Soil metal(loid)s pollution around a lead/zinc smelter and source apportionment using isotope fingerprints and receptor models

Xingyu Liang [a,b], Chuan Wang [a,b], Zhengcheng Song [a], Shaochen Yang [c], Xiangyang Bi [c], Zhonggen Li [d], Ping Li [a,*]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China
[c] State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan, 430074, China
[d] School of Resources and Environment, Zunyi Normal College, Zunyi, 563006, China

ARTICLE INFO

ABSTRACT

Soil pollution from metal(loid)s has become a severe environmental issue. Source identification of soil metal(loid)s is the basis for pollution prevention and control. In this study, a total of 31 surface soil samples were collected from farmland near a large lead/zinc (Pb/Zn) smelter in Zhuzhou City, central China. The sources of soil metal(loid)s pollution were identified with principal component analysis/absolute principal component scores (PCA/APCS), positive matrix factorization model (PMF), and Pb isotope fingerprints. Results showed significant accumulation of metal(loid)s in agricultural soils. The averages of soil Cd, Pb, and Zn concentrations were 7.90, 273, and 675 mg kg^{-1}, respectively. Metal(loid)s pollution was mainly distributed in the vicinity of the Pb/Zn smelter and the soil metal(loid)s contamination near the surface was quite high. The sources of metal(loid)s included Pb/Zn smelting, waste incineration, and natural sources. Smelting was the major source of metal(loid)s pollution. The Pb binary isotope mixing model indicated that smelting contributed 74.4% of soil Pb. PCA/APCS showed that smelting contributed 70.3%, 80.6%, and 86.5% to soil Cd, Pb, and Zn, respectively, while PMF revealed that it accounted for 73.1%, 72.1%, and 70.6%, respectively. Our study demonstrated that the combination of receptor models and isotope methods was comprehensive and effective for source identification, which provided new insights into determining the sources of soil metal(loid)s pollution.

1. Introduction

Growing levels of metal(loid)s pollution represent a severe environmental issue as soil is an important part of the ecosystem. Metal(loid)s are some of the most serious pollutants because of their toxicity and ability to bioaccumulate, which causes the loss of soil nutrients (Jansen et al., 1994), degeneration of soil biology (Praveena et al., 2015), and threat to human and animal health (Obiora et al., 2016; Rai et al., 2019). It was reported that more than 10^5 km^2 of farmland in China is seriously contaminated by metal(loid)s, such as Cd, Cu, Ni, and Pb (MEPC and MLRC, 2014). About 12 million tons of grain are contaminated by soil metal(loid)s annually, which has caused economic losses of over 20 billion Chinese Yuan (Hou and Li, 2017).

To control metal(loid)s pollution in soils, sources need to be identified. Common sources include industrial emissions, agricultural sources, and traffic emissions as well as natural geological origins. However, it is difficult to quantify the relative contributions of these sources to soil. Multiple tools, such as geostatistics, principal component analysis/absolute principal component scores (PCA/APCS), positive matrix factorization (PMF), and isotope fingerprints have been applied to determine the potential pollution sources and derived routes of metal(loid)s movement (Liang et al., 2017; Belis et al., 2013; Dash et al., 2020; Wang et al., 2019c; Yang et al., 2020b; Zhang et al., 2019). But using a single method to analyze the contribution of pollution sources is limited by the possibility of reducing or ignoring potential sources. For example, Pb isotopes have been used to explore the sources of Pb to atmosphere, soil, water, and biota (Rabinowitz, 2005; Wei et al., 2020), but the Pb isotopic compositions of different pollution sources (e.g. coal combustion and Zn/Pb ores) are too similar to be discriminated clearly (Bi et al., 2013; Chen et al., 2005). Therefore, multiple methods should be used together to complement each other and improve accuracy and reliability.

Mining and metallurgical activities, including digging, transporting, industry beneficiation as well as smelting, have caused plenty of heavy metals to be released into surrounding environment during last decades (Wang et al., 2019a; Li et al., 2013). Central China is seriously affected by metal(loid)s (particularly Cd and Pb) contamination (Li et al., 2011). The Zhuzhou smelter is one of the largest non-ferrous metals producers in China which has caused enormous impacts on the local environment. Former studies have shown that metal(loid)s concentrations in farmland around Zhuzhou City were significantly elevated compared with background values (Li and Chen, 2016). Within 4 km distance of the smelter, 75% of Pb, 47% of Zn, and 7% of Hg in soils exceeded the national limit (Li et al., 2011). Previous studies have paid more attention to the distribution and risk assessment of metal(loid)s in the soils of the local environment. These studies lack quantitative and comprehensive analysis of the sources of metal(loid)s pollution in agricultural soils.

In this study, geostatistical methods, isotope fingerprints, PCA/APCS, and PMF were employed to analyze sources of metal(loid)s in soil, towards development of a comprehensive and quantitative tool for identifying the sources of metal(loid)s in soil. The results provided scientific guidelines for risk assessment and pollution control of soil metal(loid)s in the study area and other regions.

2. Materials and methods

2.1. Study area

Zhuzhou city is a famous industrial base located in eastern Hunan province. It has a subtropical monsoon climate with average annual temperature of 17.6 °C and the predominant wind direction is NNW. Characterized by heavy industry, Zhuzhou city is one of the most severely polluted areas in China, especially by metal(loid)s pollution (Li and Chen, 2016).

The Zhuzhou Smelter mainly produces Pb and Zn as well as their alloy products, which has resulted in serious pollution in the local environment. Although several gas cleaning technologies have been employed to remove particles from flue gases, large amounts of metal(loid)s have been emitted during the production processes (Li and Chen, 2016). Previous study revealed that smelting was the largest source of metal(loid)s emissions but with no defined contribution (Li et al., 2011).

Additionally, waste incineration, which handled 360,000 tons of domestic waste annually, was established near the smelter.

2.2. Sample collection and determination

A total of 31 surface soil samples and 3 soil profiles were collected within 5 km of the smelter, as shown in Fig. 1. After removing impurity substances, soil samples were collected with five sub-samples in one site. All soil samples were air-dried, sieved (200-mesh), and packaged (polyethylene bags) for further analysis.

