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Apportionment of sources of heavy metals to agricultural soils using isotope fingerprints and multivariate statistical analyses☆

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ABSTRACT

Apportioning sources of environmental pollutants is key to controlling pollution. In this study, the sources of heavy metals to 234 agricultural soils from the Jianghan Plain (JHP) (~22454 km^2) in central China were discriminated between using Cd and Pb isotope compositions and multivariate statistical analyses. Concentrations of some metals in JHP soils (0.48 ± 0.2, 48.2 ± 15.9, 0.12 ± 0.23, 48.8 ± 16.4, 36.5 ± 9.8, and 96.8 ± 42.2 mg kg^{-1} for Cd, Cu, Hg, Ni, Pb, and Zn, respectively) were higher than background concentrations in Chinese soil. The Cd isotope compositions for the JHP soils ($\delta^{114/110}$Cd values −0.76‰ to −0.25‰) were similar to Cd isotope compositions found for smelter dust and incinerator fly ash, indicating Cd was supplied to the JHP soils by ore smelting and/or refining processes. The Pb isotope compositions for the JHP soils ($^{206}Pb/^{207}Pb$ 1.182–1.195 and $^{208}Pb/^{206}Pb$ 2.078–2.124) were between the Pb isotope compositions found for Chinese coal and natural sources, which a binary isotope mixing model indicated contributed 52% and 48%, respectively, of the Pb in JHP soils. Cluster analysis and positive matrix factorization indicated that the sources of heavy metals in JHP soils may consist of smelting and/or refining activities, coal combustion, agricultural activities, and natural sources (including Han River sediment and soil parent materials). The isotope fingerprints and multivariate statistical analyses together indicated that coal combustion and smelting and/or refining activities were the main anthropogenic sources of heavy metals polluting JHP soils.

1. Introduction

Heavy metals are some of the most serious pollutants because of their toxicities and abilities to bioaccumulate and persist in the environment (Li et al., 2014). It was concluded in a Chinese national soil pollution survey that $>10^7$ ha of farmland (8.3% of all the arable land) in China is contaminated with heavy metals such as As, Cd, Cu, Hg, Ni, and Pb (MEPC and MLRC, 2014). As much as 12×10^6 t of crops polluted with heavy metals are grown on this land each year, and this causes direct economic losses of $>20 \times 10^9$ yuan (~USD 2.91×10^9) (Hou and Li, 2017). Cd concentrations in 44% of rice samples from an open market in Guangzhou in 2013 exceeded the relevant standard (Hou and Li, 2017). Heavy metal emissions in China therefore need to be controlled urgently, and heavy metal pollution of agricultural soils needs to be minimized.

Apportioning sources of heavy metals in soil is key to preventing and controlling heavy metal pollution. Various tools, including geographic information system (GIS) maps, isotope fingerprints, and multivariate statistics, have been used to allow sources of heavy metals to be apportioned (Bi et al., 2017; Hou et al., 2017; Liu et al., 2018). GIS mapping has been widely used to determine the routes and modes through which heavy metals are transported, and could allow potential pollution sources to be identified (Zhang et al., 2009; Hou et al., 2017). Isotope fingerprints are precise proxies that allow sources of heavy metals to be identified (Huang et al., 2015; Bi et al., 2017). For example, Pb isotopes have been used to identify the sources of Pb to air, biota, ore, sediment, soil, and water (Zhu et al., 2001; Chen et al., 2005; Bory et al., 2014; Shotyk et al., 2016; Bi et al., 2017; Xu et al., 2017; Liu et al., 2018) because

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the isotopes are stable during physical and chemical processes (Sun and Zhu, 2010). Non-traditional stable isotopes (e.g., Cd, Cu, Fe, Hg, and Zn isotopes) have also been successfully used to identify sources of pollution (Cloquet et al., 2006; Weiss et al., 2008; Shiel et al., 2010; Liu et al., 2018). Biological uptake, evaporation/condensation, and precipitation cause Cd isotope fractionation (Wombacher et al., 2003; Wombacher et al., 2004; Lacan et al., 2006), which could cause fingerprints that would allow Cd sources to environmental media to be identified. Multivariate statistical methods such as cluster analysis (CA), principal component analysis (PCA), positive matrix factorization (PMF), and chemical mass balance (CMB) (Lu et al., 2005; Huang et al., 2018; Liu et al., 2018), provide a classification tool based on the relationships between different metals at different sampling points, which can be used to distinguish between the natural and anthropogenic sources (Huang et al., 2015; Liu et al., 2018). Compared to CA and PCA, PMF and CMB analyses can not only identify but also quantify the main sources of metals in various environment settings (Chen et al., 2007; Comero et al., 2014; Hu et al., 2018; Huang et al., 2018).

Agricultural soils in different Chinese regions are affected by different sources of heavy metals (Niu et al., 2013). The methods mentioned above have recently been used in numerous regional studies to identify potential sources of heavy metals in arable soils from various Chinese regions (Huang et al., 2006; Niu et al., 2013; Wang et al., 2014; Pan et al., 2016; Shao et al., 2016). For example, Niu et al. (2013) performed PCA and found that fertilizer application was a common source of Cd, Cr, Cu, Pb, and Zn to arable soils in central, Southwest, and East China. Shao et al. (2016) performed GIS mapping and CA and found that intensive coal combustion followed by atmospheric deposition was the primary source of heavy metals to arable soils in the Yangtze River Delta. Pb isotope analysis indicated that vehicle exhaust emissions and fertilization were the main anthropogenic sources of Pb to agricultural soils in the Yangtze River Delta (Wang et al., 2014; Hu et al., 2018). However, GIS mapping provides preliminary data with important uncertainties (Zhang et al., 2009), and isotope techniques can only be used to study the sources of specific metals. CA and/or PCA have been used to identify 'principal components' associated with potential sources in many studies (Huang et al., 2015; Mihailovic et al., 2015; Ali et al., 2016; Hou et al., 2017), but the relative contributions of the principal components to individual metals pollution have been studied little (Huang et al., 2018). No single method can be used to accurately and comprehensively identify the sources of heavy metals to soils (Hu et al., 2018), so combining methods is likely to be a useful way of apportioning the sources of heavy metals to soil.

