

Article

Speciation Analysis and Pollution Assessment of Heavy Metals in Farmland Soil of a Typical Mining Area: A Case Study of Dachang Tin Polymetallic Ore, Guangxi

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Abstract: To explore the distribution characteristics and degree of pollution of heavy metals in the farmland soil around the Dachang tin polymetallic mining area in Guangxi, a total of 140 soil samples were collected around the mining area in this study. The total amount and various forms of seven heavy metals (Cu, Pb, Cd, Cr, Zn, As, and Ni) were analyzed by inductively coupled plasma mass spectrometry, and the improved continuous extraction method of heavy metal speciation analysis in the soil, the potential ecological risk index (RI) , the and Nemerow evaluation index (P_N) were used to evaluate pollution characteristics of the soil and the bioavailability of heavy metals. Corresponding remediation suggestions were given according to the pollution degree. The results show that the whole soil in the study area is acidic, reducing, and the content of organic matter is low. The average content of heavy metal elements is higher than the background value of Guangxi, among which Cd, Pb, and As exceed the control value and are the main elements of pollution. The speciation analysis of heavy metals in soil shows that Cd is dominated by the ion exchange form; Cu is mainly residual and in a humic acid combined form; and the rest of the elements are mainly in residual form. Among the seven heavy metals, Cd has the strongest mobility, biological toxicity, and ecological risk, followed by As, Ni, and Zn. The overall pollution level of the soil in the study area is heavily polluted (P_N = 39.6), which is a very strong ecological risk level (*RI* = 2196.9), and the main pollutants are Pb, As, and Cd; Cd pollution is the most serious. Correlation (CA) and principal component analysis (PCA) indicate that the pollution sources of Pb, Cu, Zn, Cd, and As among the seven elements were mainly controlled by tailings accumulation, mining, and transportation, and the sources of Cr and Ni were controlled by soil-forming parent materials. Furthermore, according to the actual situation of the farmland around the mining area, two remediation suggestions are put forward: (1) use stabilization remediation technology to clean up the pollution source, such as calcium dihydrogen phosphate to reduce the bioavailability of the most polluted elements, Cd and Pb, in the soil; (2) under the concept of green environmental protection, use *Typha orientalis* Presl to repair the industrial and mining wasteland and some unused land.

Keywords: heavy metal; existing form; bioavailability; risk assessment; Dachang mining area

1. Introduction

The exploitation of mineral resources has greatly promoted the development of regional economies, but long-term mining and the stacking of tailings have also become the source of environmental hazards under economic prosperity [\[1,](#page-10-0)[2\]](#page-10-1). In particular, the release, migration, and transformation of heavy metals in the environmental medium have a great impact, causing serious pollution to the surrounding soil, water bodies, and habitats, threatening the ecological balance and human security [\[3–](#page-10-2)[5\]](#page-10-3), and restricting the construction of an ecological civilization. Soil is the most important medium to maintain balance and stability of an ecosystem, especially the soil quality of agricultural land [\[6,](#page-10-4)[7\]](#page-10-5).

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The content of heavy metals in soil is mainly controlled by soil-forming parent materials and human activities. Human activities such as sewage irrigation, mining and smelting of metal ores, and combustion of industrial wastes and fossil fuels have been proven to be the main causes of heavy metal pollution in the soil of China $[8–10]$ $[8–10]$. Among them, the mining of metals, beneficiation, and smelting activities are the main human activities that cause heavy metal pollution in soil, water, and the biosphere [\[11\]](#page-10-8). It is reported that the area of polluted soil is increasing at a rate of $46,700$ hm² every year due to mining in China [\[12\]](#page-10-9). Therefore, the phenomenon of heavy metal pollution in soil related to mining activities has always been a research hotspot.

