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Spatial distribution and source identification of heavy metals in surface soils in a typical coal mine city, Lianyuan, China☆

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ABSTRACT

In this study, we investigated the pollution degree and spatial distribution of heavy metals and determined their sources in topsoil in a typical coal mine city, Lianyuan, Hunan Province, China. We collected 6078 soil surface samples in different land use types. And the concentrations of Zn, Cd, Cu, Hg, Pb, Sb, As, Mo, V, Mn, Fe and Cr were measured. The average contents of all heavy metals were lower than their corresponding Grade II values of Chinese Soil Quality Standard with the exception of Hg. However, average contents of twelve heavy metals, except for Mn, exceeded their background level in soils in Hunan Province. Based on one-way analysis of variance (ANOVA), the contents of Cu, Zn, Cd, Pb, Hg, Mo and V were related to the anthropogenic source and there were statistically significant differences in their concentrations among different land use patterns. The spatial variation of heavy metal was visualized by GIS. The PMF model was used to ascertain contamination sources of twelve heavy metals and apportion their source contributions in Lianyuan soils. The results showed that the source contributions of the natural source, atmospheric deposition, industrial activities and agricultural activities accounted for 33.6%, 26.05%, 23.44% and 16.91%, respectively.

1. Introduction

Soil heavy metal contamination attracts great attention around the world due to rapid urbanization and industrialization (Chen et al., 2009). In a large number of soil pollutants, heavy metals already turn into an important contaminant because of their toxicity and difficult degradation (Zhong et al., 2014). Heavy metals accumulate in soils as time goes on, which can lead to the loss of soil nutrient component and the degeneration of soil biology and function (Zhang et al., 2016; Zhao et al., 2013). For instance, if the Fe concentration in soils is too high, it will affect the growth of rice. Additionally, high contents of soil heavy metal cause a serious threat to human and animals health, because heavy metal ions can be easily enter human and animals bodies by inhalation, dermal absorption or ingestion (Sun et al., 2010). For example, Cu in soils can be absorbed by the roots of crops, when Cu accumulates to a certain extent in the human body, it will be harmful to human health (the normal Cu content in soils is 2–200 mg kg^{-1}).

It is generally considered that natural and human activities are the two major origins of heavy metals. Natural sources of soil heavy metals are mainly controlled by the geological parent material (Liu et al., 2015). In addition, anthropogenic inputs of soil heavy metals are attributed to metalliferous industries, mining, vehicle exhaust, agricultural practices, coal combustion and atmospheric deposition (Alloway, 2013; Zhang, 2006). Therefore, it is very necessary to identify metal inputs before taking effective measures to protect soil quality. The spatial distribution of heavy metals in topsoil is largely influenced by natural inputs and human activities (Lu et al., 2012). Multivariate statistics combined with geostatistical methods are used to identify sources and the spatial variation of heavy metals in soils (Liang et al., 2016b; Maas et al., 2010). Positive matrix factorization (PMF) was applied to source apportionment of atmospheric particles in the early 1990s (Paatero and Tapper, 1994). And it is also effectively employed to apportion source contribution in sediments, soils and aquatic systems in recent years (Chen et al., 2016; Hua et al., 2015). Thus, this research applied the PMF model to identify twelve heavy metal's sources in soils in the Lianyuan

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city.

Lianyuan, a famous old industrial base in Hunan Province (China), possesses rich mineral resources and is known as “the sea of coal, the township of building materials, the hometown of metals and nonmetals”. Coal combustion is regarded as the most vital input of heavy metal pollution (Liaghati et al., 2004). In the Lianyuan city, many heavy industries (for instance, chemical manufacturing, metallurgical industries, iron and steel plants and so on) are related to coal combustion. What is more, there are a number of small-scale coal mines in the Lianyuan city. Coal mining can cause heavy metal pollution in different land use patterns directly or through atmospheric sedimentation. Previous studies have paid close attention to soil contamination in a single land use pattern (e.g. agricultural soil, industrial district soil, etc.), but have focused less on heavy metal pollution in soils in the coal mine city (Li et al., 2013). Consequently, it is the necessary to investigate heavy metal pollution in the surface soils from different land use patterns in a typical coal mine city, Lianyuan. This study area includes three land use patterns, which are woodland, farmland and land for construction. Our specific objectives are as follows: (1) to estimate the contamination extent of heavy metals in soils, (2) to ascertain the spatial variation characteristics of soil heavy metal concentration using geostatistics, and (3) to quantitatively identify various sources of soil heavy metals based on positive matrix factorization (PMF). This work will provide effective information to prevent further heavy metal pollution in soils in some coal mine cities.

2. Materials and methods

2.1. Study area

Lianyuan (27°27′-28°2′N, 111°33′-112°2′E), including one residential district and nineteen towns, is located in the geometrical center of Hunan province, South Central China. The city's terrain is largely mountainous, and low-lying the west to the east. The city has a subtropical humid monsoon climate. Furthermore, the annual mean temperature and rainfall are 16–17.3 °C and 1406 mm, respectively. Major industries are mining, iron and steel manufacturing, coking, machine manufacturing, metal smelting, pharmaceuticals industry, chemical planting and so on. These industry activities are closely related to heavy metal pollution in soils in the Lianyuan city.

2.2. Sample collections and concentration determination

We collected 6078 surface soil samples in the whole city from May to October, 2015 (Fig. 1). Sampling points were selected with the density of about seven every 1 km^2. In order to improve the sampling efficiency and the quality of the investigation work, the GeoSurveyPad digital survey system was applied to record geographic coordinates of the sampling points. All samples were open-air dried at room temperature in a room and selected through a 2-mm sifter after removing root and plant materials. Finally, these samples were stored in plastic bottles for concentration determination.