Central China is affected by heavy metal (particularly Cd and Pb) contamination (Niu et al., 2013). The Jianghan Plain (JHP) is one of the most important agricultural areas in central China and an important part of the Yangtze River Economic Belt, which covers 46000 km^2 and has a population of ~61.71×10^6 (HBS, 2014). The location of the JHP is shown in Fig. 1. Most previous studies of heavy metals in JHP agricultural soils have been focused on the investigation of heavy metal pollution in local scale or on areas around specific factories or sewage outlets (Tian and Cheng, 2005; Yu et al., 2008; Shen et al., 2012; Yang et al., 2016). However, there is limited comprehensive understanding of the status and sources of heavy metals in agricultural soils in the JHP. Therefore, a combination of isotope fingerprints (Pb and Cd) and multivariate statistics (CA and PMF) has been used in this study to identify the sources of heavy metals to agricultural soils in the JHP. The results will help us to develop a comprehensive and quantitative tool for identifying the sources of metals to agricultural soils.

2. Materials and methods

2.1. Samples and sample pre-treatment

Two or three sampling areas of agricultural land in each city on the JHP (which contains 10 cities covering ~22454 km^2), avoiding factories, garbage dumps, and sewage outlets, were selected. The sampling areas are shown in Fig. 1. In July 2015, eight–twelve soil samples, ~1 km apart, were collected from each sampling area. In total, 234 soil samples were collected. Each sample consisted of five 0–20 cm deep subsamples from an area 2 m × 2 m. Each sample was dried in air, ground, and passed through a ~2 mm sieve to remove large debris, stones, and pebbles, then the sample was mixed well. An aliquot of the sample was taken and the pH determined after mixing 1 g of soil with 2.5 mL of water (Niu et al., 2013). The remaining soil was pulverized and passed through a 100 mesh (~150 μm) sieve before being analyzed (Niu et al., 2013).

2.2. Chemical analysis

For Hg analysis, ~0.2 g of a sample was digested in a mixture of 3 mL HCl (38% v/v) and 1 mL HNO_3 (65% v/v) at 80 °C for 4 h in a test tube (USEPA, 2002). The mixture was cooled and then diluted to 25 mL with Milli-Q water, then the Hg concentration in the digest was measured using a MERX cold atomic fluorescence mercury analysis system (Brooks Rand Instruments, Seattle, WA, USA). The detection limit was 0.3 ng mL^{-1} (Table S1).

For other heavy metal analysis, ~50 mg of a sample was digested in a mixture of 2 mL HNO_3 (65% v/v) and 1 mL HF (40% v/v) in a sealed Teflon beaker at 190 °C for 48 h. The digest was evaporated almost to dryness on a hot plate, then digested in a mixture of 1 mL HNO_3 (65% v/v) and 0.5 mL $HClO_4$ (70% v/v) (SEPAC , 1997; Bi et al., 2017). The digest was cooled and diluted to 100 mL with HNO_3 (2% v/v), then the total heavy metal concentrations in the digest were determined using an Agilent 7900 quadrupole inductively coupled plasma mass spectrometer (Agilent Technologies, Santa Clara, CA, USA).

The heavy metal fractions in each sample were determined using the modified Community Bureau of Reference sequential extraction scheme (Rauret et al., 1999). In step 1, 40 mL acetic acid (0.11 M) was added to 1 g of sample in a centrifuge tube, and the mixture was shaken for 16 h at room temperature. The mixture was then centrifuged and the supernatant diluted to 100 mL with HNO_3 (2% v/v). In step 2, 40 mL $NH_2OH{\bullet}HCl$ (0.5 M) was added to the residue from step 1 in the centrifuge tube, and the mixture was shaken for 16 h at room temperature. The mixture was centrifuged and the supernatant diluted as described for step 1. In step 3, 10 mL H_2O_2 (8.8 M) was added to the residue from step 2 and the mixture was left at room temperature for 1 h with occasional manual shaking. The mixture was then heated to 85 ± 2 °C in a water bath until the volume had decreased to 2–3 mL. The residue was then treated with H_2O_2, and 50 mL NH_4OAc (1 M) was added to the cold mixture, which was then shaken for 16 h at room temperature. The mixture was centrifuged and the supernatant diluted as described for step 1. In step 4, the residue from step 3 was digested as described for the total heavy metal analysis.

The sample extracts were analyzed using an Agilent 7900 quadrupole inductively coupled plasma mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The Al, Cd, Cr, Cu, Fe, Ni, Pb, and Zn detection limits were 6.68, 0.003, 20.0, 0.08, 36.3, 0.06, 0.03, and 0.67, ng mL^{-1}, respectively (Table S1). The Pb isotope compositions were determined following a method presented by Bi et al. (2017) using an Agilent 7900 quadrupole inductively coupled plasma mass spectrometer (Agilent Technologies). The Cd isotope compositions were determined following a method presented by