Soil samples (50 mg) were digested with 2 mL HNO$_3$ (15.3 M) and 1 mL HF (23 M) at 185 °C for 48 h. Upon evaporation, the samples were then further digested with 5 mL mixed acid (11.6 M HCl: 15.3 M HNO$_3$ = 4:1) at 110 °C for 5 h. After that, 5 mL HNO$_3$ (1 M) was added, and the digest was heated at a temperature of 120 °C. After cooling down, the digestion was measured for metal(loid)s concentrations by inductively coupled plasma mass spectrometer (Thermo Fisher, ICP-MS X2), which utilized four internal standards including ^{103}Rh, ^{115}In, ^{187}Re, and ^{209}Bi. The quality and accuracy of soil metal(loid)s analytical results were monitored by triplicate samples, reagent blanks, and reference materials. Chinese National Standard Soils GBW07405 (GSS-5) were analyzed to monitor the quality of the metal(loid)s analysis. The relative standard deviations of the results for triplicate sample analyses were all <10%. A reagent blank was included with every 10 samples to monitor contamination.

The digested solutions were diluted with Milli-Q water to 10 µg/L of Pb in 2% HNO$_3$ (v/v). Pb isotopic compositions were measured by ICP-
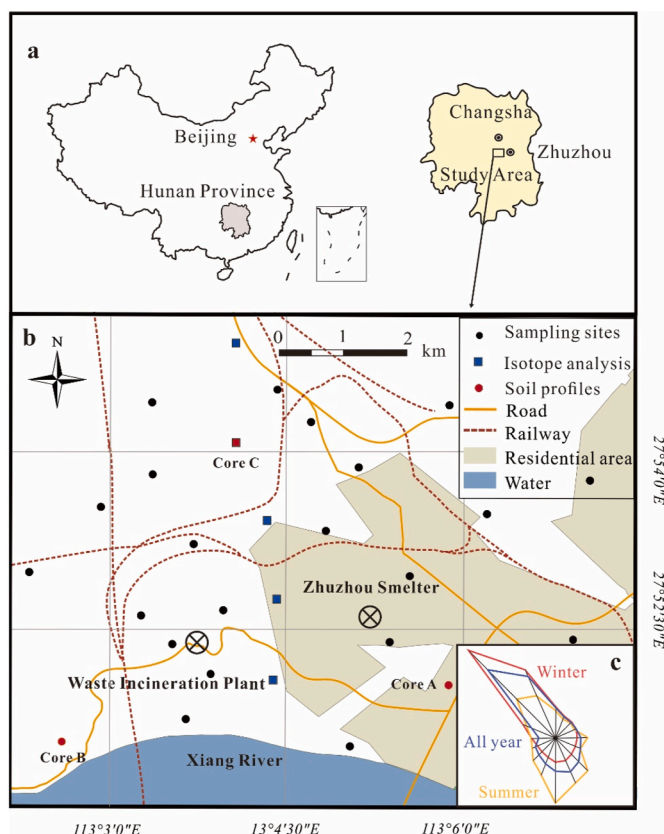

Fig. 1. Location of study area (a) and distribution of sample sites (b).

MS (Agilent 7900, USA). Pb isotopic standard (NIST SRM 981) was used for both calibration and analytical control. The relative standard deviations (RSD) of the 22 replicates were generally <0.5%. The measured ^{204}Pb/^{206}Pb, ^{206}Pb/^{207}Pb, and ^{208}Pb/^{206}Pb ratios of SRM 981 were 0.5902 ± 0.0002, 1.0936 ± 0.0025, and 2.1808 ± 0.0053, which agreed well with the reference values of 0.5904, 1.0933, and 2.1681, respectively.

2.3. Source apportionment

2.3.1. Pb isotope

According to the isotopic concentrations of soil ^{206}Pb/^{207}Pb, it is possible to quantify the contribution of sources by matching the Pb isotopic composition found at the contamination site with those of potential sources. The contributions of potential Pb sources were calculated using binary mixing model shown in Equation (1) (Cheng and Hu, 2010):

$$X_{sample} = \frac{\left(\frac{206_{Pb}}{207_{Pb}}\right)_{sample} - \left(\frac{206_{Pb}}{207_{Pb}}\right)_{background}}{\left(\frac{206_{Pb}}{207_{Pb}}\right)_{anthropogenic} - \left(\frac{206_{Pb}}{207_{Pb}}\right)_{background}} \times 100\% \tag{1}$$

where X_{sample} represents the contribution (%) of anthropogenic source (i.e. ore smelting emissions) to soil Pb. $^{206}Pb/^{207}Pb_{sample}$ represents the Pb isotopic composition for the sample, $^{206}Pb/^{207}Pb_{anthropogenic}$ represents the Pb isotopic composition for the anthropogenic source, and $^{206}Pb/^{207}Pb_{background}$ represents the composition for the natural source.

2.3.2. PCA/APCS analysis

Principal component analysis/absolute principal component scores (PCA/APCS) receptor model is composed of PCA and APCS techniques. PCA integrates and simplifies high-dimensional variables into a small number of comprehensive factors by dimensionality reduction. The APCS are used to determine the quantitative links of the factors

contributed to pollutants (detailed in SI). In this study, orthogonal rotation method of Kaiser standardization was used to extract the factors. The PCA/APCS analyses were calculated by SPSS 22.0.

2.3.3. PMF model

The positive matrix factorization (PMF) is a data analysis method proposed by Paatero and Tapper in 1994 (Norri et al., 2008). The greatest advantages of PMF are non-negativity constraints and using uncertainty to weight each data point individually (Norris et al., 2014). The goal of PMF is to solve source profiles and source contributions based on a composition dataset. The PMF model has been widely used in the apportionment of soil metal(loid)s (Zhang et al., 2019; Guan et al., 2018). In this study, PMF 5.0 was adopted according to the corresponding user guide (Norri et al., 2008; Norris et al., 2014), and the uncertainties were assigned to be 10% (Guan et al., 2018; Huang et al., 2020). PMF model was calculated by EPA PMF 5.0.

