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Original Research

Distribution, Ecological Risk and Source Analysis of Heavy Metals in Farmland Soil around Chating Copper Ore in Xuancheng Region of Southern China

Chen Cheng[1,2,3,4], Zhimin Xu[1]*, Songbao Feng[2,3,4], Ling Wang[4]

[1]School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221000, China
[2]National Engineering Research Center of Coal Mine Water Hazard Controlling, Suzhou University, Suzhou 234000, China
[3]Key Laboratory of Mine Water Resource Utilization of Anhui Higher Education Institute, Suzhou University, Suzhou 234000, China
[4]School of Resources and Civil Engineering, Suzhou University, Suzhou 234000, China

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Abstract

To study the effects of metal mineralization and mine operation on surrounding ecological environment and human health, 69 farmland soil samples of study area were collected, tested with seven heavy metals and analyzed with environmental risk assessment, spatial distribution, and source identification. The I_{geo} values of Cu and Pb indicated light-moderate pollution level and Co belonged to moderate pollution level. The EF values of Co represented moderately severe enrichment level, and Cu and Pb belonged to moderate enrichment level. The E_r^i values were in decreasing order of Co>Cu>Pb>Cr>Zn>Mn>Fe, moreover both E_r^i and RI values of seven heavy metals were at low ecological risk level. The spatial distribution of Fe, Zn, Cr and Mn showed a trend "high in northwest and low in southeast", and Co and Cu were similar with the characteristics "the closer to Chating copper ore, the higher the value", and points with higher content for Pb were distributed along the roads beside Gucheng Lake and irrigation canal. Pearson correlation analysis (CA), hierarchical cluster analysis (HACA), and principal component analysis (PCA) were adopted to gradually identified the characteristics, interactions, classifications and possible sources. PC1 was explained by Fe, Cr, Mn and Zn and might be the natural source influenced by the crust and soil parent material; PC2 was dominated by Pb and Zn and might be derived from transportation and mechanical operations; PC3 was loaded by Cu and might be greatly affected by copper mining activities.

Keywords: heavy metals, copper ore, environmental risk assessment, spatial distribution characteristics, source apportionment

*e-mail: xuzhimin@cumt.edu.cn

Introduction

In recent years, heavy metal pollution in the environment has attracted worldwide attention due to the potential toxicity, non-biodegradability, concealment and persistence [1]. In addition, metal elements can widely distribute in various environmental media such as water [2, 3], atmosphere [4, 5], sediment [6, 7], street dust [8] and soil [9-11], and have a certain cumulative effect, which poses a threat to human health over a large scale. Heavy metals in soil have a more profound impact on the surrounding environment, because soil is an important part of the natural ecosystem and the basis of the agricultural production activities of human, as the surface of the earth, connects the atmospheric, the hydrosphere and the lithosphere, and carries the influence of geological and artificial activities [12]. The rapid urbanization process, modern agriculture, mining development and other human activities cause the accumulation, enrichment and transfer of heavy metals in various of soil, and eventually heavy metals are enriched in the human body through water body, plants, animals and other food chains, and then damage human organs and the nervous system, and ultimately endanger human health and ecological environment [13].

The farmland soils have different characteristics according to the corresponding complex environment. Many scholars around the world have conducted related studies on heavy metals in farmland soil. Wei et al. [14] researched the levels, sources, and spatial distribution of eight heavy metals in farmland surface soil from the drinking water sources and found that the overall soil quality in the study area was excellent, but that the Cd, Cu, Zn, and Cr contamination risks were relatively high. Lu et al. [15] investigated the heavy metal effects under the condition of coastal reclamation in different wetland type soils in the Pearl River Delta through heavy metal evaluation, ecological risk assessment analysis. Hu et al. [16] studied the reclaimed soil of another wetland type on distribution characteristics of soil physico-chemical properties including particle size (PS), pH, soil organic matter (SOM), total nitrogen (TN), total phosphorus (TP), and nine heavy metals elements (Cr, Ni, Cu, Zn, Pb, Cd, As, V, Co) under different planting patterns.

However, a kind of agricultural soils which are more affected by mining and industrial activities have been extensively studied by scholars, such as the farmland soil of coalfired thermal power plant [17], the soil around the Pb-Zn mine [18, 19], the soil around the coal mine [20, 21] and Oil field [22], the soil around the typical industrial area [12] and so on.

The concentration characteristics, morphology analysis, pollution assessment, risk assessment, spatial distribution characteristics and source analysis of heavy metals in farmland soil have become the targets and means of researchers [23, 22]. The research methods include multivariate statistical analysis method, comprehensive pollution index method, potential ecological risk index method, enrichment factor method, geoaccumulation index method and many receptor models method including Unmix, PMF, and the chemical mass balance (CMB) [23]. Xiao et al. [24] used spatial distribution method, pollution index method and risk assessment method to study heavy metals in agricultural surface soil. Adimalla et al. [25] and Deng et al. [26] used pollution load index (PLI) and geoaccumulation index (I_{geo}) to estimate the contamination levels and status of heavy metals when they studied farmland soil in different regions around the world. Ghazban et al. [27] and Adimalla et al. [25] applied geoaccumulation index (I_{geo}) and enrichment factor index (EF) to the heavy metal datas to reveal the impact of human activities on soil. Mamat et al. [23], Deng et al. [26] and Ghazban et al. [27] all adopted risk assessment code (RAC) to reveal the impact of heavy metals on human health and ecological system. As for the source identification methods of heavy metals in soil, Dong et al. [28] carried out the multiple identification methods of correlation analysis (CA), principal component analysis (PCA), geographic information system (GIS) and positive matrix factorization (PMF) to study cropland soils. Chen et al. [29] and Yu et al. [30] studied the source apportionment progress and methods of soil heavy metal pollution in China in the past decade, and also mentioned the multivariate statistical methods such as principal component analysis (PCA), positive definite matrix factorization method (PMF), absolute factor score-multiple linear regression (APCS-MLR) receptor model methods, and a variety of combined methods to reveal the source of heavy metals in soil.

