

Characteristics and Source Analysis of Soil Heavy Metal Pollution in a Mining Area

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Abstract

It is of great significance to study the degree and source of soil heavy metal pollution in geological high background value area for remediation of local contaminated soil. The 0 - 20 cm topsoil was taken around the mining area, and the contents of Pb, Zn, Ni, Cd, Hg, Cu and As in the soil were measured. Single-factor pollution index, Nemeiro comprehensive pollution index and potential ecological risk index were used to evaluate the degree of heavy metal pollution and ecological risk. Finally, multivariate statistical analysis was used to analyze the sources of soil heavy metals. The results show that the measured elements are polluted to different degrees, mainly due to the ecological environment problems caused by extensive mining development methods and inefficient utilization of resources. The key link is the release of pollutants at the source. Effectively blocking the release at the source can cut off the possibility of pollutants entering the food chain and the circulation of materials in the ecosystem. The results of potential ecological risk index showed that the potential ecological damage of seven heavy metals was ranked as follows: Cd (97.67) > Hg (68.97) > As (14.29) > Pb (11.55) > Ni (4.62) > Zn (1.61) > Cu (1.45) had a high ecological risk coefficient, and the potential comprehensive ecological risk index was 200.16 and the degree was medium. Principal component analysis shows that the sources of heavy metals are divided into Pb, Cd, As, Zn and Hg mainly from human activities such as mining, while Ni and Cu mainly come from soil parent materials, mining and agricultural activities.

Keywords

Soil Heavy Metals, Pollution Assessment, Ecological Risk, Source Analysis

1. Introduction

Yunnan, known as the “Kingdom of Nonferrous Metals”, depends largely on the development of the nonferrous metal industry, which plays a pivotal role in Yunnan (Zhong et al., 2021). The mining of lead-zinc mines not only promotes local economic development, but also brings a series of ecological and environmental problems (Feng et al., 2020; Li et al., 2021c; Lu et al., 2014). Heavy metals are not easily degradable, easy to accumulate, have high toxicity and strong environmental persistence. Long-term discharge of heavy metals in soil will not only have a negative impact on soil functions, but also pose potential threats to humans through direct human contact, food chain, and floating and sinking. Even cause various diseases (Ning et al., 2021; Peng et al., 2013). Therefore, taking the soil in the geological high background value area as the research object, It is of great significance for the sustainable development of the study area to analyze the potential ecological hazards and sources of heavy metal pollution in the soil around the mining area.

At present, many scholars have carried out research on soil heavy metals in geologically high background areas, and there are a large number of articles on mining pollution in mining areas and serious heavy metal pollution in farmland soil. Different physical and chemical properties lead to obvious differences in soil types, pollutant distribution and characteristics. Jiang et al. (2021) analyzed and measured Cu, Cd, Pb, Zn, Mn, Hg, As The content of heavy metals and heavy metals in different soil layers were evaluated for pollution degree and potential ecological risk. Ren et al. (2021) analyzed the degree of soil heavy metal pollution in this area caused by coal mining in western Yuxi and analyzed its characteristics. Cheng et al. (2021) measured the content of heavy metals (Cd, Cu, Pb, and Zn) in the edible part of three farmland soils of corn, rice and facility vegetables in key phosphate rock distribution areas in Yunnan-Guizhou region, and analyzed the characteristics of heavy metal pollution in farmland soils. Li et al. (2021a) took an abandoned lead-zinc mine in the agricultural and animal husbandry interlaced zone in the central and southern section of the Daxing'an Mountains as an example, collected soil samples at different depths, compared and analyzed the spatial distribution characteristics of heavy metals in the mining area, and used the geoaccumulation index method and ecological risk assessment method to evaluate the mining area. For Heavy metal accumulation levels and potential ecological risks, taking Jinzhou City as the research area, Li et al. (2021b) analyzed the pollution characteristics of soil heavy metals As, Cd, Hg, Cu, Cu, Pb, Zn, and Ni. The statistical results of heavy metal content in soil samples were Cd, Cu, Cr, Hg, Ni, and Pb. The content is higher than the soil background value in Liaoning Province. Most of the current research focuses on the analysis of the characteristics of polluted areas, and even some research areas are in an unknown state of the source of heavy metal pollution in the soil of lead-zinc mining areas (Ma et al., 2019; Feng et al., 2017). Therefore, while studying the characteristics and sources of heavy metal pollution in the soil around

the mine, it is also necessary to analyze the correlation of its sources and the spatial correlation of surface changes through the reflection of the direction between the sampling points.

In this study, the content and distribution characteristics of soil heavy metals in the mining area of Shangri-La, Diqing Tibetan Autonomous Prefecture were analyzed, and 35 surface soil samples (0 - 20 cm) were randomly collected to determine the Pb, Zn, Ni, Cd, Hg, Cu and As in the soil (Lv, 2021). The single-factor pollution index, Nemerow comprehensive pollution index (Yang & Zeng, 2014) and potential ecological risk index were used to evaluate the pollution degree and ecological risk of heavy metals (Yang et al., 2022; Wan et al., 2020; Yang et al., 2018). On this basis, Pearson correlation coefficient analysis was used to determine the source of heavy metal elements (Sungur et al., 2014), and Kriging interpolation method combined (Chen et al., 2022; Guo et al., 2022) with principal component analysis was used to determine the source of pollution (Guo et al., 2012). In this paper, while studying the sources of soil pollution around the mining area, the sources of heavy metal pollution were obtained through correlation analysis and spatial correlation analysis was used to weight the measured values to obtain predictions of unmeasured values (Zhou et al., 2018; Chen et al., 2011; Luo et al., 2015). This provides data support for soil environmental quality protection and heavy metal pollution prevention and control around the mining area, and provides a theoretical basis for sustainable land use and ecological development.

