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Distribution and Source Apportionment of Heavy Metals in Soil around Dexing Copper Mine in Jiangxi Province, China

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Abstract: The soil heavy metal pollution around the mine threatens crop growth and human health. Intensively studies of the distribution characteristics and source of soil heavy metals around some typical mines are very crucial for environmental management and green development of mine. A total of eighty-nine soil samples, twenty-one sediment samples, five waste rock samples and two tailing sand samples were sampled to investigate copper (Cu), lead (Pb), zinc (Zn), arsenic (As), cadmium (Cd), chromium (Cr) and mercury (Hg) in soil, sediment, waste rocks and tailings sand around Dexing Copper Mine, Jiangxi Province, China. The concentrations of the seven heavy metals were determined using inductively coupled plasma mass spectrometry ICP-MS/atomic fluorescence spectroscopy (AFS). The I_{geo} values of soil heavy metal showed that 100% of Cu were at an unpolluted-to-moderately-polluted level (Igeo > 0), more than 50% of Cu were heavily polluted (Igeo > 3), 65.16%, and 22.47%, 7.86% and 7.87% of the soil samples for Cd, Hg, As and Zn were overly moderately polluted (Igeo > 1). A total of 13.48% and 11.24% of the soil samples for Pb and Cr, respectively, were moderately polluted (1 < Igeo < 2). The concentrations of heavy metals in soil were Compared with Risk Screening Values for Contamination of Agricultural Land (RSVCAL), with the concentration of 97.75% soil samples for Cu, and 69.21% of soil samples for Cd were higher than RSVCAL. In Dawu river basin the concentration of 50% soil samples for Pb were higher than RSVCAL. According to I_{geo} and RSVCAL, the soils around Dexing Copper Mine were polluted by heavy metals to some extent, with especially the Cu pollution of soil being the most serious. These heavy metal concentrations exceeding RSVCAL have threatened the safety of agricultural products. The results of soil profile analysis, principal component analysis (PCA) and cluster analysis (CA) indicated that the mining activities of Dexing copper mine should be the main source of Cu in the soil. High As concentration in soil obviously caused by the copper mine as well. In addition, Dexing Copper Mine should partly account for soil pollution by Zn, Pb, Cd, Hg and Cr around the mine.

Keywords: heavy metals; Dexing copper mine; soil pollution; geoaccumulation index (I_{geo}); source

Citation: Ni, S.; Liu, G.; Zhao, Y.; Zhang, C.; Wang, A. Distribution and Source Apportionment of Heavy Metals in Soil around Dexing Copper Mine in Jiangxi Province, China. *Sustainability* **2023**, *15*, 1143. https://doi.org/10.3390/su15021143

Academic Editor: Jun Wang

Received: 30 November 2022
Revised: 28 December 2022
Accepted: 2 January 2023
Published: 7 January 2023

1. Introduction

The demand for mineral resources is increasing with economic development, and the environmental problems caused by the development of mineral resources are becoming increasingly serious. The mine environment problems have become one of the research hotspots. Tailings, waste gas and wastewater from mining are often accompanied by a large number of heavy metal minerals. Due to physical, chemical and biological effects, these minerals containing heavy metals are weathered easily, which induce a great amount of heavy metals to be released and enter into the water or soils [1–3], resulting in water quality air and soil, were polluted.

Heavy metals = released from mine development enter surface water and groundwater, and the water carries heavy metals into the surrounding environment. Sadija–Kadriu et al. 2020 assessed the concentration of heavy metals in industrial discharge water from the Trepça Mine in Stantërg and flotation, and their impact in polluting the urban environment, and they concluded that the main cause of environment pollution has continuously been the mine and flotation [4]. Milaim–Sadiku et al. 2021 studied the extent of the impact of the Artana mine on heavy metal pollution of the waters of the Marec river, and they pointed that mineralogical pollution of this river resulted in almost total degradation of biota [5]. Mining is one of the major sources of anthropogenic air pollutants. Golik et al. 2021 investigate the distribution of dust from open-pit mining and the distribution of heavy metals in the soil, considering the rising wind [6].

Soil pollution is regarded as one of the most serious environmental problems caused by mine development, and soil heavy metal pollution around the mine is of great concern. Mine wastewater discharge and fine-grained mine tailings raising dust are important kinds of soil pollution. The research on soil pollution around the mine mainly focuses on three aspects: 1. soil pollution assessment [7–10], 2. pollution sources [11,12] and 3. pollution prevention or control measures [6,13,14]. The soil heavy metal pollution around the mine threaten crop growth and human health [11,15]. To prevent or control pollution, the source of pollution must be identified. The determination of pollution source is crucial for pollution prevention and treatment.

Dexing Copper Mine, a very large porphyry copper deposit in Jiangxi Province China, is an open-cast mine. In recent years, a lot of studies were carried out on the environmental problems of Dexing Copper Mine development [16–19], and these studies results have made an important contribution to the improvement of the environment in this area. However, so far, these studies of environmental problems in Dexing were mainly aimed at the Dexing Copper Mine and its surrounding ecological environment. However, only a few previous studies have systematically investigated the relationship between soil pollution and mine development. Therefore, intensively studies of the distribution and source of heavy metals in the soil around the mine are very important for environmental management and green development of mine.

In this study, the Cu, Zn, Pb, Cd, As, Hg and Cr concentrations in waste rock, slag, tailings sand and soil from the Dawu River Basin, 4# Tailings Pond and its downstream around Dexing Copper Mine were determined by ICP-MS/AFS. The geoaccumulation index (I_{geo}) was used to evaluate the level of soil pollution, and the degree of harm to agricultural product safety was assessed by comparing the heavy metal concentrations in soil with Risk Screening Values for Contamination of Agricultural Land (RSVCAL) [20]. On the basis of the heavy metal concentration comparison of the longitudinal profiles Dawu River basin, 4# Tailings Pond and its downstream, and transverse profiles (Dexing Copper Siye Family Area Section, Zhushahong Section, Xiagukou Section, Fuxikou Section), the source of soil heavy metal pollution was traced by the cluster analysis and factor analysis, and then the relationship between soil heavy metals pollution and the development of Dexing Copper Mine were discussed deeply.

2. Materials and Methods

2.1. Study Area

Dexing region is in northeastern Jiangxi Province, China (Figure 1), and it belongs to the humid monsoon region of the middle subtropical zone, with warm climate, abundant rainfall, sufficient sunshine and abundant precipitation. The annual average precipitation is 1981.7 mm. Dexing region is an important base of copper, gold, silver, lead and zinc mineral resources in China, which concentrates copper Changporphyry copper deposits, Yinshan polymetallic deposits, Jinshan gold deposits and other large and super-large deposits as one of the large ore concentration areas in the eastern metallogenic belt of China [21].