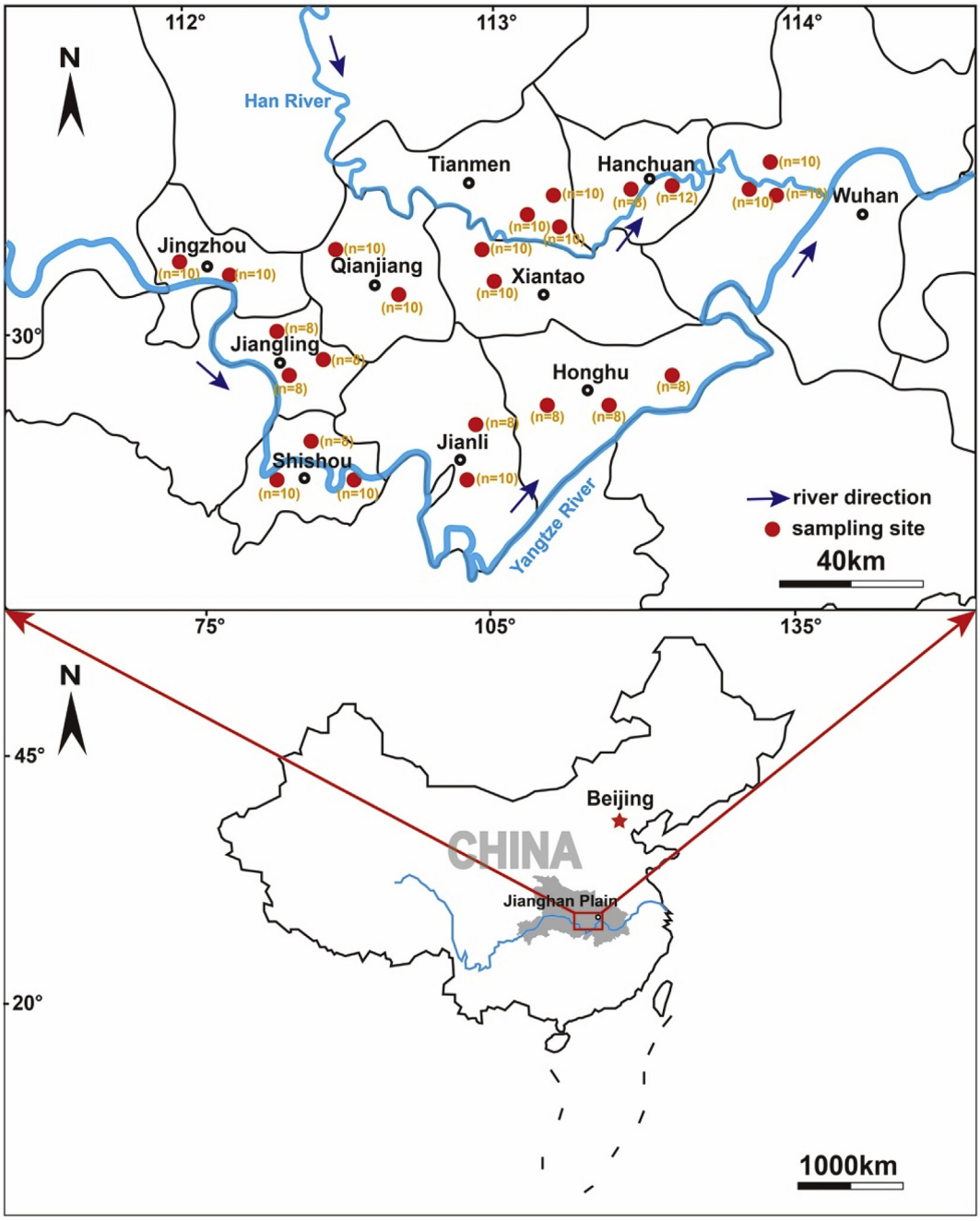

Fig. 1. Map of the Jianghan Plain with the sampling sites marked.

Gao et al. (2013) using a Nu Plasma II multi-collector inductively coupled plasma mass spectrometer (Nu Instruments, Wrexham, UK).

2.3. Quality control and assurance

The quality and accuracy of the analytical results were monitored by analyzing each sample in triplicate and analyzing reagent blanks and reference materials. The relative standard deviations of the results for the triplicate sample analyses were all <10% (Table S1). A reagent blank was included with every 10 samples to monitor contamination. Chinese National Standard Soils GBW07423 (GSS-9, a lacustrine sediment) and GBW07311 (GSD-11, a rock mixture) were analyzed to monitor the quality of the heavy metal analysis results, and standard reference materials NIST SRM3108 and NIST SRM981 were analyzed to monitor the quality of the Cd and Pb isotope analysis results. The results for the reference materials agreed with the certified values (Tables S1, S5, and S6).

2.4. Statistical analysis

The heavy metal concentrations were mapped using the inverse distance method using ArcGIS 10.2 software (ESRI, Redlands, CA, USA) to allow the spatial patterns to be assessed. CA was performed on the heavy metal concentrations using SPSS 20.0 software (SPSS, Chicago, IL, USA) using the median connection method and using the Pearson correlation coefficient as the criterion for forming clusters of metals. PMF was performed on the heavy metal

concentrations using EPA PMF 5.0 software (US Environmental Protection Agency Office of Research and Development, Washington, DC, USA), which required two inputs, the concentrations and the uncertainties. The number of sources was identified from the CA results, and the sources were identified using the most important marker species.

3. Results and discussion

3.1. Current heavy metal pollution status in the JHP

Descriptive statistics for the heavy metal concentrations in the JHP soil samples with relevant baselines and international regulatory values are shown in Table S2. The mean Cd, Cu, Hg, Ni, Pb, and Zn concentrations in the soil samples (0.48, 48.2, 0.12, 48.8, 36.5, and 96.8 mg kg^{-1}, respectively) (Table 1) were higher than the background concentrations in Chinese soil (CNEMC , 1990; Niu et al., 2013). Similar results were found in previous studies of JHP soils (Tian and Cheng, 2005; Yu et al., 2008). The concentrations in JHP soils may be higher than background soil concentrations because of industrial emissions and/or the soil parent materials in the JHP (Tian and Cheng, 2005; Yu et al., 2008; Shen et al., 2012; Yang et al., 2016). The Cd concentrations in the JHP soils were similar to concentrations found in soils from the North China Plain and Pearl River Delta but higher than concentrations found in soils from the Beijing–Tianjin–Hebei region, Songnen Plain, and Yangtze River Delta. The Cu, Ni, Pb, and Zn concentrations in the JHP soils were higher than concentrations found in soils from Hong Kong (except for Pb), the North China Plain, the Songnen Plain, and the Yangtze River Delta. The Hg concentrations in the JHP soils were similar to concentrations found in soils from the North China Plain, higher than concentrations found in soils from the Beijing–Tianjin–Hebei region, and slightly higher than concentrations found in soils from the Songnen Plain. These results indicate that heavy metal pollution is more severe in soil in the JHP and parts of South China (Hong Kong, Pearl River Delta, and Yangtze River Delta) than in soil in North China (Beijing, Hebei, and the Songnen Plain).