2. Materials and Methods

2.1. Study Area

Diqing Tibetan Autonomous Prefecture is located in the northwest of Yunnan Province, at the junction of Yunnan, Tibet and Sichuan provinces. Diqing Tibetan Autonomous Prefecture is located at the southeastern end of the “Asian Water Tower”, with an average elevation of 3380 m in the region. The upper reaches of Jinsha River and Lancang River run through Diqing Prefecture (Chen et al., 2020). The annual average temperature ranges from 4.7°C to 16.5°C, which is a subtropical monsoon climate with an annual extreme maximum temperature of 25.1°C and a minimum temperature of -27.4°C. The three-dimensional climate is obvious. There is a saying that “one mountain has four seasons, and ten miles has different days.” (He et al., 2019). There are mainly more than 30 kinds of minerals such as copper, tungsten, molybdenum, lead and zinc. In this study, a total of 35 sample points were collected in a mining area in Shangri-La, Diqing Tibetan Autonomous Prefecture (Figure 1), and 0 - 20 cm topsoil was taken from each sample point.

2.2. Sample Collection and Determination

The soil around the mining area in Shangri-La City was sampled in November 2020. Based on the environmental soil background value in my country, the soil

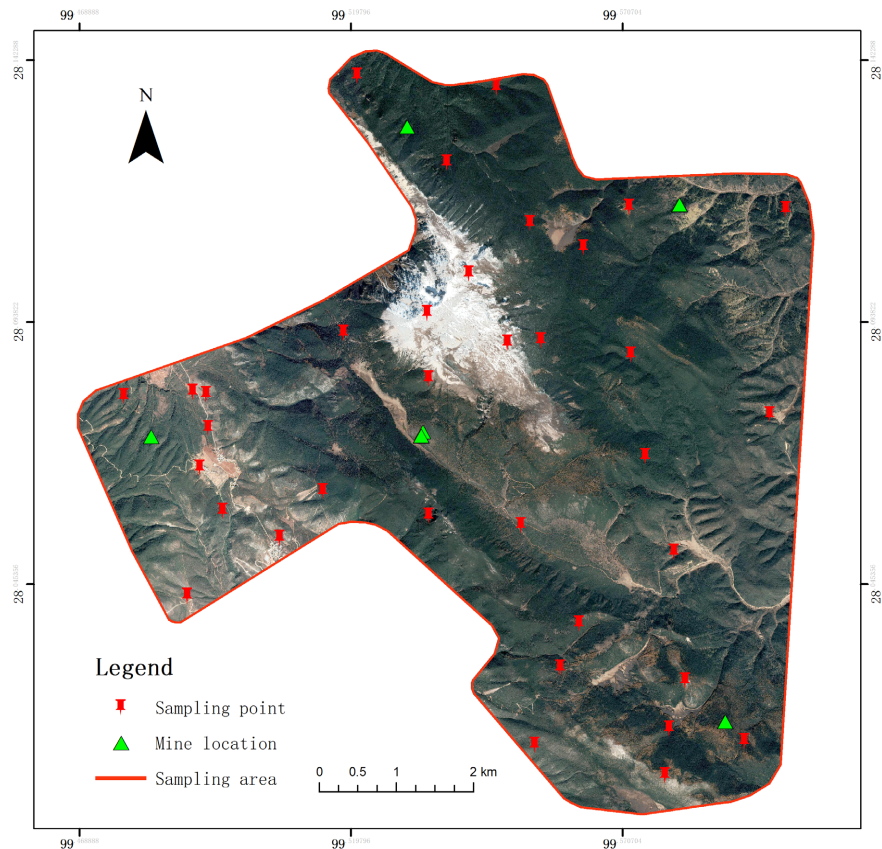


Figure 1. Distribution of the study area and sampling sites.

heavy metal pollution degree was evaluated, and the risk screening value of GB15618-2018 “Soil Environmental Quality Agricultural Land Soil Pollution Risk Control Standard (Trial)” and GB/T17141-1997 “Determination of Soil Quality Lead and Cadmium Graphite” were selected. Furnace Atomic Absorption “Spectrophotometry”, the sample determination refers to the second edition of “Sample Test Method”, combined with the soil background value in Diqing Prefecture to analyze the soil pollution degree. The single-factor pollution index method, the Nemerow comprehensive index method and the potential ecological risk assessment of soil heavy metals were used to evaluate the ecological risk of soil heavy metal pollution in the mining area of Diqing Tibetan Autonomous Prefecture. The ecological risk assessment of soil heavy metal pollution in Diqing was carried out by single factor index method and Nemerow index method. The soil samples were naturally air-dried indoors to remove impurities such as gravel and plant residues, passed through a 0.15 mm aperture nylon sieve, and stored in ziplock bags for future use.

The heavy metal elements in soil samples were Pb, Cd, As, Zn, Ni, Cu and Hg. The determination methods of each element are: lead and cadmium are determined by graphite furnace atomic absorption spectrophotometry; arsenic and mercury are determined by atomic fluorescence method; zinc, nickel and copper are determined by flame atomic absorption spectrophotometry.

2.3. Soil Heavy Metal Pollution Assessment

1) The one-factor exponential method (P_i) is calculated as: $P_i = C_i/S_i$

In the formula, C_i is the actual measured value of soil heavy metal pollution i (mg/kg); S_i is the evaluation standard of soil heavy metal i (mg/kg). Grading standards are shown in **Table 1**.

2) Nemerow index method

$$P_N = \sqrt{\frac{P_i^2 + P_{\max}^2}{2}}$$

In the formula, P_N represents the comprehensive pollution index of soil heavy metal pollutant i , P_i is the average value of the single pollution index of heavy metal i , and P_{\max} is the largest single pollution index of heavy metal i . Grading standards are shown in **Table 1**.

2.4. Potential Ecological Risk Assessment of Heavy Metals in Soil

The Swedish chemist Hankanson proposed the evaluation method of potential ecological risk index in 1980. While considering the content of heavy metals in soil, it also comprehensively considers the synergy of multiple elements, pollution concentrations, differences in biological toxicity of each element, ecological effects, and environmental sensitivity to heavy metal pollution. This method is widely used in the pollution assessment of heavy metal pollution in soil.

The calculation formula is:

1) The potential ecological hazard coefficient (T_r^i) is expressed as follows

$$E_r^i = T_r^i \frac{C_i}{S_i}$$

In the formula, $\frac{C_i}{S_i}$ is the pollution index of heavy metal i ; T_r^i is the toxicity response coefficient of heavy metal i , which reflects the toxicity level of heavy metals and the sensitivity of the environment to heavy metal pollution, and is used to consider the degree of harm caused by heavy metal elements to organisms (Liu et al., 2020). The toxicity response coefficients of elements Pb, Cd, As, Zn, Ni, Cu and Hg were 5, 30, 10, 1, 5, 2 and 40, respectively.