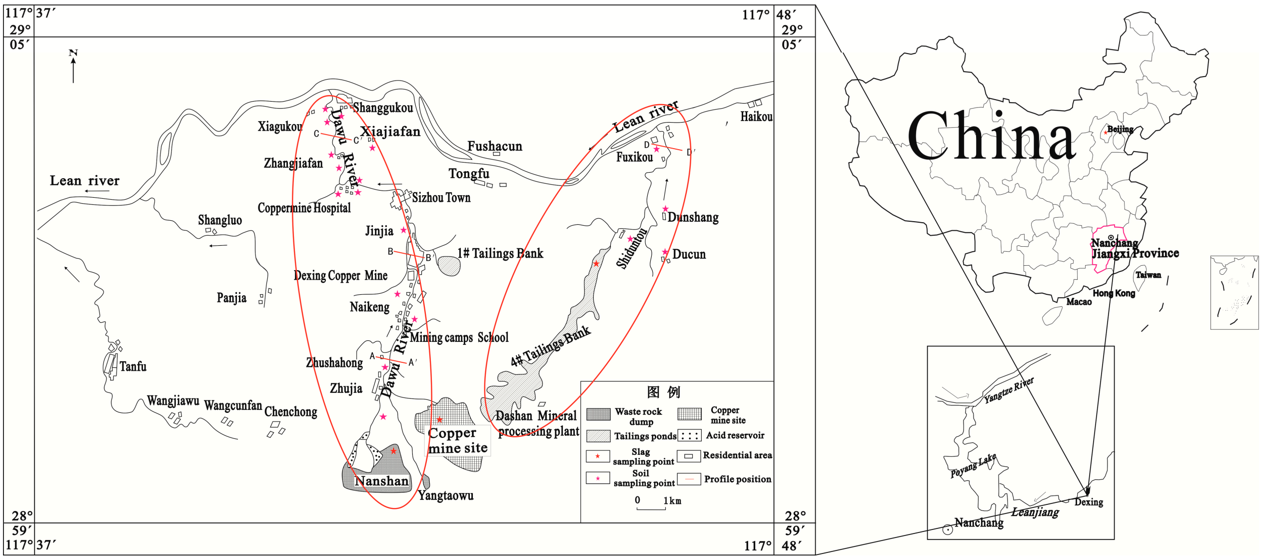

Figure 1. Locations of samples in Dawu River Basin and 4# tailings pond downstream, in Jiangxi, China.

Dexing Copper Mine in Dexing City is the largest open-pit copper mine in Asia and one of the eight super-large porphyry copper mines with reserves of more than 10,000 tons in the world. Dexing copper deposit consists of three porphyry copper (molybdenum) deposits, namely Tongchang, Fujiawu and Zhushahong.

The areas of study are Dawu river basin, 4# tailing pond and its downstream, located in Dexing Copper Mine, Jiangxi Province, China. The study areas lie between latitude 117°37′–117°48′ N and between longitude 28°59′–29°05′ E as shown in Figure 1.

Dawu River, which originates from Guanmao Mountain in the south of the waste dump of Dexing Copper Mine, has a total length of 14 km, and a catchment area of more than 34 km^2, flowing through the mining area of Dexing Copper Mine, Zhujia Village, Zhushahong, Jinjia, Zhangjiafan, Gukou and other villages, as well as flowing into Le'an River in the north of the mining area. Dawu River flows through Tongchang mining area from southeast to northwest. The mining area is divided into Nanshan and Beishan. Dexing Copper Mine has two waste dumps, Nanshan and Beishan. The waste rock from copper mining is mainly stacked in Nanshan (540 m above sea level) and Beishan (443 m above sea level). Nanshan Waste Dump is located at the upstream of Dawu River, and is designed with acid dump, three acid collecting tanks and one electrolytic copper plant. After copper recovery, acidic wastewater is used for the leaching of waste rock. There is a certain amount of acid wastewater discharged from the dam foundation of the two acid sump tanks, and part of the discharged water is pumped back to the electrolytic plant to produce copper, but some may still flow out. Sulfide in waste rock is intensively weathered under the catalysis of high temperature and rain and microorganisms, which is easy to release a large amount of heavy metal ions.

Dexing Copper Mine has the largest tailings pond in Asia—4# tailings pond. The 4# Tailings Pond (Figure 1) is composed of a reservoir and a tailing dam. It is 6 km long from north to south and has a total catchment area of 15 km^2. It receives the mineral processing wastewater and tailings discharged from Dashanzi Concentrator. After separation, the tailings are piled up into a tailing dam. The wastewater enters the reservoir and then circulates into the concentrator with a pump. Part of the wastewater is leached from the dam foundation into the stream which finally flows into the Le'an River. From near to far, the villages around the tailings pond are Shiduntou Village, Du Village and Fuxikou, in turn. The drainage at the 4# Tailings Pond downstream is discharged into Le'an River from the mouth of Fuxi River.

2.2. Sampling and Chemical Analysis

The sampling locations are in Dawu river basin, 4# tailing pond and its downstream are shown in Figure 1. A total of 117 samples were collected, including five waste rock samples from Dexing copper mining site and waste dump, two tailing sand samples from 4# tailings pond and the nearby Sizhou concentrator, 21 sediment samples along Dawu River and 89 agricultural soil samples in the mine area.

The concentrations of Cu, Cd, Cr, Pb, Hg and Zn in samples were determined by inductively coupled plasma mass spectrometry (ICP-MS), and the model is X-SERIES II. The concentrations of As in samples were determined by atomic fluorescence spectroscopy (AFS), and the model is XGY1011A. The parameters are listed in Table 1. The samples were treated and analyzed in Geological Experimental Research Institute of Anhui Provionce, China.

Table 1. Parameters describing the analytical quality of the trace elements data (mg/kg).

	Cr	Zn	Pb	Cu	Cd	As	Hg
Detection limit	3	2	2	0.8	0.02	0.2	0.0005
GSS-22 standard value	57 ± 3	59 ± 2	26 ± 2	18.3 ± 0.8	0.065 ± 0.012	7.8 ± 0.5	0.020 ± 0.002
GSS-22 determined value	56.3	59.1	26.4	18.1	0.067	8.0	0.020

2.3. Accumulation Risk Assessment for Heavy Metals in the Soil

Geoaccumulation index (I_{geo}) has been widely used to measure the pollution of soil and sediments [22–24]. The index of geo-accumulation is calculated as

$$I_{geo} = Log_2[Cn/(1.5 \times Bn)]$$

where Cn is the measured concentration of every heavy metal in the mine soil (mg/kg), and Bn is the background value of heavy metal elements in soil. The background values of heavy metals in the soil in Jiangxi Province China used to calculate I_{geo} were 20.3, 32.3, 69.4, 0.108, 0.084, 14.9 and 45.9 mg/kg for Cu, Pb, Zn, Cd, Hg, As and Cr, respectively [25]. The number 1.5 is a multiplying factor which refers to an offset of natural variability in the background data coming from the lithological variations [26]. Igeo calculations were classified into seven categories: unpolluted, Igeo < 0; unpolluted to moderately polluted, $0 \leq$ Igeo ≤ 1; moderately polluted, $1 \leq$ Igeo ≤ 2; moderately to heavily polluted, $2 \leq$ Igeo < 3; heavily polluted,$3 \leq$ Igeo < 4; heavily to extremely polluted, $4 \leq$ Igeo < 5; and extremely polluted, Igeo ≥ 5. [27].

