ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb, respectively (Table S6; Fig. 5a–b).

Despite the large variations, the Pb isotope ratios of the house foundation soils were overall less radiogenic than that of the other soil groups (Fig. 5a–b), and they mostly followed the regression line of U.S. Pb ores and overlapped with the compositional field of lead-based paint (Fig. 5c). In contrast, the Pb isotope compositions of the urban streetside soils were divergent from the Pb ore regression line, and mostly within the compositional field of eastern U.S. aerosols (Fig. 5c), implying the mixing sources of Pb in the urban streetside soils, most likely from leaded gasoline and atmospheric deposition. Likewise, the Pb isotope ratios of the city park soils, suburban streetside soils, and the Duke Forest soils were largely clustered together and within the compositional field of aerosols, indicating mixing between atmospheric deposition and the local geogenic background soils that are represented by that of the deeper soils in downtown Durham (30–50 cm) (Table S7). Indeed, the isotope composition of the deeper soils was off the Pb ore regression line with higher ²⁰⁸Pb/²⁰⁶Pb ratios (Fig. 5c), consistent with the signatures of general natural soil Pb (Wang et al., 2019b). Generally, the Pb isotope compositions of the legacy anthropogenic Pb in the U.S., including that of gasoline (Chow and Johnstone, 1965; Dunlap et al., 2000; Sherrell et al., 1992) and paint (Jaeger et al., 1998; Rabinowitz, 1987; Viczian et al., 1990), are relative non-radiogenic (i.e., higher ²⁰⁸Pb/²⁰⁶Pb and lower ²⁰⁶Pb/²⁰⁷Pb ratios), reflecting the source of relatively olderage Pb ores (Fig. 5c). However, due to the changes of Pb used in gasoline from non-radiogenic Idaho ores (i.e., $^{206}Pb/^{207}Pb = \sim 1.06$) to radiogenic and younger MVT ores since 1960s (i.e., ${}^{206}Pb/{}^{207}Pb = \sim 1.40$) (Hurst et al., 1996), and the increasing contributions of additional Pb sources in the environment since the phase-out of Pb use in both gasoline and paint (e.g., coal combustion) (Komárek et al., 2008; Wang et al., 2019b), the isotope compositions of modern anthropogenic Pb have become appreciably mixed, as reflected by the isotope variations of aerosols in the U.S. (Bollhöfer and Rosman, 2001, 2002). In addition, we did not observe any significant correlations between the ²⁰⁶Pb/²⁰⁷Pb ratios and total Pb concentrations, although the combination of the two showed a good separation between the house foundation soils and the urban streetside soils (Fig. S12b). Overall, the Pb isotope data confirm the hypothesis made in an earlier study that the high Pb levels in house foundation soils were mainly

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derived from the legacy of lead-based paint (Wade et al., 2021). Yet the mixing nature of Pb isotopic compositions of urban streetside soils reflects the influences of both the legacies of leaded gasoline and atmospheric deposition.

3.3. In vitro bioaccessibility of Pb in contaminated soils

Based on the U.S. EPA's 400 mg/kg regulatory guidance value for Pb in residential soil, samples from the house foundation soils (n = 21) and urban streetside soils (n = 13) that were above or near this threshold value were tested for in vitro bioaccessibility (IVBA) (Table S14). The IVBA of Pb for the tested house foundation soil samples ranged from 38.2% to 91.2%, averaging 55.5%, while that for the urban streetside soil samples was from 21.1% to 80.9%, with an average of 63.1%, which was significantly higher than that of the house foundation soils (p =0.04; Table S14). While the U.S. EPA Method 1340 is only intended for Pb in soil (OLEM US EPA, 2015), the bioaccessibility of other metal (loids) in the studied soils is also worth mentioning. The highest IVBA values were observed for Cd in both soil groups, averaging 89.5% for the foundation soils and 86.8% for the urban streetside soils, followed by Zn, averaging 75.2% for the foundation soil and 51.9% for the urban streetside soil. Cadium in both soil groups was more bioaccessible than Pb, which was higher in the urban streetside soils and lower in the house foundation soils than Zn (Fig. S13). The relatively high in vitro bioaccessibilities of Cd, Pb, and Zn were also found in soils elsewhere (Kelepertzis et al., 2021). This is likely due to that Cd is mostly in free inoic form, whereas Pb and Zn are more likely to exist as organic complexes in soil solutions (Ge et al., 2000). As opposed to Cd, Zn, and Pb, metal(loids) like Sb, V, and Cr were the least bioaccessible metals (<10%) in both soil groups, whereas Mn, Co, Cu, As, Ba, and Ni had intermediate bioaccessibilities, as illustrated in Table S14 and Fig. S13. As discussed earlier, Al, Fe, and Rb are dominantly derived from geogenic sources, which tend to have much less labile (i.e., bioaccessible) fraction Science of the Total Environment xxx (xxxx) xxx

