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Geochemical Response of Surface Environment to Mining of Sn-Pb-Zn Sulfide Deposits: A Case Study of Dachang Tin Polymetallic Deposit in Guangxi

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Abstract: The rational development of mineral resources provides necessary materials for economic development, but environmental pollution caused by mining activities is an inevitable consequence. Here, we present a case study of Chehe Town in Guangxi, an area with integrated metals mining and smelting. The geochemical distribution, migration, and transformation behaviors of Cd and other heavy metals were studied in detail by systematically collecting surface media such as atmospheric dust, surface water and stream sediments, ores, tailings, mine drainage, soil, and crops in and around the mining area. We used these data to explore the geochemical response of the surface environment to mining and smelting of metal sulfide deposits. The annual flux of Cd and other heavy metals near the mining and smelting sites was high. Due to the topography, heavy metals in the atmosphere are mainly transported via vertical deposition, influencing areas downwind for 25 km. The mine drainage exceeded As and Zn standards but had little impact on the surface water. The surface water quality was good, without acidification. Risks due to ore were much higher than that for tailings. Heavy metals buffered by surrounding carbonate rocks and secondary minerals mainly migrated as solid particles, resulting in the contamination of stream sediment by heavy metals. In mountainous areas, rivers are mainly affected by topography, flowing fast and dominated by downcutting, which caused heavy metal pollution in the sediment have a limited effect on the soil near the river. Heavy metal concentrations in the cultivated soil were greatly influenced by external input such as substantial atmospheric dust. However, only Cd accumulated in the crops, with very high concentrations in rice, but safe and edible levels in corn. Thus, in the mining area, the most sensitive to heavy metals was the atmospheric environment. High concentrations of heavy metals beyond the ore district are mainly concentrated in the sediment, with distant impacts. Therefore, it is necessary to monitor and control risks associated with sediment transport, conduct treatment, and adjust crop planting. The soil, river, and agriculture respond differently to mining activities, but the risk is low and can be managed as needed.

Keywords: sulfide deposit; surface environment; heavy metals; migration; transformation; Chehe Town; Guangxi

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1. Introduction

Environmental disturbance inevitably results from ore deposit development; long-term mining operations exert enormous pressure on the surrounding ecosystem. While mining is an important resource extraction activity, dumping of solid wastes and dust and effluent discharges result in environmental pollution [1–3]. The environmental effects of mining non-metallic deposits are dominated by physical disturbance, including geological hazards, noise, and dust [4,5]. The intensity of the hazards depends on factors such as the scale of the ore deposit and the mining technology. On the basis of physical disturbance, metal mine areas undergo strong chemical reactions, of which acidification and heavy metal pollution are frequently encountered. Sulfide deposits are mainly formed by endogenesis. Due to anthropogenic disturbance from deposit exploration, mining, smelting, etc., deposits originally formed under anaerobic conditions are exposed to air, water, and microbial activity, resulting in oxidation and leaching of minerals [6–8]. Under the dual effects of physical migration and chemical release, acidic discharges and heavy metals can enter the environment, causing potentially serious threats to the atmosphere, water, soil, and biological systems.

Many previous studies have been conducted on the environmental effects of sulfide mining, but most of this research has focused on a single medium such as acid mine drainage, tailings ponds, or soils, as well as discussion of surficial reaction mechanisms of sulfide minerals [9–14]. However, few of these have carried out multimedia studies of geochemical characteristics.

The overall response of the environment to mines is affected by basic factors such as contaminant concentrations in the mine, the type of ore, and mining operations, as well as characteristics of the surrounding rock, topography, hydrology, climate, etc., [15]. Thus, the distribution and migration of heavy metals in surface media such as the atmosphere dust, tailings, soil, surface water, and stream sediment are mutually influenced and closely related. Recently, as tension between the demand for mineral resources and restoration of mining environments has gradually sharpened, green mining has put forward higher requirements on the analysis of pollution sources and exploration of pollution pathways in the ore districts [16]. Only by systematically identifying the environmental pollution characteristics of multiple elements in multiple media, as well as migration pathways and constraints on heavy metals in the environment based on the geochemical behavior of sulfide minerals, can we achieve the purpose of classification management and precise policy to ensure adequate supply of resources and simultaneously maintain the quality of the ecosystem.

