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Original Research

Spatial Distribution, Pollution Characteristics and Source of Heavy Metals in Farmland Soils around Antimony Mine Area, Hunan Province

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Abstract

The heavy metal pollution of soil caused by mining activities has attracted widespread attention. This study investigates the spatial distributions, pollution characteristics, and sources of nine heavy metals (Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg) in the farmland soil around an antimony mine, Hunan Province, China. The results show that the average contents of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg are all above the background values of the surface soil in Hunan Province, and the mean concentrations of Cd and As have exceeded China's soil pollution risk screening values for agricultural land. The highest Sb content obtained in this study is 1234.3 times of the maximum allowable antimony content in the soil. The average content of heavy metal elements in the farmland soil samples shows the following trend: Sb>Zn>Cr>As>Pb>Ni>Cu>Cd>Hg. The content of each heavy metal in garden land is higher than that in arable land. Geoaccumulation index analysis results suggest the overall pollution level of the farmland soil is light. In some areas, the pollution level of Cd has reached moderate to strong pollution, the pollution levels of Sb and Zn appear to be moderate pollution to moderate to severe pollution, and the pollution levels of Ni, Cu, Pb, Cr, As, and Hg are at moderate pollution to light pollution. The correlation analysis and positive matrix factorization (PMF) analysis reveal that As, Sb, and Hg are mainly caused by the mining activity, the agricultural activity is the main reason for the accumulation of Cd, and natural factors are the main sources of Cu, Pb, Cr, Ni, and Zn in the study area.

Keywords: heavy metals, spatial distribution, pollution characteristics, source identification

Introduction

Heavy metal refers to any metal element with a density above 4.5 g/cm^3, such as cadmium (Cd), mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), chrome (Cr), nickel (Ni), antimony (Sb), and arsenic (As) [1-2]. Elevated heavy metal content in soil has a huge impact on the growth of plants, including changes in the appearance of the plants (such as color, leaf shape, and size) and even death [3]. Heavy metal pollution in soil has become a worldwide environmental problem,

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and the major pollution source is human activity, including mining, smelting, fossil-fuel combustion, and sewage sludge incineration [4-5].

Soil scientists have carried out extensive research on the spatial distribution, pollution level, and pollution sources of soil heavy metals. Rodríguez and coworkers found that the mean concentrations of Pb, Zn, Cd, and Cu in the soil samples collected at an old Spanish Pb-Zn mine were 28453.50 mg/kg, 7000.44 mg/kg, 20.57 mg/kg, and 308.48 mg/kg, respectively. Besides, a high level of Pb, Zn, and Cd pollution was also found in the samples taken from surrounding arable and pasture lands, indicating a certain extent of spreading of heavy metal pollution, which was mainly caused by acidic drainage and dust transport [6]. The study carried out by Akanchise and coworkers showed that the contents of heavy metals in the soil samples collected from abandoned dump sites in Kumasi, Ghana had the following order: Zn (166 mg/kg)>Cr (67 mg/kg) >Cu (32 mg/kg)>Ni (22 mg/kg)>Pb (11 mg/kg)>Cd (8.9 mg/kg)>As (4.2 mg/kg)>Hg (0.04 mg/kg) [7]. Wang and coworkers revealed that the soil of Dexing Copper Mine in Jiangxi, China, was heavily polluted. The average Cu content in the soil was 10 times of the normal value. The Cu pollution was mainly caused by wastewater, dust, and tailing piles of the local copper mines through sedimentation, rain, and water washing [8]. Wen and coworkers found that the Pb and Cd pollution in the topsoil around the Jinding Pb-Zn mine in China was caused by surface mines and zinc smelters [9]. In summary, industrial and mining activities are the main sources of soil heavy metal pollution in mining areas.

The Xikuangshan mine in Hunan Province has China's largest antimony deposit, and the soil in this mining area has been seriously polluted by hundreds of years of mining activities. Mo and coworkers found that the concentrations of Sb, As, and Hg in the soil near the mining area, smelting area, and tailing area of the antimony mine were 141.92~8733.26 mg/kg, 14.95~363.19 mg/kg, and 0.16~5.68 mg/kg, respectively, which largely exceeded the soil background value of Hunan Province [10]. He and Wan reported that the soil in the mining area was heavily polluted by Sb and As, and the contents of heavy metals including Hg, Cr, Zn, Cd, Pb, and Cu were also high [11]. In addition, the plants in the mining area also showed high antimony pollution. For example, the content of antimony in radish root samples and radish leave samples was 3.0~10.5 mg/kgand 1.5~121.4 mg/kg, respectively [12]. However, the aforementioned researches are mainly focused on the mining area, and there are few studies on the influence of mining activities on the farmland soil around the mining area. The long history of Sb-related mining and smelting activities caused high concentrations of heavy metals in the soils around the mine area.Therefore, the analysis of pollution status and source of heavy metals in soils around mine area is very important.

In this study, an antimony mine located at Lengshuijiang, Hunan, China is chosen to study the spatial distributions, pollution characteristics, and sources of heavy metal pollutants. The main goals of this study are: (1) to investigate the concentrations of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg in the farmland soil around the antimony mine; (2) to evaluate the pollution status using geoaccumulation index; (3) to identify possible sources of heavy metal pollutants using a positive matrix factorization (PMF) model.

Materials and Methods

Brief Description of the Study Area

Xikuangshan is located in central Hunan province of China, is well known as the world's largest Sb mine. This mine situates between 27.7°N and 111.4°E with a total area of approximately 26 km^2. As can been seen in Figure 1. It has a subtropical continental monsoon climate, with sufficient sunlight, four distinct seasons, and a mild weather condition. The average annual temperature is 16.5 °C and the average annual precipitation is 1648 mm. The elevation of the mining area is high in the north and low in the south, which is a typical low mountain and hilly landform [13]. With a total population of over 16 thousand, this area has 15 villages,14 antimony mining companies, a school, a residential community center, a market, and residential areas.

Sample Collection

A total of 130 soil samples were collected in July 2020. The sampling locations are shown in Fig. 1. The checkerboard sampling method was employed based on the landform and soil uniformity of the sampling area. Before sampling, weeds and gravel were removed. Then, a 5 m × 5 m grid pattern was laid out on the field, and the surface soil at 0-20 cm in depth was collected with a wooden shovel at the 4 corners and the center of the grid. After that, the collected soil was thoroughly mixed, and the amount of the soil sample was reduced with the quartering method until 1-2 kg was left. Finally, the sample was collected in a cloth bag and labeled.