2.4. Multivariate Statistical Analysis

Principal component analysis and cluster analysis are currently the most common methods and means to explore the sources of heavy metals in media internationally [22,28]. The concentration data of heavy metal in soils and sediments were carried out by principal component and cluster analysis using SPSS 16 software. During principal component analysis, KMO index should be >0.5 and and Bartlett value should be <0.05.

3. Results

3.1. Distribution of Heavy Metals in Waste Rock, Tailings and Slag

The concentrations of Cu and As in waste rock, slag and tailings were higher than crustal element abundance (CEA) (Figure 2, Table 2) [29]. It was worth noting that the level of Cu was much higher than CEA. Furthermore, the concentrations of Pb, Cd and As were higher than CEA. Except for Zn and Cr, the average concentrations of other heavy metals were higher than those of CEA, especially for As.

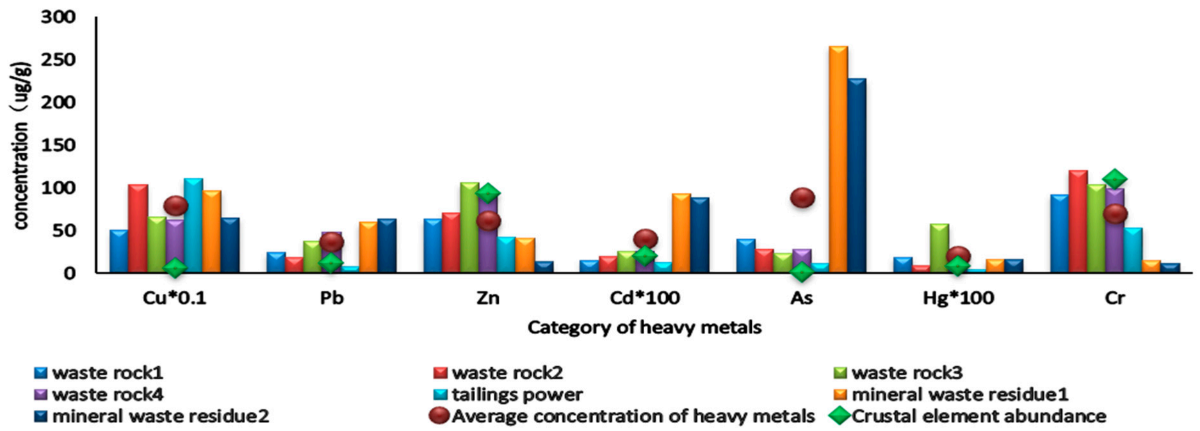

Figure 2. Distribution characteristics of heavy metals in waste rock, tailings and slag.

Table 2. Comparison of heavy metal concentration in tailings sand (mg/kg).

Sample	Cu	Zn	Pb	Cd	Cr	As	Hg	pH	Collection Time
Tailings	1107.67	41.87	7.87	0.13	53.24	11.70	0.05	7.01	2017
Tailings 1	876.00	38.20	13.60	0.09	65.70	14.00	0.05		2011–2013 ([30])
Tailings 2	1043.00	44.10	13.80	0.09	84.60	19.80	0.13		
Tailings 3	815.00	30.40	9.53	0.07	49.70	14.40	0.07		
Tailings 4	911.33	37.57	12.31	0.08	66.67	16.07	0.08		
Mean	950.60	38.43	11.42	0.09	63.98	15.19	0.08		
CEA [28]	63	94	12	0.2	110	2.2	0.089		
RSVCAL (Exclude Orchard (Cu) and Paddy Field (Zn, Pb, Cd, As, Hg, Cr)) [20]	50	200	70	0.3	40	0.3	150	pH ≤ 5.5	
	50	200	90	0.3	40	0.3	150	5.5 ≤ pH ≤ 6.5	
	100	250	120	0.3	30	0.3	200	6.5 ≤ pH ≤ 7.5	
	100	300	170	0.6	25	0.6	250	Ph > 7.5	

Heavy metal concentrations of 4# tailings in this study were comparable with the results tested by Zhao et al. from 2011 to 2013 [30]. In the last 8 years, heavy metal concentrations of tailings in 4# tailings pond have not changed significantly, and the concentrations of Cu and As were higher than the values of CEA. Cu concentration was also obviously higher than RSVCAL (Table 2).

3.2. Distribution of Heavy Metals in Soil

The concentrations of heavy metals in the soil of Dawu River basin and tailings pond downstream were compared with RSVCAL. Since the collected samples were not orchard and paddy field soil, all soil samples were compared with other soil heavy metal concentration standards (Table 2).

3.2.1. Heavy Metals in Soil of Dawu River Basin

The results showed that heavy metal concentrations in the soils of the Dawu river basin ranged from 82.7–1021.41, 64.25–477.36, 38.6–142, 0.11–1.52, 11.26–184.38, 0.04–7.23 and 54.58–271 mg/kg for Cu, Zn, Pb, Cd, As, Hg and Cr, respectively (Table 3). The average concentrations of Cu, Zn, Pb, Cd, As, Hg and Cr were 304.60, 158.14, 77.59, 0.52, 35.09, 0.51 and 108.01 mg/kg, respectively. The pH values of soil ranged from 3.15–7.76, and the average value was 5.08, by acid soil primarily.

Table 3. Basic statistical distribution parameters for selected metals (mg/kg) in soil of Dawu river and Tailings pond downstream basin.

		Number	Mean	Standard Error	Median	Stand Deviation	Skewness	Minimum	Maximum
Cu	Dawu river basin	58	304.60	25.72	271.31	195.90	1.45	1021.41	82.70
	Tailings pond downstream	31	125.74	26.06	69.18	145.08	3.09	733.90	43.00
Zn	Dawu river basin	58	158.14	10.23	133.90	77.90	2.45	477.36	64.25
	Tailings pond downstream	31	122.61	4.28	119.70	23.81	0.46	182.70	81.48
Pb	Dawu river basin	58	77.59	3.27	75.16	24.88	0.68	142.00	38.96
	Tailings pond downstream	31	43.86	2.63	40.20	14.62	1.76	97.70	18.74
Cd	Dawu river basin	58	0.52	0.04	0.43	0.32	1.01	1.52	0.11
	Tailings pond downstream	31	0.35	0.02	0.35	0.09	−0.12	0.54	0.17
As	Dawu river basin	58	35.09	5.38	22.15	40.95	2.74	184.38	11.26
	Tailings pond downstream	31	12.86	1.33	10.87	7.40	2.73	41.60	5.64
Hg	Dawu river basin	58	0.51	0.16	0.15	1.24	4.54	7.23	0.04
	Tailings pond downstream	31	0.26	0.16	0.08	0.89	5.54	5.02	0.04
Cr	Dawu river basin	58	108.01	5.27	96.65	40.17	2.16	271.00	54.58
	Tailings pond downstream	31	89.26	2.14	87.62	11.93	−0.23	113.20	57.94
pH	Dawu river basin	58	5.08	0.14	4.91	1.08	0.48	7.76	3.15
	Tailings pond downstream	31	5.45	0.11	5.42	0.63	1.34	7.12	4.33

It was worth noting that the concentration of all soil samples for Cu, 70% soil samples for Cd, 50% soil samples for Pb, 12.07% soil samples for Zn and As, 10.34% soil samples for Cr and 5.17% soil samples for Hg were higher than RSVCAL.

