ORIGINAL ARTICLE

Bioaccessibility and source identification of heavy metals in agricultural soils contaminated by mining activities

Wushuang Xie[1,2] · Chi Peng[3] · Hongtao Wang[2] · Weiping Chen[1]

Abstract

Large amounts of heavy metal are released by mining and industrial activities to the surrounding environment, raising great concerns regarding the effects of environmental exposure to pollutants on human health. A combination of total and bioaccessible contents, spatial analysis, cluster analysis, and positive matrix factorization model was successfully used to determine the status and sources of heavy metals in a small farmland under long-term influences of mining and industries activities in this study. The results show that the average contents of arsenic (As), cadmium (Cd), lead (Pb), and zinc (Zn) in agricultural soils exceed the Chinese national standard 2.18, 5.95, 3.46, and 1.33 times, respectively. Cd poses the highest potential on human health with a mean geo-accumulation index (I_{geo}) of 4.51 and a bioaccessible ratio of 37.41%, followed by Pb, which has a mean I_{geo} of 1.58 and a bioaccessible ratio of 63.24%. The significant correlation ($P < 0.01$) was found between the total and bioaccessible four contaminated metal contents (As, Cd, Pb, and Zn), indicating that total concentration of heavy metals could be effective indicators on bioaccessibility in this study. The As was attributed to the atmospheric deposition, Cd and Zn were mainly derived from mining activities, and Pb contamination is highly related with cement plant. Compared to atmospheric deposition, industrial activities, and soil parent materials, mining activities has the greatest influence on the enrichments of the total heavy metals in agricultural soils with the proportion of 47.9%.

✉ Weiping Chen
  wpchen@rcees.ac.cn

  Wushuang Xie
  wsxie_st@rcees.ac.cn

  Chi Peng
  chipeng@csu.edu.cn

  Hongtao Wang
  wanghongtao90@163.com

[1] State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, No. 18, Shuangqing Road, Beijing 100085, China

[2] University of Chinese Academy of Sciences, No. 19, Yuquan Road, Beijing 100049, China

[3] School of Metallurgy and Environment, Institute of Environmental Engineering, Central South University, Changsha 410083, China

Introduction

The rapid development of industrialization, such as metal smelting, mining, atmospheric deposition, land application of sewage sludge, and gasoline processing, has accelerated the release of toxic metals to urban and agricultural soils (Martínez and Motto 2000; Paff and Bosilovich 1995). China has been suffering from severe pollution caused by heavy metals for many decades of industrial expansion (Chen et al. 2014; Yu et al. 2016). Heavy metals pose potential threats to the environment and threaten the human health because of their persistence toxicity and non-degradability (Batayneh 2012; Kumar et al. 2012; Wang et al. 2012). Therefore, the determination of bioaccessible heavy metals and the source identification are crucial for soil contamination prevention and human safety (Li et al. 2014; Massaquoi et al. 2015; Vimercati et al. 2016).

Ingestion of soil particles is considered one of the important pathways of heavy metal exposure through hand-to-mouth transfer during outdoor activities (especially in children) (Johnson and Bretsch 2002; Mielke

et al. 1999). Heavy metals contained in the soils can be accumulated in the human body through the food chain and deteriorate human health even at low concentrations (Calabrese et al. 1999). In vitro method has been developed to solubilize the soil particles in vitro gastro-intestinal simulations, by controlling the pH, temperature, agitation, and enzyme and other chemical conditions to make it similar to the body digestion process (Schroder et al. 2003; Tao et al. 2015). The evaluation of relative bioaccessibility of heavy metals in soil would provide more accurate information on the heavy metals exposure than the total concentrations (Kang et al. 2016).

Soil heavy metal contamination affected by mining and industrial activities has drawn great concerns in China (Li et al. 2014). Source identification is a crucial step to the environmental protection. The spatial distribution of total and bioaccessible metals of the present study can be accurately assessed the possible hot-contaminated spots which would produce potential damage to human health, and confirmed the correlation between the total and bioaccessible metals. While GIS-based spatial mapping has been widely used to study spatial distribution patterns, there are a few studies to address their spatial heterogeneity in a small area such as less than 100 ha. In addition, the cluster analysis and positive matrix factorization (PMF) model were used to further identify the sources of the heavy metals and their contribution rates in this study. Although the PMF model has been successfully used to assess the pollutant source in atmospheric and sedimentary sources (Alleman et al. 2010; González-Macías et al. 2014; Gupta et al. 2012; Jang et al. 2013; Pekey and Doğan 2013), the approach to identify heavy metal sources in soils is limited.

In this study, a small farmland (about 80 ha) in Tielong town, west of Wengyuan county in Shaoguan city, Guangdong province, was selected as one of the representative mine contaminated sites. The study site is close to the Dabaoshan mining area and has experienced substantial uncontrolled mining and industrial expansion over the past 30 years. The amount of hazardous wastes released from mine and cement plant have led to severe heavy metals contamination in farmland and affected the lives of inhabitants. Based on the investigation of seven kinds of toxic elements (As, Cd, Cr, Cu, Ni, Pb, and Zn) in agricultural soils, we demonstrate the level of heavy metals in 145 agricultural surface soil samples, six soil profiles, and two different types of soil samples. The main objectives of this study are (1) to evaluate the contaminated levels and bioaccessibility of heavy metals in agricultural soils under long-term mining and industrial activities; (2) to investigate the source of heavy metals based on the spatial distribution and cluster analysis, and (3) to determine the contributions of different metal sources by PMF model.

# Materials and methods

Study area

The study area, Tielong town, covers a total area of 96.5 km^2 with a total population of 5962 inhabitants. The area has a subtropical monsoon climate with an average temperature is 19.4 °C and the annual precipitation is 1778 mm. Soil samples were collected from the farmland area in the north of Tielong town with a total area of 80 ha, directly exposed to the mining and industrial emission (Fig. 1). Non-ferrous metal company (A) and mining factory (B) were built in the north of farmland in the 1980s, but now have been closed, because large amounts of tailings were produced during mining in the Zn–Cu poly-metallic deposit. Cement plant (C) is located in the middle of farmland. The farmland has been abandoned because of severe heavy metal pollution. In addition, the farmland has two irrigation canals; one of the main irrigation canals flows down the mine.