Table 1. Grading standards of single factor pollution index and comprehensive pollution index of heavy metals in soils.

Grade	$P_i^{\textcircled{1}}$	Pollution level	$P_N^{\textcircled{2}}$	Pollution level
1	$P_i < 1$	clean	$P_N < 0.7$	clean
2	$1 \leq P_i < 2$	light pollution	$0.7 \leq P_N < 1$	moderately clean
3	$2 \leq P_i < 3$	medium pollution	$1 \leq P_N < 2$	slightly polluted
4	$P_i \geq 4$	heavily polluted	$2 \leq P_N < 3$	moderately polluted
5	-	-	$P_N \geq 3$	heavily polluted

Note: “-” means no data; ① in the table means single factor index method, ② means Nemerow index method.

2) Potential Composite Risk Index (RI)

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

The classification of soil heavy metal ecological risk factors is shown in **Table 2**.

2.5. Data Processing and Analysis

The test data were processed and plotted with Excel, SPSS 26.0 was used for multivariate statistical analysis, and ArcGIS 10.6 was used for the distribution map of sampling sites and the spatial distribution map of the content of heavy metal elements.

3. Results and Analysis

3.1. Characteristics of Heavy Metal Content in Soil

The statistical results of the content characteristics of the seven heavy metals in the study area are shown in **Table 3**. There are certain differences in the contents of heavy metal elements in the soil. The content of heavy metals in the soil

Table 2. Classification standard of potential ecological risk index.

Grade	Element Potential Ecological Risk Index		Comprehensive potential ecological risk index	
	Risk index	Risk level	Risk index	Risk level
1	$E_r^i < 40$	Low	$RI < 150$	Low
2	$40 \leq E_r^i < 80$	Medium	$150 \leq RI < 300$	Medium
3	$80 \leq E_r^i < 160$	Higher	$300 \leq RI < 600$	High
4	$160 \leq E_r^i < 320$	High	$RI \geq 600$	Extremely high
5	$E_r^i > 320$	Extremely high	-	-

Table 3. Content characteristics of 7 heavy metals in the study area.

Element	Scope (mg/kg)	Average value (mg/kg)	Standard deviation (mg/kg)	Coefficient of variation (%)	Background values ^①
Pb	18.4 - 529	93.8	106.6	113	40.6
Cd	0.22 - 1.9	0.7	0.38	56	0.218
As	7.19 - 53.9	26.3	17.06	65	18.4
Zn	66.9 - 271	144.5	51.28	35	89.7
Ni	16.1 - 85.6	39.3	15.53	39	42.5
Cu	14.6 - 138	47.4	26.38	56	65.2
Hg	0.027 - 0.199	0.1	0.05	65	0.058

Note: State environmental protection administration and China environmental monitoring station, 1990; ^① indicates the soil background value in Yunnan province.

ranges from 18.4 to 529 mg/kg of Pb, 0.22 to 1.9 mg/kg of Cd, 7.19 to 53.9 mg/kg of As, and 66.9 to 271 mg/kg of Zn. kg, Ni16.1 - 85.6 mg/kg, Cu14.6 - 138 mg/kg and Hg 0.027 - 0.199 mg/kg, the mean contents were 93.8 mg/kg, 0.7 mg/kg, 26.3 mg/kg, 144.5 mg respectively/kg, 39.3 mg/kg, 47.4 mg/kg and 0.1 mg/kg, where the contents of lead, cadmium, arsenic, zinc and mercury exceeded the background values by 2.31, 5.53, 1.43, 1.61 and 1.23 times, respectively, while the contents of Ni and Cu The mean values were lower than the soil background values in Yunnan Province, while the other elements were higher than the soil background values in Yunnan Province. The measurement results show that the study area is polluted by heavy metals to varying degrees, among which Pb, Cd and Zn pollution are the most serious, which obviously exceeded the standard.

The degree of influence of human activities in this area can be characterized by the coefficient of variation, and the grading standard is: $C_v < 10\%$ is weak variation, $10\% \leq C_v \leq 30\%$ is moderate variation, and $C_v > 30\%$ is strong variation. It can be seen from **Table 3** that the highest variation coefficient of the seven heavy metals in this area is 113% and the lowest is 35%, all of which are greater than 30% larger.

3.2. Soil Heavy Metal Pollution Assessment

The characteristics of soil heavy metal pollution in the study area are that the single-factor pollution index of Cd in the soil is 5.35, which belongs to heavy pollution; the single-factor pollution index of Pb is 2.23, which is moderate pollution; the single-factor pollution index of As, Zn and Hg is 1.43 and 1.61. and 1.23, which are lightly polluted; Ni and Cu are in the clean state (**Figure 2**).

The evaluation results of the Nemerow comprehensive pollution index of heavy metals in the soil of the mining area are shown in **Table 4**. Among them, Hg is a clean state, Cd is a light pollution, and the Nemerow comprehensive index of the remaining five heavy metal pollution is more than 3, which belongs to

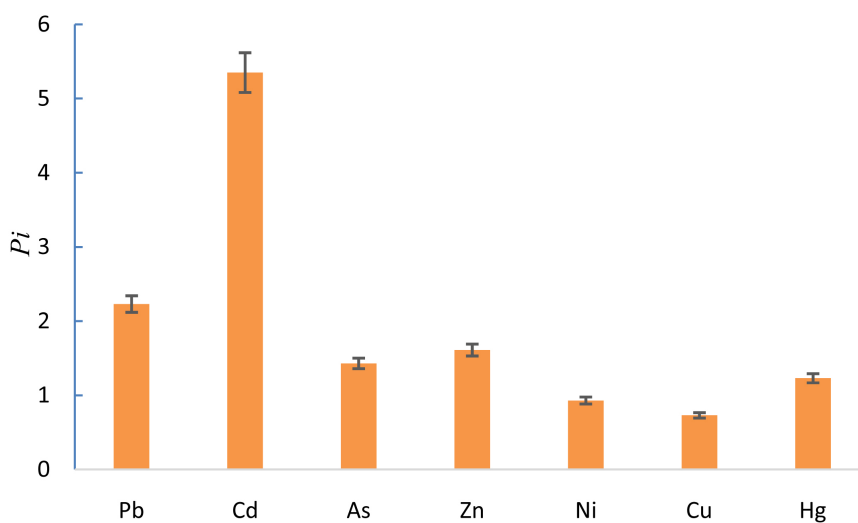


Figure 2. Soil heavy metal single factor pollution index.

