Anthropogenic Pb contribution in soils of Southeast China estimated by Pb isotopic ratios

Jianwu Li1,2, Guoshuang Hao3, Xudong Wang1, Li Ruan2,4* & Jinjie Zhou5

Isotopic ratios were used to identify the source of Lead (Pb) contamination in rural soils from Southeast China. Enrichment of Pb in surface soils was detected from three sampling locations, with the 206Pb/207Pb ratio indicating recent anthropogenic input. The 206Pb/207Pb ratio from deeper soil profiles reflected the ratio from parent basalt. Mass fractions of anthropogenic-derived Pb for soil samples in the upper profiles was as high as 50%, implying that surface soils in the current study were impacted by anthropogenic activity. The 206Pb/207Pb and 208Pb/206Pb ratios were similar to anthropogenic sources including the combustion of coal, which has been common practice in the region for 2500 years. Considering the relatively short history of petroleum use in this area and the rural location of soils, anthropogenic Pb source from coal burning was considered to be the main cause of lead pollution.

Heavy metals, such as Cu, Zn, Ni, Cd, Cr and Pb, can be major contaminants in the soil environment1–7. Lead (Pb) is one of the most widely studied metals in the soil environment due to its toxicity and widespread use8,9. Globally, soils receive and store anthropogenic Pb from sources including industrial wastes and emissions, motor vehicle emissions from Pb containing fuels and mining activities10–13. Pb is highly persistent in the environment and due to its toxicity, is of particular concern to human health14,15. Pb can be absorbed via ingestion of soil16 and water through inhalation of dust and dermal contact17,18, and consumption of vegetables grown in contaminated soil19. Pb biomagnifies through the food chain16,18,20, thus it is of concern in both developed and developing countries4,20–22. Soil Pb contamination, through the various exposure pathways, has been shown to result in elevated human blood Pb levels23–25. Literature supports the notion that children are more susceptible to elevated blood Pb concentrations, with inhibition of neurobehavioral performance, including a lower intelligence quotient (IQ), deficits in verbal memory and attention, learning failure and reading disabilities16,17. Due to the great toxicity of lead to the environment and ecology, many researchers have carried out studies of Pb pollution and remediation26–29.

Isotope methodologies have been increasingly applied to environmental studies of Pb contamination of air, soils, sediments and plants30–33. Pb in the environment has four isotopic forms, 204Pb, 206Pb, 207Pb and 208Pb34. The isotopic composition of Pb is fundamentally controlled by geological properties, and is not fractionated by weathering, transportation or biological processes. Thus, the use of Pb isotopic signatures can assist in the identification and quantification of Pb sources35,36. Therefore, assessing Pb isotopes allows us to understand anthropogenic lead pools and earth surface processes related to regolith development37,38. While there is a sound body of research globally on the distribution of Pb in soil, the source of the Pb is not always well described. This is particularly the case in Southeast China where anthropogenic contributions to soil Pb content have not been thoroughly examined. As one of the well-developed regions of China, our study area has been undergoing rapid industrialization and urbanization, thus the need to better understand the risks of Pb in the soils, as well as understanding where the main sources of contamination arise13,15,21,22,41. The objective of this study was therefore to analyze Pb concentrations and isotopic compositions of three subtropical soils in Southeast China to examine the isotopic composition of Pb through the soil profile, identify likely sources for the contamination, and to calculate the relative contribution of natural and anthropogenic Pb sources.
### Results

**Properties of studied soil profiles.** Physicochemical characteristics of the soils are shown in Table 1. The pH ranged from 5.77 to 6.42 (Table 1) and generally increased with depth across all 3 sites. The bulk density was lower in the A horizon (0.95–0.98 g cm⁻³) than in C horizon (1.03–1.09 g cm⁻³) for each soil profile. The soil organic matter shows a decreasing trend with depth, with maximum values up to 44.2 g kg⁻¹, 35.4 g kg⁻¹ and 32.3 g kg⁻¹ in the A horizon of ZSJ, ZCR and ZAJ profiles, respectively. The ZSJ, ZCR and ZAJ soil profiles represented for Sanjie, Chongren and Anjishan of Zhejiang province, respectively (Table 1).