Samples collection and analysis

Heavy metal concentrations were determined by 145 agricultural soil samples collected in the farmland (0–20 cm), and each sample was the mixture of nine subsamples. Vertical distribution of heavy metals was investigated by six randomly sampled soil profiles from farmland area, each soil depth was taken from the 100-cm profile at 20-cm intervals, and each layer was the composite of five subsamples. The distribution of sampling sites is shown in Fig. 1. Meanwhile, eight grassland samples (main public grass space soil and residential grass space soil) and seven woodland samples (0–20 cm) were collected at random to compare the soil contamination levels of heavy metals in different land uses, and each sample was the composite of five subsamples.

The soil samples were air-dried, picked for residues/stones, and sieved twice using a 2- and 0.149-mm mesh. Soil pH was determined by a pH electrode (PB-10, Sartorius, Germany) in a 1:2.5-w/v soil–liquid suspension (fine particles < 2 mm). Soil organic carbon (SOC) was measured by dry combustion in the elemental analyzer (Vario TOC, Elementar Co., German) using the air-dried 0.149 mm sieved soil samples (Schumacher 2002). To determine the heavy metal concentrations, 0.25 g soil sample (fine particles < 0.149 mm) was digested in a mixture of HCl–HNO$_3$–HClO$_4$–HF (10 mL, 7 mL, 7 mL, and 4 mL, respectively), until the solution was translucent to about 2–3 mL. The final solution was diluted to 50 mL using double-distilled water (ddH$_2$O). Heavy metal

Fig. 1 Location of study area and soil sampling sites
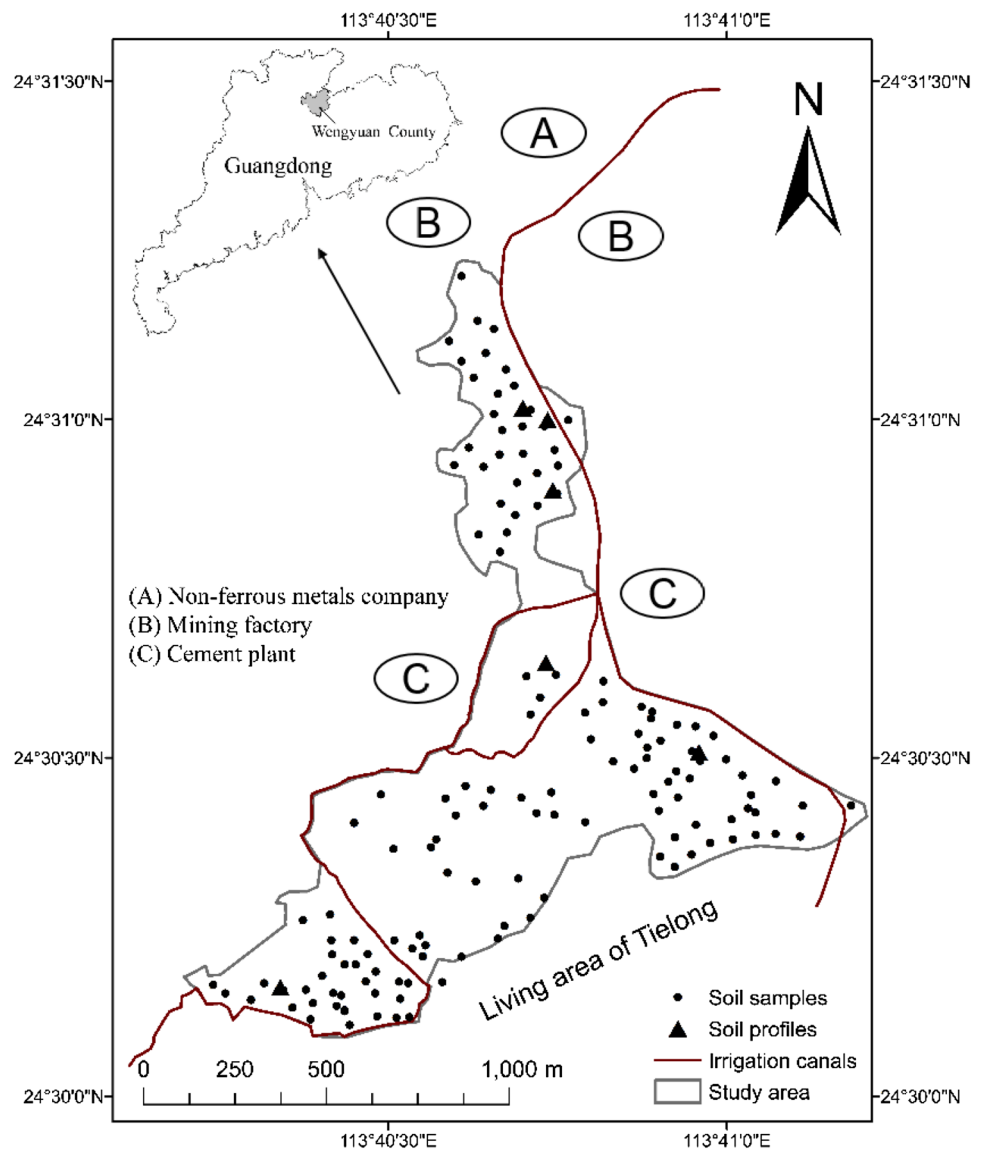
concentrations were determined by inductive-coupled plasma mass spectrometer (ICP-MS) (7500a, Agilent Technologies Inc., USA).

The in vitro digestion (IVG) model was established according to the previous studies (Boisa et al. 2014; Tang et al. 2008; Yu et al. 2010). The IVG method has two steps of sequential extraction: gastric and intestinal (Karadaş and Kara 2011): the gastric solution was prepared by dissolving 1.25 g porcine pepsin, 0.50 g sodium citrate, 0.50 g sodium malate, 420 µL lactic acid, and 500 µL of acetic acid in ddH$_2$O to a volume of 1 L. The pH was adjusted to 1.5 using concentrated HCl. Soil (0.5 g) was mixed with 50 mL of gastric solution in the reactor vessel, placed in 37 ± 1 °C constant temperature water bath (HH-6, LICHEN Technologies Inc., China) to simulate the human body temperature, and oscillated at 100 rpm/min, adjusted pH of the solution to 1.5 every 20 min. After 1 h, suspension solution was centrifuged

at 4000 rpm for 10 min; the gastric solution was modified by adjusting the pH to 7 with a saturated NaHCO$_3$ solution followed by the addition of 0.087 g bile salts and 0.025 g pancreatin to each reaction vessel. This mixture represented the intestinal digestion solution. After 4 h of digestion by the intestinal phase, 5 mL of sample was removed using a syringe. All the supernatants (gastric and intestinal) were filtered through a 0.45-µm nitrate fiber filter and maintained under refrigeration until analysis by ICP-MS.