3.2.2. Heavy Metals in Soil of Tailings Pond Downstream

The results of the analyzed soil samples (Table 3) showed that the concentrations in soil from tailings pond downstream ranged from 43.00–733.90 for Cu, 81.48–182.70 for Zn, 18.74–97.70 for Pb, 0.17–0.54 for Cd, 5.6–41.6 for As and 0.04–5.02 for Hg, 57.94–113.20'mg/kg for Cu, Zn, Pb, Cd, As, Hg and Cr, respectively. The average concentrations of Cu, Zn, Pb, Cd, As, Hg and Cr were 125.74, 122.61, 43.86, 0.35, 12.9, 0.26 and 89.26 mg/kg. The pH ranged from 4.43–7.12, and the average value was 5.45, by acid soil was, primarily. The concentration of 90.32% soil samples for Cu, 67.74% soil samples for Cd, 3.23% soil samples for Pb, and As were higher than RSVCAL (Figure 3).

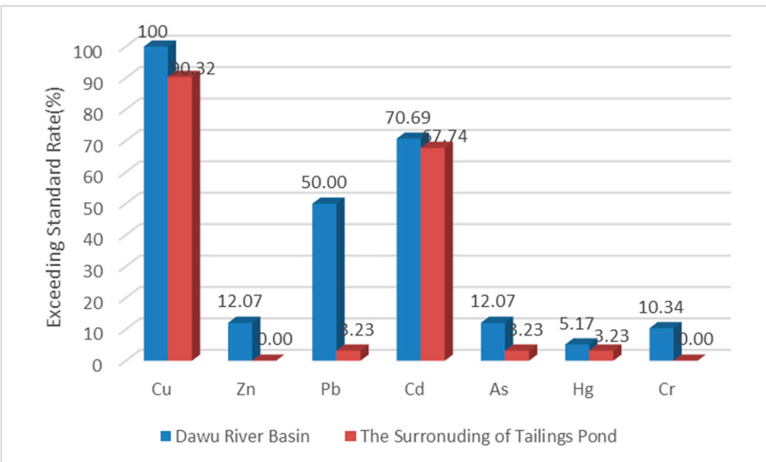

Figure 3. The heavy metal concentrations exceeding standard rate in the soil compared with RSVCAL.

4. Discussion

4.1. Environmental Hazard Assessment of Heavy Metals in Mining Waste Rock and Tailings Sand

The average concentrations of Cu, Pb, Cd, As and Hg in waste rock, slag and tailings samples were higher than Crustal element abundance. The heavy metal concentrations in 4# tailings sand were similar to those tested by Zhao Yuanyi et al. from 2011 to 2013 (Table 4), which showed that the heavy metal concentrations of 4# tailings pond tailings sand had not changed significantly in the past 8 years. The average concentrations of Cu in waste rock and ore powder samples in this test were more than ten times of crustal element abundance. Zhao Yuanyi et al. tested the element form proportion of Cu in tailings, and the proportion of water-soluble, adsorbed and carbonate forms easy to be bioabsorbed accounted for 21.49%. Vulcanized state accounted for 73.57% [30].

$$CuFeS_2 + 4O_2 = CuSO_4 + FeSO_4$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3\downarrow + 3H^+$$

$$2CuSO_4 + 2CaCO_3 + H_2O = Cu_2CO_3(OH)_2 + 2CaSO_4 + CO_2$$

$$32CuSO_4 + 3CaCO_3 + H_2O = Cu_3(CO_3)_2(OH)_2 + 3CaSO_4 + CO_2$$

Table 4. Common Factor Variance Extraction.

	Dawu River Basin	Tailings Pond Downstream
Cu	0.898	0.813
Zn	0.862	0.901
Pb	0.781	0.818
Cd	0.827	0.738
As	0.607	0.797
Hg	0.7	0.814
Cr	0.59	0.645

Mining and mineral processing are important ways for heavy metals to diffuse to soil [31]. The research shows that sulfide minerals oxidized and leached on the surface (5–10 cm) and a large amount of heavy metals were released, and then migrated vertically downward to the deep (enrichment layer, 110–115 cm) to form secondary minerals (goethite, jarosite, chloralum, tetrahydrate alum, etc.). Large heavy metals were concentrated and the underlying soil was polluted. A large number of studies showed that [32,33] the typical contaminated soils in the mining area mainly included farmland and vegetable soils irrigated by mining and mineral processing wastewater, and soils at mining sites and plant areas.

In typical smelting contaminated areas, traffic, coal combustion, smelting and mining activities are recognized as the main anthropogenic inputs of metals accumulation. The variations in metal and metalloid concentrations in soils also related to geology [34].

Chalcopyrite is the most important mineral in Dexing copper mine area. Under the action of oxygen and acidic water, copper-bearing sulfide produced water-soluble heavy metal compounds easily. Therefore, the waste rock and slag produced in the copper mine site at the upstream of Dawu River and a large amount of tailing sand stored in the $4^{\#}$ tailings dump of the copper mine threaten the surrounding environment.

4.2. Assessment of Heavy Metal Pollution and Source Apportionment of Heavy Metals in Soils

4.2.1. Evaluation of Heavy Metal Pollution in Soil around Dexing Copper Mine (Dawu River Basin and Tailings Pond Downstream)

The I_{geo} values of the seven heavy metals (Cu, Zn, Pb, Cd, As, Hg, Cr) in the soil samples and their distribution percentage are shown in Figure 4. The I_{geo} values of soil heavy metal showed that 100% of Cu were over an unpolluted-to-moderately-polluted level (I_{geo} > 0), and more than 50% of Cu were heavily polluted (I_{geo} > 3), indicating that the Cu pollution in most of the investigated sites reach the moderate to heavy contamination level. Cu pollution was serious. A total of 65.17% of the soil samples for Cd were over moderately polluted ($I_{geo} > 1$), reflecting that Cd pollution exists in this area. Totals of 22.47%, 7.87% and 7.87% of the soil samples for Hg, As and Zn were over moderately polluted ($I_{geo} > 1$), and 13.48% and 11.24% of the soil samples for Pb and Cr, and 7.87% of the soil samples for Hg, As and Zn were over moderately polluted ($I_{geo} > 1$), Pb and Cr pollution were generally moderately to lightly polluted, without moderately strong pollution.