We studied a typical Sn-Pb-Zn polymetallic sulfide mining area in Nandan County, Guangxi Zhuang Autonomous Region, including surface media such as atmospheric dust, ore, tailings, mine drainage, surface water, stream sediments, soil, and crops. Multimedia samples were systematically collected to conduct a comprehensive investigation of the migration and contamination of heavy metals in the surface environment under the influence of mining operations. Geochemical transformations of heavy metals in various environmental media in the ore district were analyzed in detail, taking into account the characteristics of secondary minerals formed by sulfide weathering, the lithology of the surrounding rocks, climatic conditions, landforms, and geotectonic background. This information provides a sufficient scientific basis for the accurate identification of ecological risks, safe utilization of land resources, and pollution remediation in areas affected by polymetallic sulfide mines.

2. Materials and Methods

2.1. The Study Area

Nandan County is located in the northern area of Hechi City, Guangxi Zhuang Autonomous Region, at the southern foot of the Yunnan-Guizhou Plateau, and is a branch of the Fenghuang Mountains. The terrain is higher in the north and lower in the south and the topography is complex and mainly mountainous. The climate has the characteristics and seasonal patterns of the plateau area. The temperatures are generally low with abundant rainfall and little sunlight. The area is rich in water resources and developed karst landforms, forming many intermittent open rivers and undercurrents; most stream segments have rapid water flow or waterfalls due to steep slopes and high rocky ridges. Nandan County is rich in mineral resources, with more than 20 non-ferrous metals such as tin, lead, zinc, silver, and manganese. Tin reserves are the largest in the country and lead and zinc reserves are also among the most abundant. The area is known as "The Hometown of Non-Ferrous Metals in China" and "Tin Capital".

The Dachang tin-sulfide polymetallic ore field is located in the central section of the Danchi (Nandan-Hechi) metallogenic belt in northwest Guangxi. Its mineral resources are mainly concentrated in the Dachang and Chehe anticlines, where the exposed strata are clastic rock-carbonate rock-siliceous assemblages of the Devonian–Triassic system [17]. This area is one of the important non-ferrous metal industrial bases in China and is globally known for its long mining history and rich mineral resources. Mining and smelting activities are mainly concentrated at the head of the Diaojiang River. In addition to a number of state-owned mining enterprises, it also accommodates hundreds of private beneficiation sites at peak times. With an annual raw ore processing volume of millions of tons, this area makes outstanding contributions to local economic development. However, it also contributes to a series of environmental problems along the Diaojiang River, resulting in abandonment of large areas of farmland and abnormal blood lead levels among residents. The ore mainly consists of cassiterite, pyrite, pyrrhotite, marmatite, galena, etc. The mine recovers Sn, Pb, Zn, Sb, and other resources from the ore for a long time while discharging a large number of sulfides such as pyrite, pyrrhotite, arsenopyrite, and gangue as tailings. Currently, there are as many as dozens of tailing ponds above medium size in the mining area, including Chehe, Changpo, Lutang, etc. Chehe Tailings Pond is circled with mountains in three sides and has a valley outlet in one side, which allows precipitation to quickly flow through the tailings pond along the hillside and merge into the river while carrying a large number of alluvium and endangering the water environment. Generally, the drainage of the tailings pond is mostly treated with lime, which to some extent alleviates the discharge of acidic water.

The Diaojiang River Basin is located in the sloping transition zone from the Yunnan–Guizhou Plateau to the Guangxi Basin. The topography is elevated in the northwest and lower in the southeast, with typical karst geomorphic development. Due to the many mountains in the area and few plains, the area of paddy fields is small, only about 20% of the total arable land area. Chehe town is located along the upper reaches of the Diaojiang River and is in the subtropical monsoon climate zone. The wind direction is mainly southeast and rainfall is concentrated from May to July annually. The primary crop is corn, mainly distributed in the hilly areas on both sides of the Diaojiang River. Rice crops are mainly planted in the karst depressions, sporadically distributed, and account for a very small percentage of the area. The town also has a variety of mining enterprises, such as concentrators, smelters, etc., and is one of the most important towns in Guangxi Zhuang Autonomous Region integrating industry, mining, commerce, and agriculture.