Quality control

All experiments conducted within strict experiment conditions to eliminate/minimize possible contamination and interference. An internal calibration of ICP-MS was done by diluting standard multi-elements containing all seven metals in 0.5% HNO$_3$ according to the manufacturer's specification.

The accuracy of the total and bioaccessible metal concentrations analysis was assessed using the standard soil samples for GSS-5 and NIST 2710; recovery rates for metal contents were controlled between 80% and 110%. Blanks and duplicate samples were analyzed with each of five samples.

Data analysis

Soil environmental quality assessment

The geo-accumulation index is calculated to assess the level of heavy metal accumulation in agricultural soils. Equation (1) is given as follows (Muller 1969):

$$I_{geo} = \log_2 \frac{C_i}{1.5B_i}, \tag{1}$$

where C_i is the concentration of metals in agricultural soil samples and B_i is the Guangdong province background value of the element. The contamination degree is classified into seven levels (Abrahim and Parker 2008; Hasan et al. 2013) by the value of the geo-accumulation index.

Bioaccessibility analysis

The metal bioaccessibility in soil is assessed as the ratio of the metal ion concentration measured in the in vitro gastric and intestinal phase solution to the total metal concentration in soil (Intawongse and Dean 2008):

$$\text{In vitro bioaccessible metal ion (BA), } \% = \frac{[\text{in vitro metal}]}{[\text{total metal}]} \times 100. \tag{2}$$

Positive matrix factorization (PMF) model

PMF is one of the receptor models for quantifying the contribution of sources to sample based on the composition of the pollution sources (Wang et al. 2009; Xue et al. 2014). In this study, PMF 5.0 was adopted to source apportionment of heavy metals in agricultural soils which was followed by the following Eq. (3), with the number of k source factors:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}, \tag{3}$$

where x_{ij} is the matrix of sample concentrations with the number of samples i and chemical species j. g_{ik} represents the contribution of each factor to soil samples, f_{kj} is the source profile species, and e_{ij} is the matrix of residual for each sample. The residual error matrix is obtained by the minimum value of the objective function Q computed by the following formula:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right)^2, \tag{4}$$

where Q is the sum of the squares of the difference (e_{ij}) between the original dataset (x_{ij}) and the PMF output ($g_{ik} f_{kj}$), weighted by the measurement uncertainties (u_{ij}).

The PMF model was run using concentration data (including 7 metals in 145 agricultural soil samples) and uncertainty data filed which encompass errors such as sampling and analytical errors.

All statistical tests were performed with SPSS 20.0 software (IBM Co., Armonk, USA) and Excel 2013 (Microsoft Co., Redmond, USA). In the statistical analysis including cluster analysis and Pearson correlation analysis, two significant levels at 5% and 1% were used in the statistics. Source apportionment of heavy metals was identified by the PMF Model (USEPA, PMF 5.0). Spatial interpolation was performed using ordinary kriging by ArcGIS 10.2 (ESRI Co., Redlands, USA).

Results and discussion

Heavy metal contamination in agricultural soils

Statistical analysis of heavy metal concentrations

Heavy metal concentrations in different land uses of Tielong town are shown in Table 1, as well as the Grade II values in the Chinese Environmental Quality Standard for Soils (GB15618-2008) (national threshold value of soil contamination) (Liao et al. 2016) and the soil background values of Guangdong province (Cai et al. 2012). The farmland has a mean pH of approximately 7.82, which belongs to the neutral soil. Mean concentrations of Cr (87.54 mg kg^{-1}), Cu (40.98 mg kg^{-1}) and Ni (39.20 mg kg^{-1}) were below the Grade II criteria, suggesting that the farmland of the study area was currently not hazardous to agricultural production and human health. The mean concentrations of As (54.65 mg kg^{-1}), Cd (2.38 mg kg^{-1}), Pb (172.76 mg kg^{-1}), and Zn (332.53 mg kg^{-1}) were relatively high compared to other metals, and were 2.18, 5.95, 3.46, and 1.33 times higher than the Grade II criteria, respectively. The minimal concentration of Cd (0.68 mg kg^{-1}) was higher than the Grade II criteria, indicating severe Cd pollution in the farmland and potential high Cd exposure risks for inhabitants.

The mean concentrations of As, Cd, Cu, Pb, and Zn in farmland were much higher than those in woodland and grassland (Table 1), suggesting that anthropogenic activities have the greatest impact in farmland. However, Cd contents in three types of soil were all higher than the national standard (GB15618-2008). Compared to woodland and grassland soil, farmers are more easily exposed to the farmland via different pathways, and, thus, should pay more attention to the contamination of agricultural soils in this area.

Table 1 Heavy metal concentrations in soil for different land uses in the study area

Land uses	No. of samples	pH	As	Cd	Cr	Cu	Ni	Pb	Zn
		Mean ± std. deviation [minimum, maximum] (mg kg^{-1})							
Farmland	145	7.82±0.45 [6.33, 8.62]	54.65±29.12 [11.43, 175.73]	2.38±2.22 [0.68, 10.06]	87.54±10.20 [57.41, 114.75]	40.98±11.67 [20.05, 89.36]	39.20±6.02 [21.33, 62.03]	172.76±106.76 [89.84, 1258.29]	332.53±114.01 [118.11, 999.83]
Woodland	8	6.61±0.91 [5.34, 7.55]	24.46±9.88 [13.64, 42.18]	1.06±0.83 [0.22, 2.69]	91.71±41.01 [41.01, 91.71]	14.31±5.43 [8.06, 24.09]	31.68±21.71 [11.57, 75.65]	89.40±19.54 [19.54, 89.40]	234.54±184.07 [30.66, 581.40]
Grassland	7	7.60±0.72 [6.18, 8.42]	5.81±4.22 [1.00, 13.73]	0.98±0.68 [0.38, 2.44]	85.29±16.69 [63.27, 106.85]	28.40±7.36 [20.77, 42.27]	37.95±23.31 [19.21, 88.74]	39.46±17.27 [23.19, 65.50]	196.92±127.79 [87.96, 432.90]
Background[1]		5.2	8.9	0.056	50.5	17	14.4	36	47.3
GB15618-2008[2]		6.5–7.5	25	0.4	200	100	80	50	250
		>7.5	20	0.6	250	100	90	50	300