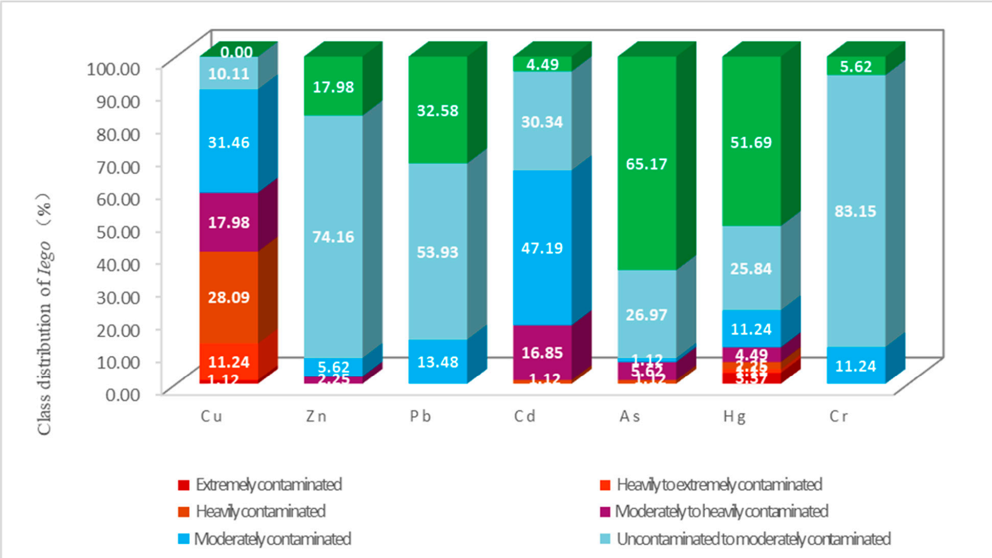

Figure 4. Geoaccumulation index (Igeo) of seven heavy metal percentage distributions in soils around Dexing Copper Mine.

The pollution levels of soil pollution in Dawu River basin were higher than that in the tailings pond downstream (Figure 5). The soil I_{geo} values showed that no matter the mean value, median value or maximum value, the concentrations of each heavy metal in the soil of Dawu River basin were greater than that in the tailings pond downstream. RSVCAL was as the standard, the exceeding standard rates of Cu, Zn, Pb, Cd, As, Hg and Cr in the soil from the Dawu River basin were higher than those from the tailings pond downstream. The exceeding standard rates of Cu in soil samples from the Dawu River basin reached 100%, while that from the tailings pond downstream reached 90%. The exceeding standard rate of Cd in soil samples from Dawu River basin were close to that from tailings pond downstream, which were 70.69% and 67.74%, respectively. The exceeding standard rate of Pb in soil samples from Dawu River basin reached 50%, and that from tailings pond downstream was only 3.23%. The exceeding standard rates of Zn, As and Cr were more than 10%, and that of Hg was 5.17% in soil samples from Dawu River. The exceeding standard rates of As and Hg soil samples were 3.23%, respectively, while Zn and Cr concentrations did not exceed RSVCAL in soil from tailings pond downstream.

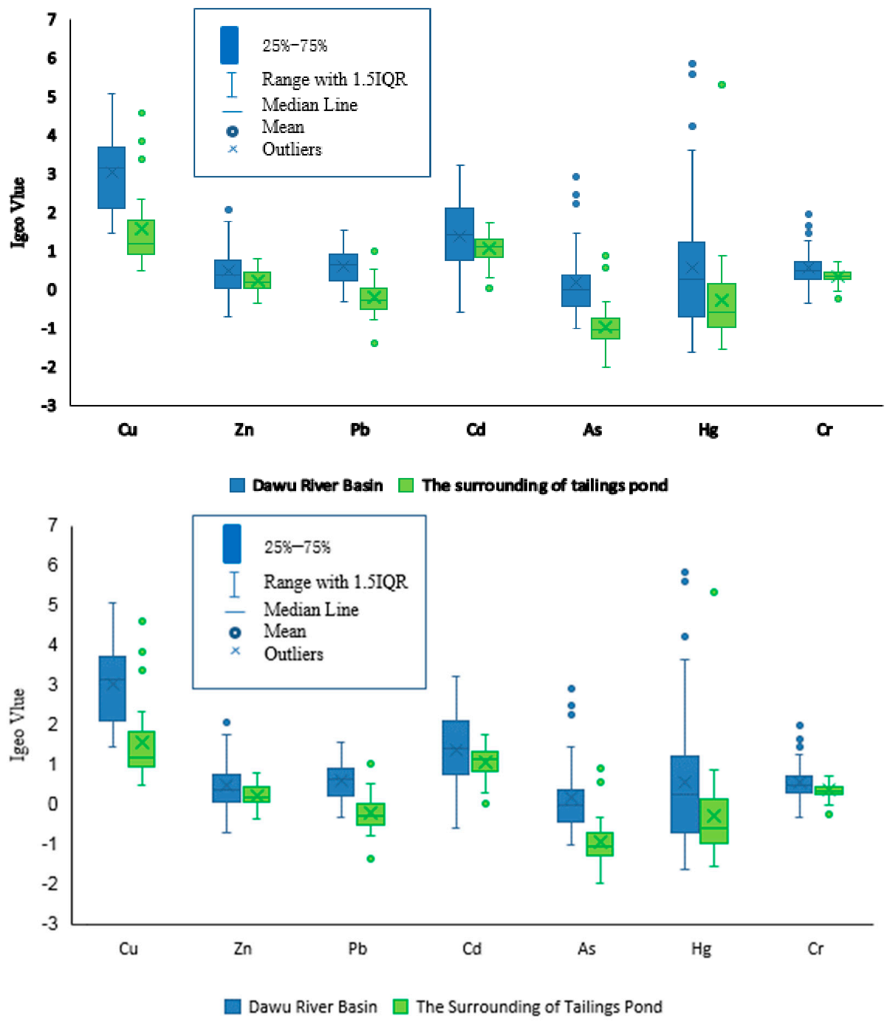

Figure 5. Geoaccumulation index (Igeo) of seven heavy metals in soil of Dawu River basin and tailings pond downstream.

According to I_{geo} and RSVCAL, the soil in the Dawu River basin and the tailings pond downstream were polluted by heavy metals to some extent, especially Cu pollution of soil was the most serious. RSVCAL refers to if the pollutant concentration in agricultural land soil is equal to or lower than RSVCAL, the risk to the quality and safety of agricultural products, crop growth or soil ecological environment is low and can be ignored generally; if the value exceeds RSVCAL, there may be risks to the quality and safety of agricultural products, crop growth or soil ecological environment. Heavy metal concentrations exceeding RSVCAL have threatened the safety of agricultural products; therefore, soil environment monitoring and agricultural product collaborative monitoring should be strengthened.

4.2.2. Changes of Heavy Metals Concentration in Soil Profile

1. Change of heavy metals concentration in soil longitudinal profile

Shown as in Figure 1, the Dawu River basin profile and tailings pond downstream profile were selected and compared from near to far according to the distance from copper mining site and tailings pond.