as opposed to anthropogenically-sourced metal(loids) (i.e., V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sb, Ba, and Pb) (Ge et al., 2000). This was reflected by our data in which Al, Fe, and Rb had negligible bioaccessibilities in both soil groups (~1%, Table S14).

Consistent with previous studies (Li et al., 2015; Sharp and Brabander, 2017), the bioaccessible Pb of the tested soil samples in this study was highly correlated with their total Pb concentration, as shown in Fig. 6a, implying that anthropogenic Pb dominantly contributes to the bioaccessible Pb in soils. Further, the measured bioaccessible Pb isotopic compositions showed significant difference between that of house foundation soils and urban streetside soils (p < 0.01; Fig. 6b), mimicking the isotopic differences between the bulk soils that reflect the differences in their dominant Pb sources. The legacy of lead-based paint for house foundation soils and the legacy of leaded gasoline and atmospheric deposition for urban streetside soils (see discussion in Section 3.2.2). While with slight variations, the Pb isotope ratios measured for the bioaccessible fraction of Pb in the tested soil samples were therefore mostly consistent with the Pb isotope ratios of the bulk soils (Fig. 6c-d). This isotopic similarity between the bioaccessible Pb and total soil Pb is different from what was reported previously in China (Li et al., 2015) and in Greece (Kelepertzis et al., 2021), which could be explained by the different isotopic signatures of the anthropogenic Pb sources in the U.S. from China and Europe (Bi et al., 2017; Komárek et al., 2008) and the differential Pb leachability in different soils. Consequently, the isotope ratios of bioaccessible Pb could be further used for tracking human exposure to soil Pb, which can be traced in biological materials such as blood, teeth, and hair in exposed populations (Gulson, 2008).

3.4. Human health implications

Considering both the U.S. EPA regulatory guidance value of 400 mg/kg for Pb in residential soils and the more conservative risk-



Fig. 6. (a) Concentration of bioaccessible Pb versus concentration of total Pb in the tested house foundation soils (n = 21) and urban streetside soils (n = 13). (b) Boxplot of Pb isotope ratios (i.e., ²⁰⁶Pb/²⁰⁷Pb) of bioaccessible Pb versus isotope ratios of total Pb in the tested soils. (c)–(d) Pb isotope ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) of bioaccessible Pb versus isotope ratios of total Pb in the tested soils.

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based screening level of 100 mg/kg adopted by European countries (Jennings, 2013), Durham soils near residential house foundations (mean Pb = 2281 mg/kg) and along urban streets (mean Pb = 321 mg/kg) certainly pose greater risks to human health than soils in city parks (mean Pb = 42.1 mg/kg) and suburban areas (mean Pb = 15.9 mg/kg). This is because elevated Pb found in residential soils is likely to be further tracked into house dusts and thus become the source for human exposure to Pb (Hunt et al., 2006; Hunt and Johnson, 2012; Laidlaw et al., 2014). Further, as suggested by the in vitro bioaccessibility assessment, over 55% (on average) of Pb in house foundation soils and 63% of Pb in urban streetside soils are likely to be bioavailable via oral ingestion.