[1](Liao et al. 2016)
[2](Cai et al. 2012)

Pollution assessment

To assess the contamination levels of the metals in the agricultural soils, the geo-accumulation index of the seven metals was calculated. As summarized in Table 2, the mean values of I_{geo} were less than 1 in agricultural soils for Cr (0.20), Cu (0.63), and Ni (0.84), which varied between 1 and 2 for As (1.83) and Pb (1.58), and the mean value of I_{geo} for Zn (2.17) varied between 2 and 3. According to the percentage of different pollution levels of the seven metals in agricultural soils (Table 3), the I_{geo} of the majority of agricultural soils samples for As (76.69%), Pb (93.98%), and Zn (96.24%) belong to the moderately to strongly contaminated level, the Cr (87.97%), Cu (78.85%), and Ni (81.95%) contamination levels of the most of agricultural soil samples were lightly. In addition, there exited severe Cd contamination in the farmland with a mean I_{geo} of 4.51, which was much higher than other metals.

Vertical distribution of heavy metals

The vertical distribution of the heavy metal concentrations along soil profiles (0–100 cm) is shown in Fig. 2. Higher levels of As, Cd, Pb, and Zn were observed in the surface layer than the subsurface and deep soil which showed the phenomenon of aggregation. Heavy metals are not easily migrated in the soil, so they are mainly concentrated in the surface soil. The decreasing pattern of As, Cd, Pb, and Zn in the soil profile indicated that the surface soil was strongly affected by the anthropogenic activities. The Cu concentrations generally kept constant along the soil profiles. Cr and Ni concentrations were increased with the depth of soil, and it may suggest that geological substrate was the important control on the distribution and concentration of soil Cr and Ni.

Heavy metal bioaccessibility in agricultural soils

Statistical analysis of heavy metal concentrations

The in vitro digestion method has been commonly used to measure the bioaccessibility of heavy metals in soil (Ljung et al. 2006; Poggio et al. 2009; Tao et al. 2015). As illustrated in Fig. 3, the seven metals in agricultural soils had quite a different bioaccessibility with mean value varying from 3.15 to 63.24%. The difference among the elements is probably due to differences in their sorption behavior. Compared with the total concentration of heavy metals, Cr (3.33±0.97%) and Ni (3.15±1.11%) showed the relative low bioaccessibility in the study. Metals derived from anthropogenic sources are commonly more bioaccessible than those derived from natural sources, the metals of natural origin are more likely to be less soluble than the more

Table 2 Descriptive statistical analysis for geo-accumulation indexes of heavy metals in agricultural soils

Index	As	Cd	Cr	Cu	Ni	Pb	Zn
Mean	1.83	4.51	0.2	0.63	0.84	1.58	2.17
SD	0.79	0.83	0.17	0.4	0.22	0.43	0.41
Minimum	− 0.22	3.01	− 0.4	− 0.35	− 0.02	0.73	0.74
Maximum	3.72	7.58	0.6	1.81	1.52	4.54	3.82

SD Standard deviation

Table 3 Percentage of different pollution levels of heavy metals in agricultural soils

Pollution level	As	Cd	Cr	Cu	Ni	Pb	Zn
≤ 0	1.50	0	12.03	3.01	0.75	0	0
0–1	14.29	0	87.97	78.95	81.95	4.51	0.75
1–2	39.10	0	0	18.05	17.29	88.72	34.59
2–3	37.59	0	0	0	0	5.26	61.65
3–4	7.52	21.80	0	0	0	0.75	3.01
4–5	0	59.40	0	0	0	0.75	0
≥ 5	0	18.80	0	0	0	0	0