(1) The Dawu River basin profile

The Dawu River basin section is a successful copper mining site—Zhujia waste rock dump-Zhujia Village-Zhushahong Village-Jinjia Village-Dexing copper hospital-Zhangjiafan Village-Xiajiafan Village-Xiagukou Village. As shown in Figure 6, the Cu concentration of waste rock in the mining site was the highest, but the Cu concentrations of soils in the

Zhujia Village Waste Dump and Zhujia Village near copper mining site were the lowest. From Zhujia waste rock dump, the Cu concentration did not reflect the trend of decreasing Cu concentration from near to far. Cd concentration was higher in copper mining sites and the midstream of Dawu River than that in the upstream and downstream. The Pb, Zn, Hg and Cr concentrations were generally lower in the mining area than other areas. In the waste dump and Zhujia Village near the mining site were generally lower than those in the downstream of Dawu River. This may be due to the fact that the sampling points in the waste rock dump and Zhujia Village were far away from the Dawu River, while other sampling points were near the Dawu River. The As concentrations were higher in the mining site and the waste dump than in other villages.

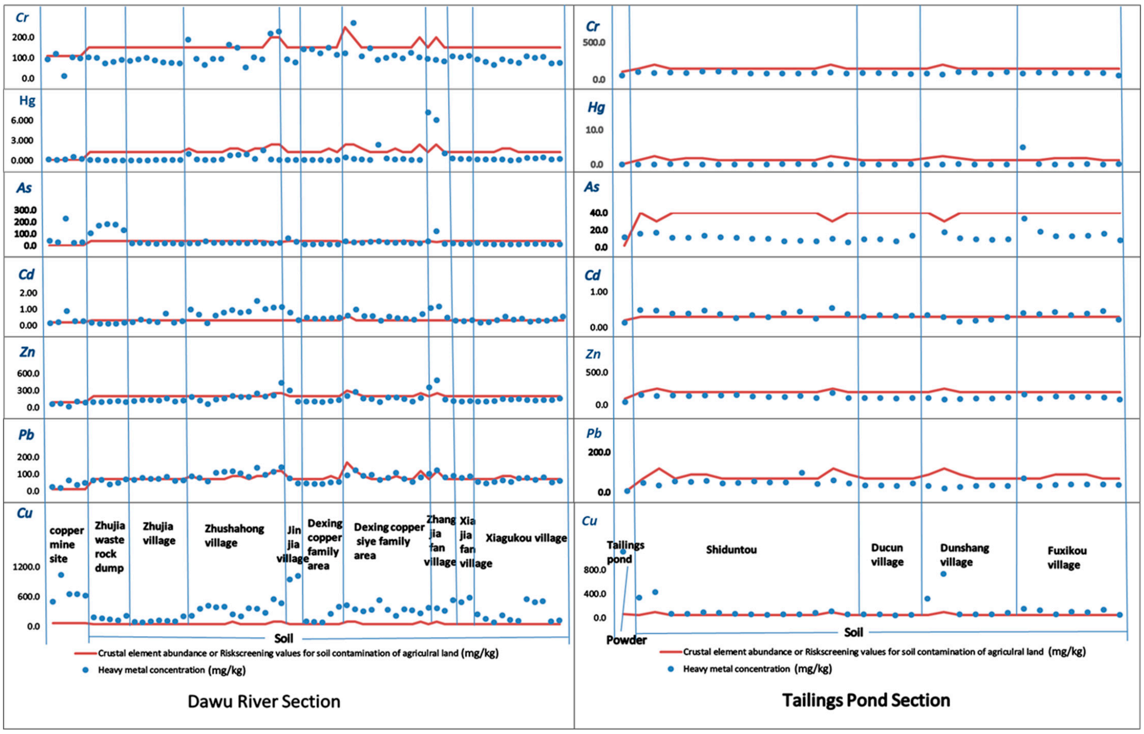

Figure 6. Distribution characteristics of heavy metals.

The results of Dawu River section showed that the concentration of Cu was the highest in the rocks of the mining site, but it did not show regular changes in the soil section. The concentrations of Cd, Pb, Zn, As, Hg and Cr did not show that the rock concentrations in the mining site were higher than other in the soil.

(2) Tailings pond downstream profile

The profile of tailings pond was successively tailings pond—Shiduntou Village-Du Village-Dunshang Village-Fuxikou Village. The Cu concentration in tailings pond was the highest, the Cu concentration in the Shiduntou soil near tailings pond was next. The Cu concentration in Dunshang Village occurred abnormally high values. The Cd, Pb, Zn, As, Hg and Cr concentrations in tailing sand was lower than that in the soil from tailings pond downstream.

2. Change of heavy metals concentration in soil transverse terrace profile

Four transverse terrace profiles of Zhushahong village, Dexing copper site family area profile, Xiagukou village and Fuxikou village were selected. The profiles of Zhushahong Village, Dexing copper site family area profile and Xiagukou Village were the profiles of Dawu River terrace. The section of Fuxikou Village was the section of tailings pond downstream. The first terrace referred to the land close to the river with low terrain, while the second terrace was higher than the first terrace and far away from the river (Figure 7).

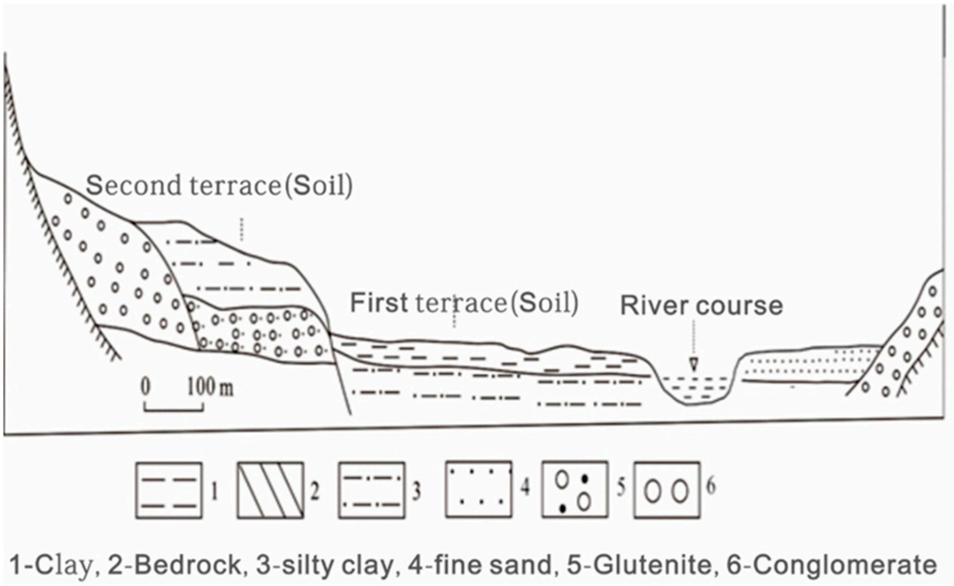

Figure 7. Schematic diagram of terrace profiles.