Farmland soil around Chating copper ore in Xuancheng, southern Anhui Province was selected as the research object of this study. This area is famous for rice and rapeseed, and crab and crayfish farming in paddy fields have also been on the rise in recent years, depending on the quality of the soil. Some metals such as Cu, Fe and Zn are important micronutrients in the activities of living organisms, and the quality of soil and water is crucial for agricultural production activities. It is directly related to human health whether the exploitation and transportation of surrounding mineral resources will cause harm to farmland soil. At the same time, the relevant studies of this area have been conducted rarely by other scholars. In this study, the following targeted researches have been carried out: (1) to determine the concentration of heavy metals Cu, Fe, Zn, Co, Cr, Mn and Pb in farmland soil; (2) to evaluate the pollution degree and potential ecological risk by using pollution index methods; (3) to analyze the spatial distribution characteristics of heavy metals; (4) to identify the contamination sources through the application of multivariate statistical techniques.

Materials and Methods

Study Area

The Chating copper ore deposit which is a new type deposit in the Xuancheng City of Anhui Province is a large deposit newly discovered in shallow overburden area of the Middle and Lower Yangtze River Valley Metallogenic Belt. It is located in the central uplift of Nanling-Xuancheng Meso-Cenozoic volcanic-sedimentary basin [31]. The alteration types of the surrounding rock of the ore deposit are dominated by silication, potash-feldspathization, biotization, sericitization (muscovitization), and pyritization. The metallic minerals in the ores are dominated by pyrite and chalcopyrite as well as a small amount of bornite, tetrahedrite, tennatite, and so on [32].

The Chating copper ore is located in northeast district of Xuancheng city in the southern Anhui province, China (Fig. 1). The north latitude is 30°34′25″ - 31°19′35″, and the east longitude is 118°27′34″ - 119°04′26″. The climate is moist, and the rainfall is plentiful with the annual precipitation over 1000 mm concentrated from March to September. The research area is rich in copper, coal, iron, molybdenum and other mineral resources.

Sampling and Testing

A total of 69 surface soil samples around the Chating porphyry copper deposit have been collected. The five-point method was used to collect 0-20 cm surface soil at the site, and the surface painted shovel was used for sampling and make sure the soil in contact with the shovel was removed, as well as weeds, gravel, animal and plant residues and other sundry objects were eliminated [33]. After mixing, more than 1kg of soil as a sample was selected by the four-point method and put in a clean zip-lock bag and brought back to the laboratory. The soil samples after air-dried in natural conditions were removed impurities such as plant roots and stems, ground with agate mortar and sieved through 20 mesh and 200 mesh, then stored in clean zip-lock bags for subsequent analysis and testing. Then the samples were compressed into a tablet by a condenser, and then analyzed by X-ray fluorescence spectrum analyzer [34, 35, 17]. The concentrations of seven kinds of heavy metals (Cu, Fe, Zn, Co, Cr, Mn, Pb) have been measured. All samples were measured parallel for 3 times with relative standard deviation less than 10%. National standard soil sample of China (GBW07430, GSS-16) was analyzed simultaneously for calibration (once per five samples), and the recovery rate of each

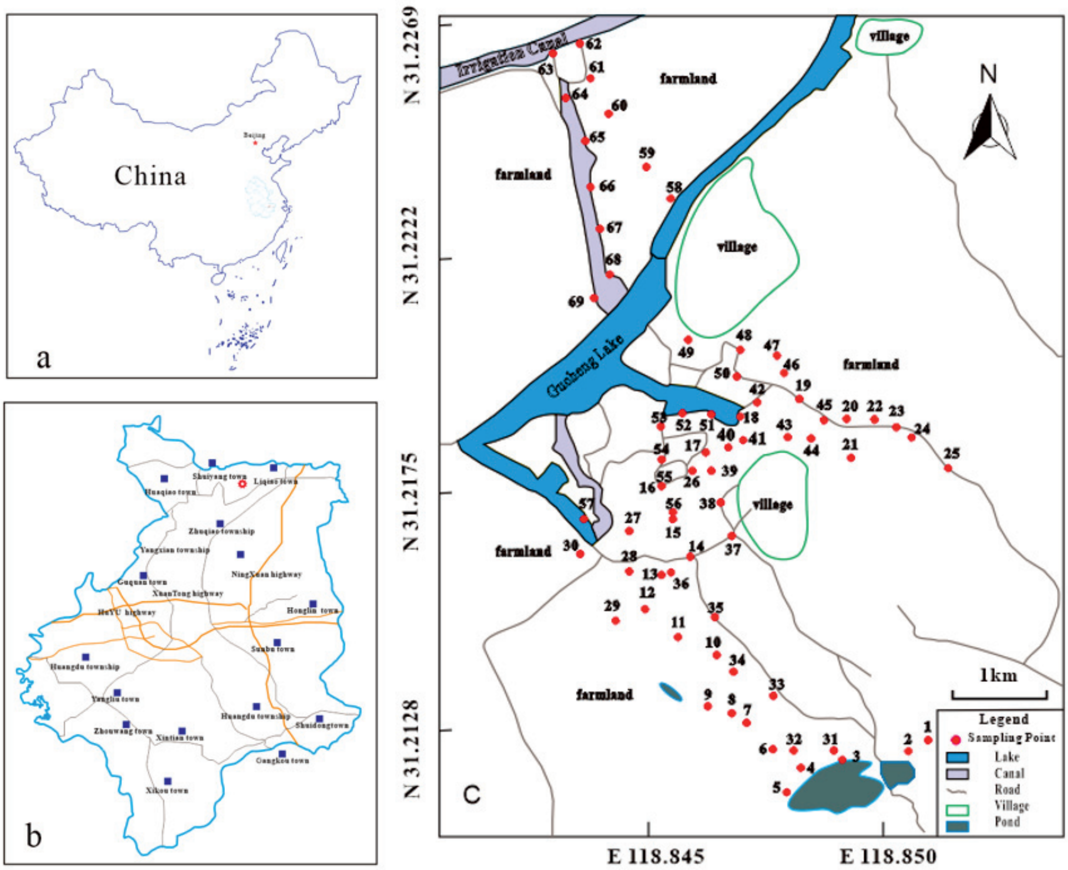

Fig. 1. The location of the study area and the samples distributions.

element was controlled in the range of 80%~120%. The experiment was carried out in the engineering and technological research centre of coal exploration, Anhui province, China. In order to ensure that the samples are not contaminated, the reagents in the test are guarantee reagent and the water is ultrapure.