The spatial distributions of heavy metals in the JHP soils were assessed. High Cd and Cu concentrations were found in soil from Hanchuan, Honghu, Jianli, Qianjang, Shishou, and Tianmen, and high Pb and Zn concentrations were found in soil from Jianli, Jingzhou, and Shishou (Fig. 2). High Ni concentrations were found in soil from Hanchuan, Tianmen, and Xiantao, which are along the Han River (Fig. 2). The Hg concentrations were low except for at several hot spots in Jingzhou and Wuhan (Fig. 2).

Sungur et al. (2015) found that heavy metals (Cd, Pb, Ni, Cu, Zn, and Cr) in uncontaminated soil are mainly bonded to silicates and primary minerals and are poorly mobile but that heavy metals in contaminated soils tend to be associated with mobile phases. In this study, the proportions of the metals in the mobile fractions (acetic acid soluble, reducible, and oxidizable fractions) decreased in the order Pb (41.0% ± 10.6%) > Cd (39.5% ± 14.7%) > Zn (36.0% ± 14.7%) > Cu (33.2% ± 11.4%) > Ni (14.6% ± 10.8%) (Table 2). A larger proportion was in the acetic acid soluble fraction for Cd (9.1% ± 4.9%) than the other metals (Table 2), indicating that Cd was mobile. The reducible Pb fraction accounted for 36.59% of the total Pb concentration, suggesting a large proportion of the Pb could be transformed into acetic acid soluble forms if the soil properties changed (Sungur et al., 2015). For example, if the soil pH decreases H^+ would compete with Pb^{2+} for binding sites on Fe–Mn oxides, causing Pb^{2+} to be released (Zeng et al., 2011). Cu and Zn were mainly in the reducible and oxidizable fractions (Table 2), which could be activated by changes in the physicochemical conditions caused by agricultural activities (Şenol Kartal et al., 2006; Han et al., 2011; Sungur et al., 2015). Ni was the least mobile metal, the immobile (residual) fraction accounting for up to 85.4% of the total Ni concentration (Table 2).

3.2. Discrimination between sources

3.2.1. Cd isotopes

The sources of heavy metals to the JHP soils were identified from the Cd isotope compositions of 20 representative samples (Table S3). The Cd isotope results are shown as $\delta^{114/110}$Cd (‰) values, calculated using equation (1) (Wombacher et al., 2004). $\delta^{114/110}$Cd is the difference between the Cd isotope composition of a sample and the Cd isotope composition of a standard.

$$\delta^{114/110}\mathrm{Cd} = \frac{\left(\frac{^{114}\mathrm{Cd}}{^{110}\mathrm{Cd}}\right)_{\mathrm{sample}} - \left(\frac{^{114}\mathrm{Cd}}{^{110}\mathrm{Cd}}\right)_{\mathrm{standard}}}{\left(\frac{^{114}\mathrm{Cd}}{^{110}\mathrm{Cd}}\right)_{\mathrm{standard}}} \times 1000 \quad (1)$$

The $\delta^{114/110}$Cd values for the JHP soils were −0.76‰ to −0.25‰, and the mean was −0.43‰ (Table S3).

Cd isotopes rarely fractionate in natural samples such as natural soils (Wombacher et al., 2003; Cloquet et al., 2005). However, evaporation/condensation at high temperatures (e.g., during coal combustion, ore smelting, and refining) can cause Cd isotope fractionation (Wombacher et al., 2003; Cloquet et al., 2005; Cloquet et al., 2006; Gao et al., 2013). Heavy Cd isotopes will be relatively enriched in slag, giving $\delta^{114/110}$Cd values > 0, and light Cd isotopes will be relatively enriched in soot and dust, giving $\delta^{114/110}$Cd values < 0 (Fig. 3) (Wombacher et al., 2003; Cloquet et al., 2005). Cloquet et al. (2006) found that $\delta^{114/110}$Cd values for soil around a smelter (−0.76‰ to +0.10‰) were affected by smelting activities and that >60% of the Cd in the soil samples was supplied by soot emitted from the smelter. Gao et al. (2013) found $\delta^{114/110}$Cd values in sediment from the Beijiang River in China of −0.45‰ to +0.25‰, and at least three sources (the local background, smelter slag, and smelter soot) were identified (Fig. 3). In this study, all the $\delta^{114/110}$Cd values were <0 and were between values previously found for incinerator fly ash and smelter dust (Fig. 3),

Table 1
Mean concentrations (mg kg^{-1}) of heavy metals in soils from the Jianghan Plain and other regions.