**Lead elemental and isotopic geochemistry.** Lead concentration of soils and basalt is shown in Table 2. Pb concentrations of soil samples were higher than the parent bedrock (2.2 mg kg⁻¹). Pb concentrations were up to 17.3 mg kg⁻¹, 15.6 mg kg⁻¹ and 15.5 mg kg⁻¹ of the A horizons for ZSJ, ZCR and ZAJ, respectively. Pb concentrations decreased with increasing soil depth. The results clearly demonstrate an enrichment of surface soil Pb concentrations.

For the deep soils, the 206Pb/207Pb ratios (Table 2) of the ZSJ, ZCR and ZAJ profiles (> 60 cm) are closer to basalt, implying an influence from the parent material with little anthropogenic Pb at depth. However, for the top soils, the Pb isotopic compositions were distinct from the parent material. The 208Pb/206Pb ratios of surface soil samples were higher than the parent material (2.079; Table 2). But the 206Pb/207Pb ratios of surface soil samples were much lower than the basalt (1.196) and increase with depth. The significantly low radiogenic 206Pb/207Pb ratio (1.175; n = 12) of the soils in the top 0–10 cm is close to anthropogenic Pb from fly ash in China. Therefore evidence is provided here that the surface soils have been substantially influenced by anthropogenic Pb inputs.

### Discussion

**Characterizing anthropogenic Pb in soils.** The ratio of 208Pb/207Pb Pb was plotted against depth in comparison with Pb content (Fig. 1) illustrating that where higher Pb concentrations were detected (i.e. surface soils), there was a correspondingly lower 208Pb/207Pb Pb ratio. The 206Pb/207Pb Pb ratios decreased approximately with the increase of Pb concentration in soils (Fig. 1), suggesting an anthropogenic contribution to soil Pb concentrations. In order to help locate the source of Pb (i.e. naturally occurring from parent material, or anthropogenic), 206Pb/205Pb versus 208Pb/206Pb of soils, basalt and anthropogenic Pb sources were plotted (Fig. 2). The influence factors of human activities on Pb pollution mainly included smelting, automobile exhaust, coal combustion and

| Profile | Location       | Horizon | Depth (cm) | pH (H₂O) | Dry bulk density (g cm⁻³) | SOM (g kg⁻¹) |
|---------|----------------|---------|------------|----------|---------------------------|--------------|
| ZSJ     | Sanjie, Shengzhou (29° 47′ N, 120° 51′ E) | A       | 0–10       | 5.99     | 0.98                      | 44.2         |
|         |                | B       | 10–25      | 5.95     | 1.02                      | 21.2         |
|         |                | BC      | 25–35      | 6.02     | 1.05                      | 8.5          |
|         |                | C       | 35–65      | 6.39     | 1.07                      | 4.3          |
| ZCR     | Chongren, Shengzhou (29° 39′ N, 120° 47′ E) | A       | 0–15       | 5.97     | 0.95                      | 35.4         |
|         |                | B       | 15–65      | 5.86     | 0.99                      | 19.8         |
|         |                | C       | 65–        | 6.42     | 1.03                      | 2.9          |
| ZAJ     | Anjishan, Xinchang (29° 27′ N, 121° 02′ E) | A       | 0–10       | 5.83     | 0.98                      | 32.3         |
|         |                | B       | 10–30      | 5.77     | 1.07                      | 22.8         |
|         |                | C       | 30–65      | 6.23     | 1.09                      | 5.9          |

Table 1. Selected physicochemical properties of the studied soil profiles.