The soil samples were digested using the method of HNO_3-$HClO_4$-HF (Chen et al., 2009). The concentration of Fe, Cu, Zn, Cr, Pb, Mn and V was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Oral et al., 2016). The inductively coupled plasma mass spectrometer (ICP-MS) was used to analyze the concentration of Cd and Mo (Huang et al., 2008; Ivanova et al., 2001). A portion of soil samples were digested with HNO_3: HCl = 1:3, after that Hg, As and Sb concentration was determined by atomic fluorescence spectrometry (AFS) (Lin et al., 2010). Soil standard reference materials, GSS-1 and GSS-4 purchased from the Center of National Reference Materials of China, were used for quality assurance and quality control (QA/QC). Recoveries ranged from 84% to 98%. Each set of 50 samples, including 1 duplicate sample, 2 standard samples and 2 external monitor samples, was used for evaluate the accuracy of analysis methods. Every soil sample was tested in triplicate (n = 3). The standard deviation was lower than 7% of all batch treatments. Detection limits were 2, 0.017, 0.0005, 3, 0.5, 0.05, 4, 0.3, 8, 0.03, 4 and 0.9 mg kg^{-1} for Pb, Cd, Hg, Zn, As, Fe, Cr, Mo, Mn, Sb, V and Cu, respectively.

2.3. Statistical and geostatistical analyses

The descriptive statistical analysis was conducted by applying SPSS 19.0 (IBM, USA), while the correlations between heavy metals were described by using Spearman correlation analysis. Prior to One-way analysis of variance (ANOVA) and geostatistical analyses, a normality test (Kolmogorov-Smirnov test) was accomplished in order to assess the normality of original concentration data. The original concentration data, which does not meet the normal distribution, was normalized by the Box-Cox transformation. The differences of heavy metal concentrations were compared from the different land use types using the ANOVA. The kriging interpolations of soil heavy metal contents were calculated using the ArcGIS 9.3 (ESRI, Redlands, California, USA).

2.4. PMF model

In our research, PMF 5.0 was adopted to source apportionment of heavy metals in soils. According to EPA PMF 5.0 user guide:

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

where x_{ij} is a measurement matrix of the j_{th} heavy metal element in i number of samples; g_{ik} is a contribution matrix of the k_{th} source factor for i number of samples; f_{kj} is a source profile of j_{th} heavy metal element for the k_{th} source factor; and e_{ij} refers to the residual value for the j_{th} metal element in i number of samples. The minimum value of the objective function Q can be computed by the following formula.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right)^2 \tag{2}$$

where u_{ij} refers to the uncertainty in the j_{th} heavy metal element for sample i.

The remarkable feature of PMF is using uncertainty to analyze the quality of every concentration data individually. If the concentration of heavy metal does not exceed the *MDL* value, the uncertainty is calculated using the following formula.

$$Unc = \frac{5}{6} \times MDL \tag{3}$$

If the concentration of heavy metal exceeds its corresponding *MDL* value, the calculation is

$$Unc = \sqrt{(Errorfraction \times concentration)^2 + (0.5 \times MDL)^2} \tag{4}$$