In recent years, studies have shown that mining activities cause soil heavy metal pollution [\[13\]](#page-10-10). In many parts of the world, heavy metals produced by mining activities cause serious environmental problems, especially when they pollute the surrounding farmland [\[14\]](#page-10-11). Concerns and research surrounding heavy metal polluted soil caused by mining are increasing all over the world. Redwan et al. evaluated the environment quality of the Barramiya gold mine area in the eastern desert of Egypt and found that there are 318–500 t tailings in the area, which cause serious heavy metal pollution to the surrounding environment due to erosion, weathering, and surface runoff [\[15\]](#page-10-12). Akoto et al. analyzed the heavy metals of different solid mine wastes in a Ghana mining area and found that the degree of ecological risk varies with the type of wastes: tailings > sulfide > oxide [\[16\]](#page-10-13). Yun et al. studied heavy metals in farmland around an abandoned gold mine in South Korea and found that farmland types have an impact on the spatial distribution of heavy metals in soil [\[17\]](#page-11-0). The geochemical characteristics of ore samples and of stream-sediment samples from the Tri-State district indicated that past mining activities and leaded gasoline have had significant effects on lead concentrations in river sediments [\[18\]](#page-11-1). Taylor et al. investigated heavy metals (Cd, Cu, Pb, and Zn) from the Pb–Zn–Ag and Cu mines at Mount Isa, Queensland, Australia, and showed that the heavy metal content in the surface soil near the mining area (within 2 km) was obviously higher than that far away and that the ecological risk level of lead was very high [\[19\]](#page-11-2).

Dachang Town in Guangxi is an important tin polymetallic production area in China. It is known as "China's Cenozoic tin capital" and has long-term mining history. However, in the process of early development and utilization, large amounts of tailings were not fully utilized and accumulated on the surface due to the constraints of technical conditions and production concepts. The tailing dumps have been under the action of oxidation for a long time, and the heavy metal elements (e.g., Cu, Pb, Zn, and Cd) have been gradually activated, invading the surrounding soil through rainwater leaching, atmospheric dust, and other ways, threatening the ecological environment of farmland soil and endangering the health of residents through food chain enrichment. Therefore, it is urgent to carry out research on heavy metal pollution of soil in the area. By collecting soil samples from farmland in natural villages around the mining area, analyzing the content of typical heavy metal elements, organic matter, and pH value, and extracting the occurrence form using the improved Tessier seven-step continuous method, we thereby reveal the spatial variation characteristics, migration laws, and pollution sources of heavy metals and comprehensively evaluate the pollution degree and environmental risk effects of heavy metals. This provides a scientific basis for the treatment and restoration of heavy metals in soil of the area and effectively promotes the protective environmental mining of metal mines in the area.

2. Materials and Methods

2.1. Study Site

Dachang mining area is situated in Dachang Town in southwestern Nandan county, Guangxi (Figure [1a](#page-2-0)–d). It is the main mineral concentration area in the county. The total coverage area of the town is 283 km², and the total urban population is more than 30,000, of which 18,000 are mining workers and their family members alone. It is a typical mining town. The study area involves 22 natural villages. The geographical coordinates are $107°33'44''~107°38'21''$ E and $24°48'36''~24°52'25''$ N. The study area is north of the Tropic of Cancer and belongs to the northern climate zone of the middle subtropical zone. It has of Cancer and belongs to the northern climate zone of the middle subtropical zone. It has the climate characteristics of a plateau mountain area. The annual mean precipitation is the climate characteristics of a plateau mountain area. The annual mean precipitation is approximately 1400 mm, and the annual mean temperature is 17.2 ◦C. The natural soil in approximately 1400 mm, and the annual mean temperature is 17.2 °C. The natural soil in the area is mainly loam, followed by sandy loam; the soil color is mainly black, gray-black, the area is mainly loam, followed by sandy loam; the soil color is mainly black, gray‐black, and yellow-brown; and the parent material of the soil is mainly sand shale, followed by and yellow‐brown; and the parent material of the soil is mainly sand shale, followed by sandstone and shale [\[20\]](#page-11-3). sandstone and shale [20].

town. The study area involves 22 natural villages. The geographical coordinates are

Figure 1. Location diagram of the study area in China and Guangxi (a-d) and distribution diagram of soil sampling (**e**). of soil sampling (**e**).