PCA/APCS and PMF receptor models described above have different intrinsic mathematical processes, which gain the PCs in PCA/APCS and factors (Fs) in PMF. The PCs and Fs are characterized by different elements and can be used to infer the sources.

2.4. Statistical analysis

SPSS 22.0 was used for Kolmogorov-Smirnov (K–S) test and spearman correlation analysis. Microsoft Excel 2010 was used for statistical analysis including mean, maximum, minimum, standard deviation, and coefficients of variation (CV). Ordinary kriging and spatial distribution maps were accomplished by Arcmap 10.2.

3. Results and discussion

3.1. Soil metal(loid)s concentrations

Descriptive statistics of metal(loid)s concentrations and basic properties in soil samples are presented in Table 1 and Table S1. Statistical distributions of soil metal(loid)s concentrations were basically conformed to normal or lognormal. The pH and SOM of soil samples ranged from 4.54 to 6.89 and 0.18%–4.90%, respectively.

Soil Cd, Pb, and Zn pollution were the main environmental issues. Both the maximum values and averages of soil Cd, Pb, and Zn (Table 1) significantly exceeded the Grade II soil criterion of China (0.4, 100, and 250 mg kg^{-1}, respectively) (CNEPA, 2018). The ratios of soil Cd, Pb, and Zn content exceeding the national limit reached 93.5% (29/31), 93.5% (29/31), and 80.5% (25/31), respectively.

The CVs of Cd, Pb, Zn, Bi, Sb, Sn, and Cu were relatively high (0.922, 0.787, 0.832, 0.639, 0.595, 0.512, and 0.434, respectively), suggesting considerable influence from artificial activities. Significant positive correlations ($p < 0.01$) were found between soil Cd, Pb, Zn, Bi, Sb, Cu, and Sn (Table S2), indicating a common source of these metal(loid)s. But uncontaminated elements (Y, Sm, Er, Nd, and Pr) showed low CVs (Table S1), and these elements correlated strongly with each other (Table S2). It was considered that these elements were derived from a natural source.

Statistical distributions of metal(loid)s concentrations revealed severe metal(loid)s pollution in the study area, especially for Cd, Pb, and Zn. Soil metal(loid)s might mainly originate from anthropogenic activities.

3.2. Spatial and vertical distribution

Spatial distributions of metal(loid)s in the soil samples were obtained with ordinary Kriging estimation as shown in Fig. 2. Spatial distributions of Cd, Pb, Zn, Bi, Sb, Cu, and Sn in surface soil showed a similar trend with higher concentrations mainly distributed in the vicinity of the Pb/Zn smelter. Particulate matter produced by smelting activities contained high contents of metal(loid)s which could enter the soil system by atmospheric deposition. The Pb/Zn smelting processes can result in Cd, Pb, Zn, Bi, Sb, Cu, and Sn emissions (Cui et al., 2004; Guo and Zhao, 2008; Yang et al., 2014). In addition, the high content of metal(loid)s found in the soil were aligned in a north-south direction, consistent with the predominant wind direction (Fig. 1c). Wind direction played an important role in metal(loid)s distribution and migration (Feng et al., 2004). Since the main wind direction was NNW in study area, metal(loid)s migrated mainly in north-south direction.

However, spatial variation of soil Cr showed a different pattern. The hotpots of soil Cr were mainly concentrated near a waste incineration power plant. Similar results were also found in previous studies (Cao et al., 2015; Li et al., 2011). Cr released from waste incineration could be enriched in the atmosphere, soil, and crops by exhaust emissions and deposition (Li et al., 2015).

The vertical variations of metal(loid)s in three soil profiles were illustrated in Fig. 3. Core A showed significantly higher metal(loid)s concentrations than those in cores B and C, because it was much closer to the smelter and received more serious impacts. There was significant increasing of Cd, Pb, and Zn concentrations in soil profiles near the surface. Except for Zn in core C, metal(loid)s in top soils (0–10 cm) were significantly elevated compared to soil at depths of >20 cm. As soil depth increased, metal(loid)s decreased sharply and reached a stable concentration at a depth of 40–80 cm. Pb/Zn smelting was a significant anthropogenic atmospheric emission source of metal(loid)s (Li et al., 2011; Li et al., 2014). High concentrations of Cd, Pb, and Zn in top soils indicated that metal(loid)s primarily originated from smelting activities rather than natural sources. But Cd, Pb, and Zn concentrations at the bottom of the soil profiles were interpreted as a local baseline (Table S2). Additionally, other elements (Y, Sm, Er, and Nd) concentrations were relatively stable throughout the soil profiles and were comparable with local baselines, suggesting that these elements were originated from natural sources (Nriagu and Pacyna, 1988) (see Fig. 3).

The spatial and vertical distributions of soil metal(loid)s reflected typical patterns of atmospheric deposition around point sources (Pb/Zn smelter and waste incineration plant). Under local climate and topographical conditions, metal(loid)s was transported to the surrounding areas by atmospheric deposition.

3.3. Source apportionment

Identification of the sources of soil metal(loid)s contamination by geostatistical and correlation analysis was not comprehensive and

Table 1
Descriptive statistics of metal(loid)s concentrations in soil (mg•kg^{-1}).