2.2. Sampling Methods

To evaluate the geochemical response of the surficial environment to the mining, dressing, and smelting activities at the Dachang tin-polymetallic ore field in Guangxi, Chehe town was selected as the sampling center as it has relatively concentrated mining and smelting activities. We studied mining activities, climate, topography, and the direction of wind and water flow, and systematically sampled atmospheric dust, surface water, stream sediment, ore, tailings, mine drainage, soil, and crops in and around the mining area. The sampling plan is shown in Figure 1. Ten atmospheric dust samples were collected at locations along the southeasterly wind direction during the dry season and the rainy season. Atmospheric dust samples are collected using high-density polyethylene bottles (25 cm in diameter) and placed at a height of 5–10 m from the ground to prevent soil resuspension. Six sets of co-located surface water and stream sediment samples were collected along the stream segment near Chehe Town in the Diaojiang River, with one sample upstream of the mine site as a background sample, three sampling locations within the ore district, and two sampling locations downstream of the mining area (Figure 1). The surface water samples were collected at the centerline of the river, 30–50 cm below the surface. Composite stream sediment samples were collected at the same locations as the surface water samples, composed of 3–5 subsamples uniformly mixed. The concentrators and tailings ponds are adjacent to each other. Ore samples were collected from the concentrator and mine drainage and tailings were collected from the tailings pond. Mine drainage is stored in an enclosed depression of the tailings dam and the ore and tailings are stored in open-air piles. Soil and crop samples were collected in agricultural fields, concentrated in mountainous areas. A total of 62 samples of corn and root soil and 3 samples of rice and root soil were collected.