Environmental Risk Assessment Methods

Geoaccumulation Index (I_{geo})

Geoaccumulation Index (I_{geo}) was proposed by a German scholar Muller in 1969 [36]. I_{geo} was initially used to evaluate the pollution degree of heavy metals in sediments [37,38], and was later widely used to evaluate the heavy metal pollution in soil [39-42]. The calculation formula is as follows:

$$I_{\mathrm{geo}} = \log_2\left(\frac{C_i}{1.5B_i}\right) \tag{1}$$

where C_i is the measured concentration of heavy metal in the sample, and B_i is the geochemical background value of heavy metal, and the concentration unit is mg/kg. The constant 1.5 is the conversion coefficient to eliminate the variation of the background value that may be caused by the difference of rocks in different places [18]. The relationship between the grade of land accumulation index and pollution degree is shown in Table 1.

Enrichment Factor (EF)

Enrichment factor is a quantitative evaluation method to assess the influence of anthropogenic activities on the enrichment of heavy metals in atmospheric particles [4, 5], street dust [1, 43], sediment [44, 45], and soil [46, 47]. In order to reduce the man-made influence in the sampling and sample preparation process and ensure the comparability and equivalence of each index factor, the elements in the test samples were normalized with reference elements as the reference standard [45]. The reference elements are required to be less affected by the environment and the analysis and test process, and their properties are stable. The commonly used reference elements are Zr [47], Mn [43], Ti [48], Al [49], Fe [46], As [45], Sc, Ca and Li.

EF is calculated as follows:

$$\mathrm{EF} = \frac{(C_i / C_{ref})_{sample}}{(B_i / B_{ref})_{background}} \tag{2}$$

where C_i and C_{ref} represent sample concentration of target metals and reference concentration of standardized elements, respectively. Similarly, B_i and B_{ref} represent background concentration in target metals and reference metals, respectively. The concentration units in all formulas are mg/kg. In this study, both Fe and Mn are selected as standardized reference elements because contents of Fe and Mn are much lower than background values, and they are rich in geochemistry and have little variation [43]. EF>1 indicates that the relative enrichment of this element is affected by human activities. The numerical classification of enrichment coefficient and corresponding pollution degree are shown in Table 1.

Potential Ecological Risk Index (RI)

The potential ecological risk index (RI) was originally used to assess the level of ecological risk from heavy metals in river sediments by Hakanson in 1980 [50]. The ecological factor (E_r^i) and potential ecological risk index (RI) of heavy metals have been applied to contamination level and environmental risk assessment of sediment, street dust and soil by this method [6-8, 48, 51], and they can be calculated by the following equations:

$$RI = \sum_{i=1}^{n} E_r^i \tag{3}$$

$$E_{\mathrm{r}}^i = T_{\mathrm{r}}^i \times P_i \tag{4}$$

$$P_i = \frac{C_i}{B_i} \tag{5}$$

Where C_i and B_i represent the measured concentration and background concentration of heavy metal elements respectively, which are consistent with the above methods; P_i is the ratio of the two concentrations, which is the single factor pollution index; T_r^i represents the toxicity response coefficient of element, and the values have been listed in the researches of Hakanson [50] and Shahab et al. [8]; RI is the cumulative value of all E_r^i values and comprehensive ecological risk index. The E_r^i can be classified into five classes and RI can be divided into four risk levels, as shown in Table 1.

Statistical Methods

It was performed to data processing and analysis using IBM SPSS Statistics 20 and Microsoft Excel 2010, in which statistical calculation, I_{geo}, EF and RI calculation analysis were conducted. Graphics and images processing and analysis were implemented via CorelDRAW 2018, Surfer 12 and OriginPro 9. Correlation analysis, hierarchical cluster analysis and principal component analysis were used to distinguish the possible sources and relationships between the metals as source identification analysis.

Table 1. Classification of geoaccumulation index (I_{geo}), enrichment coefficient (EF), ecological risk factor (E_r^i) and potential ecological risk index (RI) of heavy metals.

Geoaccumulation Index (I_{geo})	Pollution level	Enrichment coefficient (EF)	Enrichment degree
I_{geo}≤0	Non-pollution	EF≤1	Non-enrichment
0<I_{geo}≤1	Light-moderate pollution	1<EF≤2	Minor enrichment
1<I_{geo}≤2	Moderate pollution	2<EF≤5	Moderate enrichment
2<I_{geo}≤3	Moderate-Strong pollution	5<EF≤10	Moderately severe enrichment
3<I_{geo}≤4	Strong pollution	10<EF≤20	Severe enrichment
4<I_{geo}≤5	Strong-extremely strong pollution	20<EF≤40	Very severe enrichment
I_{geo}>5	Extremely strong pollution	EF>40	Extremely severe enrichment
Ecological risk factor (E_r^i)	Risk level	Potential ecological risk index (RI)	Risk level
E_r^i<40	Low risk	RI<150	Low risk
40≤E_r^i<80	Moderate risk	150≤RI<300	Moderate risk
80≤E_r^i<160	Considerable risk	300≤RI<600	Considerable risk
160≤E_r^i<320	High risk	RI>600	High risk
E_r^i≥320	Very high risk		

Results and Discussion

Concentration Analysis

Concentrations of heavy metals of surface soil in the study area are synthesized in Table 2, which also lists the background values of heavy metals in the local soils of Anhui Province [52]. The mean concentrations of heavy metal Cu, Fe, Zn, Co, Cr, Mn and Pb are respectively 42.97, 16513.7, 66.01, 66.76, 59.09, 350.16 and 42.65 mg/kg, and arranged in the following order: Fe>Mn>Co>Zn>Cr>Cu>Pb. While the background values are taken as the reference standards, Fe, Cr and Mn do not exceed the standards which show that contents of these heavy metals are close to the background values. The elements with exceedance ratio greater than 1 are Cu, Zn, Co and Pb, with ratios to soil background values of 2.11, 1.06, 4.10 and 1.60, respectively. From the perspective of sampling points, the points above the background values reach 100% for Co; to Cu and Pb, only 2 samples do not exceed the standard, and the over rates are both 97%; the proportion of Zn exceeding the standard accounts for 68%; to Fe, Mn and Cr, there are NO.1, NO.3 and NO.8 samples over the standards, and the percentages are 1.4%, 4.3% and 11.6%, respectively.