Location	Sample numbers	Pb	Cd	Zn	Cu	Ni	Hg	Reference
Beijing, China	412	36.2	0.14	69.8	22.4	–	0.07	Lu et al. (2012); Peng et al. (2018)
Hebei, China	100	18.8	0.15	70.0	21.2	25.0	0.08	Yang et al. (2009)
North plain, China	38	27.7	0.58	56.6	22.3	–	0.12	Huang and Jin (2008)
Pearl River Delta, China	38	40.0	0.58	84.7	33.0	21.2		Wong et al. (2002)
Song-nen Plain, China	20929	22.0	0.10	56.0	18.6	23.3	0.03	Xia et al. (2014)
Hong Kong, China	21	38.2	1.27	62.4	19.8	–	–	Chen et al. (1997)
China	131	33.0	0.21	92.6	40.5	28.2	–	Niu et al. (2013)
YRD, China	240	37.6	0.23	88.4	25.8	29.2	–	Shao et al. (2016)
Jianghan Plain	234	36.5	0.48	96.8	48.2	48.8	0.12	This study
Chinese baseline	–	23.5	0.10	68.0	20.7	24.9	0.04	CNEMC , 1990

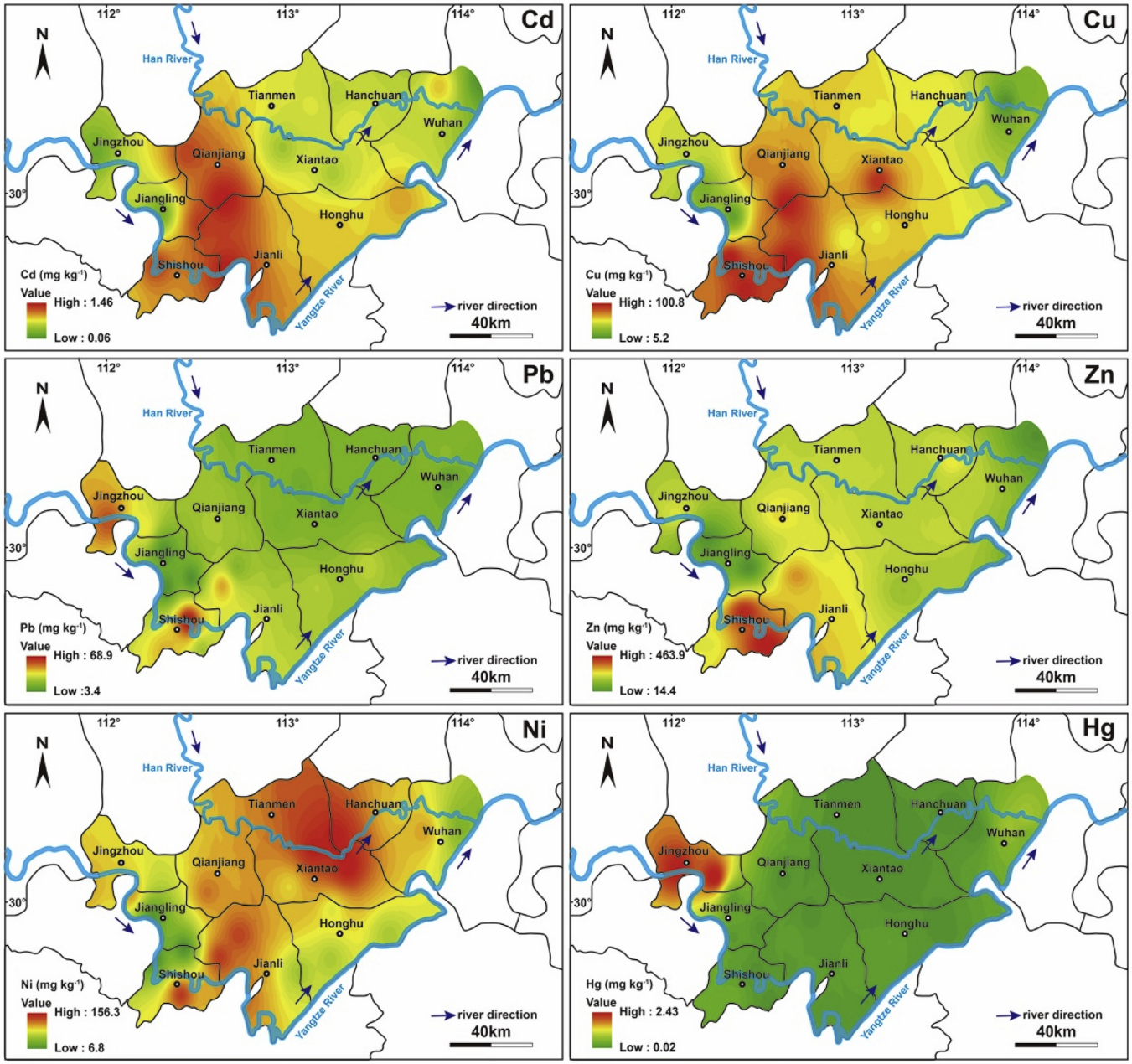

Fig. 2. Spatial distributions of the Cd, Cu, Pb, Zn, Ni, and Hg concentrations in agricultural soils from the Jianghan Plain.

Table 2
Percentages of each heavy metal in four soil fractions ($n = 32$).

Heavy metal	Acetic acid soluble fraction	Reducible fraction	Oxidizable fraction	Mobile fractions[a]	Residual fraction
Cd	9.1 ± 4.9	27.3 ± 10.3	3.2 ± 1.6	39.5 ± 14.7	60.5 ± 14.7
Cu	0.07 ± 0.02	16.1 ± 5.4	17.1 ± 8.0	33.2 ± 11.4	66.8 ± 11.4
Pb	0.09 ± 0.01	36.6 ± 9.6	4.4 ± 1.8	41.0 ± 10.6	59.0 ± 10.6
Zn	0.6 ± 0.2	18.2 ± 10.1	17.2 ± 6.6	36.0 ± 14.7	64.0 ± 14.7
Ni	0	4.5 ± 0.5	10.1 ± 6.8	14.6 ± 10.8	85.4 ± 10.8

[a] Mobile fraction = acetic acid soluble fraction + reducible fraction + oxidizable fraction.

indicating that Cd may have been supplied to JHP soils through emissions during high temperature processes including ore smelting and/or refining (Wombacher et al., 2003; Cloquet et al., 2005).