Sample Processing and Analysis

First, the soil samples were air-dried in an indoor ventilated environment. Then, the samples were sieved through a 2 mm sieve to remove non-soil materials, i.e. wood chips and grassroots. After that, the sample was ground until passing through a 0.149 mm nylon sieve, which was stored for further analysis. The soil samples need to be digested with microwave. Digestion solutions used include nitric acid (content, 65~68%), hydrofluoric acid (content, 40%), and hydrochloric acid (content, 37%).

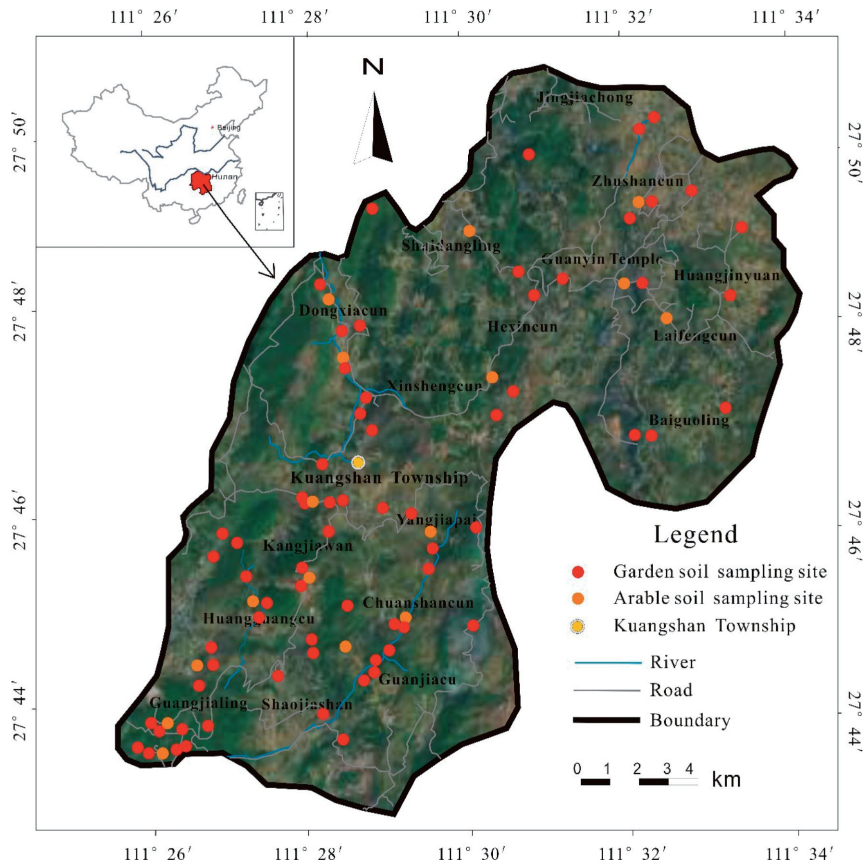

Fig.1. Geographical location and sampling point distribution map of the study.

The contents of Cu, Ni, Cd, Cr, Pb, and Zn were determined by an inductively coupled plasma mass spectrometer (ICPMS-7000, Beijing Jitian Instrument Co., Ltd., China), and the contents of As and Hg were measured using a hydride generation atomic fluorescence spectrometry (AFS-9700, Beijing Haiguang Instrument Co., Ltd., China), and the Sb content was analyzed by a flame atomic absorption spectrometry(GGX-600AAS, Beijing Kechuang Haiguang Instrument Co., Ltd., China). The quality during digestion and ultimate analysis was controlled by using national standard substances (GBW07406). Each sample was independently measured for 3 times. Blank sample tests were also performed, and the recovery rate of each heavy metal element (Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg) ranges from 90% to 110%, proving the accuracy of the measurements.

Evaluation Method

Geochemical Baseline Determination

There are three principal methods for determining the soil geochemical baseline value: standardized method, statistical method, and geochemical comparison method [14]. In this study, the standardized method is employed. The basic principle of this method is using the concentration of an inert element in the geochemical process as a reference (standard element) to obtain the concentration of active elements through the linear regression equation between them (Eq. (1)) [15].

$$C_m = aC_n + b \quad (1)$$

where C_m is the measured concentration of an active element in the sample; C_n is the measured concentration of the standard element in the sample; a and b are regression coefficients. Appling Eq. (1) to a statistical test with 95% confidence intervals, the samples falling within the 95% confidence intervals represent the range of the baseline. Then, the regression coefficients, a and b, can be determined through statistical analysis.

Based on the average content of the standard element in the soil of the study area, the average content of each active element (or the baseline value, Bm) can be calculated with Eq. (2).

$$B_m = aC_N + b \quad (2)$$

where B_m is the baseline value of active elements, and C_N is the average content of the standard element.

The standard elements for geochemical baseline study are selected based on local geological background and human activities. Al, Fe, Ti, B, Zr, and V are commonly used as standard elements [16]. Through data analysis, it was found that the overall variation coefficient and deviation of Ti in the study area are the smallest among commonly used standard elements, indicating that the content of Ti is relatively stable and less affected by human activities. Hence, in this study, Ti is used as the standard element.

Geoaccumulation Index Analysis

The geoaccumulation index method was proposed by the German scientist, Müller, in the 1960s. It can be not only used to evaluate the distribution of heavy metals in sediments but also assess the impact of human activities on the environment [17]. The heavy metal pollution classification standard [18] is shown in Table 1, and the geological accumulation index (*Igeo*, a dimensionless unit) is calculated based on Eq. (3):

$$Igeo = \log_2 \left\{ \frac{C_i}{k * B_i} \right\} \tag{3}$$

where C_i is the concentration of the heavy metal element, i, in the soil; B_i is the background value of the heavy metal, i, in the soil of Hunan Province[19], China; k is the modification index (generally, k = 1.5).