The coefficient of variation (CV) as an index showing the extent of variability in relation to the mean of pollution, can be used to identify the anthropogenic contributions degree of pollution in the environment studies. Previous studies revealed that CV<10%, 10%<CV<100% and CV>100% mean low, moderate and strong anthropogenic contributions, respectively [18, 23]. In this study, Cu, Mn, Fe and Co have relative higher CVs, which are 33%, 29%, 27% and 25%, respectively. As to Pb and Zn, they have lower CVs with

Table 2. Descriptive statistics of heavy metal concentrations (mg/kg) (n = 69).

	Cu	Fe	Zn	Co	Cr	Mn	Pb
Minimum	7.21	12274.7	50.21	29.43	51.39	187.74	7.10
Maximum	82.58	31562.4	92.41	94.58	69.11	771.18	51.71
Mean	42.97	16513.7	66.01	66.76	59.09	350.16	42.65
Standard Deviation	14.10	4466.7	7.91	16.51	5.29	101.63	6.64
Coefficient of Variation/ %	33	27	12	25	9	29	16
Background (CNEMC 1990)	20.4	31400	62	16.3	66.5	530	26.6
Excessive ratios	2.11	0.53	1.06	4.10	0.89	0.66	1.60
Over standard rates/ %	97	1.4	68	100	11.6	4.3	97

16% and 12%. The CV values of these heavy metals range from 12% to 33%, which indicate the moderate degree of spatial inhomogeneous. Cr has relative lower CV with 9% and displays low concentration variability.

Environmental Risk Assessment

Geoaccumulation (I_{geo}) and Enrichment Factor (EF)

The I_{geo} and EF values of the heavy metal concentration were calculated by using Eq. (1) and Eq. (2) to the farmland soil samples around Chating copper ore in Xuancheng, Anhui, respectively, and the pollution degree and major heavy metal contaminants were identified, and then the box diagrams of I_{geo} and EF were obtained, as shown in Fig. 2.

Referring to the grading standards of geoaccumulation index method in Table 1, as can be seen from Fig. 2a), the average I_{geo} values and mean I_{geo} of seven heavy metals are in the order of Co>Cu>Pb >Zn>Cr>Mn>Fe. The I_{geo} values of Fe, Mn, Cr and Zn are less than 0, indicate that there are no accumulations of these four metals in farmland soil samples. Most I_{geo} values of Cu and Pb fall in the range 0~1, and only I_{geo} values of a few samples are less than 0, and the proportions are 18.8% and 10.1%, respectively. Both the average value of the I_{geo} of all samples and the I_{geo} of mean value are greater than 0, implying that Cu and Pb pollution existed in the soil samples, which belonged to light-medium pollution level. For the heavy metal Co, the I_{geo} values of more than 85% samples are greater than 1 and less than 2, which belong to moderate pollution level. The I_{geo} values of other samples are between 0 and 1, which belong to light-medium pollution level. The evaluation results of geoaccumulation index method are consistent with the situation of the excessive elements and point over standard rates.

In Fig. 2b), the number 1 beside the element represents the EF value calculated with Fe as the reference element, and the number 2 means Mn as the reference element. The following conclusions can be drawn from Fig. 2b) and Table 3 according to EF grading standards in Table 1. Taking Fe as a reference, the average EF values of Cu, Zn, Co, Cr, Mn and Pb are 4.32, 2.12, 8.50, 1.76, 1.29 and 3.19, respectively, and the mean EF values are 4.01, 2.02, 7.79, 1.69, 1.26 and 3.05, respectively. The EF values of six heavy metals except Fe are in decline order of Co>Cu>Pb>Zn>Cr>Mn. The EF values of Co fall between 5 and 10, which is moderately severe enrichment level. The EF values of Cu and Pb are between 2 and 5, belonging to moderate enrichment level. The enrichment coefficients of Cr and Mn are less than 2 and greater than 1, which indicate that the heavy metals in the samples were slightly enriched. In farmland soil samples, the proportion of heavy metals Co, Cu, Cr and Mn exceeding the existing evaluation grades are 35%, 32%, 25% and 3%, respectively, while Pb and Zn do not exceed the evaluation grades. Taking Mn as the reference element, the order of heavy metal EF value is consistent with that of Fe, which is Co>Cu>Pb>Zn>Cr>Fe. In all samples, the proportion of heavy metals Co, Cu, Zn, Cr and Fe exceeding the existing evaluation grades are 13%, 10%, 23%, 3% and 19%, respectively, only Pb of all samples are within the evaluation grade. As can be seen from Table 3, under different conditions of reference elements Fe and Mn, the evaluation results of Zn are different, showing moderate enrichment and minor enrichment respectively, from the numerical point of view, the former 2.11/2.02 (average EF/EF of mean) and the latter 1.71/1.61 (average EF/EF of mean). In practice, according to another scholars' pollution classification, when the enrichment coefficient of minor enrichment is set as 1~3 [1, 37] or 1.5~3 [22], and then