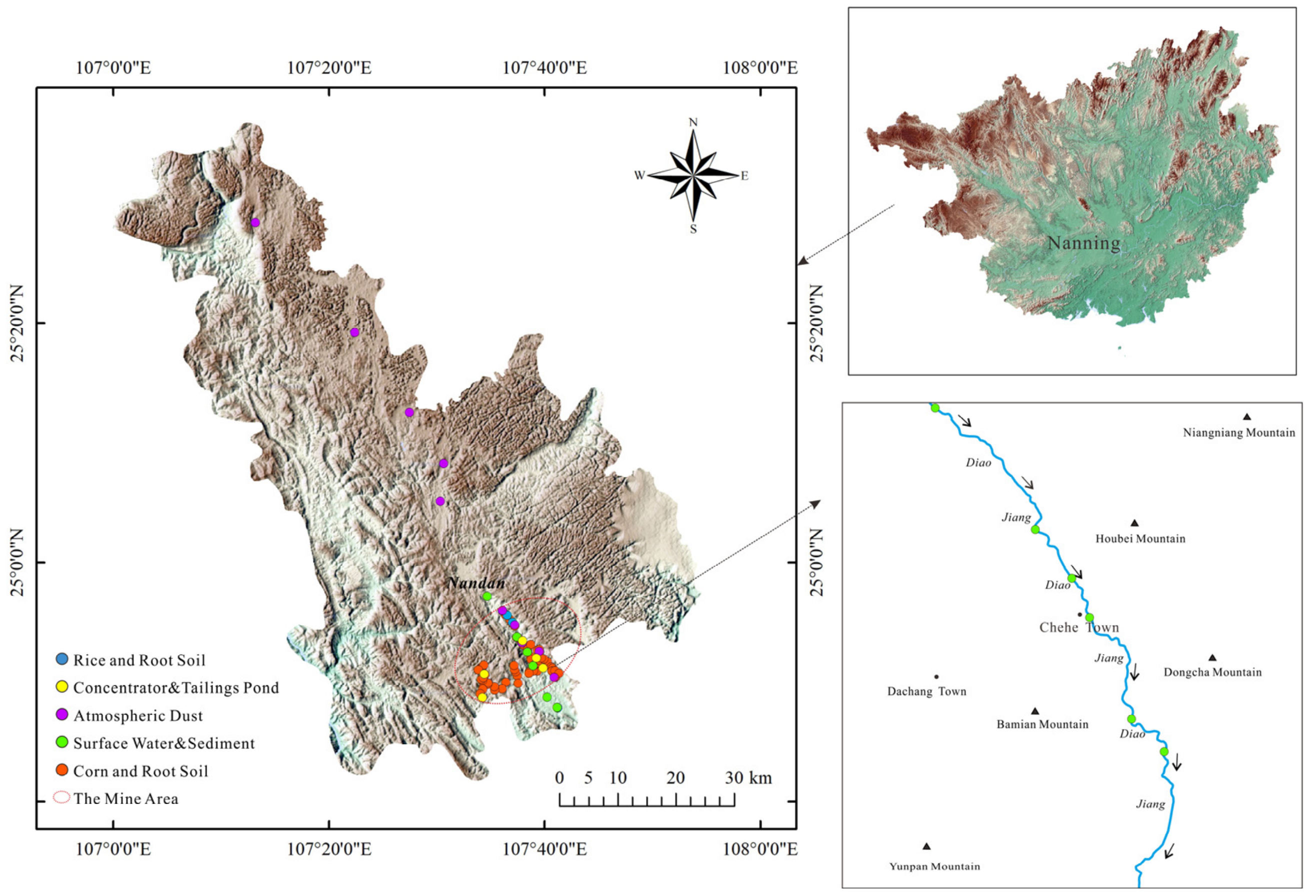

Figure 1. Distribution of sample locations.

2.3. Analysis Methods

After the atmospheric samples were collected, they left the deposition jars for 2–3 d. The supernatant was siphoned and the sediment was transferred into a beaker. We recorded the volume and total amount of the supernatant and sediment, respectively. The supernatant was added with HNO_3 (Guaranteed Reagent), and the precipitate was filtered and dried at 65 °C for testing.

The total volume of each water sample sent for analysis was 5 L. No preservatives were added to 2 L, and this original sample was used to analyze the pH, acidic ions, As, and other elements. The remaining 3 L of each sample was acidified with HCl (Guaranteed Reagent) to analyze concentrations of Cd, Pb, Zn, and other heavy metals.

Soil and sediment samples were dried under natural conditions and ground to 200 mesh. The samples were digested in a polytetrafluoroethylene tube (a mixture of $HClO_4$, HNO_3, and HF) and then dissolved in aqua regia. After stewing, transferred the liquid and diluted with HNO_3 (3%) for analysis.

After washing the crop samples with deionized water, they were ventilated and dried at 60–70 °C for 24–48 h. The dried samples were placed in an agate mortar and ground to 0.42–0.25 mm and mixed evenly for testing.

Sample analysis was conducted by Geology & Mineral Analysis & Test Research Center of Guangxi Zhuang Autonomous Region, which mainly used inductively coupled plasma mass spectrometry (ICP-MS, X-SERIES, Thermo Electron, Waltham, MA, USA; incident power 1400 W), atomic fluorescence spectrometry (AFS, Model AFS-230E, Kechuang Haiguang Instrument Co., Ltd., Beijing, China), inductively coupled plasma emission spectrometry (ICP-AES, IRIS Advantage, Thermo Fisher, Waltham, MA, USA; incident power 1150 W), X-ray fluorescence spectrometry (XRF, PW2440, Philips Co., Eindhoven, The Netherlands), and a pH meter to analyze heavy metals such as As, Cd, Pb, and Zn and other physicochemical indices in the multimedia samples. The measurement errors for the reference materials were within 5% and the errors for the coded samples were <5%. Thus, the data quality was considered reliable. X-Ray Diffraction (XRD, DMAX RAPID II, Rigaku Co., Tokyo, Japan) was completed in the Key Laboratory of Surficial Geochemistry of Ministry of Education of Nanjing University. The test used Cu targets and capillary projection method with a scanning angle of 0–40°.

2.4. Data Processing

2.4.1. Deposition Ratio

The deposition coefficient $R_{deposition}$ is calculated as shown in equations (1), where C_i is average annual atmospheric dust flux density in the mine site and C_j average annual atmospheric dust flux density outside the mine site. $R_{deposition}$ is used to assess the proportion of longitudinal deposition of elements within the mining area.

$$R_{deposition} = (C_i - C_j)/C_i \tag{1}$$

2.4.2. Content Variation Coefficient

Content variation coefficient (ΔC) is used to characterize the relative changes in the content of elements before and after geochemical migration. The formula is shown in (2). C is the concentration of the element, and i, j represents the post-migration and pre-migration assignment media of the element, respectively. $\Delta C > 0$ indicates that during geochemical migration, the element is enriched, and the greater its value, the higher the degree of enrichment. $\Delta C < 0$ indicates that during geochemical migration, the element is depleted, and the greater its absolute value, the higher the degree of dilution.