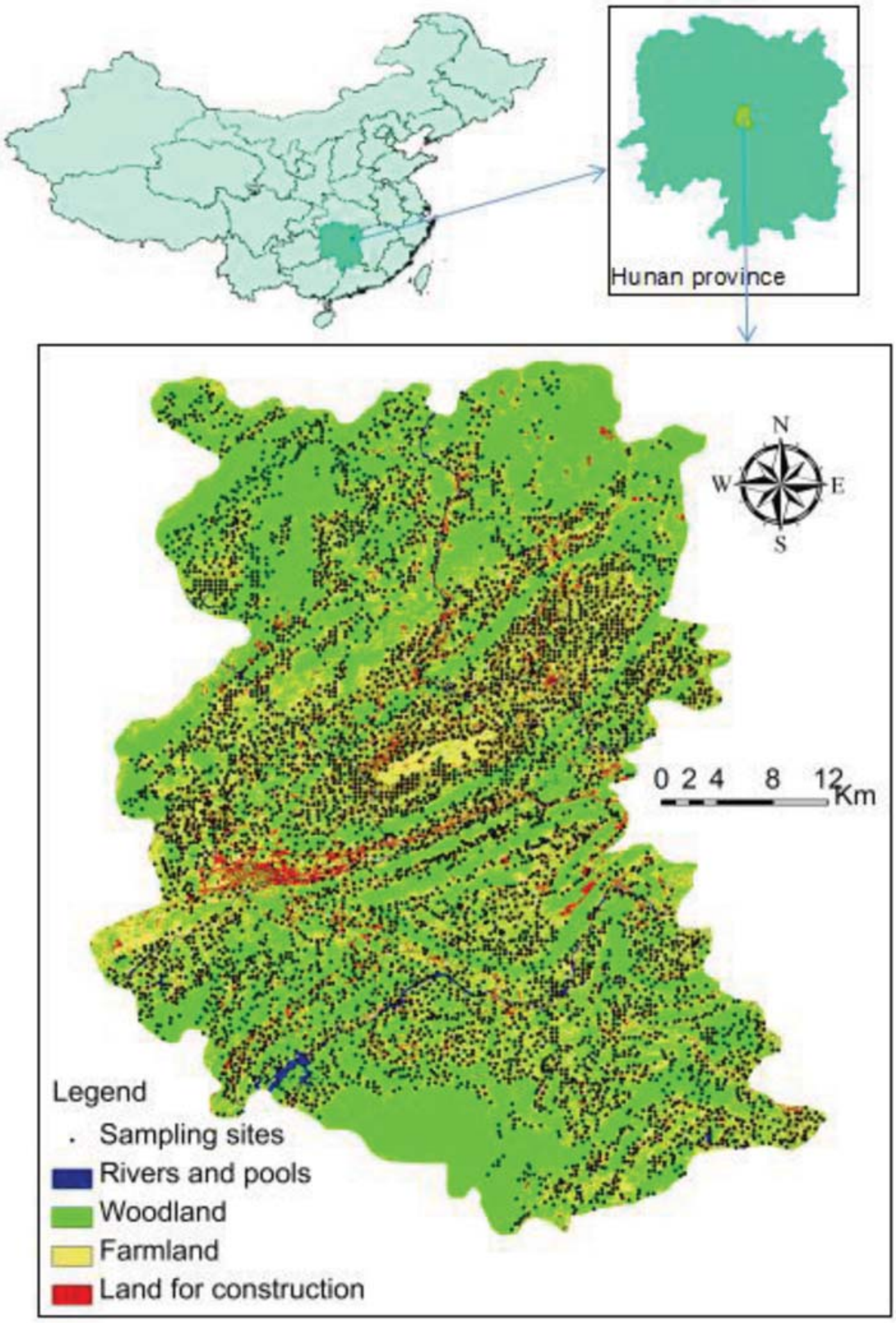

Fig. 1. Location of study area and distribution of sampling sites.

3. Results and discussion

3.1. Degree of heavy metal contamination

Basic statistical characteristics of the heavy metal concentrations in soil samples were presented in Table 1. Average concentrations of twelve heavy metals, excluding Mn, were observably higher than their background levels of soils in Hunan Province. According to the soil application function and protection target, the environment quality standards for soils are divided into three grades. The Grade I could be used as the limit value to protect the natural ecology of the region, and to maintain the natural background of soils. The Grade II could be employed for the critical value to protect human health. The Grade III could be applied to the threshold value to ensure the production of agroforestry and the normal growth of plant. Therefore, if the concentration of heavy metal in soils exceeds its corresponding Grade II value, it will be harmful to human health. In this research work, mean concentrations of Cr, Cu, As, Zn, Pb and Cd were lower than their Grade II values, in which the mean concentration (0.59 mg kg^{-1}) of the Cd was close to its Grade II value (0.6 mg kg^{-1}). Meanwhile, all of the Hg samples concentrations were higher than its corresponding Grade II value. Table S1 (Supplementary material) listed numbers of soil samples below or above the standard values to more clearly show the relationship between the concentrations of heavy metals and their corresponding standard values. According to Table 1, the

Table 1
Descriptive statistics of heavy metal concentrations (mg Kg^{-1}).

Element	min	max	Mean	SD	CV (%)	Background[a]	Grade I[b]	Grade II[b]	Grade III[b]
Cr	21.49	206.20	93.03	23.75	26	68	90	250	300
Cu	7.92	719.60	33.26	15.01	45	25	35	100	400
As	0.78	512.05	14.96	13.25	89	13.41	15	25	30
Sb	0.22	196.85	3.79	5.04	133	1.1	–	–	–
Hg	1.20	3601.10	178.19	132.07	74	0.07	0.15	0.5	1.5
Zn	21.13	1112.00	107.24	35.56	33	96	100	250	500
Mo	0.29	52.69	1.63	2.45	151	0.6	–	–	–
Cd	0.05	8.71	0.59	0.46	78	0.07	0.2	0.6	1
Mn	39.74	8254.00	552.50	82.88	15	777	–	–	–
Pb	8.69	744.70	37.82	23.83	63	30	35	300	500
Fe	6.89	86.59	34.39	8.84	26	28.5	–	–	–
V	38.97	618.90	113.60	39.76	35	91.6	–	–	–

[a] Background: According to the Environment Quality Report of Hunan Province (GB 15618-2013).
[b] Soil environmental quality standard (GB15618-1995).

heavy metals of Hg, Zn, Cd, Pb, Cu, As, Mo, V and Sb had higher coefficients of variation (CV) and wide concentration ranges, which showed that these heavy metal importing soils in this research area would put down to anthropogenic sources (Manta et al., 2002). Cr, Mn and Fe had lower coefficients of variation (CV<30%), indicating that anthropic imports of these metals were low.

The above discussion indicated that soils in the Lianyuan city have been contaminated by heavy metals in different degree. On the whole, Hg and Cd pollution was more serious. Therefore, it is essential to recognize “hot spot” region with high contents of heavy metal and confirm the probable sources by the spatial interpolations of heavy metal concentrations.

3.2. *Spatial distributions of heavy metal concentrations*

The spatial variations of heavy metal contents in soils in the Lianyuan city were shown in Fig. 2. Spatial distribution trends for Zn and Cu in soils were highly similar. Despite the Zn and Cu concentrations were different in some of the same areas, suggesting that Cu and Zn may have had the same source. A small area where soils were contaminated with Zn and Cu was situated at the city center surrounded with farm machinery plants and rubber machinery factories. The Grade I to the Grade II value of Zn and Cu concentrations accounted for about 68.62% and 30.83% of the study area, respectively. And they were principally found in the middle part of the Lianyuan city, where agricultural regions were concentrated. Agricultural inputs such as commercial fertilizer, animal manure, pesticides and fungicides, etc. include large quantities of Zn and Cu (Nicholson et al., 2003; Yuan et al., 2015), which can largely explain their existence in the middle part.