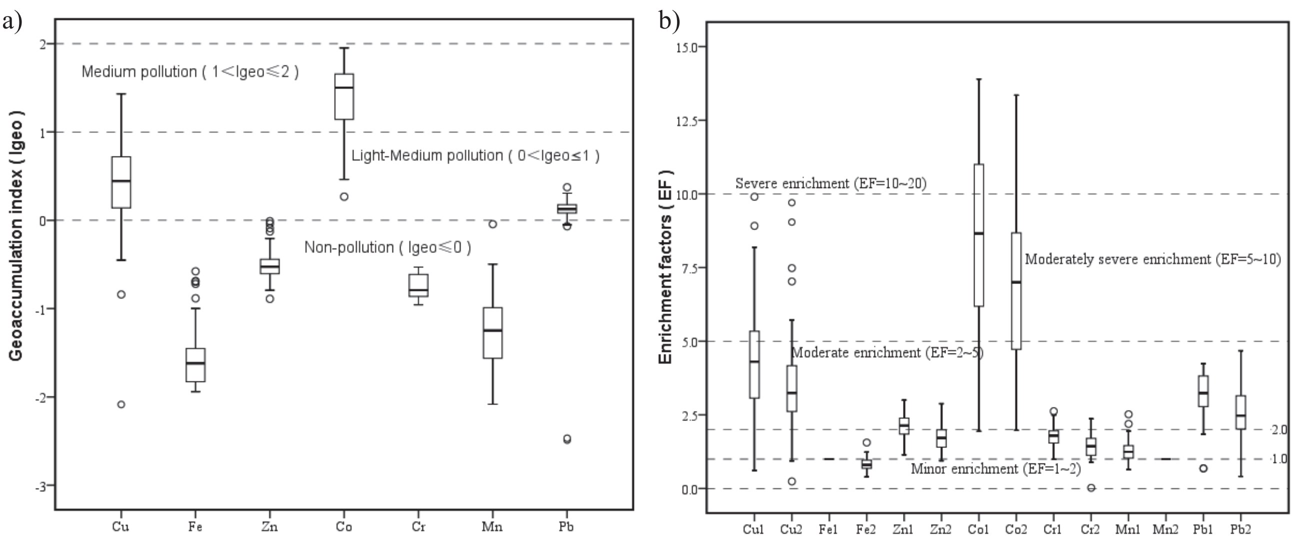

Fig. 2. Box plots of I_{geo} and EF for heavy metals in farmland soil samples: a) Geoaccumulation Index (I_{geo}) values of heavy metals, b) Enrichment factors (EF) coefficient of heavy metals.

Table 3. Pollution classification of I_{geo} and EF for heavy metals in farmland soil samples

	I_{geo}		EF_{Fe}		EF_{Mn}	
Co	1.40	1.45	8.50	7.79	6.84	6.20
	Moderate pollution		Moderately severe enrichment		Moderately severe enrichment	
Cu	0.40	0.49	4.32	4.01	3.49	3.19
	Light-moderate pollution		Moderate enrichment		Moderate enrichment	
Pb	0.05	0.10	3.19	3.05	2.60	2.43
	Light-moderate pollution		Moderate enrichment		Moderate enrichment	
Zn	-0.50	-0.49	2.11	2.02	1.71	1.61
	Non-pollution		Moderate enrichment		Minor enrichment	
Cr	-0.76	-0.76	1.76	1.69	1.43	1.34
	Non-pollution		Minor enrichment		Minor enrichment	
Mn	-1.24	-1.18	1.29	1.26	1	1
	Non-pollution		Minor enrichment		Non-enrichment	
Fe	-1.56	-1.51	1	1	0.83	0.80
	Non-pollution		Non-enrichment		Non-enrichment	

the same pollution level (minor enrichment) will be received.

The assessment results of heavy metal pollution by the geoaccumulation index method and the enrichment factor method are basically consistent. Table 3 shows that the pollution grades of seven heavy metal elements are in the same order in the two methods. This is mainly because the influence caused by natural anomalies can be eliminated using normalization on the basis of soil environmental background values in the evaluation process. The results are more reliable for the validation from different evaluation methods.

Potential Ecological Risk Assessment

Using the Hakanson potential risk index method, single potential ecological risk coefficient (E_r^i) and the comprehensive potential ecological risk index (RI) can be calculated by the Eqs. (3-5). According to the classification criteria of potential ecological risk levels in Table 1, E_r^i and RI are obtained, as shown in Fig. 3.

According to the averages of single potential ecological risk index, and as provided in Fig. 3a), potential ecological risk factors for Cu, Fe, Zn, Co, Cr, Mn and Pb are in decreasing trend of Co>Cu>Pb >Cr>Zn>Mn>Fe. The results are roughly the same as those of I_{geo} and EF, and the difference is reflected in the heavy metals Zn and Cr. Zn and Cr are at the same pollution level in the former two evaluation methods, and Zn is greater than Cr, while the potential ecological risk assessment result is that Cr is greater than Zn. The main reason for this difference is that the toxicity response coefficient of Cr ($T_r = 2$) is higher than that of Zn ($T_r = 1$). The E_r^i values of seven heavy metals range from 0.35 to 29, lower than the risk value of 40, which indicates that all metal elements are at low ecological risk level. The comprehensive potential risk indices for heavy metals in sampling points range from 31 to 56, lower than the risk value of 150, which indicates that all sampling points are at low ecological risk level. The evaluation level of potential ecological risk assessment are lighter than those of geoaccumulation index method and enrichment factor method, which have also been appeared in other scholars' researchers. Rahman et al. [45] found that the average I_{geo} values for Cr and Fe were (−0.44±1.87) and (1.59±1.87), during moderate pollution level to strong pollution level, while it was observed that E_r^i of Cr, Pb, Cu and Mn were all lower than 40, which belong to low ecological risk, besides all the sampling sites were at low risk level where the RI values were much lower than 150. Jamil et al. [12] carried out agricultural soil assessment in Hayatabad industrial estate, the EF and I_{geo} assessment results were consistent (Pb>Mn>Cr>Cu>Zn), while RI results were different (Pb>Cu>Mn>Cr>Zn). These studies well support the evaluation results of this paper, as for the inconsistent results of environmental risk assessment may be caused by: 1) single element exceeding the standard in a certain extent cannot cause ecological risk; 2) the background value and the toxicity response coefficient of ecological risk contribution factors are different.