| Profiles | Horizon | Sample numbers | Pb (mg kg⁻¹) | 206Pb/204Pb | 207Pb/204Pb | 208Pb/204Pb | 206Pb/207Pb | 208Pb/206Pb |
|----------|---------|----------------|--------------|-------------|-------------|-------------|-------------|-------------|
| ZSJ      | A       | 4              | 16.2 ± 0.5   | 18.342 ± 0.009 | 15.595 ± 0.008 | 38.503 ± 0.011 | 2.099 ± 0.006 | 1.176 ± 0.004 |
|          | B       | 3              | 8.9 ± 0.3    | 18.428 ± 0.008 | 15.624 ± 0.005 | 38.717 ± 0.015 | 2.101 ± 0.003 | 1.179 ± 0.002 |
|          | BC      | 2              | 5.4 ± 0.2    | 18.529 ± 0.007 | 15.630 ± 0.007 | 38.833 ± 0.009 | 2.096 ± 0.002 | 1.185 ± 0.002 |
|          | C       | 4              | 6.7 ± 0.2    | 18.392 ± 0.005 | 15.597 ± 0.009 | 38.640 ± 0.012 | 2.101 ± 0.005 | 1.179 ± 0.003 |
| ZCR      | A       | 4              | 15.1 ± 0.5   | 18.410 ± 0.006 | 15.610 ± 0.010 | 38.585 ± 0.010 | 2.096 ± 0.004 | 1.179 ± 0.004 |
|          | B       | 6              | 8.6 ± 0.4    | 18.517 ± 0.009 | 15.597 ± 0.006 | 38.698 ± 0.008 | 2.090 ± 0.002 | 1.187 ± 0.003 |
|          | C       | 5              | 2.5 ± 0.1    | 18.511 ± 0.008 | 15.611 ± 0.009 | 38.770 ± 0.011 | 2.094 ± 0.003 | 1.186 ± 0.001 |
| ZAJ      | A       | 4              | 15.2 ± 0.6   | 18.445 ± 0.006 | 15.680 ± 0.007 | 38.806 ± 0.009 | 2.104 ± 0.004 | 1.176 ± 0.002 |
|          | B       | 5              | 5.9 ± 0.2    | 18.515 ± 0.009 | 15.618 ± 0.009 | 38.768 ± 0.013 | 2.094 ± 0.006 | 1.185 ± 0.005 |
|          | C       | 4              | 3.2 ± 0.1    | 18.637 ± 0.008 | 15.718 ± 0.008 | 39.138 ± 0.008 | 2.100 ± 0.005 | 1.186 ± 0.002 |
| Basalt   | Parent rocks | 3             | 2.2 ± 0.1   | 18.630 ± 0.007 | 15.572 ± 0.007 | 38.733 ± 0.009 | 2.079 ± 0.003 | 1.196 ± 0.001 |

Table 2. Lead concentrations and isotopic composition in soils.
so on. Firstly, the early Pb pollution was caused by emissions from the crude smelting technologies in copper production in Europe and China\(^43\). With the improvement of smelting technology and strict control of industrial pollution discharge, the contribution of smelting Pb to it is relatively small. Meanwhile, our research areas were remote from industrial areas, so smelting is not the main anthropogenic source of lead. Secondly, the anthropogenic Pb derived from the combustion of leaded petrol, often occurred in urban environments\(^44\), rather than in the rural areas. Our sample sites were far away from urban areas, so the effect of gasoline lead on it is relatively small. In addition, considering the shorter time usage of petroleum in China and the lower \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios for petroleum combustion (~1.11), its contribution to the change in soil Pb isotope ratios from ZSJ, ZCR and ZAJ could be considered as negligible\(^{20,45,46}\). Importantly, Pb ores from north China were different from the values of ZSJ, ZCR and ZAJ soils, with much higher \(^{208}\text{Pb}/^{206}\text{Pb}\) ratios (2.15–2.33) and lower \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios (1.03–1.13)\(^47,48\). However, coal has been used in China for more than 2500 years. Coal combustion may be an important source of lead pollution in soil. The emission indicators of flue gas can be used to prove the conjecture

Figure 1. Pb content and \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios for soils in Southeast China.