$$\Delta C_{i-j} = (C_i - C_j)/C_j \times 100\% \tag{2}$$

3. Results and Discussion

3.1. Atmospheric Dust

Heavy metal releases to the atmosphere include dust created by transportation of uncovered ore and smelting emissions. The study area is surrounded by mountains and the dust is not easily dispersed, resulting in significant concentrations of heavy metals in the atmosphere (Figure 2). Annual deposition flux density characteristics of atmospheric heavy metals in the study area are shown in Table 1. There were significant seasonal differences in the deposition flux density of heavy metals such as As, Cd, Pb, and Zn, significantly influenced by rainfall. The deposition flux density of heavy metals in the rainy season was generally higher than that in the dry season, with lower concentrations and high deposition, while the dry season has the opposite characteristics (Figure 3). Over the entire year, the annual deposition flux density for each element was high in the mining area. The annual deposition flux density of Cd was two-times higher than the standard (30 $g/hm^2 \cdot a$) of DZ/T 0295-2016 “Specification of Land Quality Geochemical Assessment [18]”, indicating that the concentrations of heavy metals in atmospheric dust is sufficient to produce significant harm to surface environments such as soil.

Figure 2. Smelter emission in the research area.

Table 1. Geochemical characteristics of heavy metal flux in atmospheric dust (g/hm^2/a; n = 10).

	Dry Season				Rainy Season			
	As	**Cd**	**Pb**	**Zn**	**As**	**Cd**	**Pb**	**Zn**
Min	1.27	0.78	22.55	52.12	4.65	1.24	24.08	74.75
Max	552.15	58.70	197.71	2632.15	1628.54	76.19	1161.17	3173.91
Mean	89.18	13.68	87.95	577.33	196.22	27.86	421.26	1123.85
Annual deposition flux density of heavy metals in the atmosphere of different regions [19–24]								
	Nandan	**Guixi**	**Dinghu Mountain**	**Dabaoshan**	**Changchun**	**Daqing**	**Chengdu**	
As	285	-	-	-	47.9	8.1	27.7	
Cd	41.55	65.6	5.7	1.97	2.5	1.7	17.7	
Pb	509	700	428.4	-	123.1	157.1	459.5	
Zn	1701	2250	1857.8	-	481.5	788.1	1478.3	

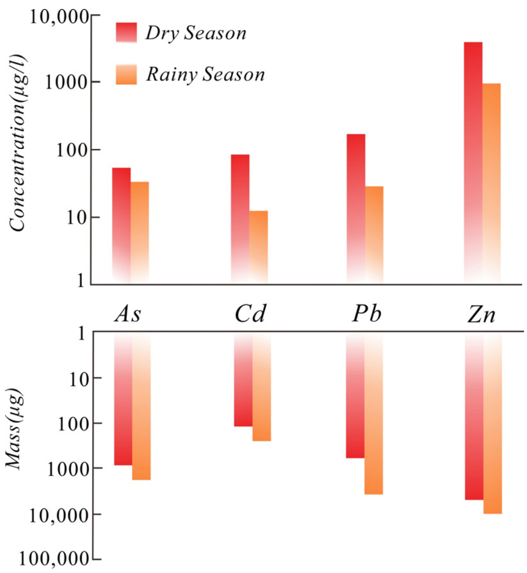

Figure 3. Comparison of characteristics of heavy metals in the atmosphere in different seasons. Log-rithmic coordinates. Comparison of differences in concentration and quality of heavy metals in atmospheric deposition during the dry season and rainy season.

The annual deposition flux densities of heavy metals in the ore district were much higher than those of typical mining agglomerations (Dabaoshan mine), heavy industrial areas (Dinghushan, Guangdong; Daqing; Changchun), economic development zones (Chengdu), and other high-emissions functional areas, and equivalent to those of copper smelting areas (Guixi) (Table 1). The effects of smelting operations on air quality are far greater than those of ore mining, industrial production, and other activities, and there is a risk of secondary pollution by deposition of dust onto the surface environment [19–24].