PMF Source Analysis Method

PMF is a multivariate factor analysis technique that is commonly used in environmental pollution source analysis [20]. This model uses uncertainty to analyze the quality of each concentration data. If the concentration of a heavy metal element is below the detection limit of the determination method (MDL), the uncertainty, U_{nc}, is calculated according to Eq. (4):

$$U_{nc} = 5/6 * \text{MDL} \tag{4}$$

If the concentration of a heavy metal element exceeds the MDL value, the following equation is applied.

$$U_{nc} = \sqrt{\left(\text{EF} * X_{ij}\right)^2 + (0.5 * \text{MDL})^2} \tag{5}$$

where EF is the determination precision, which is 0.2 in this study (it generally lies between 0.05-0.3); X_{ij} is the concentration of the jth element in the ith sample.

Statistical Analysis

All statistical analyses are performed by SPSS 19.0, including descriptive statistical analysis of heavy metal elements and Pearson correlation analysis. The PMF5.0 software is used to analyze the sources of heavy metals in soil. The ArcGIS10.2.2 is used to determine the pollution distribution of heavy metal elements contents in the study area.

Results and Discussion

Characteristics of Soil Heavy Metal Content

The statistical characteristics of the contents of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg in the 130 samples were listed in Table 2. It can be seen that the average content of heavy metals show the following trend: Sb (413.21 mg/kg)>Zn (167.33 mg/kg)>Cr (86.23 mg/kg) >As (52.73 mg/kg)>Pb (46.16 mg/kg)>Ni (32.31 mg/kg) >Cu (32.52 mg/kg)>Cd (2.56 mg/kg)>Hg (0.88 mg/kg), and the corresponding concentration ranges are 3.74~4320.00 mg/kg, 50.00~2275.62 mg/kg, 45.00~156.00 mg/kg, 9.57~552.00 mg/kg, 8.20~193.25 mg/kg, 15.88~95.70 mg/kg, 13.90~129.00 mg/kg, 0.15~42.89 mg/kg, and 0.08~8.07 mg/kg. The average contents of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg are all above the soil background values in Hunan Province, while the average concentrations of Ni, Cu, Zn, Cr, As, Sb, and Hg still below China's soil pollution risk screening values (GB15618-2018) [21] except for Cd and Pb. The average concentrations of Cd and Pb are 8.5 times and 1.8 times of the screening values, indicating that part of the farmland in the study area has the risk of Cd and As pollution.

The antimony content obtained in this study is much higher than that reported in previous studies. In 2002, He and coworkers collected representative antimony contaminated soil and found that the Sb content ranged

Table 1. Evaluation standard classification of geological accumulation index.

Pollution rank	I_{geo}	Pollution degree
0	$I_{geo} \leq 0$	Non pollution
1	$0 < I_{geo} \leq 1$	Light pollution
2	$1 < I_{geo} \leq 2$	Moderate pollution
3	$2 < I_{geo} \leq 3$	Moderate pollution to strong pollution
4	$3 < I_{geo} \leq 4$	Strong pollution
5	$4 < I_{geo} \leq 5$	Strong pollution to extreme pollution
6	$I_{geo} > 5$	Extreme pollution

Table 2. Statistical characteristics of heavy metal content in soil samples.

Element	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	Standard deviation (mg/kg)	Coefficient of Variation	Background values (mg/kg)	Filter values (mg/kg)
Ni	15.88	95.70	32.31	11.29	0.35	32.00	100
Cu	13.90	129.00	32.52	15.29	0.47	26.00	100
Pb	8.20	193.25	46.16	30.21	0.65	27.00	120
Zn	50.00	2275.62	167.33	235.83	1.41	94.00	250
Cr	45.00	156.00	86.23	21.76	0.25	68.00	200
Cd	0.15	42.89	2.56	4.83	1.88	0.085	0.3
As	9.57	552.00	52.73	61.55	1.17	14.00	30
Sb	3.74	4320.00	413.21	698.33	1.69	2.98	-
Hg	0.08	8.07	0.88	1.28	1.46	0.096	2.4

from 100.6 mg/kg to 5045 mg/kg [22]; In 2012, Ku and coworkers reported the Sb content in the antimony mining areas ranged from 83.6 mg/kg to 2247.5 mg/kg [23]; In 2020, Huang and coworkers revealed that the average Sb content in this area reached 3619.38 mg/kg [24]. These studies show that with the progress of mining, the pollution of farmland soil is getting more and more pollution. Crommentuijn and coworkers reported that the maximum allowable antimony content in soil is 3.50 mg/kg [25], and the Sb content of all farmland soil samples has exceeded this value by up to 1234.3 times.

The coefficient of variation can be used to assess the interference of human factors on the accumulation of soil heavy metals. Generally, distributions with CV>1.0 are considered as strong variance, distributions with CV between 0.1 and 1.0 are regarded as medium variance, and distributions with CV<0.1 are recognized as weak variance [26]. The coefficient of variation of the soil heavy metals show the following order: Cd>Sb>Hg>Zn>As>Pb>Cu>Ni>Cr. The coefficients of variation of Cd, Sb, Hg, Zn, and As are all greater than 1 (strong variance) with significant spatial variance, indicating the elevated contents of Cd, Sb, Hg, Zn, and As are likely to be affected by human factors; the coefficients of variation of Pb, Cu, Ni, and Cr all lie between 0.1 and 1, corresponding to medium variance.

Spatial Distribution of Heavy Metals in Farmland Soil

The concentration distributions of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg in the farmland soil in the mining area were plotted by using ArcGIS based on the coordinates of the sampling points and the content data of each element, as shown in Fig. 2.

The spatial distributions of Cu, Pb, Zn, Cr, and Cd show excessively high concentrations in the southwest, which may be related to point pollution. After investigation, it was found that the tailing ponds of the mining area are located in that area, indicating that Cu, Pb, Zn, and Cd in farmland soil may come from the tailing ponds; Ni and Cr show band-shaped distributions, and the high Ni content area is mainly located in the northeastern part of the antimony mine, which is far away from the mining area, suggesting the Ni pollution is controlled by background sedimentation; The spatial distribution of As, Sb, and Hg are similar, and the high pollution areas are mainly located inside the mining area with non-point source distribution, indicating the contents of As, Sb, and Hg are influenced by mining activities. Mining activities generate a large amount of solid waste, such as waste rock and tailings. These solid wastes are piled in open places for a long time and pollute farmland soil through rainfall leaching [27]; Besides, heavy metal air pollutants, i.e. As, Sb and Hg, emitted by the smelters in this area is the cause of regional surface pollution through dry and wet precipitation [28].