Figure 2. \(^{208}\text{Pb}/^{206}\text{Pb}\) vs. \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios. The ZSJ, ZCR and ZAJ soil profiles were represented for Sanjie, Chongren and Anjishan of Zhejiang province, respectively.
of the source of Pb pollution. Recent studies have shown that the atmospheric lead emission from coal burning in China exceeded 10,000 t a⁻¹ from 2001 to 2005, and the annual growth rate is 14.5%⁴⁹. The highest average amount of lead discharged was in North China and the Shanxi, Shandong and Jiangsu province ranked the top three in terms of Pb discharge intensity. Lead emissions from these areas will be deposited in the study area along with the northeast monsoon⁵⁰. Mukai et al.⁴⁸ and Komárek et al.⁵¹ showed that the combustion of coal has an impact on aerosol Pb isotope ratios. The lower ²⁰⁶Pb/²⁰⁷Pb values in soil samples strongly indicate the coal combustion was the main cause of lead pollution in studied area. As shown in Fig. 2, the ²⁰⁸Pb/²⁰⁶Pb ratios are from 2.090 to 2.104, which were between basalt (2.079) and anthropogenic source from coal combustion (2.114), while the ²⁰⁶Pb/²⁰⁷Pb ratios range from 1.176 to 1.187, which are lower than their parent rocks (1.196) but higher than anthropogenic source from coal combustion in south China (1.162)⁴¹. After comprehensive consideration, we chose the average Pb isotope ratios of anthropogenic sources from coal combustion in Jiangsu-Zhejiang region to be ²⁰⁶Pb/²⁰⁷Pb = 1.162, and ²⁰⁸Pb/²⁰⁶Pb = 2.114.

**Calculation of anthropogenic Pb pools in soils of Southeast China.** During thousands of years, different sources of anthropogenic Pb have been deposited on the surface of the soils. A two end-member model based on the isotope mass balance has been developed to calculate the percentage contribution of anthropogenic and natural Pb sources to total Pb in soils¹³. The Pb isotope ratio of basalts and anthropogenic source¹¹ is ²⁰⁶Pb/²⁰⁷Pb = 1.196 and ²⁰⁶Pb/²⁰⁷Pb = 1.16, respectively.

\[
\frac{f_{\text{anthropogenic}}^{\text{Pb}}}{f_{\text{anthropogenic}}^{\text{Pb}}} = \frac{R_{\text{soil}}^{\text{Pb}} - R_{\text{basalt}}^{\text{Pb}}}{R_{\text{Pb}}^{\text{anthropogenic}} - R_{\text{basalt}}^{\text{Pb}}}
\]

where \(f_{\text{anthropogenic}}^{\text{Pb}}\) represented the percentage contribution of anthropogenic Pb source in soils, and the \(R_{\text{Pb}}^{\text{soil}}\) and \(R_{\text{Pb}}^{\text{basalt}}\) are the Pb isotope ratios of soils, anthropogenic-derived and basalt-derived, respectively. Soils developed on the basalt from the study area are significantly influenced by contributions of anthropogenic Pb sources. The mass fraction (Fig. 3) of anthropogenic Pb from the ZSJ, ZCR and ZAJ profiles ranged from 25.78 to 55.20%, 24.33 to 46.26% and 29.24% to 54.71%, respectively. Moreover, the \(f_{\text{anthropogenic}}^{\text{Pb}}\) values showed a prominent increase from the lower horizon to the surface horizon for all profiles tested. For the lower horizon (C horizon), the \(f_{\text{anthropogenic}}^{\text{Pb}}\) values are lower, which indicates a primary influence from parent material. In contrast, for the topsoil (especially the A horizon), contributions of anthropogenic Pb were high (> 50%), implying large anthropogenic Pb addition to the soils in Southeast China.