As was shown in Fig. 2, Cd had a relatively scattered spatial distribution. The Cd hotspots included the city center, northwest, northeast and southeast of Lianyuan, and these areas have metallurgy and steel industries. In addition, the iron and steel industry has been proved to be an important source of Cd by atmospheric emissions (Bi et al., 2006). The Grade I to the Grade II value of Cd concentrations distribution was similar with the Zn, which accounted for approximately 61.95% of all samples. Phosphate fertilizers are considered as a crucial source of Cd (Blumberg, 2006), indicating that the Cd, Cu and Zn input soils by the same human activities.

The spatial variations of Pb and Zn concentrations were consistent in a certain area. The Pb hotspots, located in the city center, were mainly distributed in highway sides and commercial district with the high density of population. However, other hotspots for Pb were present at the southwest edge. Coal combustion was the main cause of the Pb pollution in this area. It is reported that general sources of Pb are vehicle exhaust and industrial fumes (Charlesworth et al., 2003; Jiang et al., 2014; Liang et al., 2015b). In addition, the Grade I limit (30 mg kg^{-1}) was exceeded by 65.58% of all samples and these samples were mainly situated in the south of Lianyuan.

The hotspots with the high content of Hg mostly coincided with the coal mine and chemical industrial district. A number of small-scale coal mines were located in a different region of Lianyuan. There have been a number of statements about Hg coming from the use of coal in industrial activities and atmospheric deposition (Berg et al., 2006; Monna et al., 2004). In this research region, Hg pollution in the south was more serious than that in the north, and nearly all of the Hg samples exceeded its corresponding Grade III value (1.5 mg kg^{-1}). It was suggested that soils in the Lianyuan city were affected by different degree of Hg pollution, which might cause serious harm to human health.

Some regions where soils with high contents of As were discovered in the south of the Lianyuan city, especially at the southwestern edge of the top. There were plenty of industrial activities in this area, such as chemical manufacturing, coking plants and non-ferrous metal smelting industries. These industries have been shown to cause As enrichment in soils through atmospheric deposition (Luo et al., 2012; Zhu et al., 2014). The sample points between the Grade I value and the Grade II value of As concentrations had no obvious spatial distribution, and these sample points accounted for about 27.92% of the study area. Therefore, further research of the As sources in this area soils may be needed. The varied tendency of Sb concentrations in soils was gradually reduced from southwest to northeast in the Lianyuan city. A small area with higher contents of Sb was found in the northwest. It was due to antimony ore in the southwest and northeast of the Lianyuan city. In addition, the highest content of Sb, as the same as As, was abundant in the hotspot.

As listed in Fig. 2, it revealed some similar varied tendency for Mo and V. High contents of Mo and V were discovered in the northwest, southwest and from the middle to the northeast of the research region. This point source pollution was associated with the long-term coal mining and steel smelting. Moreover, a hotspot with high concentrations of V was also discovered near a coal mine at the southeastern edge. Apart from a hotspot in the middle, Cr concentrations in soils were generally low. Moreover, no concentration was higher than the Grade II value, indicating that soils in this study area do not show significant Cr pollution. The Fe hotspots were found in the middle, where the iron and steel factories was concentrated. Besides, Fe concentrations were less variable in other regions. Two zones with higher concentrations of Mn were discovered in the city center and the southeast edge, respectively.