Spatial Distribution Characteristics

In order to understand the spatial distribution characteristics of all metal elements and the concentrated distribution areas of pollution, Kriging

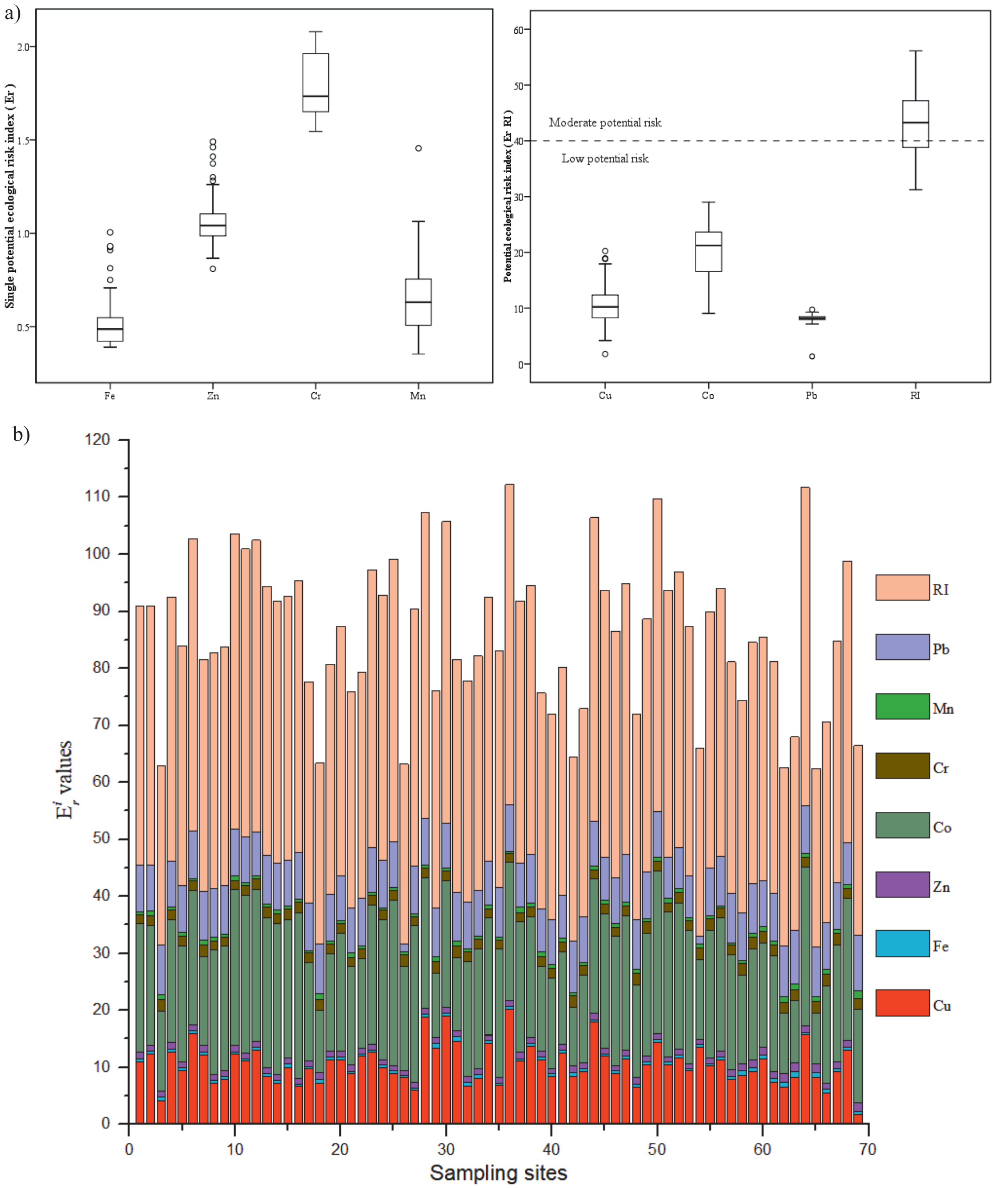

Fig. 3. Potential ecological risk index (E_r^i , RI) for heavy metals in the farmland soil of Chating copper ore: a) Box plots of E_r^i and RI of heavy metals in farmland soil samples, b) Potential ecological risk index of heavy metals in sampling sites.

spatial interpolation technology [41] in Surfer software is used to analyze the spatial distribution characteristics, and the results are shown in Fig. 4.

From the contour maps of metal element content combined with the sampling point map, it can be seen that the spatial distribution of concentration reflects a certain regional concentration, and the spatial distribution similarity is found in some elements. The high values of Fe, Zn, Cr and Mn are concentrated in the northwest corner of the study area, the high values of other areas are scattered sporadically and presented island or banded distributions. The high values of Cu