2.2. Sample Collection and Chemical Analysis 2.2. Sample Collection and Chemical Analysis

Using geographic information system technology and the grid method, the sample Using geographic information system technology and the grid method, the sample points are evenly distributed in the whole study area. During the sampling process, accessibility and safety were carefully considered, and 140 sampling points were determined in combination with the actual topography around the Dachang mining area (Figure [1e](#page-2-0)). Each sample was collected from a 0–20 cm thick layer of soil. To maximize the representativeness of the samples, five subsamples collected from each square were mixed into a comprehensive soil sample on site. We removed impurities such as stones and debris from the samples. The weight of each composite sample was about 1 kg. After being crushed with a wooden mallet, all the samples were passed through 100 mesh sieves, were fully mixed and weighed, and were put into a polyethylene sample bottle before chemical analysis.

The sample pretreatment for the determination of the total amount of heavy metals in soil was in accordance with the Ministry of Ecology and Environment of the People's Repub-

lic of China (HJ832-2017) [\[21\]](#page-11-4). After the sample was digested by $HNO₃-HCl-HF-HClO₄$ (Mars 6 classic, CEM) it was determined by inductively coupled plasma mass spectrometry (ICP-MS). The pH value and organic matter content of the soil were determined by the potentiometric method and the potassium dichromate oxidation colorimetric method, and the EH value was analyzed by an OPR-422 redox potentiometer. The speciation analysis of heavy metals in soil was extracted step-by-step in strict accordance with the technical standard for evaluation and analysis of eco-geochemical samples (DD2005-03) [\[22\]](#page-11-5). The reagents used for analysis were superior grade pure. We simultaneously analyzed the total amount, weak acid extraction form, reducible form, and oxidizable form of the reagent blank and sediment reference material BCR701 to reduce errors. The recovery of heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) in the reference materials was 118%, 86%, 88%, 120%, 87%, 109%, and 97%, respectively, which met quality control standards.

2.3. Risk Assessment and Data Processing

2.3.1. Single Factor Pollution Index (SFPI)

The SFPI is one of the most effective methods to evaluate heavy metal pollution degree. The equation is as follows; however, its results do not reflect the level of pollution in the whole area:

$$
P_i = \frac{C_i}{B_i} \tag{1}
$$

where P_i is the pollution index of element *i*, C_i is the measured data for metal *i*, and B_i is the soil background value. The heavy metal content of the soil in Guangxi measured in 1990 was used as the background value of the study. The values of Cd, As, Cu, Pb, Zn, Cr, and Ni are 0.27, 20.5, 27.8, 24.0, 75.6, 72.1, and 26.6 mg/kg, respectively.

2.3.2. Nemerow Integrated Pollution Index (NIPI)

The NIPI is a perfect supplement to the shortcomings of the SFPI. It can comprehensively evaluate the overall pollution level of the study area and make comparisons between different areas [\[23,](#page-11-6)[24\]](#page-11-7). The index is calculated using the following equation:

$$
P_N = \sqrt[2]{\left(\frac{(Pi)_{ave}^2 + (Pi)_{max}^2}{2}\right)}
$$
 (2)

where P_N is the soil pollution index and (P_i) *ave* and (P_i) *max* are the average and maximum values of the pollution element *i* within a specific area, respectively. The classification criteria for assessment of the soil heavy metal pollution index are shown in Table [1](#page-3-0) [\[25\]](#page-11-8).