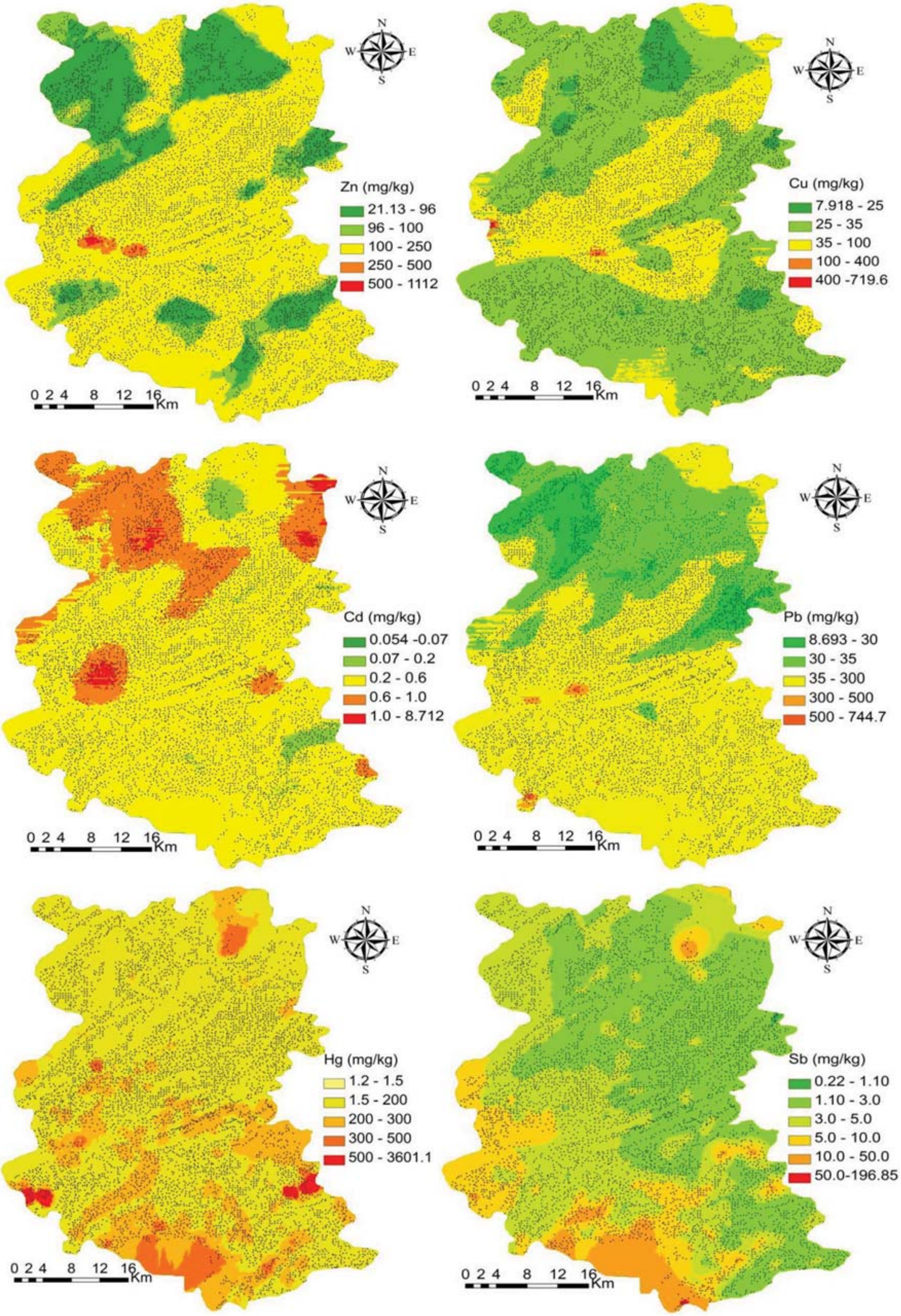

Fig. 2. Spatial distribution of heavy metal concentrations in soils.

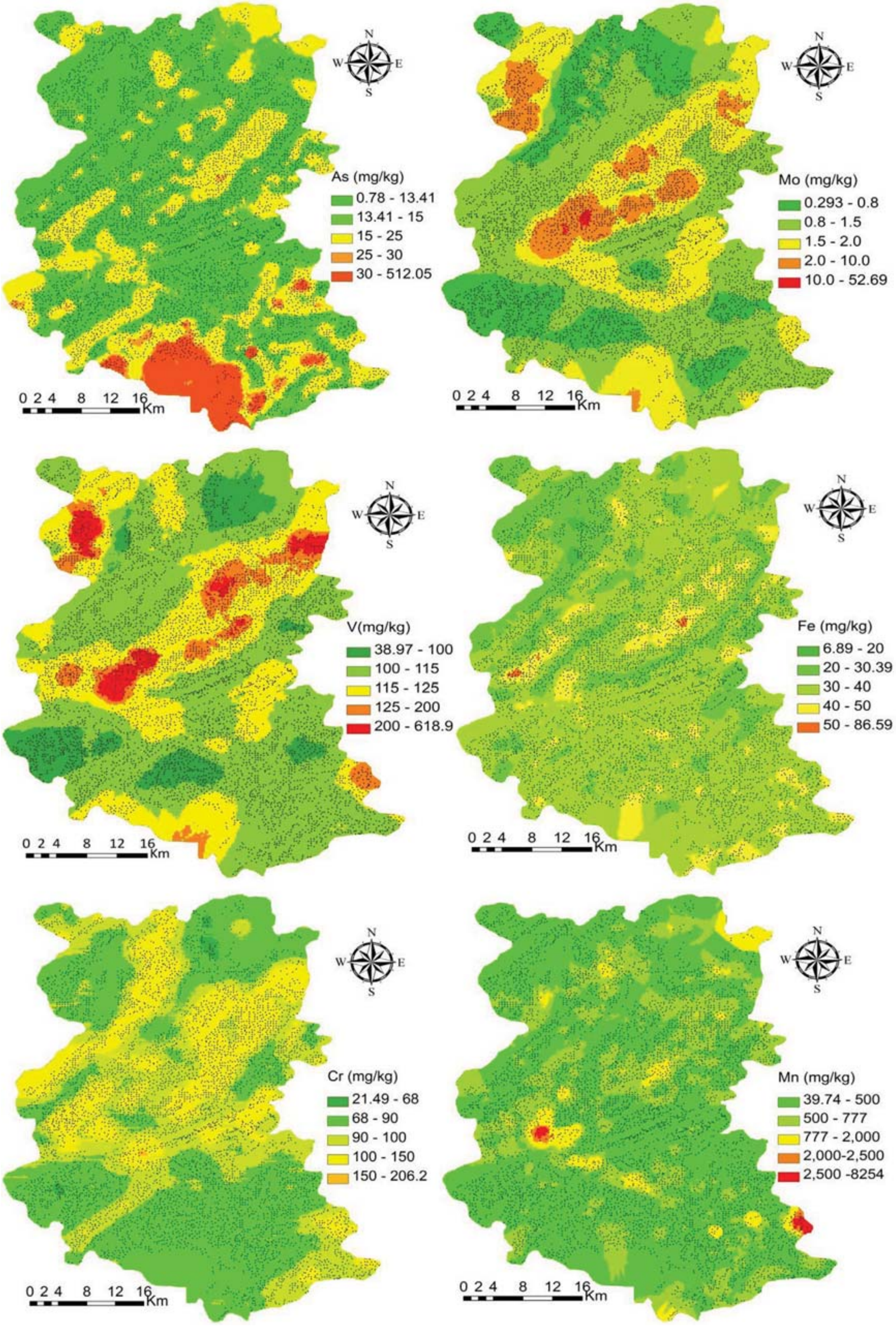

Fig. 2. (*continued*).