3.2.2. Pb isotopes

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotope ratios for 32 representative soil samples were 1.182–1.195 and 2.078–2.097, respectively, which were within the ranges for Chinese coal ($^{206}Pb/^{207}Pb$

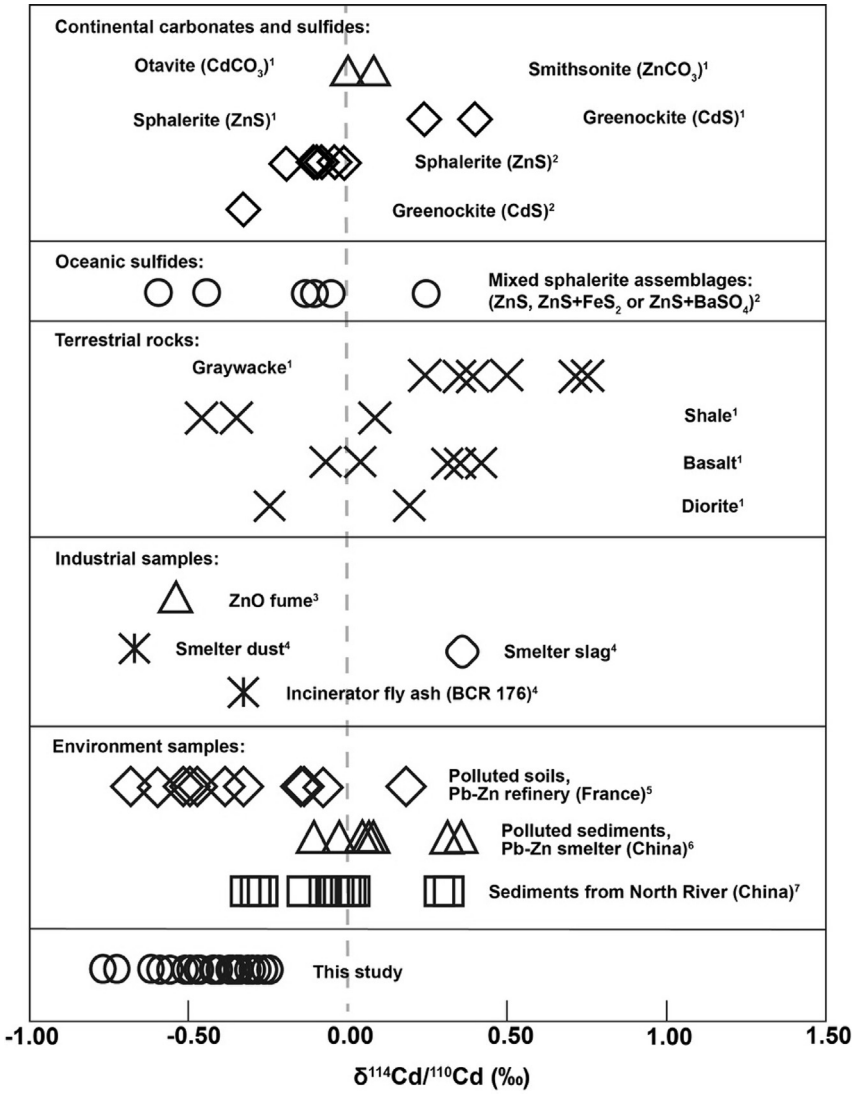

Fig. 3. Cd isotope compositions of samples from the Jianghan Plain and in previous studies. Data sources: [1]Wombacher et al. (2003), [2]Schmitt et al. (2009), [3]Shiel et al. (2010), [4]Cloquet et al. (2005), [5]Cloquet et al. (2006), [6]Gao et al. (2008), [7]Gao et al. (2013).

1.181–1.182 and $^{208}Pb/^{206}Pb$ 2.099–2.101) and natural sources ($^{206}Pb/^{207}Pb$ 1.190–1.208 and $^{208}Pb/^{206}Pb$ 2.066–2.084) (Fig. 4a) (Bi et al., 2017) but clearly different from the ranges for vehicle exhaust ($^{206}Pb/^{207}Pb$ 1.147–1.162 and $^{208}Pb/^{206}Pb$ 2.106–2.126) (Fig. 4a) (Bi et al., 2017). This indicated that traffic emissions made limited contributions to the Pb concentrations in JHP soils but that coal combustion made important contributions to the Pb concentrations in JHP soils (Zhao et al., 2014).

The contributions of different Pb sources to Pb in JHP soils were calculated using the binary mixing model shown in equation (2) (Komarek et al., 2008),

$$X_{\text{sample}} = \frac{\left(\frac{^{206}Pb}{^{207}Pb}\right)\text{sample} - \left(\frac{^{206}Pb}{^{207}Pb}\right)\text{background}}{\left(\frac{^{206}Pb}{^{207}Pb}\right)\text{anthropogenic} - \left(\frac{^{206}Pb}{^{207}Pb}\right)\text{background}} \times 100\%, \quad (2)$$

where X_{sample} is the contribution (%) of anthropogenic Pb (i.e., coal combustion emissions) to Pb in the sample, $(^{206}Pb/^{207}Pb)_{sample}$ is the Pb isotope composition for the sample, $(^{206}Pb/^{207}Pb)_{anthropogenic}$ is the Pb isotope composition for the contaminant (i.e., Pb emitted during coal combustion), and $(^{206}Pb/^{207}Pb)_{background}$ is the Pb isotope composition for background Pb.

The $(^{206}Pb/^{207}Pb)_{anthropogenic}$ value used was 1.182, which is the weighted mean Pb isotope composition for Chinese coal since 2010 (Bi et al., 2017). The $(^{206}Pb/^{207}Pb)_{background}$ value used was 1.197, which is the mean of the $^{206}Pb/^{207}Pb$ values for marine sand in Hainan Province, loess in Jingchuan and Xifeng, and uncontaminated soil in Guangzhou (Bi et al., 2017). The results indicated that 37%–87% (mean 52%) of the Pb in the JHP soils was supplied by coal combustion emissions (Table S4). Coal combustion contributed 74% and 87% of the total Pb burden of soil in Shishou and Jingzhou, respectively (Table S4), where most of the coal-fired power plants in the JHP are located. These results were consistent with the high Pb concentrations found in these two areas (Fig. 2).