The Impact of Land-Use Types on Heavy Metal Contents

Based on the land-use type, the sampling sites can be divided into garden land and arable land. Fig. 3 shows the statistics of heavy metal content in the surface soil with different land-use types. As can be seen in the figure, the content ranges of Cu, Pb, Zn, Cr, Ni, Cd, As, Sb, and Hg in garden land are 13.9~70.4 mg/kg, 24.6~185 mg/kg, 66.5~930 mg/kg, 52.6~156 mg/kg, 16.5~95.7 mg/kg, 0.15~16.8 mg/kg, 10.4~137 mg/kg, 3.74~4320 mg/kg, and 0.09~8.07 mg/kg, respectively; Their average contents are in the following order: Sb>Zn>Cr>Pb>As >Ni>Cu>Cd>Hg. The content ranges of Cu, Pb, Zn, Cr, Ni, Cd, As, Sb, and Hg in arable soil are 16.50~129 mg/kg, 15.60~148.00 mg/kg, 50~1060.00 mg/kg, 50.6~152 mg/kg, 17.7~73 mg/kg, 0.18~16 mg/kg, 9.57~180 mg/kg, 7.26~3240 mg/kg and 0.12~7.25 mg/kg, respectively; Their average contents are in the following order: Sb>Zn>Cr>Pb>As>Ni>Cu>Cd>Hg.

The average contents of heavy metal elements in garden land, especially Sb and Zn, are higher than those of arable land, which indicates that different farming modes affect the accumulation of Sb and Zn. The large difference in Sb content may be related to the higher usage of Sb-contaminated irrigation water in garden land than the arable land.

Fig. 4 shows the influence of different planting modes on the chemical state of As and Sb. Compared with the As composition in garden land, the reducible arsenic in arable land was reduced by 3.30%, while the residual As content was increased by 3.88%. This may due to the geochemical behavior of As. The As(III) in arable land has more interaction with oxygen resulting in forming a higher percentage of As(V), and the poor migration rate of As(V) leads to the accumulation of Ab in the residual state. The planting mode has little effect on the chemical state of Sb, which may be related to the higher migration rate of Sb(V) than that of Sb(III).

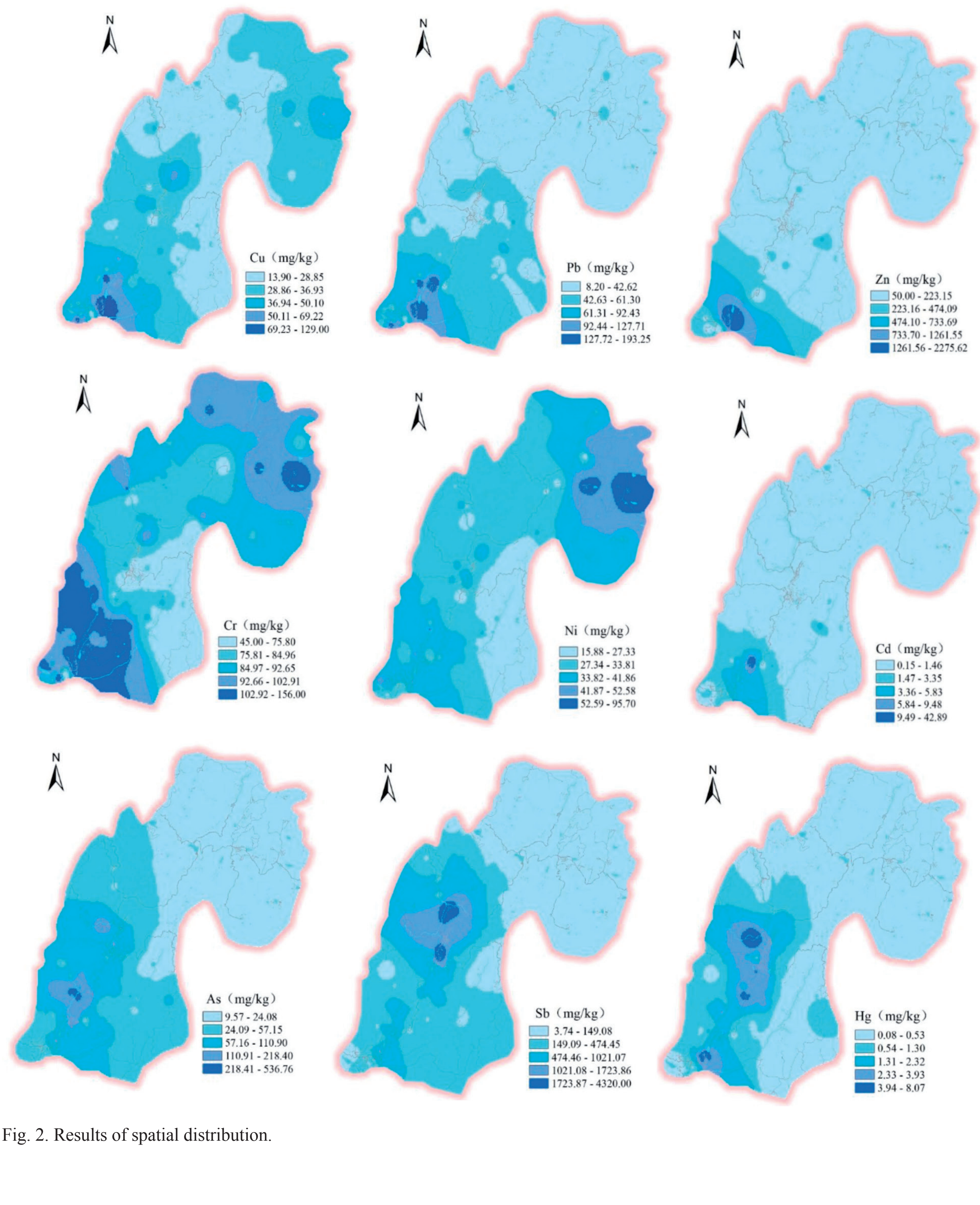

Fig. 2. Results of spatial distribution.