However, there were no obvious point sources of Mn. Additionally, the average concentrations of Fe and Mn were close to their background contents. And Fe and Mn have relatively lower coefficients of variation. Therefore, it indicates that Fe and Mn in soils were primarily controlled by parent materials.

3.3. *Influences of different land use patterns on heavy metal contents in soils*

One-way analysis of variance (ANOVA) was employed to confirm whether land use had any effect on the trace metal concentration in Lianyuan soils. Tamhane's T2 test and Tukey test were applied to heavy metals (Zn, Cd, Pb, Hg, Sb, Mo, V, Mn, Cr and Fe) with homogeneity of variance and heavy metals (Cu and As) with heterogeneity of variance, respectively. The conclusions were shown in Table 2. Cu, Zn and Cd contents were significantly higher in the soils of farmland and land for construction than in woodland soils, reflecting Zn, Cu and Cd pollution came from agricultural and industrial practices. In addition, the contents of Hg, Pb, Mo and V in the land for construction soils exceeded that in farmland and woodland soils, suggesting these metals pollution derived from industrial activities and atmospheric sedimentation. From Table 2, the land uses exerted no influence on the As, Sb, Cr, Fe and Mn concentrations. Combined with the spatial variation characteristics of these trace metal contents, it can be inferred that Cr, Fe and Mn in soils were primarily controlled by parent materials, but sources of As and Sb need to be further determined.

3.4. *Source apportionment of heavy metals*

Spearman correlation coefficients of twelve heavy metals were listed in Table 3. A very significant positive correlation was discovered between Fe and Cr, Cu and Cr, Mn and Fe, Zn and Cr, Zn and Cu, Cd and Zn, As and Fe, Pb and Hg ($P < 0.01$); Fe, Zn, Cr, Cu and Mo were closely related to V ($P < 0.01$). Sb did not display obvious correlation with any other trace metals. This may be because the major source of Sb was antimony ore, independently. Significant correlated coefficients between metal elements in soils suggest that these metal elements existed like contamination sources (Li and Feng, 2012). For instance, Zn was noted to be highly correlated

Table 2
Result of ANOVA for soil samples among different land use patterns.

		Woodland	Farmland	Land for construction	F	Sig. (p-value)
Zn[b]	mean	85.23	128.12	108.37	5.520	0.004
	CV (%)	25.00	32.30	35.38		
Cu[a]	mean	22.59	38.86	38.33	5.315	0.005
	CV (%)	31.55	51.66	38.90		
Cd[b]	mean	0.39	0.61	0.77	4.360	0.013
	CV (%)	50.81	89.31	78.69		
Hg[b]	mean	175.35	176.64	202.31	8.978	0.000
	CV (%)	68.57	65.75	112.39		
Pb[b]	mean	30.91	32.18	50.37	13.515	0.000
	CV (%)	35.79	27.11	83.06		
As	mean	15.59	15.19	14.64	2.152	0.116
	CV (%)	97.67	69.78	127.17		
Sb	mean	3.73	3.77	4.23	2.112	0.121
	CV (%)	132.44	110.88	208.75		
Mo[b]	mean	0.61	0.81	3.47	1.698	0.015
	CV (%)	82.25	90.36	163.18		
V[b]	mean	90.02	100.31	150.47	1.784	0.002
	CV (%)	20.05	26.78	31.48		
Cr	mean	91.75	94.56	92.95	9.853	0.168
	CV (%)	19.91	21.15	30.31		
Fe	mean	33.32	35.39	34.44	39.091	0.328
	CV (%)	26.59	24.87	23.81		
Mn	mean	447.34	477.00	500.35	1.899	0.150
	CV (%)	11.61	16.91	16.54		

[a] Tukey test.
[b] Tamhane's test.

Table 3
Correlation coefficients between different heavy metals.

	Cr	Cu	Fe	Mn	Pb	Zn	Mo	Cd	As	Sb	Hg	V
Cr	1.000	0.528**	0.561**	0.334**	0.215**	0.551**	0.388**	0.263**	0.392**	−0.013	0.199**	0.740**
Cu		1.000	0.368**	0.218**	0.390**	0.748**	0.449**	0.377**	0.248**	0.157**	0.300**	0.708**
Fe			1.000	0.516**	0.498**	0.390**	0.327**	−0.082**	0.622**	0.023	0.026**	0.561**
Mn				1.000	0.163**	0.283**	0.222**	0.175**	0.428**	−0.120**	−0.077**	0.202**
Pb					1.000**	0.456**	0.149**	0.050**	0.412**	0.377**	0.582**	0.318**
Zn						1.000	0.243**	0.448**	0.346**	0.225**	0.424**	0.581**
Mo							1.000	0.125**	0.371**	0.049**	0.110**	0.561**
Cd								1.000	−0.045**	0.138**	0.236**	0.255**
As									1.000	0.293**	0.244**	0.421**
Sb										1.000	0.349**	0.123**
Hg											1.000	0.234**
V												1.000

**Correlation is significant at $P < 0.01$ (two-tailed).
*Correlation is significant at $P < 0.05$ (two-tailed).

with Cd and Cu in the present study, which was consistent with the investigation reported by Pan et al. (2016). Additionally, anthropogenic inputs from agricultural activities were considered to be a predominant origin for Zn, Cu and Cd (Sun et al., 2013). Actually, relationships between the twelve heavy metals have been influenced by various factors, and the conclusions of Spearman correlation coefficients were not comprehensive. So, deeper Positive matrix factorization (PMF) model was employed to search the relationships between twelve metal elements and their pollution sources further.