$I_{geo} \leq 0$—uncontaminated; $0 < I_{geo} < 1$—uncontaminated to moderately contaminated; $1 < I_{geo} < 2$—moderately contaminated; $2 < I_{geo} < 3$—moderately to strongly contaminated; $3 < I_{geo} < 4$—strongly contaminated; $4 < I_{geo} < 5$—strongly to extremely contaminated; $I_{geo} \geq 5$—extremely contaminated
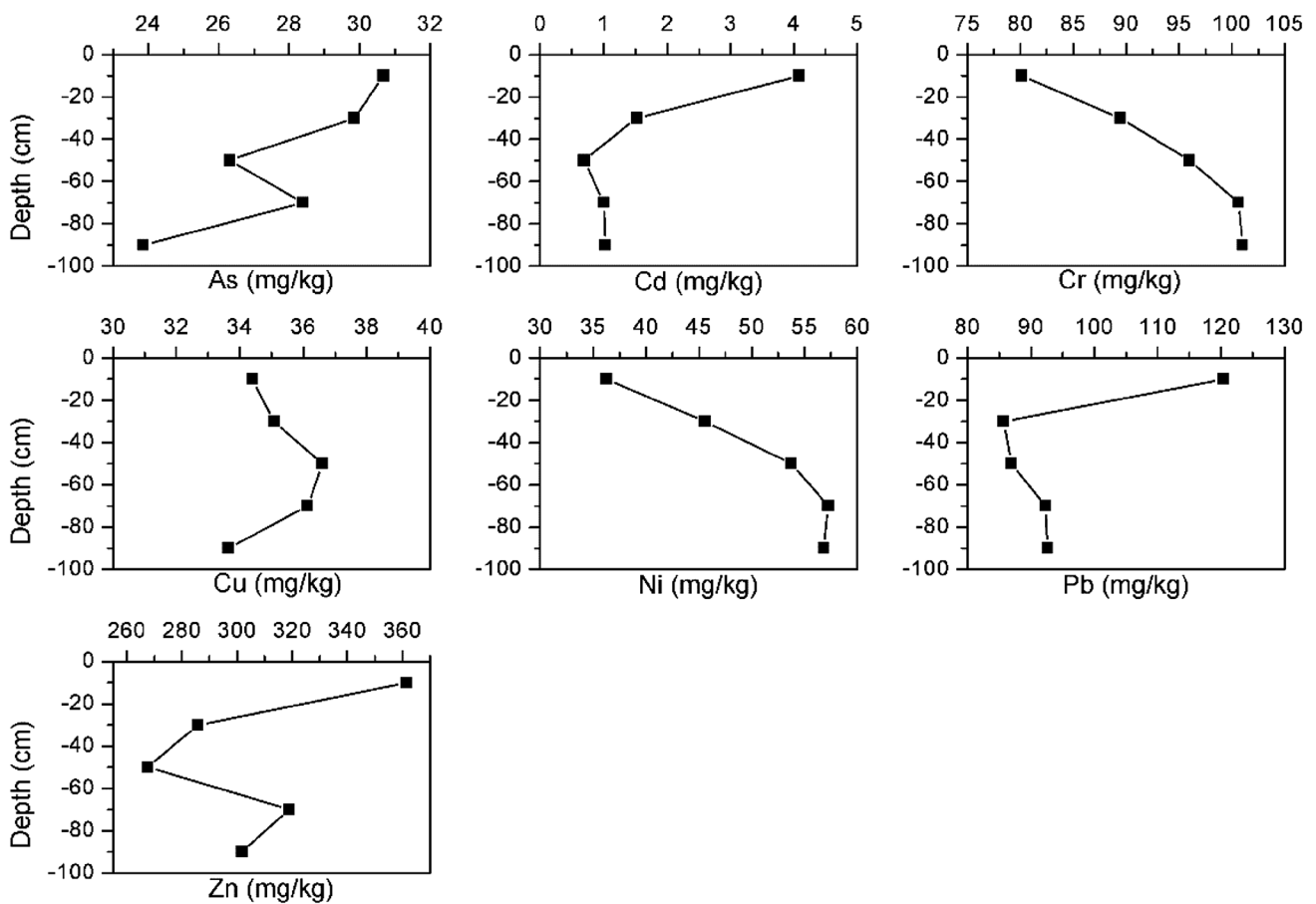

Fig. 2 Vertical distribution of the mean concentrations of heavy metal in agricultural soil profiles
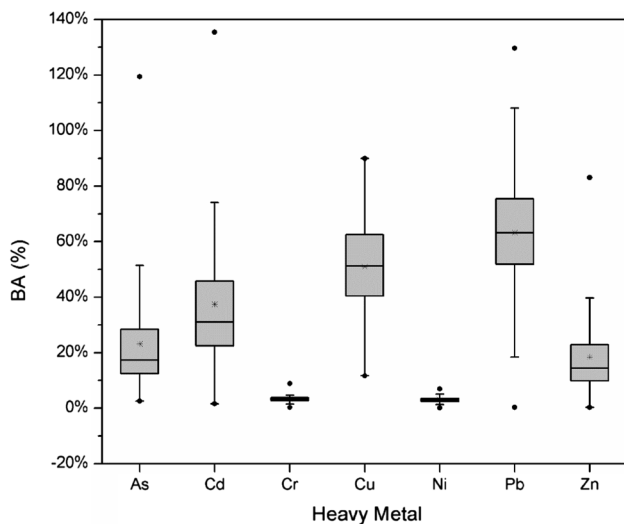
Fig. 3 The bioaccessibility of heavy metals in agricultural soils (The box in the box plot gives the interquartile range of the values, the line in the box is the median value. The asterisk represents the mean value, circles outside the box indicate the extreme value)
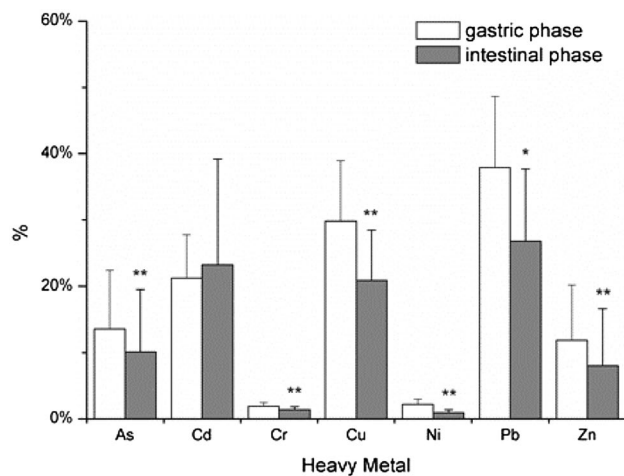

Fig. 4 Bioaccessibility of heavy metals in gastric and intestinal phases using in vitro method (** = $p < 0.01$, * = $p < 0.05$)

recent inputs from anthropogenic sources because of limiting rate (Ljung et al. 2006). Thus, Cd (37.41%) and Pb (63.24%) which were highly affected by the mining activities around showed relative high bioaccessibility; Cd and Pb posed a high potential risk on human health if they were ingested. However, it is contradictory to find the relative high Cu bioaccessibility (50.85%), maybe because Cu^{2+} has the higher affinity with pepsin compared with other heavy metals (Kang et al. 2016).

Except for Cd, the bioaccessible heavy metals in gastric phase (1.93–37.92%) were significantly higher than that in intestinal phase (1.39–26.79%) (Fig. 4), which was consistent with that observed in the previous studies (Ljung et al. 2007; Lu et al. 2011; Schroder et al. 2003). The gastric phase produced the higher bioaccessibility of heavy metals than the intestinal phase mainly because of the low pH; heavy metals were likely to be precipitated in the intestine and associated with Fe or Mn oxides when the pH was increased from gastric (1.5) to the intestinal phase (7) (Juhasz et al. 2010). The bioaccessibility of Cd in gastric phase showed comparable value with that in the intestinal phase, possibly due to the species of Cd in soils showed different absorption efficiency in gastric and intestinal phases (Kang et al. 2016).