2.3.3. Potential Ecological Risk Index (PERI)

The PERI has been proposed by Swedish scientist Hakanson. It is a method to evaluate heavy metal pollution in soil or sediment from the perspective of sedimentology according to the properties and environmental behavior characteristics of heavy metals. The method not only considers the content of heavy metals in soil, but also comprehensively considers the synergistic effect of multiple elements, toxicity level, pollution degree, and environmental sensitivity to heavy metal pollution, so it has been widely used in environmental risk assessment [\[26\]](#page-11-9). The expression is as follows:

$$
RI = \sum_{i}^{k} E_{r}^{i} = \sum_{i}^{k} T_{n}^{i} \times \frac{C_{i}}{B_{i}}
$$
(3)

where *RI* represents the PERI of various heavy metals in soil; *Er i* is the potential ecological risk coefficient of type *i* heavy metal; *Cⁱ* is the concentration of type *i* heavy metal (mg/kg); B_i is the parameter ratio of type *i* heavy metal (mg/kg); T_n^i is the toxicity coefficient of type *i* heavy metal. In this study, the toxicity coefficients of As, Ni, Cd, Cr, Cu, Pb, and Zn are 10, 5, 30, 2, 5, 5, 5, and 1, respectively [\[27\]](#page-11-10). Table [2](#page-4-0) shows the corresponding values of ecological risk levels and different indexes.

Table 2. Corresponding range of ecological risk level in soil.

2.3.4. The Migration Coefficient (MC) and Bioavailability Coefficient (BC)

Among the seven forms of heavy metals, the water-soluble form and the ion exchange form are the most easily exchanged by other ions, and easy to be directly used by plants [\[28\]](#page-11-11). They have a strong migration ability and are sensitive to environmental changes. These two forms are usually used to calculate the mobility of heavy metals and are important indicators for evaluating soil heavy metal pollution. The carbonate-combined form can be extracted by mild acid, which is easily absorbed and utilized by organisms. Therefore, the bioavailability of heavy metals in soil is calculated by the sum of the water-soluble form, the ion exchange form, and the carbonate combined form [\[7\]](#page-10-5). The MC and BC are calculated as follows:

Migration coefficient (MC) =
$$
\frac{(F1 + F2)}{(F1 + F2 + F3 + F4 + F5 + F6 + F7)}
$$
(4)

Bioavailability coefficient (BC) =
$$
\frac{(F1 + F2 + F3)}{(F1 + F2 + F3 + F4 + F5 + F6 + F7)}
$$
(5)

where *F*1 and *F*2 represent the water-soluble form and the ion exchange form, *F*3 and *F*4 represent the carbonate combined form and the humic acid combined form, *F*5 and *F*6 represent the iron–manganese oxide combined form and strong organic combined form, and *F*7 represents the residual form.

2.3.5. Data Processing

Arithmetic mean and range were used to analyze the concentration of heavy metals in the study area. The Pearson's correlation analysis (CA) and principal component analysis (PCA) were used to explore the sources of metal elements and establish the relationships between heavy metals and other variables in the soil. All analyses were carried out using SPSS 26.0 Origin Pro 2021, and Excel. ArcGIS 10.8 and CorelDRAW 2020 were used for drawing.

3. Results

3.1. Content Characteristics of Heavy Metal in Soil

Table [3](#page-5-0) shows the descriptive statistical data of physical and chemical properties and heavy metal content in the soil around the mining area. The overall soil is acidic, with the pH value ranging from 3.7 to 7.7 and an average value of 5.9. Among them, 86% of the soil is acidic and 34% is strongly acidic. The range of organic matter content is 0.5–10.5 g/kg, with an average of 4.3 g/kg , which indicates that organic matter content in soil is small