Because the relatively short history of petroleum use in this area and the rural location of ZSJ, ZCR and ZAJ, with little vehicular access, local anthropogenic Pb source from gasoline are likely to have only a very minor influence on soil contamination. However, coal usage had long history in China. Ancient mining and utilization of coal were begun at Spring and Autumn and Warring States (470 B.C.), especially in the Sui and Tang Dynasties, the scale of coal mining and utilization was further expanded⁵². Large coal mines distribution include Hancheng (Shanxi Province), Taiyuan and Changzhi (Shanxi Province), Yangzhou (Jiangsu Province) and Huainan and Huaibei (Anhui Province). In addition, as the largest coal mine in Zhejiang Province, Changxing coal mine is the nearest to the research area. In the northern winter season, cold air from high latitudes is controlled by the continental high-pressure system, and propagates southward to form the strongest northerly dry and cold winter monsoon in the world. The northern winter monsoon can controls the atmospheric circulation⁵⁰ and carry the Pb pollutants from above coal mines to the study area during the dry season from November to April⁵³. Meanwhile, Pb isotope ratios of the soils in this area were similar to that of anthropogenic Pb from coal combustion.
in China, particularly that of Jiangsu-Zhejiang region\textsuperscript{41}, which is neighboring with Xinchang-Shengzhou Basin. Thus, we conclude that coal combustion is the main factor for the enhanced Pb contamination in surface soils.

In conclusion, three soil profiles from rural Southeast China been shown to have elevated surface Pb contamination. Using isotopic methodologies, this elevated Pb was shown to result mainly from anthropogenic activity. The $^{206}$Pb/$^{207}$Pb values of deep horizons were close to the parent material suggesting contamination was restricted to the surface soil and did not leach through the profile. Our study suggested that the combustion of coal was the main source of soil contamination, and to avoid future contamination, lower particulate emissions will be required to avoid continued accumulation of Pb in surface soils in the region.

**Methods**

**Study region and soil sampling.** The study area is located in Xinchang-Shengzhou Basin, Southeast China, between 120°2′E–121°0′E and 29°1′N–29°5′N (Fig. 4). It belongs to the southern fringe of the northern subtropics\textsuperscript{44} and has a mean annual air temperature of 16.6 °C, with yearly extremes ranging from −5.3 to 40.3 °C. The region has a mean annual precipitation of 1500 mm with nearly 70% falling during the wet season (April–September). Basalt is the dominant bedrock in the region\textsuperscript{55} with the resulting soil most commonly derived from in situ weathering of basalt. The soil is classified as either Udic Ferrosols\textsuperscript{56}, or Ultisol according to USDA Soil Taxonomy\textsuperscript{57}. The soils support plants that are dominated by *Machilus thunbergii* and *Camellia* sp.

Three basaltic weathering profiles i.e. native forest soils (ZCR and ZAJ) and farmland soil (ZSJ), were selected in a rural area of Chongren, Anjishan and Sanjie respectively, in Zhejiang province (Fig. 4, Table 1), with locations being relatively remote from cities and obvious influences of human activity. The typical basalt platforms in the study area are distributed in triangles. We chose the north, southeast and southwest of the triangle platform as the sampling sites, in order to make the sampling points have better typical representative. The parent rock from all profiles was fresh tholeiitic basalt, which was collected beneath the sampling profiles. Soils were excavated to bedrock and sampled from small concavities in an otherwise convex portion of the landscape by genetic horizon.

**Laboratory analytical methods.** Collected soil samples were air-dried, ground and passed through a 2 mm sieve. The soil pH was determined in a suspension of 1:2.5 soil:water solution (w/v). Soil bulk density was measured from the 100 cm$^{-3}$ undisturbed soil cores by drying the cores for 24 h at 105 °C. A homogenized sub-sample of soil was digested with an acid solution (5 ml concentrated HNO$_3$ (65%, v/v), 5 ml concentrated HCl (30%, v/v) and 5 ml concentrated HF (40%, v/v)). Diluted and filtered samples were assayed using an inductively coupled plasma mass spectrometer (ICP-MS) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry in the Chinese Academy of Science\textsuperscript{58}. The standard reference materials were GSR-3, BCR-1, GXR-5 and GXR-6. Analytical uncertainties were less than ±5%.