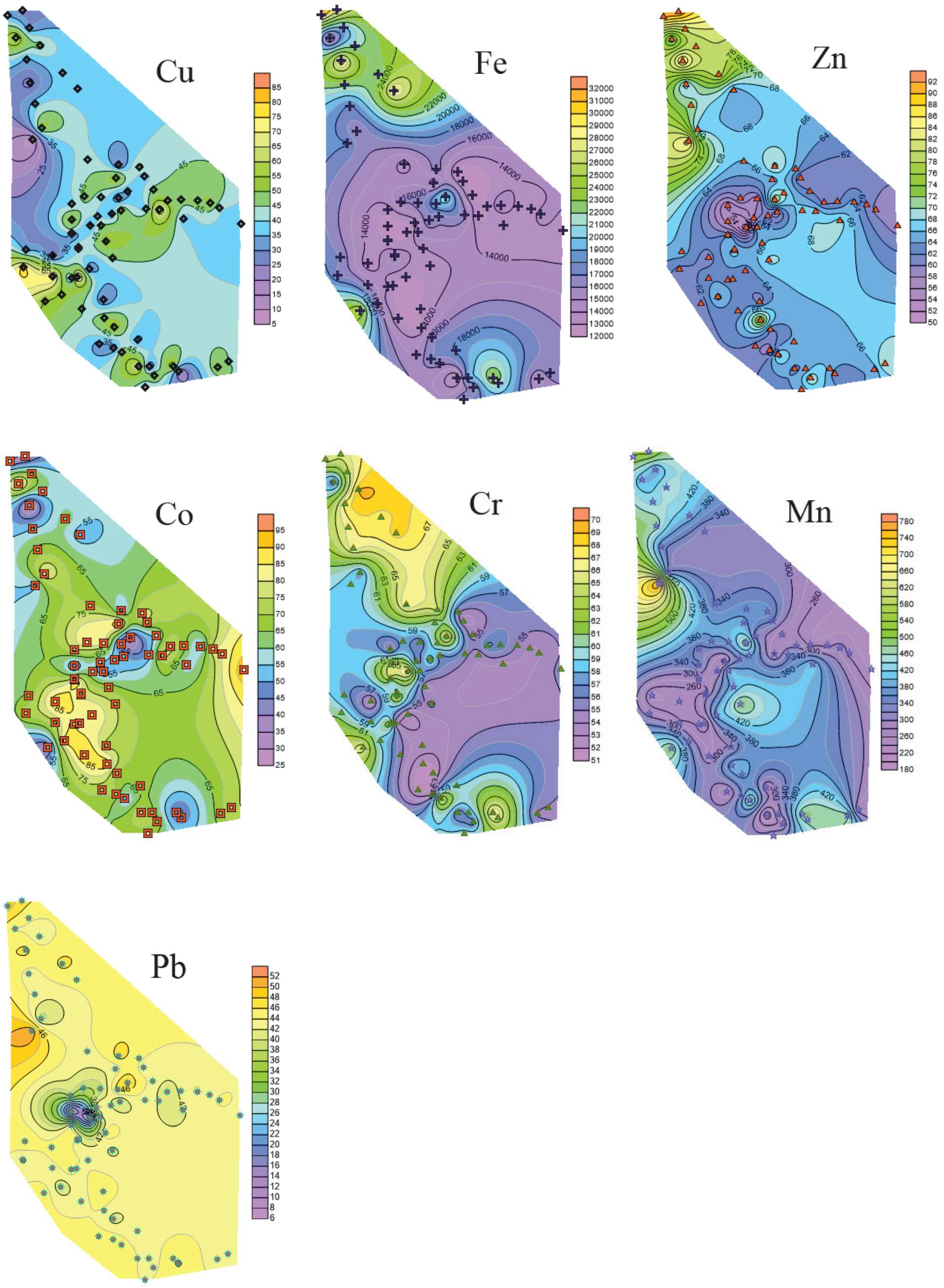

Fig. 4. Spatial distributions of heavy metals in farmland soil samples from Chating copper ore.

are island and banded in the middle and southwest of the study area. Combined with the location of sampling points in Fig. 1, the maximum Cu value are the samples No.28 and No.30. The Chating copper ore is located in the southeast of the sampling area, and the concentration distribution of Cu in the study area is higher in the southeast than in the northwest. In the isoline map of Co, most points of study area is in the range of high value, and Co concentration in all sampling points exceed the geochemical background value (16.3mg/kg). The spatial distribution of Co concentration is similar to Cu, and the concentration value near Chating copper ore is higher than that far away. Based on the spatial distribution characteristics of Pb and Fig. 1, it can be seen that contents of only samples 26 and 54 located in the center of study area are lower than the environmental background value (26.6mg/kg), while contents of other samples are higher. The points with higher content of Pb are distributed along the roads beside Gucheng Lake and irrigation canal.

Source Identification

The correlation matrix is useful as it can point out associations between variables, and thus indicate the participation of the individual chemical parameters

Table 4. Correlation matrix of heavy metals concentrations in farmland soil samples.

	Cu	Fe	Zn	Co	Cr	Mn	Pb
Cu	1.000						
Fe	-0.289*	1.000					
Zn	-0.226	**0.610****	1.000				
Co	0.253*	-0.673**	-0.367**	1.000			
Cr	-0.224	**0.628****	**0.355****	-0.537**	1.000		
Mn	-0.268*	**0.491****	**0.573****	-0.456**	**0.318****	1.000	
Pb	-0.172	0.306*	**0.454****	-0.028	-0.119	0.192	1.000

Note: **extremely significant at $\alpha = 0.01$ level; *significant at $\alpha = 0.05$ level

in several influences factors. The results of Pearson correlation method about soil samples collected from Xuancheng farmland are shown in Table 4. As can be seen from the statistics, close relationships have been identified among the metals Fe-Cr-Zn-Mn (r_α = 0.318~0.628) and Pb-Zn (r_α = 0.454), with extremely significant positive correlation at $\alpha = 0.01$ level, which suggest that Fe, Cr, Zn, Mn may have similar sources or have been affected by similar factors. While the correlation coefficient of Co to Fe, Zn, Cr, Mn are -0.673, -0.367, -0.537, -0.456 at extremely significant negative level, which indicate that there is a different source between Co and other four metals. The correlation coefficients between Cu and other elements with exception of Co are negative, demonstrating similar characteristics or common origin.

Cluster analysis has been used for environment studies for a long time. In this study, the hierarchical cluster analysis (HACA) with the "Ward" linkage and the "Euclidean" distance [27] being chosen for calculation has been applied to the metal contents of farmland soil samples from Xuancheng Chating copper ore, which are standardized using z-scores before calculation, and the results are shown in Fig. 5 as a dendrogram. According to the generated dendrogram, two major groups, cluster 1 and cluster 2, and three sub-clusters are obtained. Subgroups 1 (Sub-1) is connected by Fe, Cr, Zn and Mn, and Subgroups 2 (Sub-2) is composed of Pb, and Subgroups 3 (Sub-3) is consisted of Cu and Co, which shows the similarities of these three subgroups and agree with the results of Pearson correlation analysis (CA).

Principal component analysis (PCA) is performed for farmland soil samples from Xuancheng Chating copper ore so as to assist in identifying the contaminants' sources. The Kaiser-Meyer-Olkin value is 0.727 which is greater than 0.6 for soil samples, and Bartlett test significance probability P = 0.000 which is less than