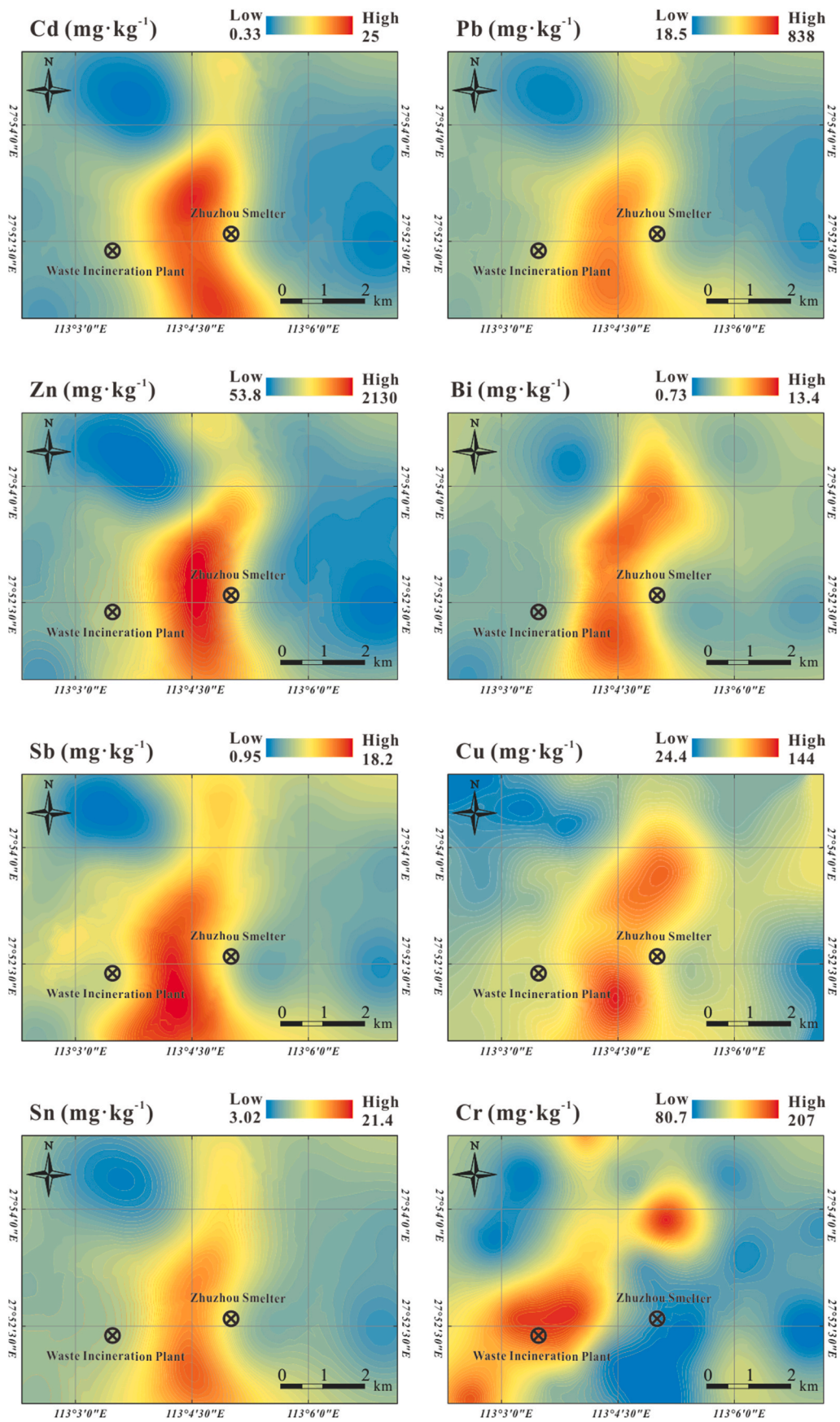|	Mean	SD	Max	Min	CV	Background of Hunan Province	Accumulation index
Cd	7.90	7.28	25.0	0.329	0.922	0.126	62.7
Pb	273	214	838	18.5	0.787	29.7	9.18
Zn	675	561	2130	53.8	0.832	94.4	7.15
Bi	5.28	3.38	13.4	0.733	0.639	1.05	5.03
Sb	7.60	4.52	18.2	0.951	0.595	1.87	4.07
Cu	67.8	29.4	144	24.4	0.434	27.3	2.48
Sn	8.90	4.56	21.4	3.02	0.512	4.30	2.07
Cr	131	41.7	208	80.7	0.319	71.4	1.09

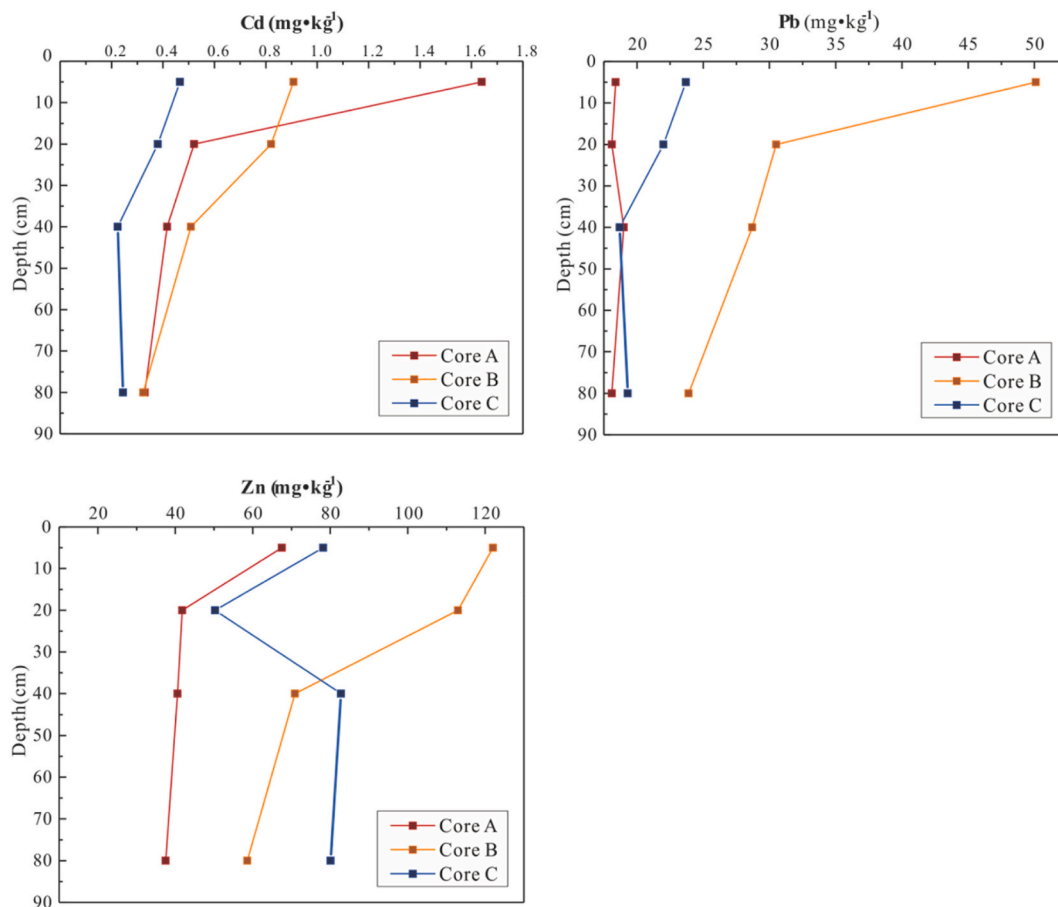**Fig. 2.** Spatial distribution of soil metal(loid)s.