Table 4. Nemerow index of soil heavy metals.

	Pb	Cd	As	Zn	Ni	Cu	Hg
Maximum value	529	1.9	53.9	271	85.6	138	0.199
Average value	93.8	0.7	26.3	144.5	39.3	47.4	0.1
P_N	385.64	1.515	59.57	240	66.6	103.18	0.173
Degree of pollution	Heavy	Light	Heavy	Heavy	Heavy	Heavy	Clean

the heavy pollution level. The results of the Nemerow index method showed that 5 of the 7 heavy metals in the soil of the mining area were severely polluted, which seriously exceeded the evaluation standard. Since the Nemerow index method highlights the impact and effect of high concentrations of heavy metals on environmental quality, in this study, the concentration of heavy metals in the sampling points near the lead-zinc mining area is relatively high, and the impact of these high concentrations of heavy metals is artificially amplified, making The evaluation results of the Nemerow comprehensive pollution index of most heavy metals are heavy pollution levels, which indicates that the impact of high-concentration heavy metal pollution at these sampling points on the overall environment around the mining area cannot be ignored and needs to be paid attention to.

3.3. Evaluation of Potential Ecological Risk Index of Heavy Metals in Soil

The potential ecological risk coefficient E_r^i and ecological risk index RI of heavy metals in the soil of the study area are shown in **Table 5**. The order of potential ecological risk coefficients of each heavy metal element in the soil of this mining area is: Cd (97.67) > Hg (68.97) > As (14.29) > Pb (11.55) > Ni (4.62) > Zn (1.61) > Cu (1.45). Among them, the potential ecological risk level of Cd is high pollution, Hg is medium pollution, and the rest of the heavy metal elements belong to low risk level.

3.4. Source Analysis of Heavy Metals in Soil

3.4.1. Correlation Analysis

The study used Pearson correlation analysis to determine the relationship between heavy metal content in soil parts. The soil Pearson correlation coefficient and its significance level are shown in **Table 6**. The correlations were significant at the level of $P \leq 0.05$, and there were significant correlations between Pb and Cd, Cd and Ni, and Zn and Hg. At the level of $P \leq 0.01$, there is a very significant positive correlation between Pb, Zn and Cd, a very significant positive correlation between Cu and Ni, and a very significant positive correlation between Hg and As. There is a very significant positive correlation between Cu and Ni, and no significant correlation with other heavy metals. There is a very significant positive correlation between Pb, Cd and Zn, and the correlation coefficient is the

Table 5. Potential ecological hazard coefficient (E_r^i) and potential comprehensive ecological risk coefficient (RI) of soil heavy metals.

Statistics	Potential Ecological Hazard Factor							$Rf^{\text{①}}$
	Pb	Cd	As	Zn	Ni	Cu	Hg	
minimum	2.3	50.68	3.91	0.75	1.9	0.45	15.34	75.33
maximum value	65.1	444.29	49.86	3.02	10.07	4.23	137.29	713.86
Overall average	11.55	97.67	14.29	1.61	4.62	1.45	68.97	200.16
Level of risk	Low	Higher	Low	Low	Low	Low	Medium	Medium

Table 6. Correlation analysis of soil heavy metal content.

	Pb	Cd	As	Zn	Ni	Cu	Hg
Pb	1						
Cd	0.402*	1					
As	-0.096	0.476**	1				
Zn	0.619**	0.709**	0.330	1			
Ni	-0.038	0.395*	0.278	0.319	1		
Cu	0.139	0.200	0.256	0.158	0.457**	1	
Hg	-0.029	0.131	0.511**	0.353*	-0.110	0.062	1

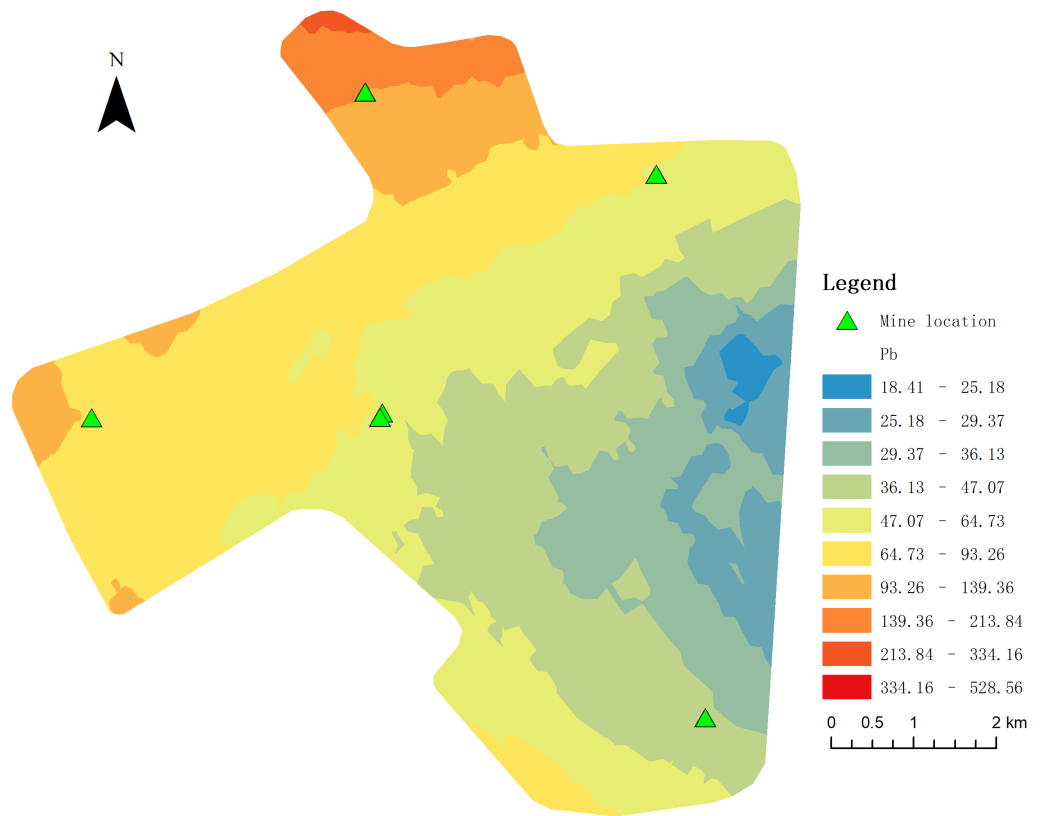
Note: *, ** indicate significant correlation at the 0.05 level and the 0.01 level.

highest, indicating that these three heavy metals have similar sources. There is a negative correlation between Pb and As, Ni, and Hg, indicating that there are different sources among them. There is a negative correlation between Hg and Ni, and their sources are different.