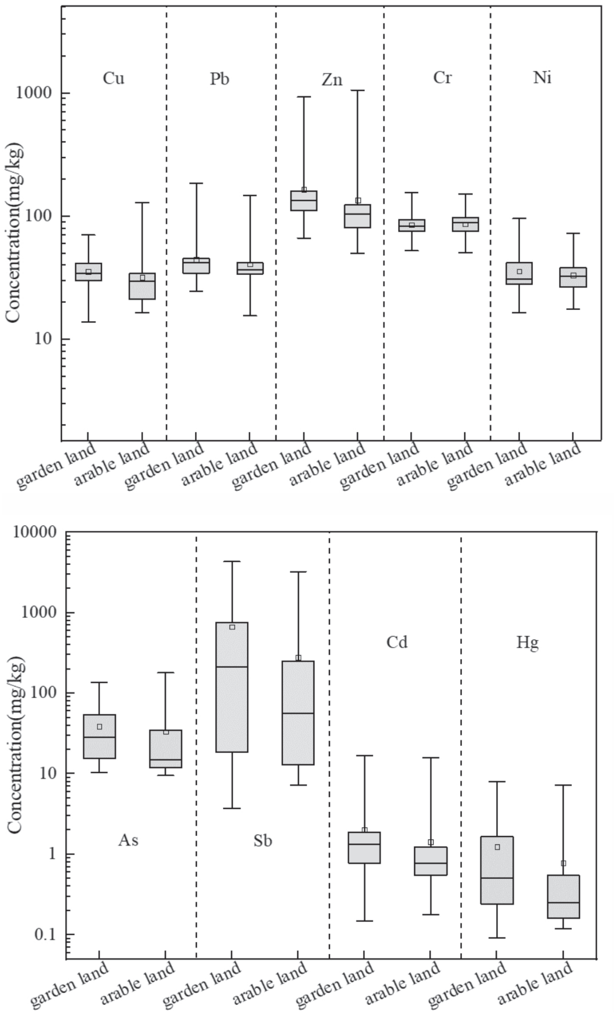

Fig. 3. Characteristics of heavy metal content under different land-use types.

Pollution Evaluation with Geoaccumulation Index

Determination of Geochemical Baseline Values

In this study, Ti is selected as the standard element. The linear regression equations between Ti and other heavy metal elements (As, Sb, Cu, Ni, Cd, Hg, Cr, Pb, and Zn) were first established based on Eq. (1). Then, the geochemical baseline value of each heavy metal element (Table 3) was obtained using Eq. (2).

Compared with the soil background values of Hunan Province, the obtained baseline values of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg are generally higher, especially for As and Sb. The increase in the baseline values of these elements indicates the influence of human factors such as mining and smelting on the accumulation of heavy metals in the soil. Therefore, utilizing the baseline value as an evaluation method can objectively reflect the accumulation of heavy metal pollutants in the soil.

Table 3. Geochemical baseline values.

Element	Baseline equation	R	Baseline value
Ni	$B_m = 0.008C_N - 7.479$	0.528	34.44
Cu	$B_m = 0.005C_N + 2.871$	0.318	29.07
Pb	$B_m = 0.006C_N + 4.391$	0.259	35.83
Zn	$B_m = 0.022C_N + 18.44$	0.144	133.72
Cr	$B_m = 0.013C_N + 9.428$	0.564	77.55
Cd	$B_m = 0.000C_N + 0.963$	0.036	0.96
As	$B_m = -0.009C_N + 90.29$	0.182	43.13
Sb	$B_m = -0.151C_N + 1332.6$	0.154	541.36
Hg	$B_m = 0.000C_N + 1.799$	0.095	1.80

Pollution Evaluation Results

The geological accumulation index (*Igeo*) of each heavy metal in the soil samples and the corresponding pollution levels were calculated using Eq. (3) and the geochemical baseline values (Table 3). The results are shown in Fig. 5. It can be seen that the farmland soil has been polluted by heavy metals to varying degrees, and the overall pollution level is light. In some areas, the Cd pollution level has reached moderate to strong pollution, and the Sb and Zn pollution levels have reached moderate to moderate to severe pollution.

According to the average *Igeo*, the pollution levels of these heavy metals show the following trend: Cr>Cu>Pb>Cd>Ni>Zn>As>Sb>Hg. The *Igeo* value of Cd varies from -3.26 to 3.54, which covers all five pollution levels. Among them, the percentage of the samples with non Cd pollution, light Cd pollution, moderate Cd pollution, moderate to strong Cd pollution, and strong Cd pollution are 72.45%, 19.39%, 4.08%, 2.04%, and 2.04%, respectively; The max geological accumulation index of Sb and Zn are more than 2, and they are in a moderate to strong pollution state, indicating that the pollution risk of heavy metal elements in Sb and Zn is high. The geological accumulation index of As varies from -2.76~1.48, in which As is non pollution, light pollution and moderate pollution state, and the proportions of sample points account for 77.55%, 14.29%, and 8.16% of the total number of samples respectively. The pollution levels of Ni, Cu, Pb, Cr, and Hg are all at the light pollution.

Based on the geological accumulation pollution index, the pollution distribution maps of the nine heavy metal elements were plotted, as shown in Fig. 6. Ni and Cr are generally at the non pollution level and their *Igeo* values are affected by the soil background value. The farmland in the southwest of Kuangshan township, close to the Longwangchi tailing dam, is strongly polluted by Zn and Cd. As the river water in this area is polluted by the infiltration and seepage of tailings, irrigation

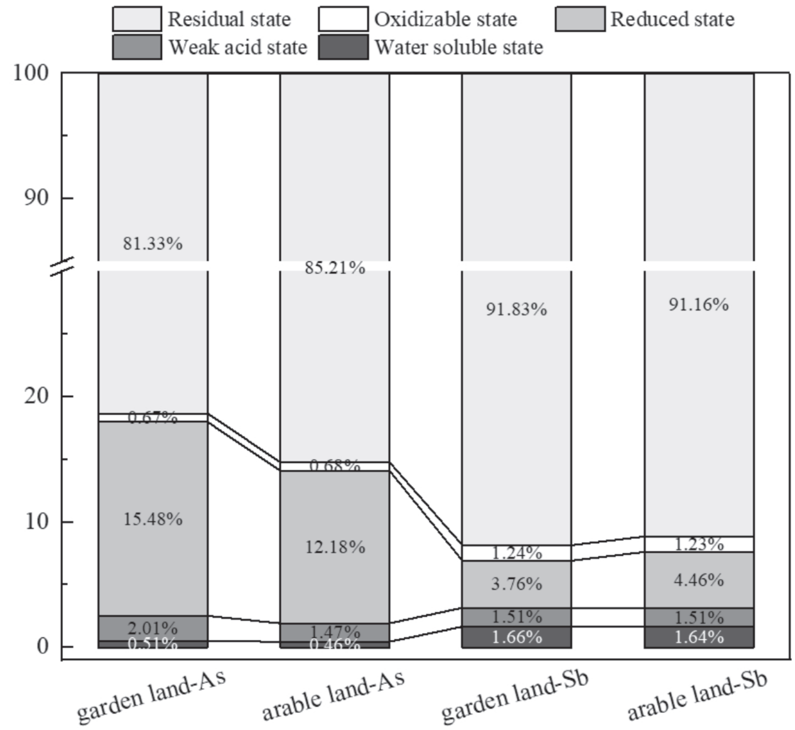

Fig. 4. The morphological composition diagram of the elements As and Sb under different planting modes