Emissions characteristics and migration of heavy metals through atmospheric dust transport in the study area were preliminarily evaluated (Figure 4). Due to isomorphism, the migration of Cd, Zn, and other heavy metals in the atmosphere showed similar geochemical behaviors and variations along the wind direction. Namely, the annual deposition flux densities were highest in the mine area and gradually decreased with increasing distance from the ore district. Pb and Zn show similar trends to some extent, but their distribution is also different due to ore type and grade limitations. As is the main component of gangue minerals and also exhibits characteristics with high concentrations in the mining area, but its fluctuations are relatively low. The annual precipitation flux densities of heavy metals in the mine area were closely related to the distribution of ore deposits and mining activities, with significant fluctuations along the wind direction. Heavy metal fluxes in mining areas with strong human disturbance were higher than those in areas with weak human disturbance. Under the combined influences of topography, climate, and the specific gravity of the metal sulfide or metal oxide, diffusion in the atmosphere demonstrated hysteresis. Longitudinal deposition was greater than lateral migration; the proportion of longitudinal deposition for each element was calculated according to (1): As (97.49%), Cd (92.26%), Zn (89.64%), and Pb (88.36%). Beyond about 25 km away from the mine area, the annual atmospheric deposition flux density of heavy metals decreased rapidly and the impact of mining activities on the atmosphere gradually disappeared.

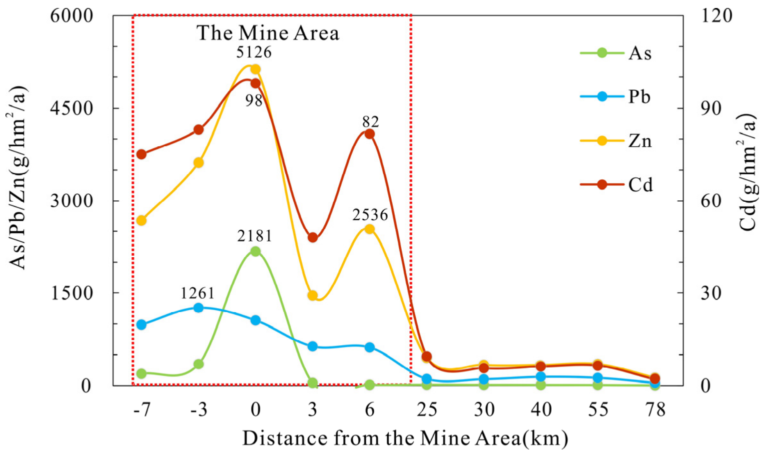

Figure 4. Spatial migration of heavy metals in the atmosphere. (Changes in the concentration of heavy metals migrating along the wind).

3.2. Mine Drainage and Surface Water

Environmental and geochemical characteristics of the mine drainage and surface water within the mine site were analyzed (Table 2). The mine drainage from the tailings pond/dam showed various degrees of exceedance for As and Zn over the limits specified in GB 25466-2010 "Emission Standard of Pollutants for Lead and Zinc Industry", while the concentrations of Cd and Pb were relatively low and did not exceed the limits [25]. Due to oxidation of sulfide minerals in the ore, concentrations of SO_4^{2-} in the mine age were high, with a maximum value of 1472 mg/L. However, SO_4^{2-} readily reacts with Ca^{2+} in the surrounding carbonate rocks to precipitate gypsum, so, after discharge into the river, SO_4^{2-} concentrations in the surface water appear to have been significantly reduced through precipitation and dilution.

Heavy metal concentrations in the river water were much lower than those in the mine drainage. Cd, Pb, and Zn concentrations complied with the Class III limits of GB 3838-2002 "Environmental Quality Standards for Surface Water", indicating low risk, while As exceeded the standard [26]. According to previous data, in 1992, the Diaojiang River was affected by mining activities. The contamination with heavy metals such as As (114 mg/L), Cd (0.64 mg/L), Pb (54.8 mg/L), and Zn (50.5 mg/L) was very high [27]. In 1996, the river remained contaminated by multiple chemicals and the area of pollution had significantly expanded [27]. By 1998, the mine area had implemented large-scale corrective measures, the water quality had significantly improved and dissolved heavy metals concentrations met the national surface water Class III standards [27]. The present study demonstrates that the physical and chemical properties of the surface water in the ore district have remained stable over the past 20 years, with neutral to alkaline pH and good water quality.

Table 2. Geochemical properties of water in the study area (mg/L).