In addition, the co-occurrence and significant enrichment of other potentially toxic metal(loids) such as Zn, Cd, and Sb and fallout radionuclides excess ²¹⁰Pb and ¹³⁷Cs in house foundation soils due to long-term accumulation and lack of disturbances furthermore raises concerns about multi-element exposure. Given that over 90% of house foundation soils investigated in this study were from pre-1978 properties, which account for 85% of single-family homes citywide (Wade et al., 2021), residents in oldage houses are undoubtedly more vulnerable to such exposure than those living in newly-built homes. In contrast, soils from urban streetside are more likely subjected to soil disturbances, yet which could also be problematic due to the likelihood of resuspension of contaminant-containing dusts (Laidlaw et al., 2012; Zahran et al., 2013a).

4. Conclusions

Through integrative geochemical analyses, this study aimed to comprehensively understand the sources and implications of urban soil Pb contamination by investigating the co-occurrence of Pb with other metal(loids), isotopic fingerprints of anthropogenic Pb, and in vitro bioaccessibility of Pb in surface soil samples from Durham, NC. Results showed that Pb in soils near residential house foundations markedly exceeded the U.S. EPA regulatory guidance value of 400 mg/kg, with Pb isotope ratios indicative of significant input of legacy lead-based paint and co-occurring with Zn, Cd, and Sb, whereas soils from urban streetside had systematically lower Pb and metal(loids) concentrations and were of mixed origins, dominantly the legacies of leaded gasoline and atmospheric deposition. In addition, the high ¹³⁷Cs activities and high correlations with Pb and other metal(loids) in house foundation soils indicate less soil disturbances that could lead to the preservation of multiple contaminants near homes and thus pose risks to human exposure via dusts tracked into homes. The in vitro bioaccessibility assessment showed that on average, 55% of Pb for house foundation soils and on average, 63% of Pb for urban streetside soils were potentially bioavailable. The isotopic similarity between the bioaccessible and total Pb in contaminated soils reinforced the utility of Pb isotope as a sensitive tracer for delineating the sources of Pb in the human body. The integrated analyses presented in this study could be applicable for other urban environments.

CRediT authorship contribution statement

Zhen Wang: Conceptualization; Data curation; Investigation; Writing - original draft; Writing - review & editing. **Anna M. Wade:** Conceptualization; Writing - review & editing. **Daniel Richter:** Conceptualization; Writing - review & editing. **Heather M. Stapleton:** Writing - review & editing. **James M. Kaste:** Writing - review & editing. **Avner Vengosh:** Conceptualization; Investigation; Supervision; Writing - original draft; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Boxplots of total elemental concentrations and enrichment factors of metal(loids) in different soil groups (Figs. S1-3); bivariate plots of total concentrations of metal(loids) versus Pb in different soils groups (Figs. S4–7); PCA plot (Fig. S8); boxplots of ¹³⁷Cs and excess ²¹⁰Pb in studied soils (Fig. S9); bivariate plots of ¹³⁷Cs and excess ²¹⁰Pb versus metal(loids) concentrations (Fig. S10); metal(loids) profiles of Duke Forest soils (Fig. S11); plots of ²⁰⁸Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁷Pb versus 1/[Pb] (Fig. S12); boxplots of bioaccessibilities of Pb and other metal(loids) (Fig. S13). Total elemental concentrations of NIST SRM 2711a (Table S1); in vitro bio-accessibility of Pb in NIST SRM 2711a (Table S2); total elemental concentrations, excess ²¹⁰Pb and ¹³⁷Cs activities, and Pb isotope ratios of different soil groups (Tables S3-7 and S13); U.S. EPA regional screening levels (RSL) of potentially toxic metal(loids) for residential soil (Table S8); enrichment factors of metal(loids) (Tables S9-12); in vitro bioaccessibility of Pb and other metal(loids) in tested soils (Table S14). Supplementary data to this article can be found online at https://doi.org/10.1016/j. scitotenv.2021.151276.

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