The relationship between bioaccessibility and total metal contents

Correlation coefficients between the bioaccessible and total concentration of heavy metals, pH, and SOC in soils are shown in Table 4. Significantly positive correlations between the bioaccessible and total concentrations of Cd ($R^2 = 0.735$, $P < 0.01$) and Zn ($R^2 = 0.739$, $P < 0.01$) were detected. The total and bioaccessible As ($R^2 = 0.320$, $P < 0.01$) and Pb ($R^2 = 0.263$, $P < 0.01$) also showed a significant correlation, but the coefficients were relative low. The bioaccessible heavy metals were not significantly correlated with the soil pH and SOC, except for Cu, Ni and Pb. The variation of bioaccessible most metals in fractions of agricultural soils may be influenced by soil properties other than soil pH and SOC or anthropogenic factors such as mining and industrial activities.

Table 4 Correlation coefficients between the bioaccessible concentrations of heavy metals and total concentrations of heavy metals, pH, and SOM in agricultural soils

	As	Cd	Cr	Cu	Ni	Pb	Zn
Total concentration	0.320**	0.735**	0.150	0.275**	0.156	0.263**	0.739**
pH	− 0.093	− 0.033	− 0.296	− 0.092**	− 0.178**	0.039	0.031
SOC	− 0.048	− 0.017	− 0.138	0.073	0.032	0.307**	0.104

Levels of significance: **$P < 0.01$, *$P < 0.05$

Spatial distribution of heavy metal concentrations and bioaccessibility

Spatial distribution of metal concentrations

Spatial distribution patterns of heavy metals were established by ArcGIS 10.2 (Fig. 5). The spherical model was chosen to fit semi-variogram and ordinary Kriging was chosen to interpolate, after data transformation of all the non-normal distribution data. The soil As concentration mainly ranged from 40 to 80 mg kg^{-1}, which were relatively high and exceed the national standard 2–3 times. The total concentration of soil Cd showed a tendency of reducing from north to the south. The highest pollution region of Cd located in the north of the study area, where old mining factory is located in the upstream of the farmland. Even though soil Cr, Cu, and Ni concentrations in the farmland were higher than the background values, there did not exist great difference in spatial distribution of these three metals, indicating that the accumulation of these heavy metals is mainly due to parent material and pedogenic processes. The region with the highest Pb total concentrations was located in the middle of the study area. Pb pollution was more severe when closer to the cement plant, indicating that the main source of Pb may be due to the emissions from the cement plant. The patches of higher concentrations for Zn mainly confined in the north and east (near the main canal) of the study area, indicating that Zn pollution may be mainly affected by the discharge of sewage from the mine.

In general, the spatial distribution of Cd, Pb, and Zn in the study area maintains such a pattern that the levels of metals are high both in the north and center of the study area, and the spatial distribution characteristics are mainly attributed to the influence of mining and industrial activities. Prior to the remediation work, the first step is cutting off the source of pollution, and then, different remediation approaches should be taken according to the concentration spatial distribution.

Spatial distribution of bioaccessible metals

The spatial distribution of bioaccessible metals indicates the risk level due to pollutant exposure (Fig. 6). The concentration ranges of bioaccessible As, Cr, Cu, and Ni varied slightly. Cd is considered as a proved human carcinogen and has potential to damage the ecological communities, and the total bioaccessible concentration of soil Cd samples in the study area was higher than the Grade II criteria (0.4 mg kg^{-1}). Highly bioaccessible concentrations of Cd, Pb, and Zn were recognized in the middle and north of the study area, and Pb and Zn concentrations were higher when closer to the main canals. Frequent activities in north and central regions of the study area, thus,
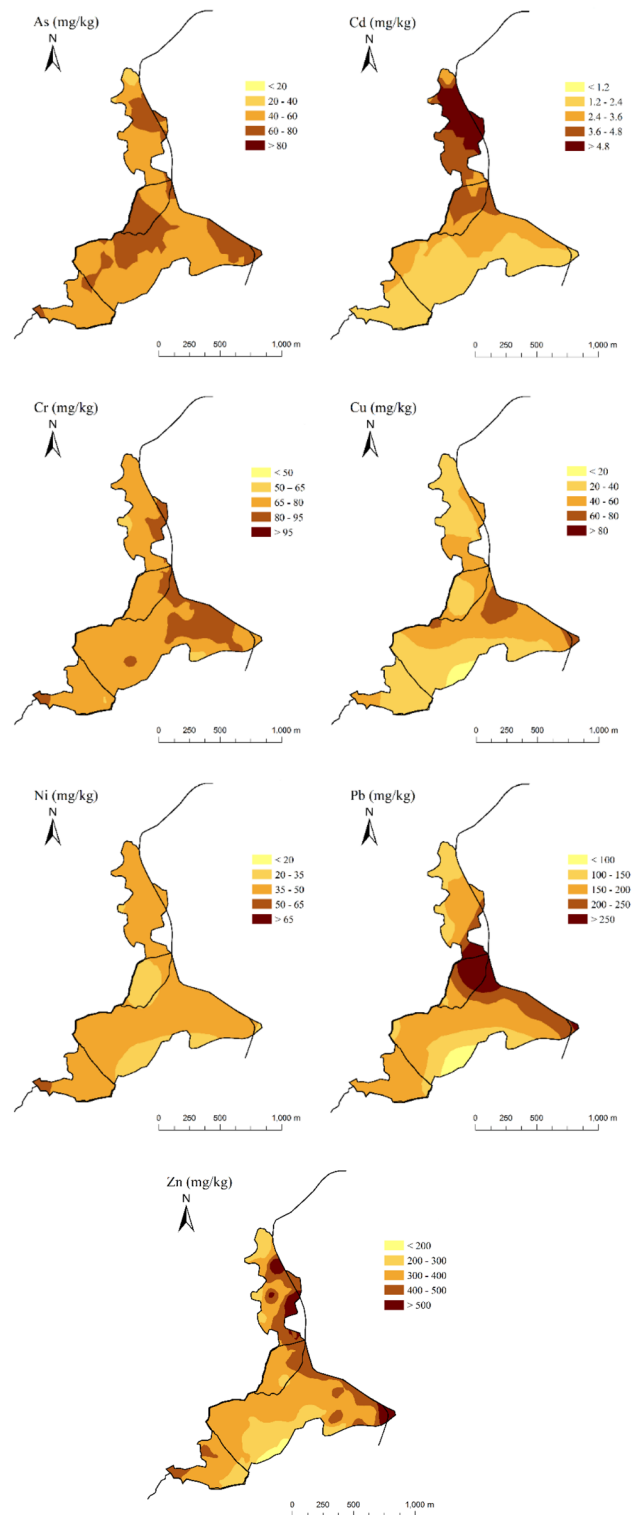