For the determination of Pb isotopes, soil samples (0.05 g) were digested in a mixture of 4 ml concentrated HNO$_3$ (65%, v/v) and 1 ml concentrated HF (40%, v/v) in Teflon vessels on a hotplate at 200 °C for 8 h. The vessel was then uncovered to allow evaporation to almost dryness. This procedure was repeated until the samples were completely dissolved\textsuperscript{59}. Pb isotopes were measured on a GV Isoprobe-T thermal ionization mass spectrometer (TIMS) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry in the Chinese Academy of Science. The reagent blank was also measured and blank subtraction was done for the final intensity of each isotope of Pb in the sample. The relative standard deviations (RSD) of 10 replicate readings of samples were better than 1% for $^{206}$Pb/$^{207}$Pb and 0.6% for $^{208}$Pb/$^{206}$Pb. The average of measured $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb of the National Institute of Standards and Technology (NIST 981) were 0.9147 ± 0.0084 and 2.1681 ± 0.0099 with the certified values of 0.9147 and 2.1683, respectively.

Received: 20 April 2020; Accepted: 30 November 2020
Published online: 17 December 2020

---

**Figure 4.** The location of sampling sites.
References

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

2. Mohamed, Y. M. et al. Isolation and characterization of a heavy metal-resistant, thermophilic esterase from a Red Sea brine pool. *Sci. Rep.* **3**(7477), 3358 (2013).

3. Li, S. et al. Accumulation and localization of cadmium in moso bamboo (*Phyllostachys pubescens*) grown hydroponically. *Acta Physiol. Plant.* **37**(3), 1–7 (2015).

4. Yan, W. et al. Spatial distribution and risk assessment of heavy metals in farmland along mineral product transportation routes in Zhejiang, China. *Soil Use Manage.* **32**(3), 338–349 (2016).

5. Wu, W. et al. Unraveling sorption of lead in aqueous solutions by chemically modified biochar derived from coconut fiber: a microscopic and spectroscopic investigation. *Sci. Total Environ.* **576**, 766–774 (2017).

6. Lu, K. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *J. Environ. Manage.* **186**, 285–292 (2017).

7. Yang, X. Bioavailability of Cd and Zn in soils treated with biochars derived from tobacco stalk and dead pigs. *J. Soils Sedim.* **17**, 751–762 (2017).

8. Monastra, V., Derry, L. & Chadwick, O. Multiple sources of lead in soils from a Hawaiian chronosequence. *Chem. Geol.* **209**, 215–231 (2004).

9. Liu, D. et al. Lead accumulation and tolerance of Moso bamboo (*Phyllostachys pubescens*) seedlings: applications of phytoremediation. *J. Zhejiang Univ. Sci. B* **16**(2), 123–130 (2015).

10. Burghart, W. Soils in urban and industrial environments. *J. Plant Nutr. Soil Sci.* **157**, 205–214 (1994).

11. Markus, J. & McBratney, A. B. A review of the contamination of soil with lead II. Spatial distribution and risk assessment of soil lead. *Environ. Int.* **27**, 399–411 (2001).

12. Lu, Y. et al. Concentrations and chemical speciations of Cu, Zn, Pb and Cr of urban soils in Nanjing, China. *Geoderma* **115**, 101–111 (2003).

13. Li, H. et al. Contamination and source differentiation of Pb in park soils along an urban-rural gradient in Shanghai. *Environ. Pollut.* **159**, 3536–3544 (2011).

14. Zahran, S. et al. Children’s blood lead and standardized test performance response as indicators of neurotoxicity in metropolitan New Orleans elementary schools. *Neurotoxicology* **30**, 888–897 (2009).

15. Lei, K. et al. Contamination and human health risk of lead in soils around lead/zinc smelting areas in China. *Environ. Sci. Polllut. Res. Int.* **23**(13), 13128–13136 (2016).

16. Rasmussen, P. E. et al. A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. *Sci. Total Environ.* **267**, 125–140 (2001).