The concentrations of Cu, Cd, Pb, Zn, As, Hg and Cr in the soil of the first terrace were compared with the second terrace. As shown in the Figure 8, the concentrations of Cu, Cd, Pb, Zn, As and Cr of the first terrace were higher than that of the second terrace in four profiles. The concentration of Hg of the first terrace was higher than that of the second terrace, except for Xiagukou profile.

Figure 8. Comparison Diagram of Heavy Metal Concentration of Terrace profiles.

The concentration of heavy metal increased in each profile generally from the first terrace to the second terrace, reflecting that river water was an important source of heavy metals in the soil. The Dawu River flowing through the profiles of Zhushahong Village, Dexing copper siye family area profile and Xiagukou Village is the drainage river of Dexing Copper Mine. The Fuxi River flowing through the profile of Fuxikou Village is connected with 4# Tailings Pond small stream. To a large extent, this means that the concentration of heavy metals in the soil beside the river were affected by the development of copper mine.

4.3. Discussion on the Source of Heavy Metal Pollution in Soil around Dexing Copper Mine

The Cu concentrations in waste rocks and tailing sand were highest in the Dawu River profile and the tailings pond downstream, and the concentrations of Cu, Cd, Pb, Zn, As and Cr of the first terrace in four profiles were higher than that of the second terrace. All results point to that the development of Dexing Copper Mine may be the source of Cu pollution in the soil. Except Cu, the other heavy metal of Cd, Pb, Zn, As, Hg and Cr did not show significant high values in waste rocks and tailing sand. Principal component analysis (PCA) and cluster analysis (CA) were performed with SPSS 16 to explore the sources of heavy metals in soils. This study discussed the impact of mine development on the distribution of heavy metals in soil, and deeply analyzed the possible sources of heavy metals in soil.

A total of 79 soil and sediment samples were selected for principal component analysis and cluster analysis in the Dawu River basin. This is because the principal component analysis showed that the common factor variance extraction of 58 soil samples Cu concentration in Dawu River basin was only 0.139, and the principal component analysis could not reflect the soil Cu information. The common factor variance extraction of 79 soil and sediment samples for Cu concentration in Dawu River basin reached 0.898 (Table 4), the principal component analysis could reflect most of the information of Cu. KMO index and Bartlett value of soil and sediment heavy metal concentration data in Dawu River basin were 0.718 and 0.000, respectively, which indicated that principal component analysis could be applied. In the tailings pond downstream, only 31 soil samples were selected, no sediment, and the common factor variance extractions of the soil samples heavy metal concentrations were above 0.5, which could reflect the information of heavy metals (Table 4). The KMO index and Bartlett value of the soil heavy metal concentration data were 0.541 and 0.000, respectively, which indicated that principal component analysis could be applied. In the interpretations of PCA patterns, factor loadings greater than 0.71 are typically considered excellent, while those less than 0.32 are regarded as meaningless [35,36].

As shown in Table 5, three principal components, extracted from the variables with eigenvalues > 1, were retained for further analysis which accounted for 75.21% of the total variance of the data in Dawu River basin.

Table 5. Significant Principal Component Loadings (>0.32) using varimax normalized rotation on the dataset of selected metals in the soil of Dawu river basin.

	Component		
	1	2	3
Cu	0.153	0.260	**0.898**
Zn	**0.912**	0.170	−0.030
Pb	**0.846**	−0.178	−0.183
Cd	**0.894**	−0.080	0.149
As	−0.042	**0.686**	**−0.367**
Hg	**−0.570**	**0.607**	−0.084
Cr	**0.543**	**−0.534**	−0.102
% of Variance	42.721	17.978	14.509
Cumulative %	42.721	60.699	75.208
eigenvalues	2.991	1.258	1.016

Note: The bolding represent Significant Principal Component Loadings (>0.32).

Factor 1 consisted of high significant positive loadings of Zn, Pb, Cd, Hg and Cr, which accounted for 42.72% of the total variance of the variables with an eigenvalue of 2.991. Factor 2 consisted of significant loadings of As, Hg and Cr, which accounted for 17.99% of the total variance of the variables with an eigenvalue of 1.258. Factor 3 consisted of significant positive loadings of Cu and As, which accounted for 14.51% of the total variance of the variables with an eigenvalue of 1.016. Soil heavy metal distribution can be affected by human activities severely [37,38]. The main factors of soil heavy metal pollution contained mineral development, industrial processing, sewage irrigation, fertilizer application, vehicle traffic, urban development, etc. [39]. Factor 1 might be interpreted as representing influences from multiple factors, such as the vehicular exhaust from vehicle traffic, daily human activities, mining and smelting activities, because the Concentrations of Zn, Pb, Cd, Hg and Cr were lower in rocks of the mining site than in soil. Mining activity influence should account for a small part, and vehicle traffic and daily human activities (fertiliser application et al.) should be the major factors. In all Dawu River basin samples the Cu concentration in the rocks of the mining site was the highest, Cu concentration should be influenced mainly by Dexing copper development. Cu and As formed factor 3, As might be influenced by a mixed source of both Dexing copper development and human origin in agricultural soils. Cluster analysis (Figure 9) reflected that Zn, Pb and Cd had a closer relationship than other heavy metals.

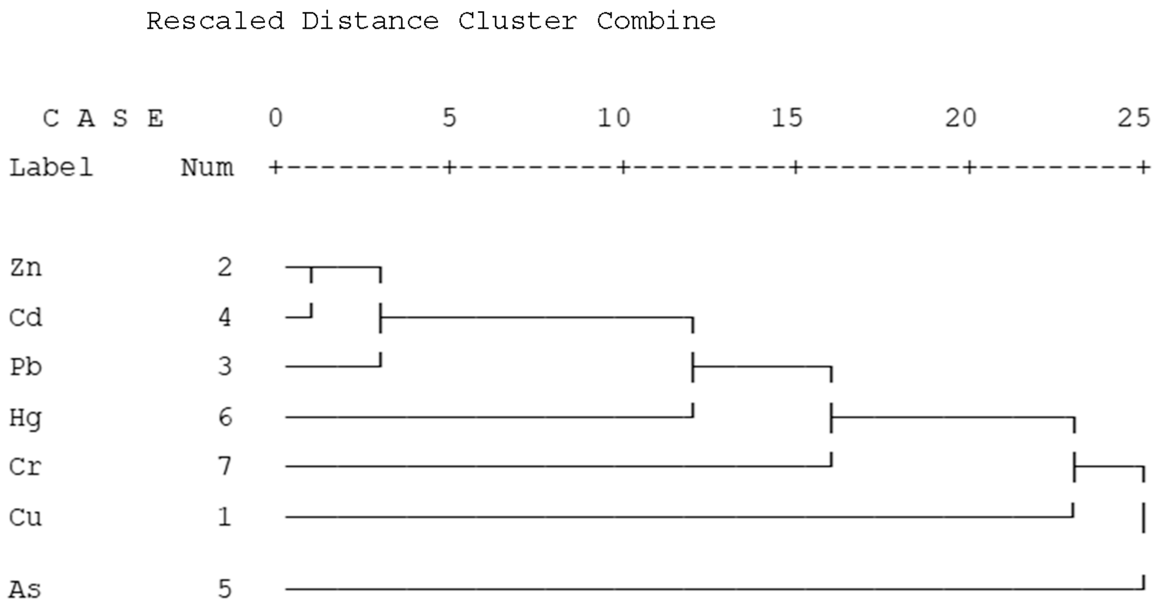

Figure 9. Dendrogram of the metals showing the clustering behaviour of metals in the soil of Dawu river drainage area.