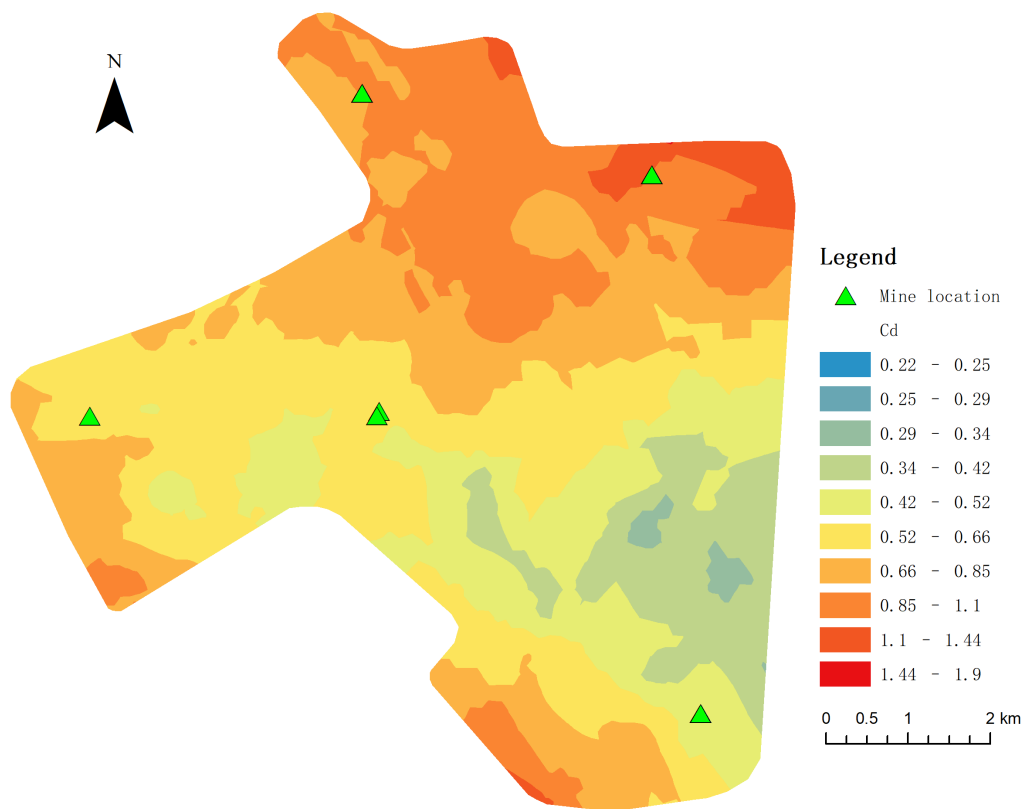
3.4.2. Spatial Correlation

Kriging is based on weighting surrounding measurements to arrive at a prediction of unmeasured values. By reflecting the distance or direction between sampling points, it can be used to account for the spatial correlation of surface changes. Both Pb and Zn are distributed in a band in the north of the study area; the highest value of Cd is mainly concentrated around the mining site in the north of the study area; As is highly concentrated in the low area near the mining site, with a planar distribution; Hg is the highest. The values are concentrated in the northern mining point group and decrease in turn toward the south (**Figure 3**). The results of the spatial correlation analysis of Pb, Cd, Zn, As and Hg show that the peaks are all around the northern mines or near the mining points in the study area, indicating that The sources of these five elements are correlated, which is consistent with the results of correlation analysis.

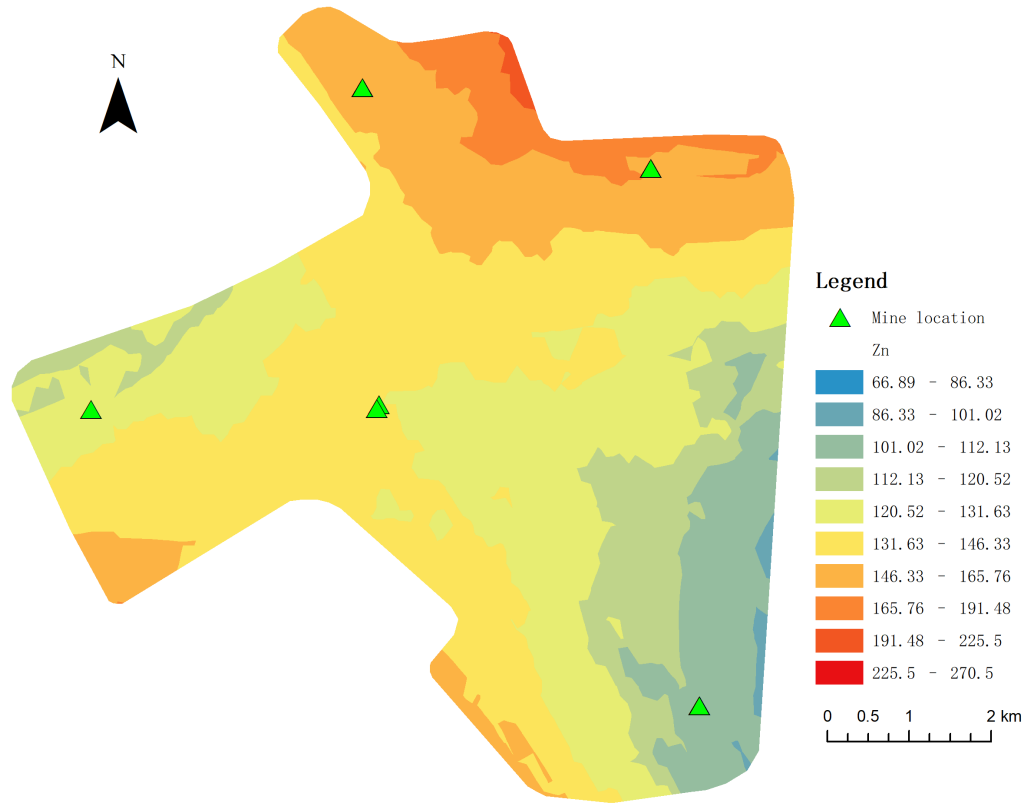
Ni in the soil mainly comes from rock weathering, atmospheric deposition or