17. Ogawa, M., Nakajima, Y., Kubota, R. & Endo, Y. Two cases of acute lead poisoning due to occupational exposure to lead. *Clin. Toxicol.* **46**(4), 332–335 (2007).

18. Laidlaw, M. A. S. & Filippelli, G. M. Resuspension of heavy metals during co-composting of sewage sludge with lime. *Chemosphere* **63**, 980–986 (2006).

19. Wang, S. Q. & Zhang, J. L. Biolead levels in children, China. *Environ. Res.* **101**, 412–418 (2006).

20. Zhang, S. M. et al. Surveillance of childhood blood lead levels in 14 cities of China in 2004–2006. *Biomed. Environ. Sci.* **22**, 288–296 (2009).

21. Bolan, N. et al. Remediation of heavy metal(loid) contaminated soils—to mobilize or to immobilize?. *J. Hazard. Mater.* **266**, 141–166 (2014).

22. Surkan, P. et al. Neuropsychological function in children with blood lead levels <10 mg/dl. *Neurotoxicology* **28**, 1170–1177 (2007).

23. Kamenov, G. D. & Gulsom, B. L. The Pb isotopic record of historical to modern human lead exposure. *Sci. Total Environ.* **490**, 861–870. https://doi.org/10.1016/j.scitotenv.2014.09.031

24. Etter, V. et al. ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution. *Anal. Bioanal. Chem.* **378**, 311–317 (2004).

25. Wong, J. W. C. & Selvam, A. Speciation of heavy metals during co-composting of sewage sludge with lime. *Chemosphere* **63**, 980–986 (2006).

26. Wang, S. Q. & Zhang, J. L. Blood lead levels in children, China. *Environ. Res.* **101**, 412–418 (2006).

27. Zhang, S. M. et al. Surveillance of childhood blood lead levels in 14 cities of China in 2004–2006. *Biomed. Environ. Sci.* **22**, 288–296 (2009).

28. Bolan, N. et al. Remediation of heavy metal(loid) contaminated soils—to mobilize or to immobilize?. *J. Hazard. Mater.* **266**, 141–166 (2014).

29. Surkan, P. et al. Neuropsychological function in children with blood lead levels <10 mg/dl. *Neurotoxicology* **28**, 1170–1177 (2007).

30. Chen, H. H. et al. Enhanced Pb immobilization via the combination of biochar and phosphate solubilizing bacteria. *Environ. Int.* **127**, 395–401 (2019).

31. Tian, D. et al. A new insight into lead (II) tolerance of environmental fungi based on a study of Aspergillus Niger and *Penicillium roqueforti*. *Environ. Microbiol.* **21**, 471–479 (2019).

32. Li, Z. et al. Induced biotransformation of lead (II) by Enterobacter sp. in SO4-PO4-Cl para solution. *J. Hazard. Mater.* **357**(5), 491–497 (2018).

33. Ellam, R. M. The graphical presentation of lead isotope data for environmental soil acropportionment. *Sci. Total Environ.* **408**, 3490–3492. https://doi.org/10.1016/j.scitotenv.2010.01.082

34. Hyoung, K. et al. Pb, Nd and Sr isotope records of pelagic dust: Source distinction and the effects of dust extraction procedures and authigenic mineral growth. *Chem. Geol.* **269**(3–4), 240–251 (2011).

35. Albaerdem, F., Desautels, A. M. & Blichtert-Toft, J. A geological perspective on the use of Pb isotopes in archaeology. *Archaeometry* **54**, 853–867 (2012).

36. Shi, G. et al. Sr-Nd-Pb isotope systematics of the Permian volcanic rocks in the northern margin of the Alxa Block (the Shalazhashan Belt) and comparisons with the nearby regions: implications for a Permian rift setting. *J. Geodyn.* **115**, 43–56 (2018).

37. Fature, G. *Principles of Isotope Geology* (Wiley, New York, 1986).

38. Chen, J. et al. A lead isotope record of Shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline. *Atmos. Environ.* **39**, 1245–1253 (2005).