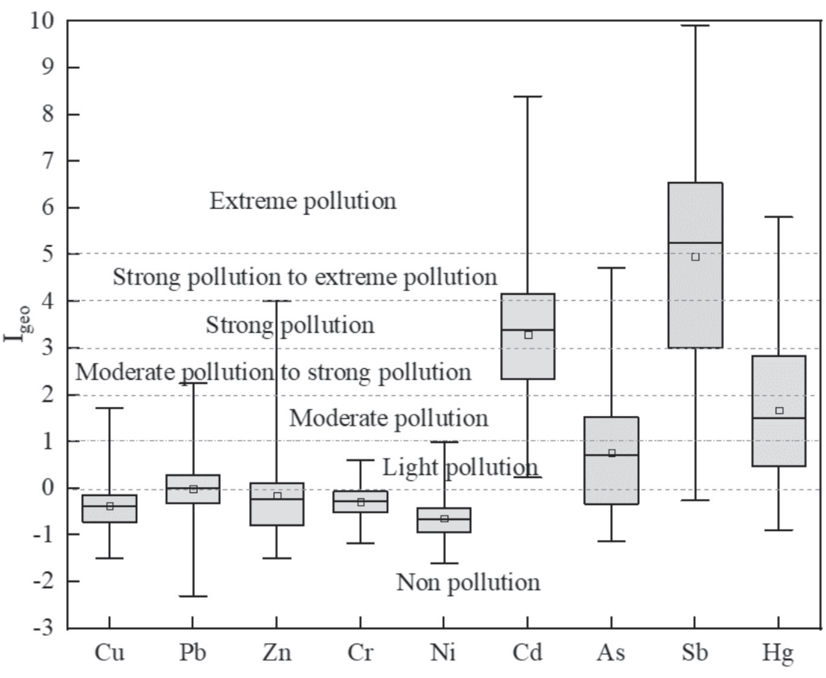

Fig. 5. Box diagram of Geological accumulation index evaluation.

with the polluted river water results in a high degree of enrichment of Zn and Cd. The high Sb polluted area is mainly located near the Nankuang smelter area, where the heavy metal polluted wastewater discharge ports of two mining and smelting companies (Jinbo Antimony Development Co. Ltd and Shizishan Antimony Co. Ltd) are located. And the Sb in the wastewater enters the surface soil through rainwater infiltration. Besides, the high Hg polluted area also appears in the same area, which is caused by the dry and wet sedimentation of the Hg-containing waste gas generated from the smelting process.

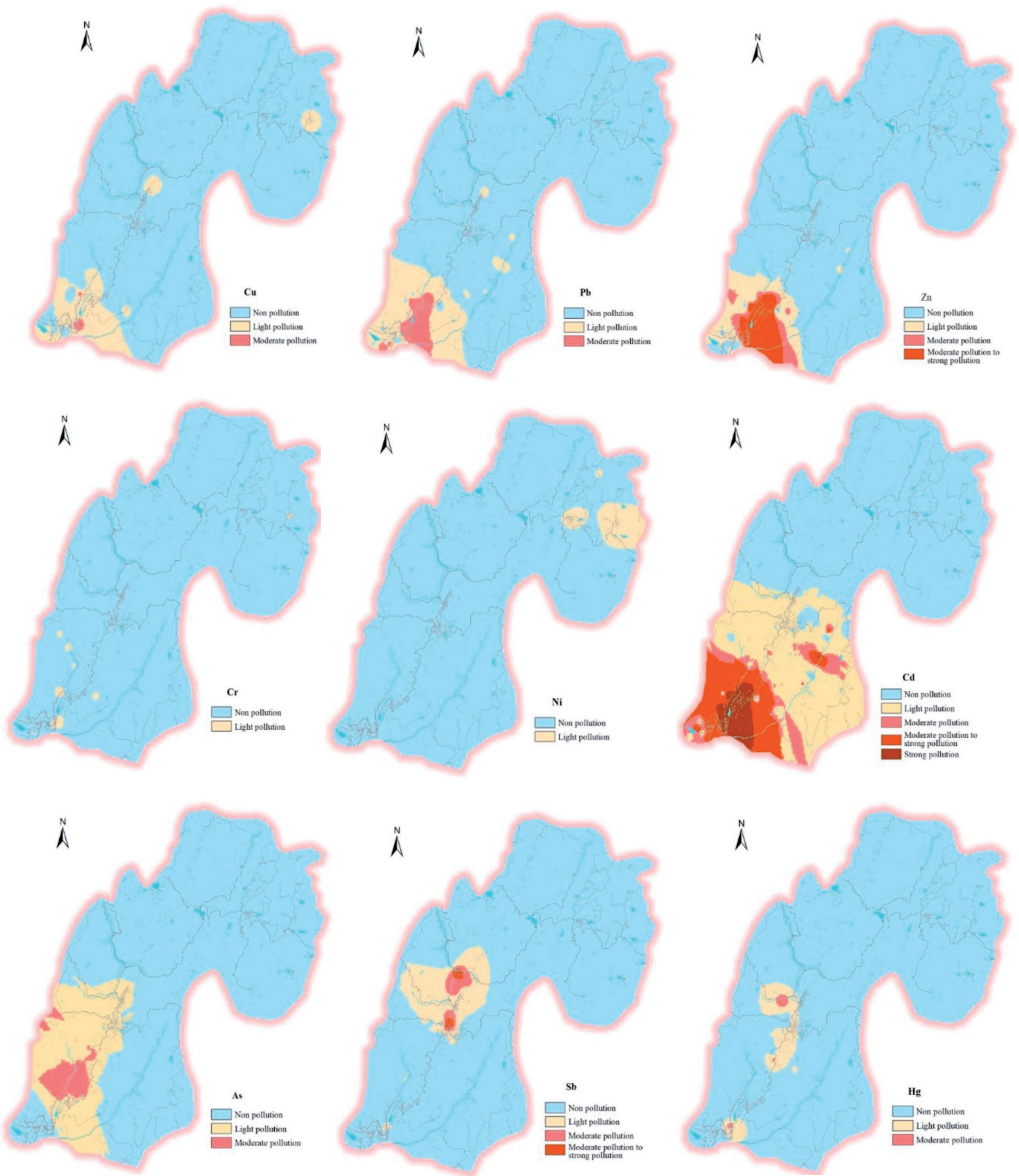

Fig. 6. Results of Pollution distribution.