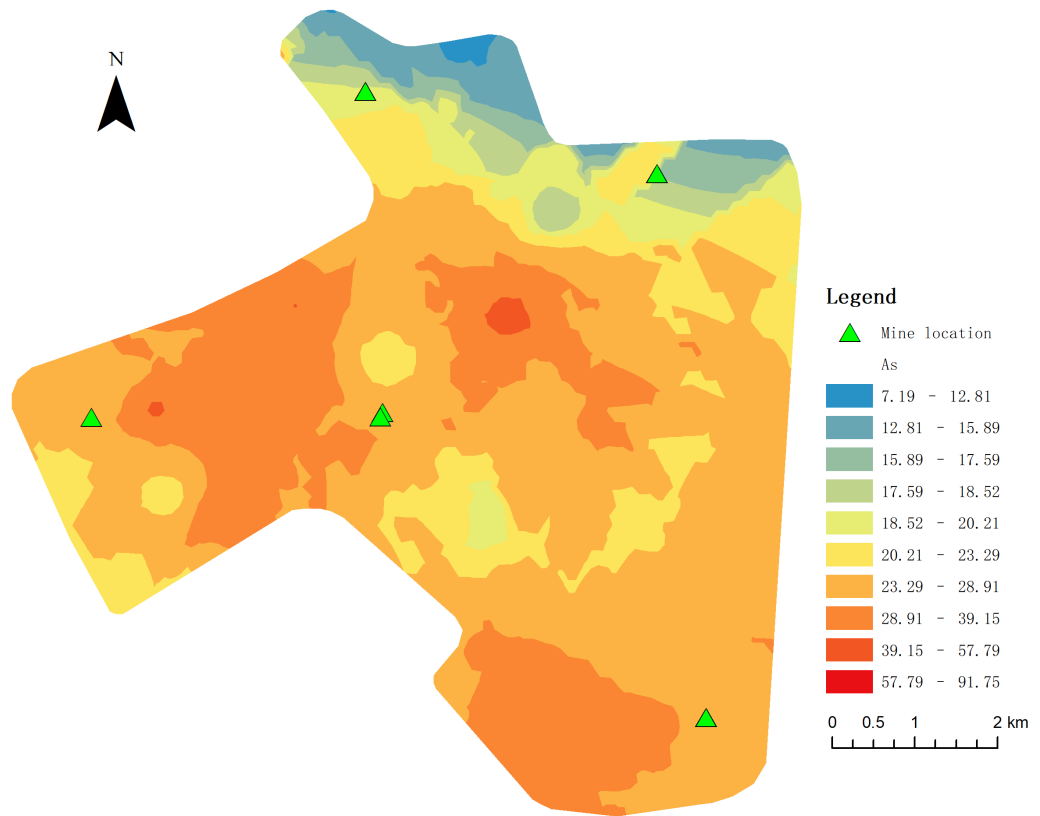
(a)



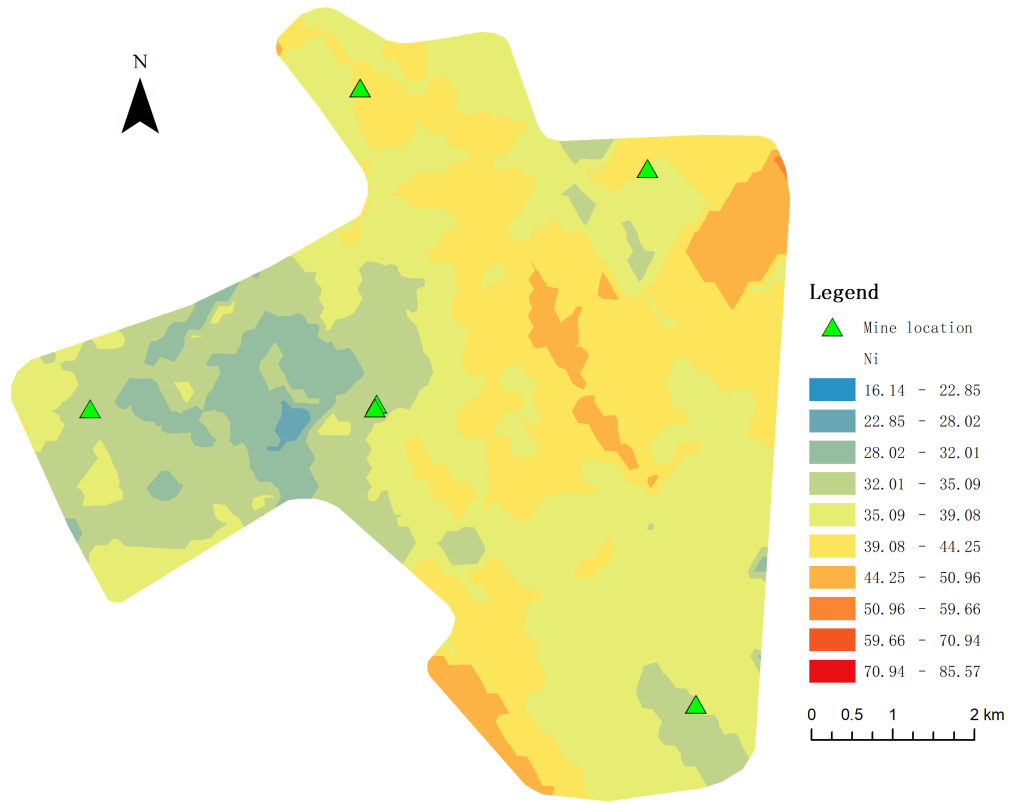
(b)