Fig. 3. Vertical distribution of Cd, Pb, and Zn concentrations in soil profiles.

multiple methods should be used to improve accuracy and reliability. The receptor model and isotope approach were employed to quantify the contributions from different sources in this study.

3.3.1. Pb isotope approach

The regression lines for Chinese coal, mean Hunan Province coal, ores, natural sources in China, and vehicle exhausts in China were taken from Bi et al. (2017) (detailed in Table S4). Values for waste incineration were taken from Li et al. (2019).

As shown in Fig. 4, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios for most topsoil (0–20 cm) samples varied from 1.169 to 1.186 and 2.097–2.114, respectively. Isotopic compositions for surface soil were within the ranges for South Chinese ore ($^{206}Pb/^{207}Pb$: 1.020–1.183 and $^{208}Pb/^{206}Pb$: 2.088–2.309), 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) and natural sources ($^{206}Pb/^{207}Pb$: 1.190–1.208 and $^{208}Pb/^{206}Pb$: 2.066–2.084) (Bi et al., 2017). All Pb isotopic compositions in topsoil were located between the ore smelting and waste incineration, suggesting the potential influence of refuse burning (Li et al., 2019). But it was hard to distinguish the impacts of smelting and waste incineration as the isotopic compositions of each were quite similar.

Different from isotopic compositions for surface soil, the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in deeper soil (20–80 cm) ranged from 1.191 to 1.194 and 2.087–2.092, respectively. Pb isotopic compositions were within the extent of background, indicating that soil Pb was derived from natural sources rather than anthropogenic activities. This agreed with the vertical distribution pattern of low Pb concentration in deep soil (Section 3.2).

Distance was also an important factor affecting Pb isotopic compositions in topsoil. Soil samples far away from the smelter indicated
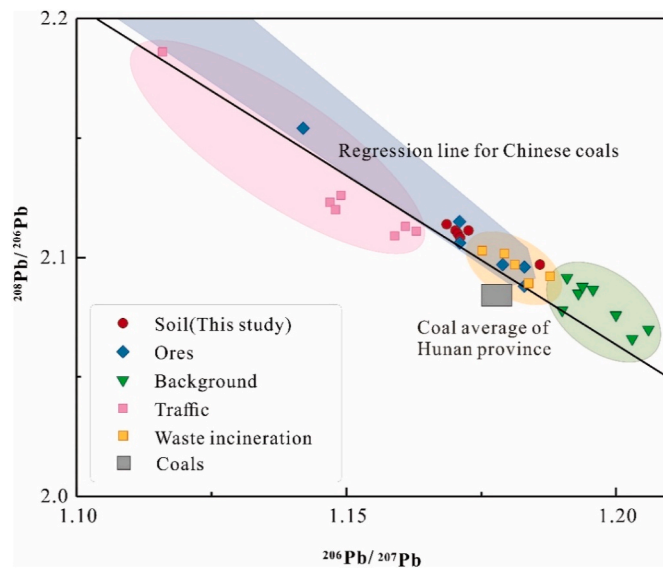

Fig. 4. Pb isotopic compositions of agricultural soils in the study area.

higher $^{208}Pb/^{206}Pb$ and lower $^{206}Pb/^{207}Pb$ ratios. This could be explained by noting that with the increasing of distance to the smelter, the relative contribution from smelting decreased.

The isotopic compositions of Pb fit well using a binary mixing model as the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$ ratios in soils exhibited a linear correlation ($R^2 = 0.98$). Two end-members including ore smelting and

natural sources were developed and the composition of $^{206}Pb/^{207}Pb$ for smelting and background were assigned as 1.162 and 1.205, respectively (Bi et al., 2017). According to Eq. (1), ore smelting contributed 74.4% to soil Pb on average, while natural sources accounted for 25.6%. Soil Pb concentrations in the study area were mainly affected by ore smelting activities.

As discussed in Section 3.1, the concentrations of several metal(loid)s (Cu, Zn, Cd, Sn, Sb, and Bi) and Pb in topsoil samples had a significant positive correlation, revealing that these metal(loid)s originated from the same pollution source. Therefore, the sources of soil Pb and other metal(loid)s highly correlated with Pb can be identified.

3.3.2. PCA/APCS analysis

Five principal components were extracted by PCA/APCS, using more than 80% of the information from the original data.

PC1 was composed of Cu, Zn, Cd, Sn, Sb, Tl, Pb, and Bi with factor loading of over 0.7 (Table S3). Correlation analysis and spatial distribution proved that these elements were derived from the same source and greatly affected by Pb/Zn smelting. Smelting activity was considered as the most important pollutant emitted in the study area during recent decades (Li et al., 2011; Li et al., 2014). The raw materials contained large amounts of metal(loid)s, which could be released to the atmosphere during the ore refining process (Li et al., 2015; Wei et al., 2020). The smoke and dust that fell to the surface of the soil resulted in metal(loid)s pollution (Cao et al., 2015; Li et al., 2018).