Fig. 5 Spatial interpolation of total heavy concentration in farmland

would lead to large amounts of soil particles ingestion and inhalation and then pose a threat to residents' health. In general, the spatial distribution of bioaccessible contaminated metals (As, Cd, Pb, and Zn) in the study area is
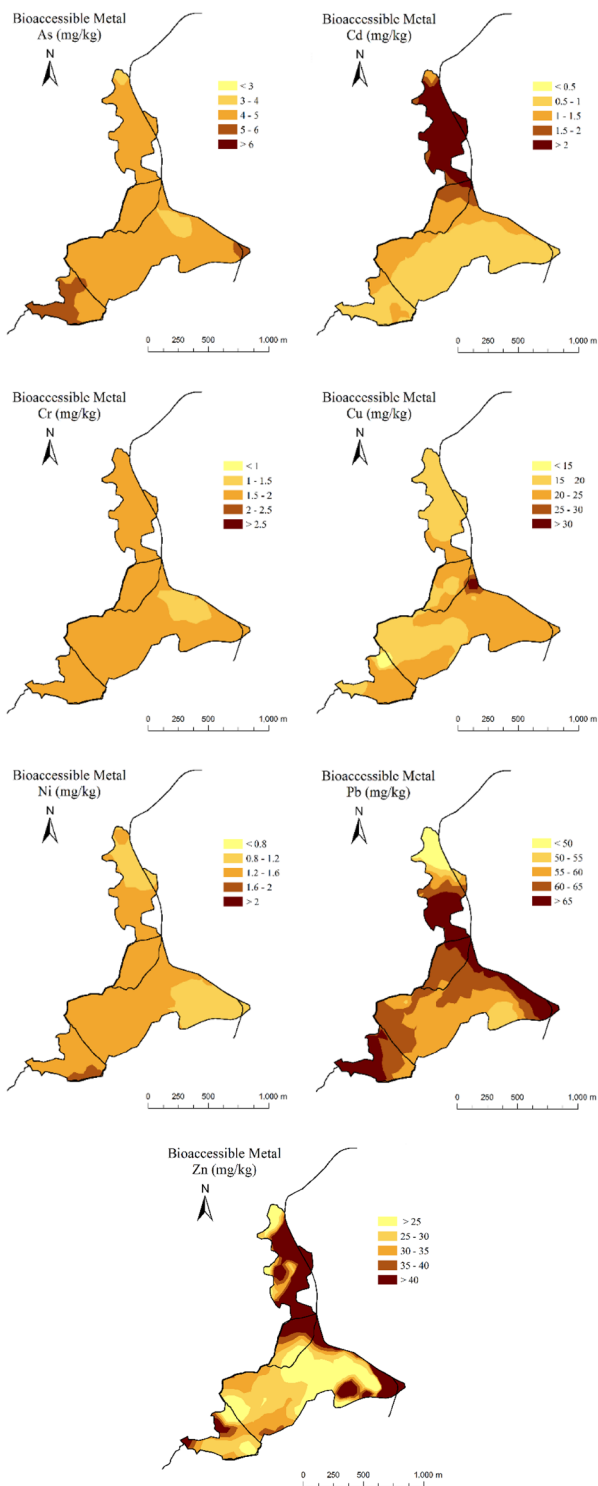
Fig. 6 Spatial interpolation of bioaccessible concentrations of heavy metals in farmland

Fig. 7 Cluster tree of elements using cluster analysis based on Pearson's correlation coefficient

metals (including spatial distribution) could be effective indicators on bioaccessibility in this study.

Source identification and contribution rate determination

Cluster analysis

Figure 7 illustrates the cluster tree for the seven metals in soils. The seven elements can be classified into four groups (the groups were used a criteria value of rescaled distance 15: group 1: Cr, Ni and Cu; group 2: Cd and Zn; group 3: As, and group 4: Pb). Cu, Cr, and Ni contents in agricultural soils were all far under the Grade II values, so the Cu, Cr, and Ni accumulation was dominated by the natural source. Cd and Zn were the main anthropogenic contaminants in the agricultural soils. Combined with the results of the spatial analysis, the main source of Cd and Zn may be due to the emissions from non-ferrous metals and mining companies in the north of the study area, As contamination may be attributed to the atmospheric deposition, and Pb pollution may come from the combustion process of the cement plant.

Source apportionment of heavy metals by positive matrix factorization (PMF) model

To further identify the source apportionment of heavy metals in agricultural soils, the PMF analysis is conducted in Table 5. It is necessary to minimum Q and control the residual matrix E to ensure the rationality of the analysis, and then determine a reasonable number of factors. In this study, four factors were determined. The source contribution

apparently similar with the spatial distribution pattern of total metals, which confirmed the significant positive correlations ($P < 0.01$) between bioaccessibility and total contents (Table 4). Therefore, the total concentration of heavy
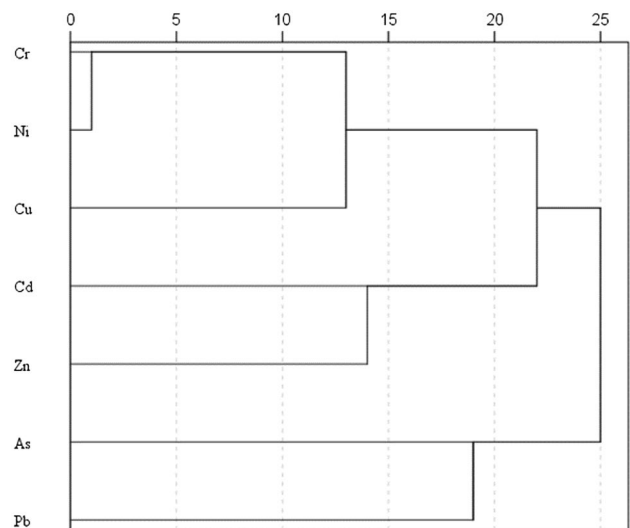
Table 5 Source contribution for different heavy metals as estimated by the PMF model