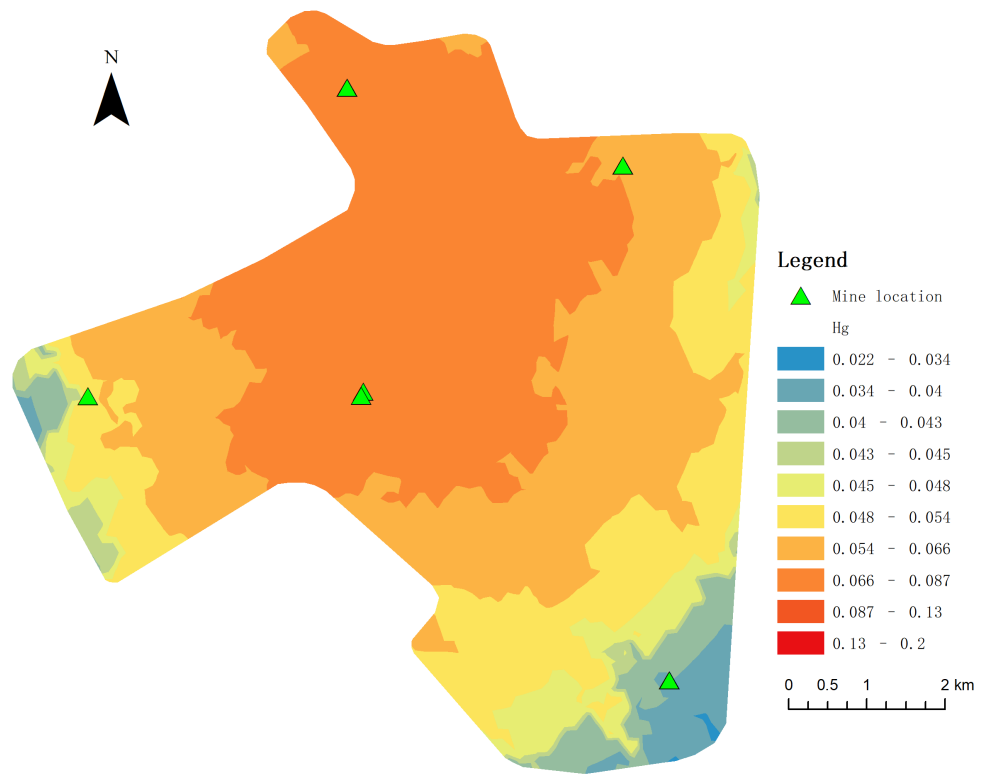
(c)



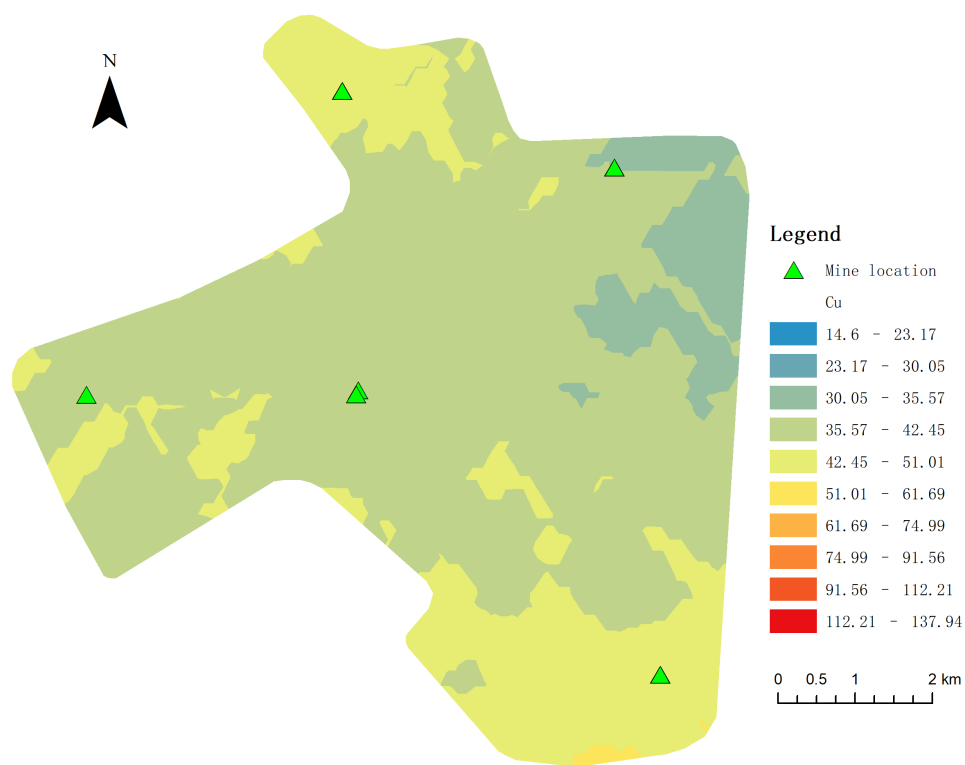
(d)