and might affect the activity of heavy metals. The content ranges of heavy metals (Cr, Ni, Cu, Pb, Zn, As, and Cd) were 32.7–169.2 mg/kg, 9.1–151.7 mg/kg, 13.4–328.7 mg/kg, 1.8–7104.5 mg/kg, 16.8–20,075 mg/kg, 1.2–4097.9 mg/kg, and 0.2–255.9 mg/kg, respectively. The average content shows a change in the trend of Zn (2422.0 mg/kg) > Pb (730.0 mg/kg) > As (307.1 mg/kg) > Cu (86.5 mg/kg) > Cr (66.9 mg/kg) > Ni (42.7 mg/kg) $>$ Cd (16.4 mg/kg). Except for Cr and Ni, the average contents of the other five elements are higher than background values in Guangxi, indicating that the heavy metal elements in the soil are enriched to different degrees. Among them, Cd and Zn reach 61.4 times and 32.0 times their background values, respectively. Pb reaches 30.4 times the background value, and As and Cu are 5.3 times and 3.1 times higher than their background values, respectively. The results show that the mining and smelting of non-ferrous metals can obviously lead to the accumulation of some heavy metals (e.g., Cd, Zn, Pb) [\[29](#page-11-12)[,30\]](#page-11-13). According to the Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (GB15618-2018) [\[31\]](#page-11-14), Cd, As, Pb, and Zn exceed the risk screening values, and Cd, As, and Pb even exceed the risk intervention values, indicating that Cd, As, Pb, and Zn are obviously enriched and the main pollution elements in the soil, a fact that needs special attention.

3.2. Speciation Characteristics of Heavy Metals

The speciation characteristics of heavy metal in the soil around the mining area are presented in Table [4](#page-6-0) and Figure [2.](#page-6-1) Cr is mainly in residual form, with an average content of 58.67 mg/kg, accounting for 82.04% of the 7 forms, followed by humic acid combined form of 9.52%. Arsenic is mainly in residual form, with an average content of 172.02 mg/kg, accounting for 69.15% of the 7 forms. Ni, Pb, and Zn are mainly in residual form, accounting for 59.85%, 57.34%, and 61.11%, respectively, followed by iron– manganese oxide combined form, of which Pb accounts for the highest proportion, reaching 22.86%. Some studies show that Pb in air dust is mainly in iron–manganese oxide form [\[32\]](#page-11-15). Cu is mainly in residue form and humic acid combined form, followed by iron–manganese oxide combined form and strong organic combined form. Cd is mainly in ion exchange form, with an average content of 26.72 mg/kg, accounting for 24.12%, and the proportions of other forms are in the following order: strong organic combined form > humic acid combined form > iron–manganese oxide combined form > residual form > carbonate combined form > water-soluble form.

Table 3. Statistical parameters of pH value, organic matter, and heavy metal content of the farmland soil around Dachang mining area.

* Refers to China National Environmental Monitoring Center [\[33\]](#page-11-16).

Element	Water-Soluble Form	Ion Exchange Form	Carbonate Combined Form	Humic Acid Combined Form	Iron-Manganese Oxide Combined Form	Strong Organic Combined Form	Residual Form
Cr^*	0.16	0.41	0.56	6.81	1.35	3.55	58.67
$Ni*$	0.36	0.44	1.44	2.36	6.02	5.01	23.30
Cu *	0.40	0.49	2.85	62.38	25.93	20.29	76.84
Pb^*	4.26	0.60	61.50	625.74	1017.02	188.54	2551.00
Zn *	115.21	93.73	387.57	546.96	1253.83	959.23	5273.57
As*	7.01	0.97	6.43	43.51	7.27	11.55	172.02
Cd *	4.72	26.72	10.53	17.64	16.08	20.03	15.04

Table 4. Contents of different forms of heavy metals in soil around Dachang mining area.

* Represents the arithmetic mean contents of different speciation.