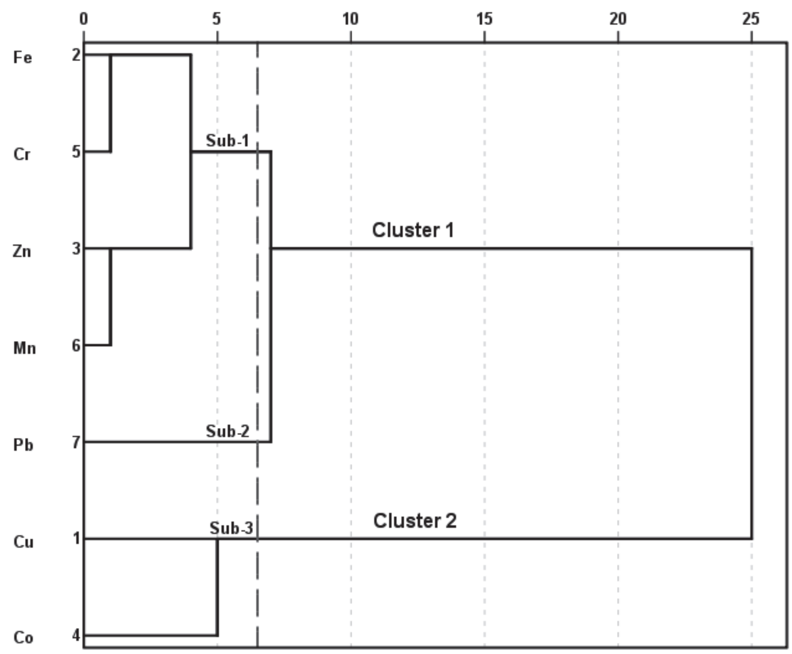

Fig. 5. Dendrogram of the hierarchical cluster analysis of heavy metal.

Table 5. Principal component analysis of farmland soil heavy metal concentrations.

Heavy metals	PC1	PC2	PC3
Cu	-0.172	-0.116	0.976
Fe	0.800	0.390	-0.110
Zn	0.499	0.722	-0.026
Co	-0.825	-0.058	0.127
Cr	0.850	-0.127	-0.090
Mn	0.564	0.448	-0.134
Pb	-0.129	0.895	-0.112
Eigenvalue	3.250	1.281	0.851
Variance contribution (%)	46.43%	18.29%	12.16%
Accumulative variance contribution (%)	46.43%	64.72%	76.88%

0.001 prove that the data are suitable for PCA [2]. The PCA results including factor loading after Varimax rotation as well as eigenvalues, Variance contribution and cumulative of variance are displayed in Table 5. Three significant principal components with eigenvalues > 0.8 are extracted, accounting for 76.88 % of the total variance, while eigenvalue is 1, the total variance explained is 64%. The first component is explained by Fe, Cr, Mn and Zn, accounting for 46.43 % of the total variance; the second component is dominated by Pb and Zn, accounting for 18.29 % of the total variance; the third component is loaded by Cu with high coefficient 0.976, although the eigenvalue is 0.851 less than 1, the extraction information of Cu increased from 21.6% when the eigenvalue was 1 to 99.5%.

Based on anthropogenic source evaluation results and spatial distribution characteristics, three possible sources of principal components have been discussed. The PCA results are in good agreement with the findings of HACA and CA. The above results and discussions indicate that the similar origin of Fe-Cr-Mn-Zn that is principal component 1 may be the natural source influenced by the crust and soil parent material [49]; principal component 2 contained the main element Pb could be derived from transportation and mechanical operations; principal component 3 included the dominant element Cu might be greatly affected by copper mining activities. The heavy metals assessment of the paddy soil in Xiangtan city, China, by Deng et al. [26] found that slight anthropogenic activities can cause accumulation of Pb and Cu.

Conclusions

The heavy metals of 69 soil samples from the farmland around Chating copper ore in Xuancheng area, southern Anhui Province, China, were tested and analyzed. Analysis of metal concentration characteristics, multivariate statistical analysis, environmental risk assessment, spatial distribution characteristics and source apportionment were adopted to explore the study area. The results revealed that human activities have a certain impact on the soil environment. The specific conclusions are listed as follows.

The concentrations of all the detected metal elements showed the decline order: Fe (16513.7)>Mn (350.16)>Co (66.76)>Zn (66.01)>Cr (59.09)>Cu (42.97) >Pb (42.65), and the multiples of Cu, Zn, Co and Pb over the background value are 2.11, 1.06, 4.10 and 1.60, respectively. To 69 sampling points, 100% of metal Co exceeds the standard, and the ratio of Cu and Pb are both 97%. The I_{geo} values were sorted as Co>Cu> Pb>Zn>Cr>Mn>Fe, and the I_{geo} values of Cu and Pb fell in the range 0~1, which indicated slight-medium pollution level; the I_{geo} values of Co with more than 85% samples were in the range 1~2, which belong to moderate pollution level. Taking Fe and Mn as the reference elements respectively, EF values of the heavy metal content were both in the order of Co>Cu>Pb>Zn>Cr. The EF values of Co fell in the range 5~10, which is moderately severe enrichment level; the EF values of Cu and Pb were between 2 and 5, belonging to moderate enrichment level. The E_r^i values were in decreasing order of Co>Cu>Pb>Cr>Zn>Mn>Fe, moreover both E_r^i and RI values of all heavy metals were at low ecological risk level.

The spatial distribution of metal elements was inhomogeneous, in general, the concentration of Fe, Zn, Cr and Mn showed a trend of "high in northwest and low in southeast". The spatial distribution of Co and Cu were similar with the characteristics of "the closer to Chating copper ore, the higher the value". The points with higher content of Pb were distributed along the roads beside Gucheng Lake and irrigation canal.

Close relationships had been identified among the metals Fe-Cr-Zn-Mn and Pb-Zn, with extremely significant positive correlation at α = 0.01 level. The correlation coefficient of Co to Fe, Zn, Cr, Mn were negative at α = 0.01 level, while the correlation coefficient of Co to Cu was positive at α = 0.05 level. Two major clusters (Cluster 1 and Cluster 2) and three sub-clusters (Sub-1, Sub-2, Sub-3) were obtained by hierarchical cluster analysis. Cluster analysis further expressed the correlation results intuitively which Sub-1 was connected by Fe, Cr, Zn and Mn, and Sub-2 was composed of Pb, and Sub-3 was consisted of Cu and Co. Principal component analysis further identified possible contamination sources: PC1 was explained by Fe, Cr, Mn and Zn accounting for 46.43% and might be the natural source influenced by the crust and soil parent material; PC2 was dominated by Pb and Zn accounting for 18.29 % and could be derived from transportation and mechanical operations; PC3 was loaded by Cu with high coefficient 0.976 and accounting for 12.16% and may be greatly affected by copper mining activities.

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Conflict of Interest

The authors declare no competing interests.

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