PC2 (Cr, V, Fe, Ni, Sr, and Zr) was associated with waste incineration (Bi et al., 2018; Li et al., 2015). Atmospheric deposition of metal(loid)s released by waste incineration was also a non-negligible source of soil metal(loid)s (Li et al., 2017; Wang et al., 2019b).

PC3, PC4, and PC5 were combined in a natural source. PC3 contained high loadings of Y, Pr, Nd, Sm, and Er, while PC4 was composed of Mg, Ca, and Ti. PC5 featured high levels of Mn, Co, and Mo. The amount of these elements was found to be close to background values, suggesting the contribution of natural processes (Luo et al., 2015; Ostro et al., 2007).

It was calculated by APCS that smelting contributed 70.3%, 80.6%, and 86.5% to total Cd, Pb, and Zn in the soils, while waste incineration accounted for 2.2%, 7.6%, and 5.1%, respectively. Natural sources contributed 27.5%, 11.8%, and 8.4% to soil Cd, Pb, and Zn, respectively, on average (Fig. 5a). Pb/Zn smelting was the major source of soil metal(loid)s pollution, especially for Cd, Pb, and Zn.

3.3.3. PMF model

The results of PMF fit well with PCA/APCS. Five factors were chosen based on the outcome of the PMF model.

F1 featured high levels of Cu, Zn, Cd, Sn, Sb, Pb, and Bi, which was highly consistent with PC1 (Fig. S1). These elements showed quite a close relationship to Pb/Zn smelting activities. It had been widely reported that Pb/Zn smelting was one of the major sources of metal(loid)s to environment, especially in China (Cui et al., 2004; Li et al., 2015; Wei et al., 2020; Wang et al., 2019a). F1 was defined as being from the smelting source.

F2, F3, and F5, weighted primarily on Mn, Ca, Mg, Ti, and other elements (Fig. S1). The spatial distribution of these elements was relatively uniform, with no obvious specific pattern. These elements were usually considered as natural background source (Gilkes and McKenzie, 1988; Micó et al., 2006). The geological environment in the study area was quite complex and trace elements behaved variously in geological processes. The PMF model separated these elements into multiple sources. These Fs were inferred as soil parent materials.

F4 (V, Cr, Fe, Co, and Ni) was comparable with PC2 and considered as having a waste incineration source (Fig. S1). Waste incineration released many kinds of metal(loid)s including Cr (Li et al., 2017, 2019; Wang et al., 2019b; Yang et al., 2020a). Li et al. (2015) found a remarkable concentration for soil Cr around a waste incineration plant.

As presented in Fig. 5b, Pb/Zn smelting explained 73.1%, 72.1%, and 70.6% to total soil Cd, Pb, and Zn, while waste incineration accounted for 7.1%, 6.0%, and 6.4%, respectively. Natural sources contributed 19.8%, 21.9%, and 22.9% on average. The results were similar with those calculated by PCA/APCS (Section 3.3.2), revealing that soil metal(loid)s pollution came primarily from Pb/Zn smelting.

3.3.4. Comparison between different methods

In the study area, three main sources of soil metal(loid)s were recognized, covering Pb/Zn smelting, waste incineration, and natural sources. Pb/Zn smelting was identified as the largest contributor to soil metal(loid)s in surrounding areas. The contributions obtained by Pb isotope, PCA/APCS, and PMF were relatively consistent, indicating that these three methods can verify each other very well.

4. Conclusions

This study investigated metal(loid)s pollution and quantified the relative contribution from different sources in agricultural soils nearby a Pb/Zn smelter using isotope fingerprints, PCA/APCS, and PMF. Serious Cd, Pb, and Zn pollution in the surface soils were observed. The spatial and vertical distribution of soil metal(loid)s, except for Cr, showed an obvious pattern of atmospheric deposition around the smelter. The outcomes of PCA/APCS, PMF, and Pb isotope were consistent and revealed that the sources of metal(loid)s included Pb/Zn smelting, waste incineration, and natural sources. Pb/Zn smelting was identified as the primary source of soil metal(loid)s. Combining Pb isotope and receptor models (PCA/APCS and PMF) can effectively identify the sources of soil metal(loid)s. Anthropogenic emission of metal(loid)s from the smelter should be strictly reduced in the study area and other regions with similar industries. The bioaccumulation of metal(loid)s in crops and
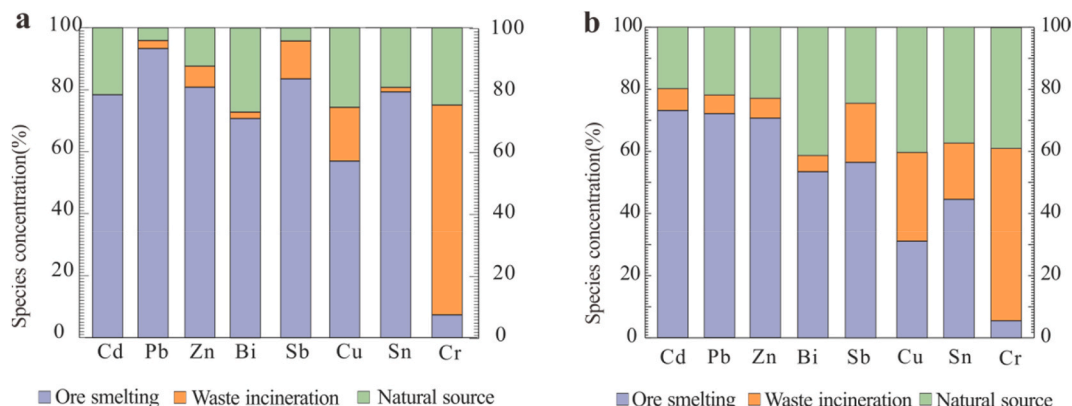
Fig. 5. Contributions of different sources calculated by PCA/APCS (a) and PMF (b).

health risks to humans should also be investigated in future studies.

Declaration of competing interest

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2021.105118.

References

Belis, C.A., Karagulian, F., Larsen, B.R., Hopke, P.K., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos. Environ. 69, 94–108. https://doi.org/10.1016/j.atmosenv.2012.11.009.