Figure 2. The proportion chart of different forms of heavy metals in the farmland soil around the Dachang mining area. Dachang mining area. **Figure 2.** The proportion chart of different forms of heavy metals in the farmland soil around the

with the change in environmental conditions is in the following order: Cd > As > Ni > Zn \sim Cr $>$ Cu $>$ Pb; the order of the biological availability of each heavy metal element with the change in environmental conditions is: Cd > Zn > As > Ni > Cu > Cr > Pb. Compared with other elements, the absolute content of water-soluble, ion exchange, and carbonate combined forms of Cd is higher. Cd is the most active and easily absorbed and utilized by plants, thus accumulating toxicity in organisms, followed by As, Ni, and Zn. The residual form of Cr, Cu, and Pb elements are higher, and the biological activity and mobility of these heavy metals are poor. Figure [3](#page-7-0) shows that the migration ability of each heavy metal element in farmland soil

Figure 3. Column diagram of mobility coefficient and bioavailability coefficient of heavy metal. **Figure 3.** Column diagram of mobility coefficient and bioavailability coefficient of heavy metal.

3.3. Ecological Hazard Assessment 3.3. Ecological Hazard Assessment

these heavy metals are poor.

According to the measured data and Equations (1) and (2), corresponding values (the P_i and *P_N*) can be obtained. The single pollution index range of each pollutant is 0.3–0.6 for P_{Cr}, for PC reduced $\frac{1}{2}$. $\frac{1}{2}$ for $\frac{1}{2}$ for $\frac{1}{2}$ for $\frac{1}{2}$, $\frac{1}{2}$, for P_{Cd}. The level of P_i in the farmland soils around the Dachang mining area can be ordered
for P_{Cd}. The level of P_i (2.3) s P₁ (2.4) s P₁ (2.4) s P₁ (2.6) s P₁ (2.6) s P₁ (2.4) In the subgla as: P_{CA} (8.1) > P_{Zn} (12.1) > P_{PB} (8.1) > P_{AS} (7.7) > P_{CB} (1.7) > P_{NI} (6.6) > P_{CF} (6.1). In the whole polluted by the soil is not polluted by Cr and Ni, is slightly polluted by Cu, and is extremely polluted by the other four elements (Cd, Zn, Pb, and As) $[18,19]$ $[18,19]$. The Nemerow integrated pollution index (P_N) is 39.6, and the pollution level is extremely polluted. Notably, Cd pollution matrix (*P_N*) is 39.6, and the pollution index, with a contribution rate ranging contributes the most to the comprehensive pollution index, with a contribution rate ranging from 33% to 89%, and its contribution rate is as high as 68% in the whole study area. 0.3–1.5 for P_{Ni} , 0.4–4.2 for P_{Cu} , 0.7–32.5 for P_{Pb} , 2.0–44.9 for P_{Zn} , 0.5–17.4 for P_{As} , and 3.3–258.3 as: P_{Cd} (54.7) > P_{Zn} (12.1) > P_{Pb} (8.1) > P_{As} (7.7) > P_{Cu} (1.7) > P_{Ni} (0.6) > P_{Cr} (0.4). In the whole

According to Equation (3), the PERI of soil samples can be calculated, and the results are as follows. The level of E_i heavy metals in the farmland soils around the Dachang mining area can be ordered as: E_{Cd} (1842.6) > E_{Pb} (152.1) > E_{As} (150.0) > E_{Zn} (12.1) > E_{Cu} (1.7) > E_{Ni} (0.6) > E_{Cr} (0.4). The risk of Cd is the most significant, which belongs to the extremely strong ecological hazard level, followed by As and Pb, which belong to the relatively strong ecological hazard level. Zn, Cu, Ni, and Cr belong to the slight ecological risk level. The potential ecological hazard index (*RI*) of the study area is 2196.9, which belongs to the extremely strong ecological hazard level. The contribution rate of Cd is as high as 84%, which is the main pollution element. This result is highly consistent with the evaluation result of the Nemerow integrated pollution index.