39. Cheng, H. F. & Hu, Y. N. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environ. Pollut.* **158**, 1134–1146 (2010).

40. Zhang, W. et al. Lead (Pb) isotopes as a tracer of Pb origin in Yangtze River intertidal zone. *Chem. Geol.* **257**, 257–263 (2008).

41. Bird, G. Provenancing anthropogenic Pb within the fluvial environment: developments and challenges in the use of Pb isotopes. *Environ. Int.* **37**, 802–819 (2011).

42. Chrusty, V. et al. Geochemical position of Pb, Zn and Cd in soils near the Olkusz mine/smelter, South Poland: effects of land use, type of contamination and distance from pollution source. *Environ. Monit. Assess.* **184**, 2517–2536 (2012).

43. Blichtert-Toft, J. L. et al. Large-Scale tectonic cycles in Europe revealed by distinct Pb isotope provinces. *Geochem. Geophys. Geosyst.* **17**(10), 3854–3864 (2016).

44. Zhang, G. L. et al. Historical change of soil Pb content and Pb isotope signatures of the cultural layers in urban Nanjing. *CATENA* **69**, 51–56 (2007).

45. Rollhofer, A. & Rossman, K. J. R. Isotopic source signatures for atmospheric lead: the Northern Hemisphere. *Geochim. Cosmochim. Acta* **65**(11), 1727–1740 (2001).

https://doi.org/10.1038/s41598-020-79203-3
43. Hong, S. et al. History of ancient copper smelting pollution during Roman and Medieval times recorded in Greenland ice. *Science* **272**, 246–248 (1996).

44. Nageotte, S. M. & Day, P. Lead concentrations and isotope ratios in street dust determined by electrothermal atomic absorption spectrometry and inductively coupled plasma mass spectrometry. *Analyst* **123**, 59–62 (1998).

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

46. Duzgoren-Aydin, N. S., Li, X. D. & Wong, S. C. Lead contamination and isotope signatures in the urban environment of Hong Kong. *Environ. Int.* **30**(2), 209–217 (2004).

47. Chen, Y. W., Mao, C. X. & Zhu, B. Q. Lead isotopic composition and genesis of phanerozoic metal deposits in China. *Geochemistry* **9**(3), 215–229 (1980).

48. Mukai, H. et al. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. *Environ. Sci. Technol.* **35**(6), 1064–1071 (2001).

49. Qin, J., Li, Z. & Lou, M. 2001–2005 China’s provinces estimation of atmospheric lead emissions from coal-fired. *Guangdong Trace Element Sci.* **17**(5), 31–38 (2010) (*in Chinese*).

50. An, Z. The history and variability of the east Asian paleomonsoon climate. *Quatern. Sci. Rev.* **19**(1), 171–187 (2000).

51. Komárek, M. et al. Lead isotopes in environmental sciences: a review. *Environ. Int.* **34**, 562–577 (2008).

52. Long, Y. W. Development and utilization of coal in ancient China. *Econ. Soc. Dev.* **4**, 41–49 (2018) (*in Chinese*).

53. Chen, H. S. et al. Isotope tracing of major sources of lead pollution in the atmosphere of Hangzhou city. *Bull. Geochem. Miner. Rocks* **3**(5), 146–149 (1998) (*in Chinese*).

54. Xiong, Y. & Li, Q. K. Soils in China (*in Chinese*) (Science Press, Beijing, 1987).

55. Zou, H. et al. Major, trace element, and Nd, Sr and Pb isotope studies of Cenozoic basalts in SE China: mantle sources, regional variations, and tectonic significance. *Chem. Geol.* **171**(1–2), 33–47 (2000).

56. Soil Survey Staff. *Keys to Soil Taxonomy* 12th edn. (United States Department of Agriculture (Natural Resources Conservation Service, Washington DC, 2014).

57. Chinese Soil Taxonomy Research Group (CST). *Chinese Soil Taxonomy* (Science Press, Beijing, 2001).