Bi, C., Zhou, Y., Chen, Z., Jia, J., Bao, X., 2018. Heavy metals and lead isotopes in soils, road dust and leafy vegetables and health risks via vegetable consumption in the industrial areas of Shanghai, China. Sci. Total Environ. 619–620, 1349–1357. https://doi.org/10.1016/j.scitotenv.2017.11.177.

Bi, X., Li, Z., Wang, S., Zhang, L., Xu, R., Liu, J., Yang, H., Guo, M., 2017. Lead isotopic compositions of selected coals, Pb/Zn ores and fuels in China and the application for source tracing. Environ. Sci. Technol. 51 (22), 13502–13508. https://doi.org/10.1021/acs.est.7b04119.

Bi, X., Liang, S., Li, X., 2013. A novel in situ method for sampling urban soil dust: particle size distribution, trace metal concentrations, and stable lead isotopes. Environ. Pollut. 177, 48–57. https://doi.org/10.1016/j.envpol.2013.01.045.

Cao, X., Zhang, S., Tan, C., Hu, P., Cui, X., Zhou, T., Wu, L., Luo, Y., 2015. Heavy metal contamination characteristics in soils around a nonferrous metal smelter in central southern China. Soils 47 (1), 94–99 (in Chinese).

Chen, J., Tan, M., Li, Y., Zhang, Y., Lu, W., Tong, Y., Zhang, G., Li, Y., 2005. 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 (7), 1245–1253. https://doi.org/10.1016/j.atmosenv.2004.10.041.

Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. Environ. Pollut. 158 (5), 1134–1146. https://doi.org/10.1016/j.envpol.2009.12.028.

CNEPA (National Environmental Protection Agency of China), 2018. Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018) (In Chinese).

Cui, Y., Zhu, Y., Zhai, R., Chen, D., Huang, Y., Qiu, Y., Liang, J., 2004. Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. Environ. Int. 30 (6), 785–791. https://doi.org/10.1016/j.envint.2004.01.003.

Dash, S., Borah, S.S., Kalamdhad, A.S., 2020. Application of positive matrix factorization receptor model and elemental analysis for the assessment of sediment contamination and their source apportionment of Deepor Beel, Assam, India. Ecol. Indicat. 114, 106291. https://doi.org/10.1016/j.ecolind.2020.106291.

Feng, X., Li, G., Qiu, G., 2004. A preliminary study on mercury contamination to the environment from artisanal zinc smelting using indigenous methods in Hezhang county, Guizhou, China—Part 1: mercury emission from zinc smelting and its influences on the surface waters. Atmos. Environ. 38 (36), 6223–6230. https://doi.org/10.1016/j.scitotenv.2005.09.036.

Gilkes, R.I., McKenzie, R.M., 1988. Geochemistry and Mineralogy of Manganese in Soils, pp. 23–35.

Guan, Q., Wang, F., Xu, C., Pan, N., Lin, J., Zhao, R., Yang, Y., Luo, H., 2018. Source apportionment of heavy metals in agricultural soil based on PMF: a case study in Hexi Corridor, northwest China. Chemosphere 193, 189–197. https://doi.org/10.1016/j.chemosphere.2017.10.151.

Guo, C., Zhao, Y., 2008. Recovery of Pb and Zn from smoke dust. Environ. Protect. Chem. Ind. (1), 77–80 (in Chinese).

Hou, D., Li, F., 2017. Complexities surrounding China's soil action plan. Land Degrad. Dev. 28, 2315–2320 (in Chinese).

Huang, H., Lin, C., Hu, G., Yu, R., Hao, C., Chen, F., 2020. Source appointment of heavy metals in agricultural soils of the Jiulong river basin based on positive matrix factorization. Environ. Sci. 41 (1), 430–437. https://doi.org/10.13227/j.hjkx.201907156.

Jansen, E., Michels, M., van Til, M., Doelman, P., 1994. Effects of heavy metals in soil on microbial diversity and activity as shown by the sensitivity-resistance index, an ecologically relevant parameter. Biol. Fertil. Soils 17 (3), 177–184.

Li, K., Gu, Y., Li, M., Zhao, L., Ding, J., Lun, Z., Tian, W., 2018. Spatial analysis, source identification and risk assessment of heavy metals in a coal mining area in Henan, Central China. Int. Biodeterior. Biodegrad. 128, 148–154. https://doi.org/10.1016/j.ibiod.2017.03.026.

Li, N., Kang, Y., Pan, W., Zeng, L., Zhang, Q., Luo, J., 2015. Concentration and transportation of heavy metals in vegetables and risk assessment of human exposure to bioaccessible heavy metals in soil near a waste-incinerator site, South China. Sci. Total Environ. 521–522, 144–151. https://doi.org/10.1016/j.scitotenv.2015.03.081.

Li, P., Lin, C., Cheng, H., Duan, X., Lei, K., 2015. Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. Ecotoxicol. Environ. Saf. 113, 391–399. https://doi.org/10.1016/j.ecoenv.2014.12.025.

Li, T., Wan, Y., Ben, Y., Fan, S., Hu, J., 2017. Relative importance of different exposure routes of heavy metals for humans living near a municipal solid waste incinerator. Environ. Pollut. 226, 385–393. https://doi.org/10.1016/j.envpol.2017.04.002.

Li, X., Chen, X., 2016. Characteristics of heavy metals pollution and health risk assessment in farmland soil of Zhuzhou. J. Guilin Univ. Technol. 36 (3), 545–549 (in Chinese).

Li, Y., Zhang, H., Shao, L., Zhou, X., He, P., 2019. Impact of municipal solid waste incineration on heavy metals in the surrounding soils by multivariate analysis and lead isotope analysis. J. Environ. Sci.-China 82, 47–56 (in Chinese).

Li, Z., Feng, X., Li, G., Bi, X., Sun, G., Zhu, J., Qin, H., Wang, J., 2011. Mercury and other metal and metalloid soil contamination near a Pb/Zn smelter in east Hunan province, China. Appl. Geochem. 26 (2), 160–166. https://doi.org/10.1016/j.apgeochem.2010.11.014.