Medium	Sampling Site	As	Cd	Pb	Zn	SO_4^{2-}	pH
Mine Sewage (n = 3)	Tailings pond/dam	0.33 0.007 1.61	0.0005 0.019 0.016	0.0007 0.0007 0.04	0.037 2.45 0.079	1372 215 1472	6.61 7.29 7.28
GB 25466-2010	Direct Discharge Indirect Discharge	0.3 0.3	0.05 0.05	0.5 0.5	1.5 1.5	- -	6–9 6–9
	Concentration	**As**	**Cd**	**Pb**	**Zn**	**SO_4^{2-}**	**pH**
Surface Water (n = 6)	Range Mean	0.018–0.18 0.07	0.0001–0.0032 0.0011	0.0006–0.0007 0.0007	0.0095–0.047 0.0218	87.4–250 155	7.75–8.06 -
GB 3838-2002	Class III	0.05	0.005	0.05	1.0	250	6–9

3.3. Solid Wastes

As the primary solid waste resulting from mining and the source of heavy metal pollution, tailings have been the focus of much research on mine pollution. However, in our study area, in addition to large accumulations of tailings, there is also ore that has not been smelted after grinding. The ore is more sensitive to the supergene environment than tailings due to its much higher sulfide content prior to smelting. As a source of pollution, it presents a greater risk than tailings (Table 3). Stream sediment is an important medium that is both a "source" and "sink" for heavy metals. The geochemical characteristics of the sediment are the result of the combined effects of chemical weathering and physical migration of pollutants from the upstream mines. The sediment also acts as a carrier of heavy metals in the river and can be a source of secondary pollution. Heavy metal concentrations in the sediment of the study area were high (Table 3).

Table 3. Statistics of heavy metals characteristics of solid wastes.

		Fe_2O_3	S	As	Cd	Pb	Zn	pH
		%	%	μg/g	μg/g	μg/g	μg/g	-
Tailings (n = 2)	Min	3.57	2.51	5484	22.6	328	2833	7.71
	Mean	6.64	3.45	5908	47	2203	6397	-
	Max	9.70	4.39	6331	71	4078	9960	7.85
Ore (n = 4)	Min	21.42	21.87	32,440	85.90	3395	10,310	3.20
	Mean	21.52	24.57	65,073	91.98	3759	10,663	-
	Max	21.69	27.14	99,080	99.30	4010	11,210	4.88
Sediment (n = 6)	Min	5.00	0.06	32.60	1.60	34	243	7.32
	Mean	7.98	0.73	2321	35.70	218	3710	-
	Max	10.86	1.34	3788	64.70	334	5850	8.80
$\Delta C_{sediment\text{-}tailings}$	-	20.25%	−78.77%	−60.71%	−23.72%	−90.10%	−42.01%	-
$\Delta C_{sediment\text{-}ore}$	-	−62.93%	−97.02%	−96.43%	−61.19%	−94.20%	−65.21%	-

Based on the mineral compositions of various media (Figure 5), the ore is mainly composed of primary sulfide minerals such as sphalerite, pyrite, and pyrrhotite. It has a strongly acidic pH and very high concentrations of various metals related to mineralization, such as S, Fe, As, Cd, Pb, and Zn, which present a great potential risk. Tailings and sediment that are exposed to hypergene conditions for a long time, in addition to retaining some primary sulfide minerals, quartz and calcite, are mainly composed of secondary minerals such as kaolinite, goethite, illite, and gypsum. The pH becomes neutral to alkaline and the concentrations of S and metals precipitously decline compared to those in the ore. The tailings had undergone the processes of mining, smelting, and open storage, the heavy metals were mainly in the form of oxides, and the potential risk was greatly reduced compared with that of ore. Heavy metal concentrations in sediment are the result of the combined action of chemical weathering and physical migration of ore and tailings. Although the concentrations of As, Cd, Pb, and Zn in sediment had decreased significantly compared to the source material, it was still elevated relative to other surface media such as soil and crops, and poses a threat to the safety of the environment.