Source Analysis of Soil heavy Metals

Correlation Analysis

Table 4 shows the Pearson correlation coefficients of the 9 heavy metal elements in the agricultural topsoil of Kuangshan township. If the correlation of two elements is significant, the two elements have similar geochemical behaviors such as source or migration [29]. Wang found that that the pH value of the soil affects the adsorption-desorption of heavy metal ions [30]. As shown in Table 4, the correlation coefficients between soil pH value and various metal elements are small, indicating the correlation between soil pH and each heavy metal element is not significant. Hence, soil pH is not the main factor influencing heavy metal pollution. In addition, the correction coefficients between Cu and Pb (r = 0.780), Cu and Cr (r = 0.647), Pb and Zn (r = 0.783),

Table 4. Correlation analysis of heavy metal elements.

	Cu	Pb	Zn	Cr	Ni	Cd	As	Sb	Hg	pH
Cu	1.000									
Pb	0.780**	1.000								
Zn	0.602**	0.783**	1.000							
Cr	0.647**	0.448**	0.335**	1.000						
Ni	0.481**	0.138	0.156	0.746**	1.000					
Cd	0.546**	0.806**	0.953**	0.300**	0.074	1.000				
As	0.194*	0.188*	0.296**	0.130	0.125	0.299**	1.000			
Sb	0.140	0.029	0.080	-0.102	-0.006	0.056	0.341**	1.000		
Hg	0.280**	0.319**	0.325**	-0.017	0.002	0.299**	0.485**	0.496**	1.000	
pH	-0.059	-0.085	0.090	0.025	-0.054	0.049	0.173	0.098	-0.004	1.000

** the correlation was significant at P<0.01 level (bilateral);
* the correlation was significant at P<0.05 level (bilateral).

Pb and Cd (r = 0.806), Zn and Cd (r = 0.953), as well as Ni and Cr (r = 0.746) are all greater than 0.5 (significant positive correlation, P<0.01), indicating that Cu, Pb, Cr, and Ni may have similar pollution sources, and Zn and Cd may have similar geochemical behaviors. Besides, Hg has significant positive correlations with As (r = 0.485) and Sb (r = 0.496), suggesting they may have similar pollution sources. According to the correlation coefficient analysis, the sources of the heavy metal elements in the study area are complex, which requires further analysis.

PMF Source Analysis

The EPA PMF5.0 model was applied to analyze the sources of the nine heavy metal pollutants. The pollution sources and contribution ratios of the nine heavy metals are shown in Fig. 7.

Factor 1 is dominated by As (69.7%), Sb (96.1%), and Hg (58.6%), and this factor is mainly associated with the mining and smelting activities of antimony. Frequent mining activities and long-term piling of waste rocks and slag results in the pollution of Sb and other

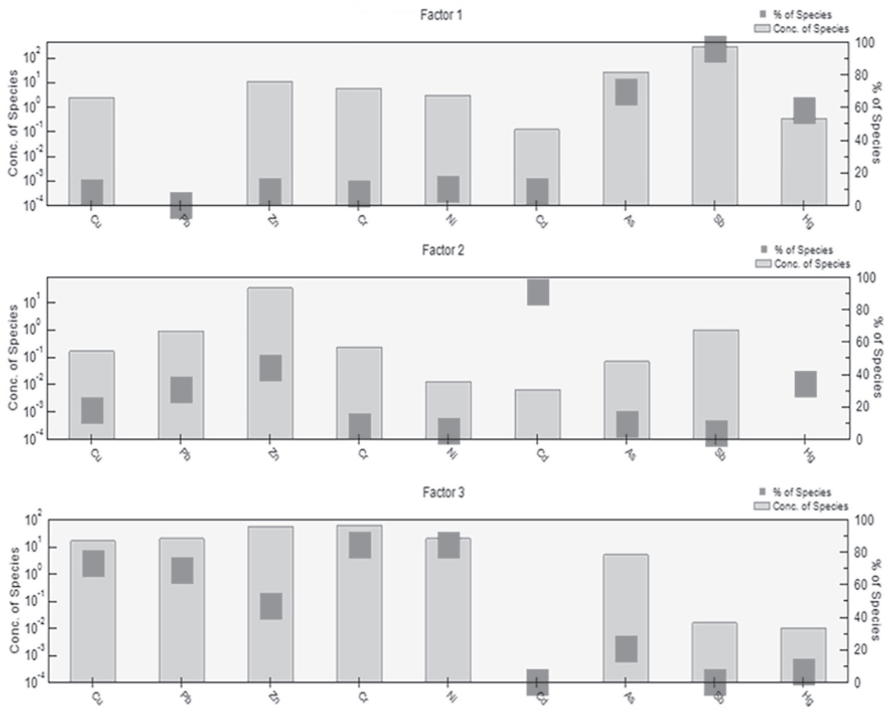

Fig. 7. Contributions of three main factors to nine heavy metals.