Li, Z., Feng, X., Li, G., Bi, X., Zhu, J., Qin, H., Dai, Z., Liu, J., Li, Q., Sun, G., 2013. Distributions, sources and pollution status of 17 trace metal/metalloids in the street dust of a heavily industrialized city of central China. Environ. Pollut. 182, 408–416. https://doi.org/10.1016/j.envpol.2013.07.041.

Li, Z., Ma, Z., van der Kuijp, T.J., Yuan, Z., Huang, L., 2014. A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. Sci. Total Environ. 468–469, 843–853. https://doi.org/10.1016/j.scitotenv.2013.08.090.

Liang, J., Feng, C., Zeng, G., Gao, X., Zhong, M., Li, X., Li, X., He, X., Fang, Y., 2017. Spatial distribution and source identification of heavy metals in surface soils in a typical coal mine city, Lianyuan, China. Environ. Pollut. 225, 681–690. https://doi.org/10.1016/j.envpol.2017.03.057.

Luo, X., Xue, Y., Wang, Y., Cang, L., Xu, B., Ding, J., 2015. Source identification and apportionment of heavy metals in urban soil profiles. Chemosphere 127, 152–157. https://doi.org/10.1016/j.chemosphere.2015.01.048.

MEPC (Ministry of Environmental Protection of China)., MLRC (Ministry of Land and Resources), 2014. National Soil Pollution Survey Communique (in Chinese).

Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere 65 (5), 863–872. https://doi.org/10.1016/j.chemosphere.2006.03.016.

Norri, G., Vedantham, R., Wade, K., 2008. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. The National Exposure Research Laboratory, Washington.

Norris, G.A., Duvall, R., Brown, S.G., Bai, S., 2014. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide Prepared for the US. Environmental Protection Agency Office of Research and Development, Washington, DC. DC.EPA/600/R-14/108.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative Assessment of World Contamination of Air, Water and Soils by Trace Metals, pp. 134–139.

Obiora, S.C., Chukwu, A., Davies, T.C., 2016. Heavy metals and health risk assessment of arable soils and food crops around Pb–Zn mining localities in Enyigba, southeastern Nigeria. J. Afr. Earth. Sci. 116, 182–189. https://doi.org/10.1016/j.jafrearsci.2015.12.025.

Ostro, B., Feng, W.Y., Broadwin, R., Green, S., Lipsett, M., 2007. The effects of components of fine particulate air pollution on mortality in California: results from CALFINE. Environ. Health Perspect. 115 (1), 13–19. https://doi.org/10.1289/ehp.9281.

Praveena, S.M., Yuswir, N.S., Aris, A.Z., Hashim, Z., 2015. Contamination assessment and potential human health risks of heavy metals in Klang urban soils: a preliminary study. Environ. Earth Sci. 73 (12), 8155–8165. https://doi.org/10.1007/s12665-014-3974-2.

Rabinowitz, M.B., 2005. Lead isotopes in soils near five historic American lead smelters and refineries. Sci. Total Environ. 346 (1–3), 138–148. https://doi.org/10.1016/j.scitotenv.2004.11.021.

Rai, P.K., Lee, S.S., Zhang, M., Tsang, Y.F., Kim, K., 2019. Heavy metals in food crops: health risks, fate, mechanisms, and management. Environ. Int. 125, 365–385. https://doi.org/10.1016/j.envint.2019.01.067.

Wang, J., Su, J., Li, Z., Liu, B., Cheng, G., Jiang, Y., Li, Y., Zhou, S., Yuan, W., 2019a. Source apportionment of heavy metal and their health risks in soil-dustfall-plant system nearby a typical non-ferrous metal mining area of Tongling, Eastern China. Environ. Pollut. 254, 113089. https://doi.org/10.1016/j.envpol.2019.113089.

Wang, P., Hu, Y., Cheng, H., 2019b. Municipal solid waste (MSW) incineration fly ash as an important source of heavy metal pollution in China. Environ. Pollut. 252, 461–475. https://doi.org/10.1016/j.envpol.2019.04.082.

Wang, S., Cai, L., Wen, H., Luo, J., Wang, Q., Liu, X., 2019c. Spatial distribution and source apportionment of heavy metals in soil from a typical county-level city of Guangdong Province, China. Sci. Total Environ. 655, 92–101. https://doi.org/10.1016/j.scitotenv.2018.11.244.

Wei, X., Zhou, Y., Jiang, Y., Tsang, D.C.W., Zhang, C., Liu, J., Zhou, Y., Yin, M., Wang, J., Shen, N., Xiao, T., Chen, Y., 2020. Health risks of metal(loid)s in maize (Zea mays L.) in an artisanal zinc smelting zone and source fingerprinting by lead isotope. Sci. Total Environ. 742, 140321. https://doi.org/10.1016/j.scitotenv.2020.140321.

Yang, X., Li, H., Li, C., 2014. Characterization and Leachability of lead smelting dust. Environ. Protect. Chem. Ind. 34 (5), 493–498 (in Chinese).

Yang, D., Liu, Y., Liu, S., Li, C., Zhao, Y., Li, L., Lu, S., 2020a. Exposure to heavy metals and its association with DNA oxidative damage in municipal waste incinerator workers in Shenzhen, China. Chemosphere 250, 126289. https://doi.org/10.1016/j.chemosphere.2020.126289.

Yang, Y., Yang, X., He, M., Christakos, G., 2020b. Beyond mere pollution source identification: determination of land covers emitting soil heavy metals by combining PCA/APCS, GeoDetector and GIS analysis. Catena 185, 104297. https://doi.org/10.1016/j.catena.2019.104297.

Zhang, J., Li, R., Zhang, X., Bai, Y., Cao, P., Hua, P., 2019. Vehicular contribution of PAHs in size dependent road dust: a source apportionment by PCA-MLR, PMF, and Unmix receptor models. Sci. Total Environ. 649, 1314–1322. https://doi.org/10.1016/j.scitotenv.2018.08.410.