3.2.3. CA and PMF

The sources of heavy metals to the JHP soils were investigated further by performing CA to standardize the bulk concentration data. Three clusters were identified, (1) Cr and Ni, (2) Al, Cd, Cu, Fe, Pb, and Zn, and (3) Hg (Fig. 5a, the Pearson correlation coefficients are shown in Table S5). Heavy metals with statistically significantly

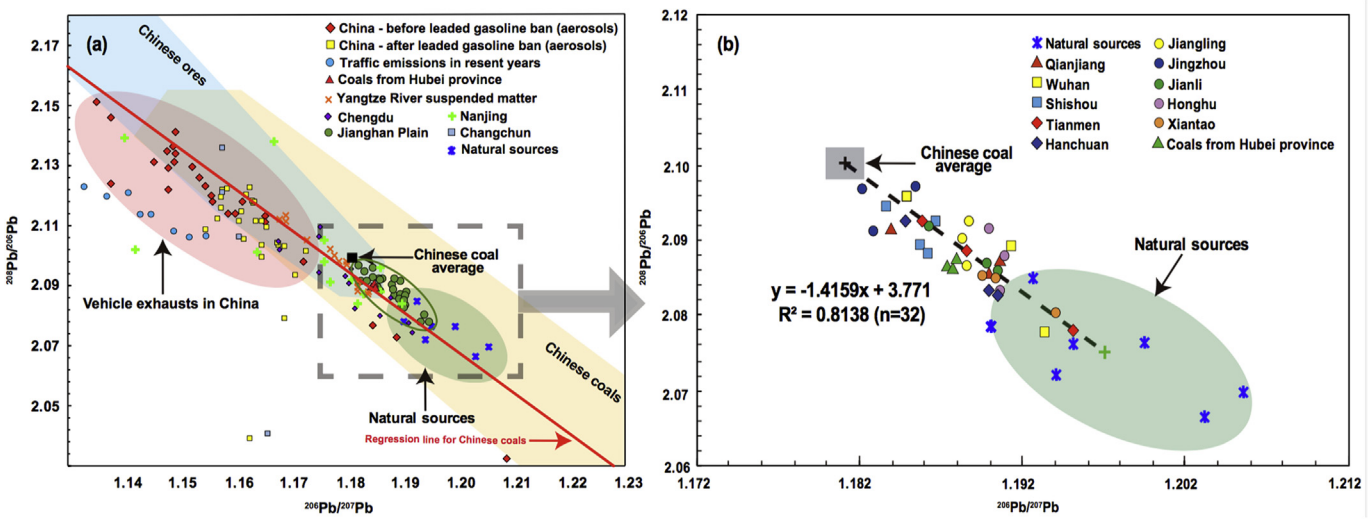

Fig. 4. Pb isotope compositions of agricultural soils from the Jianghan Plain. The regression lines for Chinese coal, mean Chinese coal, natural sources in China, and vehicle exhausts in China were taken from Bi et al. (2017). Values for Chengdu were taken from Gao et al. (2004). Values for Nanjing and suspended matter in the Yangtze River were taken from Wang et al. (2014). Values for soils in Changchun were taken from Yang et al. (2008). Values for coal from Hubei Province were taken from Bi et al. (2017).

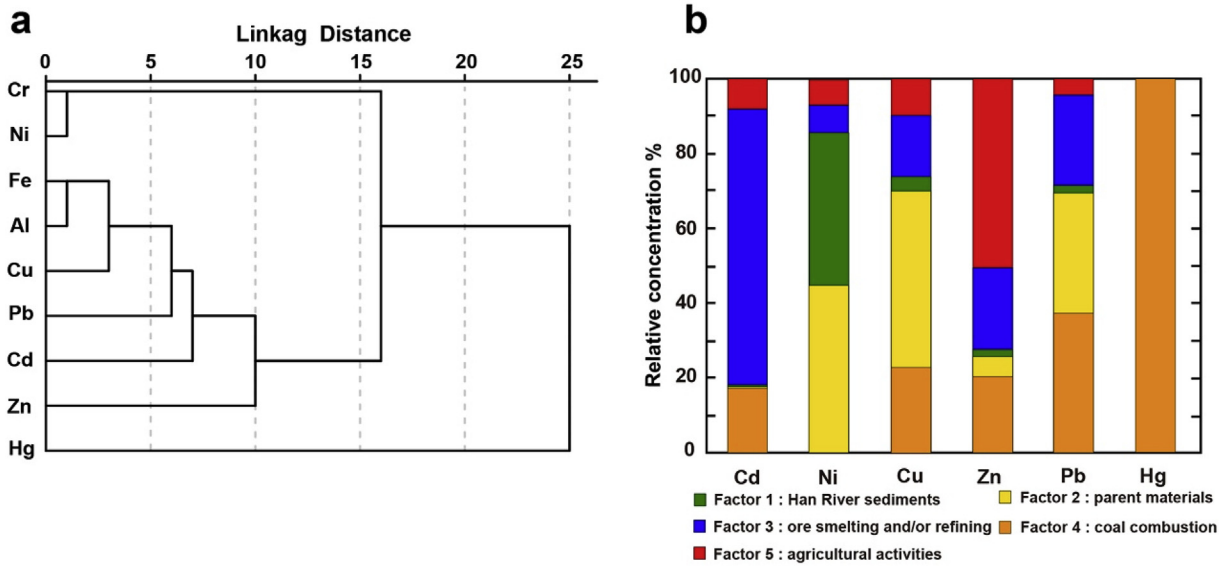

Fig. 5. (a) Hierarchical dendrogram for nine metals obtained using the median connection method (each distance reflects the degree of correlation between metals). (b) Relative contributions of different sources to the heavy metal concentrations in agricultural soils from the Jianghan Plain.

correlated concentrations are likely to have similar sources (Gramatica et al., 2006). The concentrations of Al, Cu, and Fe (in cluster 2) correlated and the Al, Cu, and Fe linkage distances were <5, but the linkage distances between Cd, Pb, and Zn and Al, Cu, and Fe were 5–10 (Fig. 5a), suggesting that the metals in cluster 2 had more than one source.