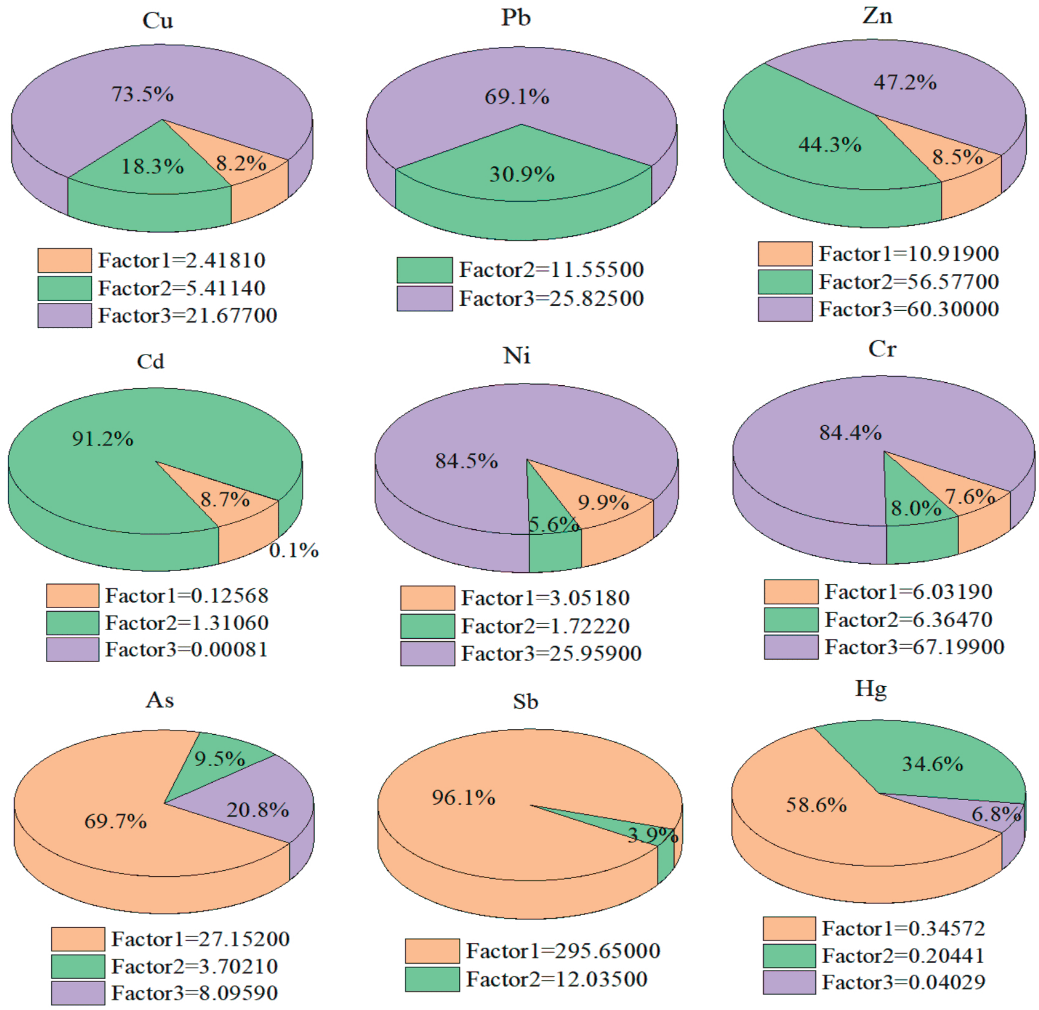

Fig. 8. The factor contribution rate of each heavy metal.

associated heavy metal elements (i.e. As and Hg) in the farmland soil in the mining area. In addition, arsenic-alkali slag (mainly Na_2AsO_4) is a characteristic pollutant produced from the mining and smelting process in this area [31]. During the antimony smelting process, the crude antimony is refined by adding sodium carbonate to remove arsenic. The by-product of this process, Na_2AsO_4 [32], is toxic and highly water-soluble, and it can enter the farmland soil through surface runoff, resulting in the As pollution of farmland soil. Therefore, factor 1 is assumed to be a mining activity source.

Factor 2 is represented by Cd (91.2%). The main pollution source of Cd in farmland soil is agricultural activities, including the usage of organic fertilizers, chemical fertilizers, and pesticides [33]. Therefore, factor 2 represents an agricultural activity source.

Factor 3 is characterized by the presence of Cu (73.5%), Pb (69.1%), Cr (84.4%), Ni (84.5%), and Zn (47.2%). Generally, heavy metals related to soil parent materials are the elements with low pollution levels [34]. Researches on the sources of Cu, Cr, and Ni shows that Cu, Cr, and Ni mainly come from soil parent materials [35]. The sources of Pb and Zn are more complicated, and their contributions are lower than that of Cu, Cr, and Ni and can be ignored. Therefore, factor 3 can be identified as a natural source.

Fig. 8 shows the pie charts of the pollution sources of the nine heavy metal elements: The contributions of the mining activity source, the agricultural activity source, and the natural source to the As pollution are 69.70%, 9.50%, and 20.80%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Sb pollution are 96.10% and 3.90%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Hg pollution are 58.60%, 34.60%, and 6.80%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Cd pollution are 8.70%, 91.20%, and 0.10%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Cu pollution are 8.20%, 18.30%, and 73.50%, respectively; The contributions of the agricultural activity source and the natural source to the Pd pollution are 30.90% and 69.10%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Zn pollution are 8.50%, 44.30%, and 47.20%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Cr pollution are 7.60%, 8.00%, and 84.40%, respectively; The contributions of the mining activity source, the agricultural activity source, and the natural source to the Ni pollution are 9.90%, 5.60%, and 84.50%, respectively.

Conclusion

(1) The average contents of Ni, Cu, Pb, Zn, Cr, Cd, As, Sb, and Hg in the farmland soil of antimony mine are higher than the background values of the surface soil in Hunan province. And the mean concentrations of Cd and As have exceeded China's soil pollution risk screening values for agricultural land. The highest Sb content obtained in this study is 1234.3 times of the maximum allowable antimony content. The average content of heavy metal elements in the farmland soil shows the following order: Sb>Zn>Cr>As>Pb>Ni> Cu> Cd>Hg. The content of each heavy metal in garden land is higher than that in arable land.

(2) Geoaccumulation index analysis results suggest the overall pollution level of the farmland soil in the study area is slightly polluted. In some areas, the pollution level of Cd has reached moderate to strong pollution; the pollution levels of Sb and Zn appear to be moderate pollution to moderate to severe pollution; the pollution levels of Ni, Cu, Pb, Cr, As, and Hg are at moderate pollution to light pollution.

(3) The correlation analysis and PMF analysis reveal that As, Sb, and Hg are mainly caused by the mining activity, the agricultural activity is the main reason for the accumulation of Cd, and natural factors are the main sources of Cu, Pb, Cr, Ni, and Zn in the study area.

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Conflict of Interest

There is no potential conflict of interest in what is stated herein.

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