3.4. Source Identification index.

3.4.1. Correlation Analysis (CA)

The correlation analysis between heavy metals can reflect whether they have homology and provide rich information for judging the source of substances. Table [5](#page-8-0) shows that Cr is positively correlated with the other 6 elements, but the correlation is not significant. Ni is significantly correlated with Cu ($p < 0.01$) and negatively correlated with Pb ($p < 0.05$). There is a significant positive correlation between Cu and Zn, Cd, Pb, and As ($p < 0.01$). The correlation coefficients of Zn, Cd, Pb, and As are Zn/Pb, (0.758), Zn/As (0.815), Zn/Cd (0.964), Pb/As (0.839), Pb/Cd (0.785), and As/Cd (0.831), which are all greater than 0.75, indicating a significant positive correlation, meaning they have similar formation causes or common influence factors. The content of organic matter in soil is negatively correlated with Cr and Ni $(p < 0.05)$ and positively correlated with Pb and As. The correlation is

significant, which is in line with the law that the content of Pb and As increases when the soil changes from acid to neutral. The Eh value is significantly negatively correlated with Ni, Cu, Pb, Zn, As, and Cd $(p < 0.01)$, indicating that, the lower the Eh value, the stronger the soil reduction ability and the higher the content of heavy metals.

Table 5. Correlation coefficients among heavy metals, pH, Eh, and organic matter.

Item	Cr	Ni	Cu	Zn	C _d	Pb	As	Organic Matter	pН	Eh
Cr										
Ni	0.113									
Cu	0.148	$0.358**$								
Zn	0.174	0.086	$0.712**$							
C _d	0.160	$-0.570*$	$0.631**$	0.964 **						
Pb	0.037	-0.058	$0.633**$	$0.758**$	$0.785**$					
As	0.072	-0.047	$0.596**$	$0.815**$	$0.831**$	$0.839**$				
organic matter	$-0.560**$	$-0.338**$	0.129	0.301	0.211	0.266 **	$0.385**$			
pH	-0.083	$0.369**$	$0.443**$	$0.547**$	$0.628**$	$0.518**$	$0.512**$	0.248		
Eh	0.132	$-0.338*$	$-0.449**$	$-0.507**$	$-0.581**$	$-0.482**$	$-0.498**$	-0.206	$-0.945**$	

Notes: ** Correlation is significant at the 0.01 level (double-tailed), * Correlation is significant at the 0.05 level (double-tailed).

3.4.2. Principal Component Analysis (PCA)

To identify and quantify the sources of the seven heavy metals in soil, PCA was used to further analyze the sources of heavy metals in soil more accurately. Firstly, the data were tested by KMO and Bartlett sphere, and the KMO value of the test result was 0.886. Therefore, the dataset was suitable for PCA. The analysis results are shown in Tables [6](#page-8-1) and [7.](#page-9-0) The cumulative variance percentage contribution of the front three principal components is 87.137%, which basically represents the indicators of heavy metal in the study area. The variance contribution rate of the first principal component is 54.72%. The load values of Cu, Pb, Zn, Cd, and As are relatively large among the 7 elements, all of which are greater than 0.6. Meanwhile, they are significantly correlated with each other in the CA. Field investigation also found that they are high in the farmland soil near the mining area and along the road, and the mining of tin polymetallic ore produces a large number of tailings containing a certain amount of Cd, Pb, and Cu. The oxides and sulfides of the above elements may enter the environment through the weathering process and cause serious pollution to the surrounding soil [\[34,](#page-11-17)[35\]](#page-11-18). Therefore, it is speculated that the first principal component is enriched by the influence of tailings accumulation, mining, and transportation. The contribution rate of PC2 (the second principal component) is 17.82%, and the highest load value is Ni. Ni has a significant positive correlation with Cu, but not with other elements. It is speculated that it may be related to sewage irrigation, pesticides, and soil-forming parent materials. The load value of Cr is the highest in the third principal component, with a contribution rate of 14.60%. The correlation between Cr and the other six elements is not significant. It is considered that Cr is related to the soil–forming parent materials.

Table 6. Total variance explained and component matrices for heavy metals.