The sources of the metals were investigated further by performing PMF and calculating the relative contributions of each source of heavy metals to the JHP soils. The CA results were combined, and five factors were set up in the PMF analysis, which is described in detail in the supplementary material (Figs. S2 and S3).

Factor 1 had the strongest relative intensity of Ni (Fig. S2). Chen et al. (1999) and Sajn et al. (2011) found that Ni concentrations in soil may be affected by certain geological features such as volcanic rocks that contain high Ni concentrations. The high proportion of Ni in the immobile fractions in the JHP soils supported the possible natural origin of Ni in the JHP soils (Table 2). The Ni concentrations were higher in soils from cities adjacent to the Han River (e.g., Hanchuan, Qianjiang, Tianmen, and Xiantao) than in soils from other parts of the JHP (Ma et al., 2005). In factor 2, the relative intensities of Al and Fe were higher than the relative intensities of the other metals (Fig. S2). Al and Fe are the main metals in soil, and the Al and Fe contents of soil are stable, rarely affected by anthropogenic activities, and mainly related to the parent materials (Allen-Gil et al., 2003; Zhu et al., 2016). Factors 1 and 2 in the PMF could therefore be defined as natural sources (Han River sediment and parent materials, respectively).

In factor 3, the relative intensity of Cd was higher than the relative intensities of the other metals (Fig. S2). The Cd isotope compositions indicated that Cd was mainly supplied by ore smelting and/or refining emissions (Fig. 3). The mobile fraction contributed 39.5% ± 14.7% of the total Cd concentrations in the soils

(Table 2). These results suggested that factor 3 could be defined as anthropogenic sources related to smelting and/or refining activities.

In factor 4, the relative intensities of Hg (in particular) and Pb were higher than the relative intensities of the other metals (Fig. S2). Streets et al. (2005) found that coal combustion is the main source of Hg to soil in China, contributing 38% of the total Hg concentrations. Tian et al. (2010) found that ~43.3% of the Hg in soil in China was supplied by coal-fired power plants. Site-specific sources of Hg to soil in Jingzhou and Wuhan may have included plants at which coal is combusted (e.g., Wuhan iron and steel plant and coal-fired power plants). Taking the Pb isotope composition results into account, factor 4 could be defined as coal combustion sources (Zhao et al., 2014; Yang et al., 2016).

In factor 5, the relative intensity of Zn was higher than the relative intensities of the other metals (Fig. S2). Zn and its compounds are widely used as additives in agricultural fertilizers to act as antimicrobial agents and growth promoters, and Zn may enter agricultural soil through livestock manure (Chen et al., 1997; Mcbride and Spiers, 2001; Niu et al., 2013). Zn enrichment in agricultural soil is strongly related to agricultural activities (Nicholson et al., 2003), and farmyard manure is one of the main sources of metals to soils, and may contribute 51% of Zn in soil (Luo et al., 2009). Factor 5 could therefore be defined as anthropogenic sources related to agricultural activities.

The relative contributions of different sources to the heavy metal concentrations in the JHP soils, determined by PMF, are shown in Fig. 5b and Table S6. Coal combustion supplied 99.9% of the Hg, ore smelting and/or refining and coal combustion supplied 74.0% and 17.5% of the Cd, respectively, and Ni mainly had natural sources (41.3% from Han River sediment and 44.5% from soil parent materials). Coal combustion supplied 39.1% of the Pb, parent materials 31.8%, and ore smelting and/or refining 24.4%. These results were somewhat different from the Pb isotope composition results (which indicated that the mean contribution of coal combustion to the total Pb concentration was 52%). This could have been because of limitations in the ability of the binary mixing model to separate coal combustion (39.1%) and ore smelting and/or refining (24.4%) in the PMF model (Fig. 4a). Agricultural activities contributed 50.5% and 9.5% of the Zn and Cu, respectively. The low contribution of agricultural activities to Cu may have been related to changes in agricultural practices (Li et al., 2015). For example, promotion of organic fungicides means farmers now rarely use copper-based fungicides such as Bordeaux mixture ($CuSO_4$ and $Ca(OH)_2$) (Li et al., 2015).

4. Conclusions

Elevated heavy metal concentrations (especially Cd and Pb concentrations) relative to background concentrations were found in JHP soils. The speciation results indicated that the heavy metals except Ni in the JHP soils were very mobile and bioavailable. The $\delta^{114/110}Cd$ values for the soils were similar to values for smelter dust and incinerator fly ash, indicating that Cd may have been supplied to the JHP soils through smelting and/or refining plant emissions. The Pb isotope compositions of the JHP soils were between the mean compositions for Chinese coal and for natural sources, indicating that coal combustion has made considerable contributions of Pb to JHP soils, particularly in Jingzhou and Shishou. The CA and PMF results indicated that heavy metals in JHP soils have both natural and anthropogenic sources. Overall, coal combustion and ore smelting and/or refining have been the main anthropogenic sources of heavy metal pollution in JHP soils, and agricultural activities have made limited contributions of heavy metals except Zn. Combining stable Cd and Pb isotope analyses and multivariate statistical analyses (CA and PMF) is an effective way of identifying the sources of metals to agricultural soils.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.03.034.

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