The input files of EPA PMF 5.0 model included concentration data of twelve metals in 6078 soil samples and uncertainty data associated with these concentrations. In order to ensure the optimization of results, the number of factors was set 3, 4 and 5, respectively. Furthermore, the "random start seed number" option was selected and the number of runs was set 20. When the number of factors was four, the *Q* value was minimum and stable, then scaled residuals of all soil samples was within 3.0 and −3.0 and R^2 values was greater than 0.75.

As shown in Fig. 3, Factor 1 was predominantly loaded on Pb (82.83%) and Sb (66.73%) and moderately loaded on Hg (50.69%) and As (44.53%). The primary sources of Pb are vehicle emissions

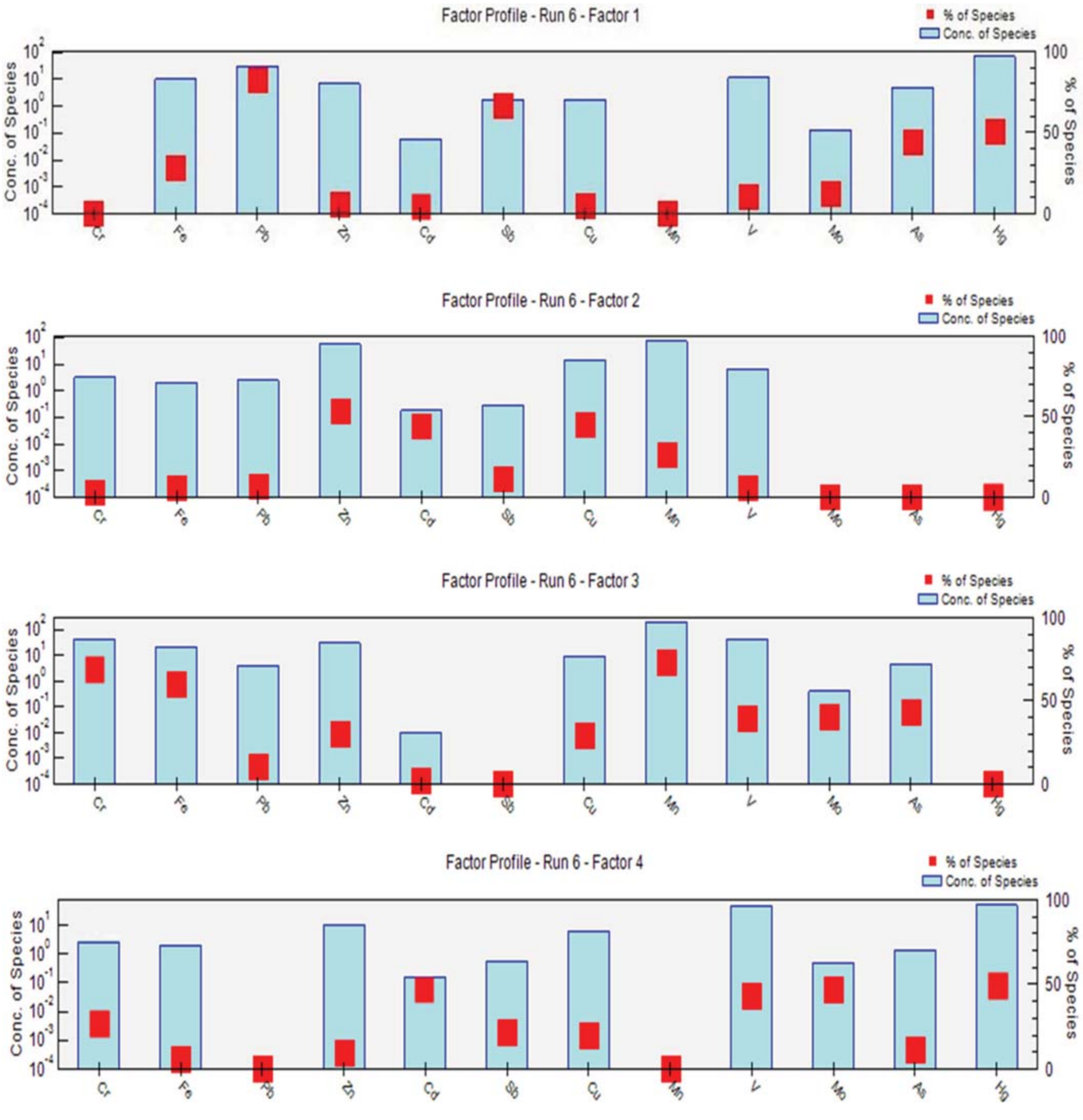

Fig. 3. Factor profiles from PMF model using soils heavy metals concentrations data.

and atmospheric deposition (Sabin et al., 2006). Additionally, high contents of Pb, Hg and As may be associated with coal combustion and industrial production by atmospheric deposition (Bhuiyan et al., 2015). The investigation reported that the content of As in coal of China was well above average in other countries (Wang et al., 2006). Sb mainly comes from the antimony ore by atmospheric deposition in the Lianyuan city. As mentioned above, in the Lianyuan city, there were many small-scale coal mines. The gaseous contaminants including Pb, Hg and As, were emitted from coal mining. And these metals were largely concentrated in the surrounding soils through atmospheric precipitation. Thus, the Factor 1 was related to coal burning and automobile exhaust emission through atmospheric deposition.