		Principal Components Factor Load		Rotated Principal Components Factor Load			
Elements	PC ₁	PC2	PC ₃	PC ₁	PC ₂	PC ₃	
Сr	0.184	0.488	0.852	0.065	0.063	0.994	
Ni	0.132	0.866	-0.396	-0.039	0.959	0.052	
Cu	0.750	0.365	-0.199	0.664	0.538	0.069	
Zn	0.953	-0.044	0.039	0.941	0.107	0.119	
Cd	0.963	-0.039	0.014	0.951	0.125	0.100	
Pb	0.843	-0.255	-0.016	0.877	-0.070	-0.036	
As	0.884	-0.208	0.009	0.908	-0.034	0.012	

Table 7. Composition matrix of heavy metals.

3.5. Suggestions for Pollution Remediation

Remediation of heavy metal contamination in soil refers to the process of removing heavy metals from soil or immobilizing them in soil to reduce their mobility and bioavailability, thereby reducing the health and environmental risks of heavy metals. Common methods include physical, chemical, and biological methods. According to the heavy metal pollution elements and the pollution degree of the soil around the mining area, combined with the actual situation, the following two suggestions are given:

(1) Clean up the pollution source by using stabilization repair technology. The pollution in the Dachang mining area and its surrounding areas is related to the discharge of waste slag, wastewater, and exhaust gas in the early stage. Therefore, the remediation of the soil in this area must start with cleaning up the pollution sources. Due to the large area of contamination, the guest soil and soil replacement methods are obviously not economically feasible. Considering the advantages and disadvantages of various remediation technologies and the actual situation in the field, it is recommended that stabilization reagents be added in the soil to reduce the mobility and bioavailability of heavy metals in the soil and prevent the transfer of heavy metals to the food chain. Referring to the study results of [\[36\]](#page-11-19), it is suggested to use calcium dihydrogen phosphate to reduce the bioavailability of Pb and Cd in the soil. After soil remediation is completed, it is useful to plant Pb and Cd resistant crops, such as corn.

(2) There are serious Cd, As, and Pb pollution issues in the industrial and mining wasteland and some unused land in the study area. Studies have shown that *Typha orientalis* Presl can absorb As, Cd, and Pb in the soil, accumulate, and fix them in the root [\[37\]](#page-11-20). Therefore, it is suggested to plant *Typha orientalis* Presl in these regions to achieve the goal of remediating and beautifying the environment.

4. Conclusions

(1) The study concludes that the mean concentrations of heavy metals in the farmland soil around Dachang mining area are in the decreasing order of Zn (2422.0 mg/kg) > Pb (730.0 mg/kg) > As (307.1 mg/kg) > Cu (86.5 mg/kg) > Cr (66.9 mg/kg) > Ni (42.7 mg/kg) $>$ Cd (16.4 mg/kg). The soil is generally acidic, in a reduced state, with low organic matter content. Cd, As, and Pb even exceed the risk intervention values, indicating that Cd, As, and Pb are significantly enriched and that they are the main pollution elements of soil.

(2) Speciation analysis of heavy metals shows that Cd in soil is mainly in ion-exchange form, Cu is mainly in residual form and humic acid combined form, and the other elements are mainly in residual form. Among the seven heavy metal elements, Cd has the strongest mobility and biological toxicity, followed by As, Ni, and Zn; Cr, Cu, and Pb have poor biological activity and mobility.

(3) The assessment results show that the overall pollution level of the study area is heavy, which means a very strong ecological risk level. The main pollutants are Pb, As, and Cd; Cd is the most serious pollution. CA and PCA showed that the pollution sources of Cu, Pb, Zn, Cd, and As are mainly affected by tailings accumulation, mining and transportation, while Cr and Ni sources are controlled by soil-forming parent materials.

(4) According to the actual situation of the farmland around the mining area, it is proposed to clean up the pollution source by using stabilization remediation technology, such as using calcium dihydrogen phosphate to reduce the bioavailability of the most polluted elements, Pb and Cd, in the soil. In the industrial and mining wasteland and some unused land, *Typha orientalis* Presl can be used for repair in order to achieve the goal of green governance and beautification of the environment.

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