	Source profile (mg kg^{-1})				Percentage contribution (%)			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
As	0	3.609	46.305	4.198	0	6.7	85.6	7.8
Cd	0.120	0.993	0.118	0.363	7.5	62.3	7.4	22.8
Cr	41.659	23.499	0	22.298	47.6	26.9	0	25.5
Cu	20.640	11.463	8.485	9.942	40.9	22.7	16.8	19.7
Ni	14.942	7.168	4.123	12.698	38.4	18.4	10.6	32.6
Pb	21.043	50.710	26.893	60.813	13.2	31.8	16.9	38.1
Zn	0.377	265.540	65.534	0.000	0.1	80.1	19.8	0

of Cr, Cu, and Ni for the first factor was up to 47.6%, 40.9%, and 38.4%, respectively. In the study area, Cr, Cu, and Ni contamination did not exist, and they were mainly influenced by the natural geological substrate by analyzing the vertical distribution. Besides, the spatial distribution of Cr, Cu, and Ni belongs to the low spatial variability category. Thus, we can infer that the first factor is allocated to soil parent materials. Factor 2 is prominent for Cd and Zn which accounted for 62.3% and 80.1%, respectively. Cd and Zn are categorized in the same group by the cluster analysis, and the accumulation of Cd and Zn was highly related to the mining activities according to the spatial distribution of total and bioaccessible concentrations. Therefore, the second factor represents mining activities. We should take into consideration that although both Cd and Zn contamination are mainly caused by point source pollution (mining area), different pollution pathways may exist, because the spatial distribution of Cd is not totally consistent with Zn. Combined with the results of spatial distribution, the total concentration of soil Cd showed a tendency of reducing from north to the south, but the total Zn concentration was higher when closer to the main channel according to the spatial map. Thus, we assume that Cd is mainly affected by atmospheric deposition in the mining area, while Zn is mainly affected by direct discharge of sewage from the mine. Factor 3 was highly related to As which received the highest weighting (85.6%) than the other metals. Bhuiyan et al. (2014) and Hu et al. (2018) found the emission from transportation and coal combustion may be vital contributors of As in atmospheric deposition, and Wang et al. (2006) investigated that As contents in coal of China were well above the average in other countries. Mining and industrial activities require burning large amounts of coal in the study area. It was found that soil As concentration mainly ranged from 40 to 80 mg kg^{-1} by spatial interpolation which belongs to the contaminated level. The average As content in woodland (24.46 mg kg^{-1}) is much higher than that in grassland (5.81 mg kg^{-1}), because some areas of woodland are close to cement plants and mines. Thus, the third source factor is attributed to atmospheric deposition. For the fourth source factor, Pb (38.1%) received relative higher weighting than the other metals. The spatial distribution indicates that Pb accumulation in agricultural soils was directly affected by the discharge of the cement plant. Therefore, the fourth factor can be considered the industrial activities.

From the discussion above, four sources were apportioned including soil parent materials, mining activities, atmospheric deposition due to emission from transportation and coal combustion, and industrial emissions caused by the cement plant, which consistent with the result of cluster analysis. The total percent contribution of each source was computed and the results are listed in Fig. 8. It can be seen that mining activities were apportioned as the largest contribution (49.7%) for the heavy metals in agricultural soils, followed by atmospheric deposition (20.9%), industrial activities (15.2%), and natural source (14.2%). Therefore, mining activities had a great influence on the heavy metals in agricultural soils in the study area. Besides, the local mining
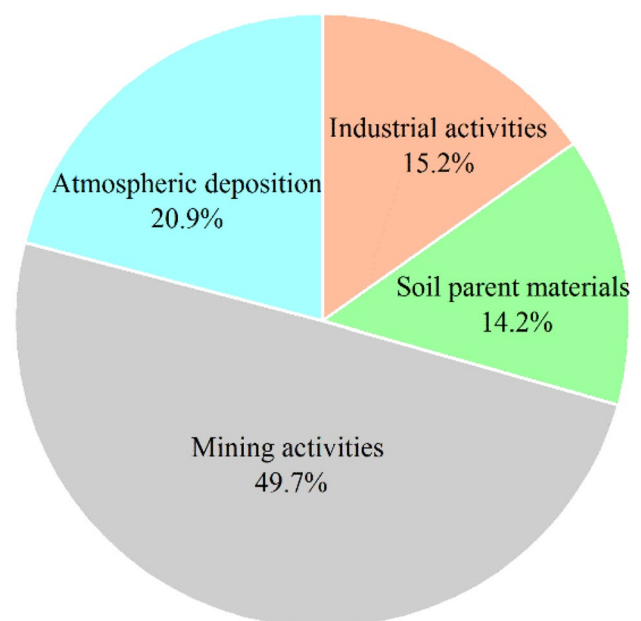
Fig. 8 Factor contribution of heavy metals calculated by PMF model

and industrial activities should be strictly adjusted or limited to prevent the heavy metal contamination.

Conclusions

The study depicted the contamination levels and bioaccessibility of seven metals, and then evaluated the source identification of these seven metals in agricultural soils affected by mining activities. Long-term mining and industries activities had resulted in significant enrichments of As, Cd, Pb, and Zn in the agricultural soils, with the mean I_{geo} value of 1.83, 4.51, 1.58, and 2.17, respectively. The contents of these four contaminated elements in the surface layer are higher than that in the deep layer. All these results suggested that concentrations of As, Cd, Pb, and Zn in the surface soil were strongly affected by the surrounding anthropogenic activities. In addition, the potential risk of Cd and Pb on human health if they should be ingested could not be ignored that about 37.41% and 63.24% of them were bioaccessible with relatively high soil concentration. Significant correlations were found between bioaccessible and total concentrations of the four contaminant metals (As, Cd, Pb, and Zn), which suggested that total concentration of the contaminant metals (distribution) could be effective indicators on bioaccessibility (distribution). The analysis on the spatial distribution of total and bioaccessible heavy metals in the soil affirmed the feature of the exterior source for the four contaminated elements in agricultural soils. The significant spatial variation means that different remediation approaches are needed in the study area. Combined results of spatial distribution, cluster analysis, and PMF model indicated that As contamination is attributed to the atmospheric deposition, mining activities have brought most of the Cd and Zn contamination, and the cement plants account for most of the pollution of Pb.

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