Factor 2 was dominated by Zn (53.60%), Cu (45.29%) and Cd (43.90%). In China, Zn, Cu and Cd elements are widely applied to agricultural production. For example, Cu is extensively used to Bordeaux mixture as pesticides or fungicides for vegetable and fruit, while Zn is an effective ingredient of some bactericides that are used to food and cash crops (Lei et al., 2009; Liang et al., 2015d). According to statistics, in China, approximately 55 million tons of fertilizers are used in farmland every year (Liang et al., 2014; Tang et al., 2008; Xiao-Nan et al., 2005). Cd is commonly regarded as an important element for phosphate fertilizer (Spiers, 2001). In addition, animal wastes are ordinarily considered as another primary origin of Zn, Cu and Cd in topsoil (Wu et al., 2010). As mentioned above, these examples proved the views in the “Spatial distribution and Correlation between heavy metals” section once again. Therefore, the Factor 2 was an anthropogenic source due to agricultural activities.

Factor 3 was weighted on Mn (73.10%), Cr (72.73%) and Fe (60.26%). Many previous researches reported that Mn, Cr and Fe in soils may be controlled by the soil parent material (Liang et al., 2016a; Rodríguez Martín et al., 2007; Yuan et al., 2016; Zeng et al., 2009). In this research, the average value of Mn, Cr and Fe contents were not very high. Besides, the CVs of Mn, Cr and Fe were 15%, 26% and 26%, respectively, which belong to the low spatial variability category. Most of concentrations of Mn, Cr and Fe were close to the natural background level in soils that were dominated by the parent material. As mentioned above, these discussions were consistent with the statistical analysis for Table 1. Hence, the Factor 3 was a natural source.

Factor 4 was defined by Hg (49.31%), Cd (48.58%), Mo (47.22%) and V (43.43%). Previous studies showed that Hg contaminant in soils in China originated from non-ferrous metal smelting, coal-mining industries and farraginous activities, accounting for 46%, 39% and 15%, respectively (Liang et al., 2015a; Streets et al., 2005). Metallurgical industries and municipal solid waste have been regarded as the significant source of Cd (Charlesworth et al., 2003; Liang et al., 2015c). As noted above, in the research region, there were a number of chemical, metallurgical and metal smelting industries. Therefore, the Factor 4 was mainly derived from industrial activities.

According to the factor fingerprints of each heavy metal, the overall percent contribution of each source was computed. The result was listed in Fig. 4. Natural source was apportioned as the largest percent contribution (33.61%) for the heavy metals in soils of the Lianyuan city, followed by atmospheric deposition (26.05%), industrial activities (23.44%), and agricultural activities (16.91%). In general, anthropogenic sources occupied the predominant factors, influencing the contents of metal elements in Lianyuan soils with the proportion of approximately 66.39%. Particularly, coal mining, non-ferrous metal smelting, chemical industries, vehicle emission, use of agrochemicals and fertilizers were considered as the possible contamination sources of heavy metals. These pollutants input soils of the Lianyuan city through direct emission, atmospheric deposition and agricultural activities. Therefore, human activities had a great influence on the heavy metals in soils of the Lianyuan city, which can not be ignored. Besides, to protect this area, small-scaled coal mines, industrial and agricultural activities should be properly adjusted and strictly limited.

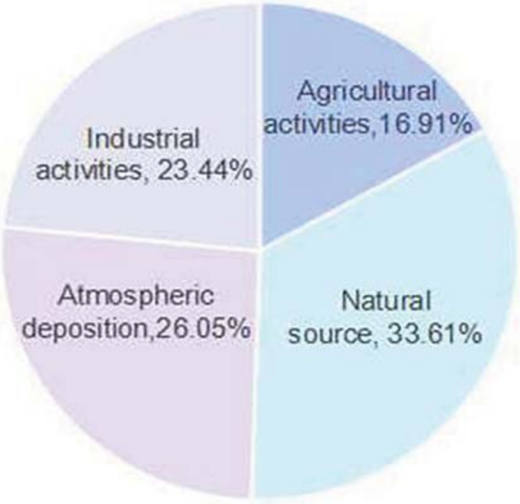

Fig. 4. Factor contributions of heavy metals calculated by PMF model.

4. Conclusion

The conclusions of this research suggested that the average concentrations of Zn, Cu, Cd, Hg, Pb, As, Sb, Mo, V, Cr and Fe were higher than their background contents in soils in Hunan Province. But the average concentration of Mn was lower than its background level. Additionally, Zn, Cu, Cd, Hg, Pb, As and Cr concentrations exceeded their corresponding Grade II value by 1.46%, 0.14%, 37.96%, 100%, 0.6%, 6.73%, 0.06% of all samples, respectively. Consequently, Hg and Cd pose a serious threat to human health. The ANOVA suggested that Zn, Cu and Cd contents were significantly higher in soils of farmland and land for construction than in woodland soils. And the contents of Hg, Pb, Mo and V were higher in the land for construction soils than in farmland and woodland soils. But the land uses exerted no influence on the As, Sb, Cr, Fe and Mn concentrations. Through spatial distribution and PMF analysis, Zn, Cu and Cd mainly came from agricultural and industrial activities. Pb, Sb, Hg and As mainly originated from vehicle emissions and coal combustion by atmospheric deposition. Industrial practices such as coal mining, chemical industries and metal smelting were the main sources of Hg, Cd, Mo and V. The parent materials played a vital role in Mn, Cr and Fe enrichment in soils. These results are useful for the prevention and reduction of heavy metal contamination in soils by various effective measures in some topical coal mine city.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.03.057.

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