As shown in Table 6, three principal components, extracted from the variables with eigenvalues >1, were retained for further analysis, which accounted for 78.95% of the total variance of the data in tailings pond downstream.

Table 6. Significant Principal Component Loadings (>0.32) using varimax normalized rotation on the dataset of selected metals in the soil of tailings pond downstream.

	Component		
	1	2	3
Cu	−0.093	**0.752**	**0.489**
Zn	**0.935**	−0.117	0.112
Pb	**0.779**	−0.230	**−0.397**
Cd	**0.791**	0.076	**0.327**
As	0.269	**0.850**	0.040
Hg	**0.457**	**0.510**	**−0.587**
Cr	**0.444**	**−0.368**	**0.559**
% of Variance	37.07	25.088	16.79
Cumulative %	37.07	62.157	78.948
eigenvalues	2.595	1.756	1.175

Note: The bolding represent Significant Principal Component Loadings (>0.32).

Factor 1 consisted of high significant positive loadings of Zn, Pb, Cd, Hg and Cr which accounted for 37.07% of the total variance of the variables with an eigenvalue of 2.595. Factor 2 consisted of significant positive loadings of Cu, As, Hg and Cr, which accounted for 25.088% of the total variance of the variables with an eigenvalue of 1.756. Factor 3 consisted of significant positive loadings of Cu, Pb, Cd, Hg and Cr, which accounted for 16.79% of the total variance of the variables with an eigenvalue of 1.016.

Principal Component Analysis of the tailings pond downstream dataset, compared with Dawu River basin dataset, showed that the components of factor 1 were similar, also reflected the influences on the concentration of Zn, Pb, Cd, Hg and Cr from multiple factors, such as the vehicular exhaust from vehicle traffic, daily human activities, mining and smelting activities, etc., with factor 2 and 3 containing Cu indicating the influences from copper mine development. The differences of factor 2 and 3 between the tailings pond downstream dataset and Dawu River basin dataset possibly reflect that the influences of heavy metal (Cu, Pb, Cd, Hg and Cr) pollution from mining were greater on the tailings pond downstream than on Dawu River basin. The results of the cluster analyses (Figure 10) indicated that the relationships among different heavy metals.

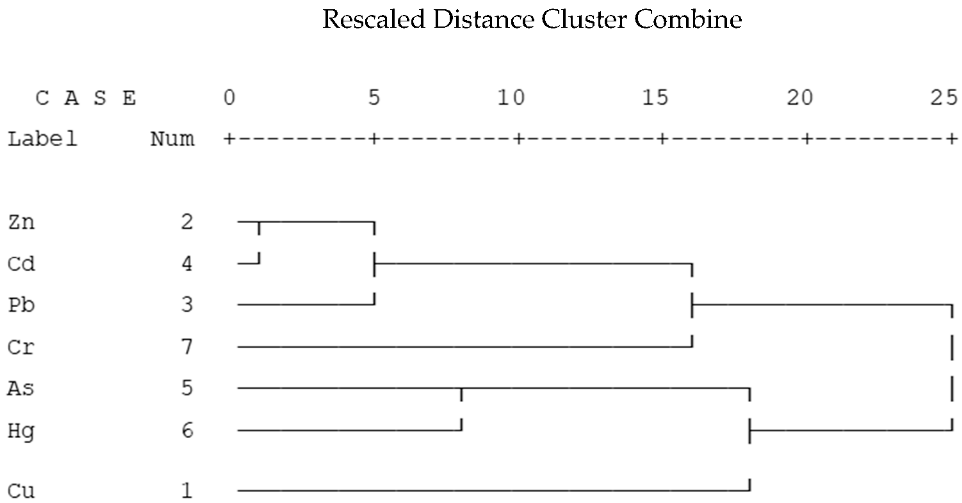

Figure 10. Dendrogram of the metals showing the clustering behavior of metals in the soil of the surrounding of tailings pond.

5. Conclusions

1. The soil around the Dexing Copper Mine (Dawu River basin and 4# tailings pond Downstream) was polluted by heavy metals of Cu, Zn, Pb, Cd, As, Hg and Cr to some extent. Cu pollution of soil was the most serious.

The I_{geo} values of soil heavy metal showed that 100% of Cu was over an unpolluted-to-moderately-polluted level (I_{geo} > 0), more than 50% of Cu was heavily polluted (I_{geo} > 3), and 65.16%, 22.47%,7.86% and 7.87% of the soil samples for Cd, Hg, As and Zn were over moderately polluted (I_{geo} > 1). Totals of 13.48% and 11.24% of the soil samples for Pb and Cr were moderately polluted (1< I_{geo}< 2). The concentrations of heavy metals in soil were compared with Risk Screening Values for Contamination of Agricultural Land (RSVCAL), and the concentration of 97.75% soil samples for Cu, and 69.21% soil samples for Cd were higher than RSVCAL. In Dawu river basin the concentration of 50% soil samples for Pb were higher than RSVCAL. According to I_{geo} and RSVCAL, the soils around Dexing Copper Mine were polluted by heavy metals to some extent, with Cu pollution of soil especially being the most serious.

2. Mine development should be the main factor leading to soil Cu pollution in this area. The profile analysis showed that the Cu concentrations in the waste rocks and tailings sand of Dexing Copper Mine and tailings pond were higher than in soils of Dexing Copper Mine and tailings pond profiles. Mine development should be the main factor leading to soil Cu pollution in this area.
3. High As concentration in soil obviously caused by the copper mine, Dexing Copper Mine, should partly account for soil pollution by Zn, Pb, Cd, Hg and Cr around the mine.

PCA and CA showed that the sources of Cu and As have a certain internal relationship. The sources of Zn, Pb, Cd, Hg and Cr are closely related, but they do not show a close relationship with Cu. Therefore, it is inferred that high As concentration in soil mainly caused by the copper mine development. In addition, Dexing Copper Mine should partly account for soil pollution by Zn, Pb, Cd, Hg and Cr around the mine. The Zn, Pb, Cd, Hg and Cr pollution main source of soil in this area should be further investigated.

Author Contributions: S.N. designed the study, and drafted, revised and refined the manuscript; G.L. contributed to revised and refining of manuscript; Y.Z., C.Z. and A.W. contributed to the collection and determination of the samples. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by Management of Central Pubfic-interest Scientific Institution Basal Research Fund (Grant Nos. K1711, KK2109) and the National Natural Science Foundation of China (41807134).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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