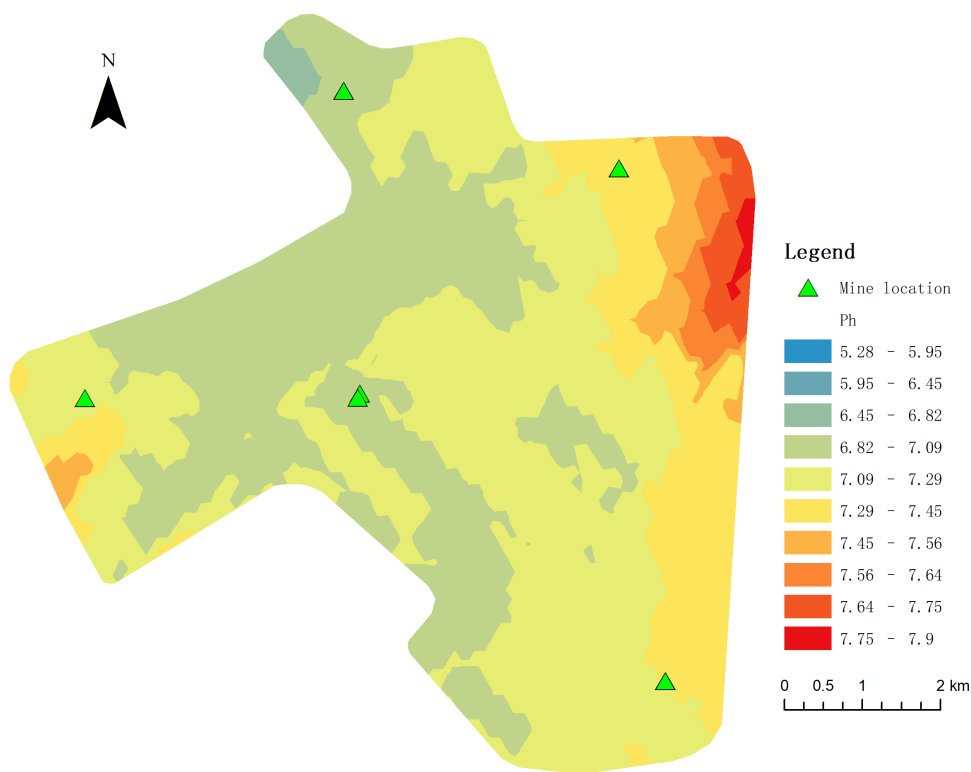
(e)



(f)



(g)



(h)

Figure 3. The spatial distribution of heavy metals in the study area, (a), (b), (c), (d), (e), (f), (g) and (h) represent (Pb), (Cd), (Zn), (As), (Ni), (Hg) (Cu) and (Ph).

symbiosis and copper ore. From the analysis of **Figure 3(g)**, it can be concluded that the high value of Cu is mainly around the ore point, which is also in line with the correlation between Ni and Cu. significant correlation. Therefore, soil-forming parent material and Cu ore mining are the main sources of Ni in soil.

3.4.3. Principal Component Analysis

To further study the relationship between heavy metals, principal component analysis was performed. PCA was used to reduce the dimensionality of seven heavy metal elements, and multiple single indicators were converted into a few comprehensive indicators, and a total of 3 comprehensive factors were obtained. The results show that the contribution rates of the first to third principal components are 39.124%, 20.034% and 18.760%, and the total contribution rate is 77.919% (**Table 7**). Through the analysis of the four principal components, it is concluded that:

The loading factors of Pb, Cd, As and Zn in the first principal component are higher, especially the two elements dominated by Cd and Zn reflect the enrichment in the soil (Liu et al., 2011). The study shows that the zinc in the soil mainly comes from zinc Lead mining, smelting and processing, etc., cadmium is extracted from zinc-lead ores and sulfur-cadmium ores as by-products. The enrichment of cadmium and zinc in soil is closely related to lead-zinc mining in the study area, which is related to **Table 6**. The analysis results are consistent, so the first principal component mainly represents human activities such as mining operations.

The proportion of Hg and As in the second principal component contributed 20.023%, and the positive load was higher, which also reflected the source of Hg and As. Correlation analysis showed that Hg was significantly significant with As and Zn, and negatively correlated with Pb, indicating that its sources are not similar, and the significant sources of As and Cd indicate that they have similar sources. The data show that Hg and As are the main sources. It is enriched in the vicinity of the mining site, and is released in the mining and smelting of the mining area and finally enters the soil environment after migration and transformation.

The third main component of nickel and copper is 18.76%. Ni is mainly from geological sources, reflecting the accumulation of soil parent materials and their weathering products. There is very little elemental Cu in the natural environment, mainly in the minerals, there is a significant correlation between Cu and Ni, so it is judged that there is a similar source or there is complex pollution. Through the observation of **Table 7** and **Table 8**, it can be concluded that the general situation of heavy metal pollution can be reflected objectively by these three principal components. Therefore, the selected three principal components are analyzed, using these three comprehensive factors (PC1, PC2, PC3). It can fully reflect a large amount of information in the original data.

Table 7. Principal component analysis of soil heavy metals.

Element	Initial eigenvalues			Extract the load sum of squares		
	Total	Variance %	Accumulation %	Total	Variance %	Accumulation %
1	2.739	39.124	39.124	2.739	39.124	39.124
2	1.402	20.034	59.158	1.402	20.034	59.158
3	1.313	18.760	77.919	1.313	18.760	77.919
4	0.747	10.674	88.593			
5	0.442	6.310	94.903			
6	0.236	3.368	98.271			
7	0.121	1.729	100.000			

Table 8. Initial factor load matrix of soil heavy metals.

Heavy metal	Element		
	1	2	3
Pb	0.483	-0.772	-0.140
Cd	0.841	-0.160	0.005
As	0.637	0.609	-0.182
Zn	0.857	-0.317	-0.216
Ni	0.536	0.193	0.687
Cu	0.462	0.210	0.558
Hg	0.399	0.478	-0.657

4. Conclusion

In the 0 - 20 cm soil layer of the mining area, the content, ecological risk and correlation of each heavy metal element were analyzed. Pb, Cd, As, Zn and Hg exceeded the soil background values in Yunnan Province by 2.31, 5.53, 1.43, 1.61 and 1.23 times, respectively, and Pb, Cd and Zn were the most polluted. The coefficients of variation are all greater than 30%, indicating that the soil heavy metal content in the study area is very likely to be polluted by external factors.

The single-factor pollution degree of heavy metal pollution in soil was as follows: Cd and Pb were heavily polluted and moderately polluted, As, Zn, Hg were mildly polluted, and Ni and Cu were clean. Using the Nemerow comprehensive index evaluation method, it is concluded that the Pb, As, Zn, Ni and Cu in this area are heavily polluted, and the rest are light or clean.

The potential ecological risk index evaluation method found that the potential ecological risk level of Cd was high pollution, Hg was medium pollution, and the rest of heavy metal elements belonged to low risk level. Its potential comprehensive ecological risk index is 200.16, which is a medium risk level.

The PCA results show that the sources of heavy metals can be divided into Pb, Cd, As, Zn and Hg mainly from anthropogenic activities such as mining, while Ni and Cu are mainly from the combined effects of soil-forming parent materials, mining operations and agricultural activities.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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