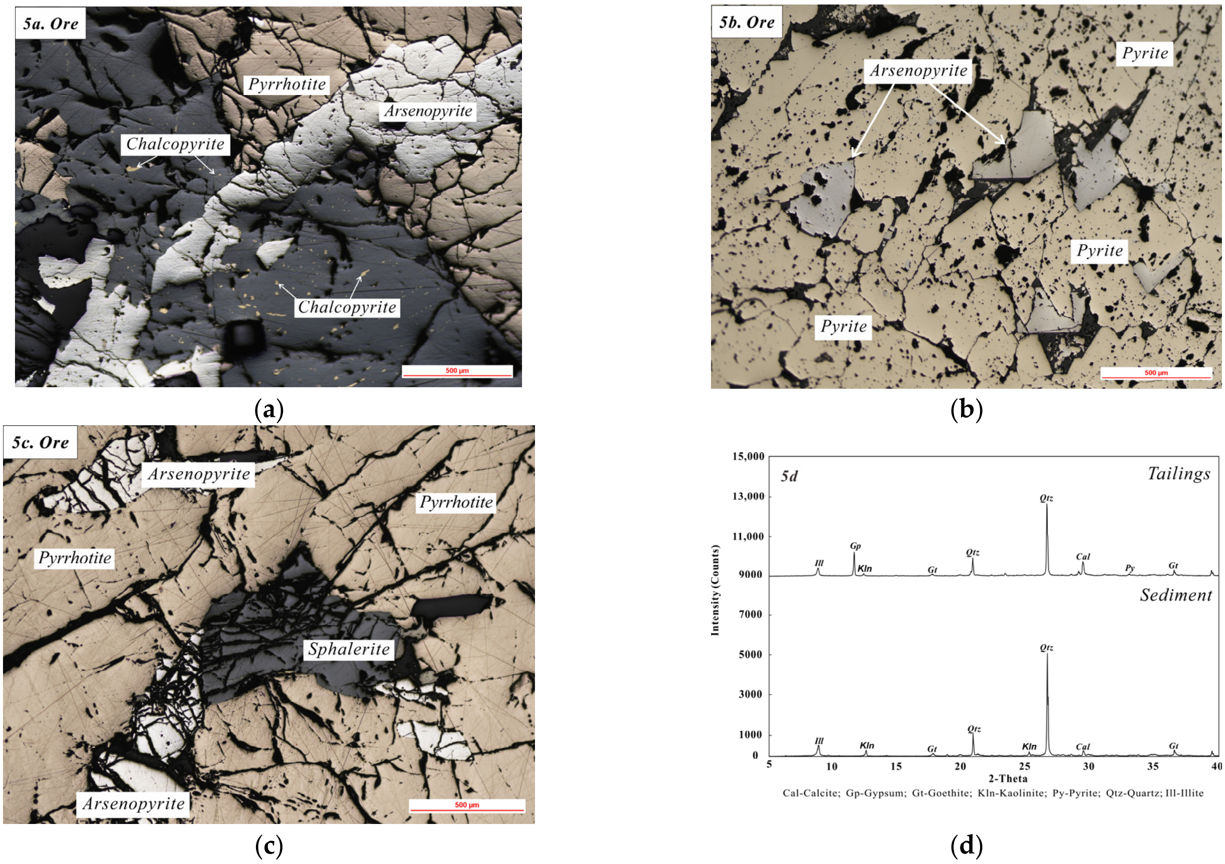

Figure 5. Mineral composition of ore, tailings, and stream sediment. (**a**–**c**) Show the microscopic results of rock slices, and (**d**) shows the analysis of XRD of tailings and sediments. Figure 5 reflects the mineral composition of the samples.

The migration and transformation of elements during the supergene process can be characterized by ΔC. The heavy metals in the river sediments, driven by both physical and chemical dynamics, underwent different degrees of leaching compared to the ore and tailings samples. As and Pb were leached more heavily, followed by Zn and Cd with a similar ΔC. The tailings had gone through the dressing and smelting process and, thus, the heavy metals were relatively stable, with leaching rates far lower than those of the ore. One of the primary sulfide minerals constituting the deposit is pyrrhotite, which has a defect structure. Some of the Fe^{2+} in the crystal structure is replaced by Fe^{3+} and the cation position has some vacancies, resulting in instability of the crystal structure. Thus, it oxidizes before other minerals, forming a dissolution-acid supply system based on Fe^{2+} oxidation and Fe^{3+} hydrolysis [28–30]. As oxidation continues, pyrite also begins to weather and dissolve, and the low-pH pore water continuously leaches and releases additional Fe^{3+} to the elemental cycle. This process greatly increases the decomposition rate of primary sulfides such as arsenopyrite, sphalerite, and galena [28–30].

The stability of sphalerite is intermediate between that of pyrrhotite and pyrite, and the weathering and dissolution of sphalerite results in release of large amounts of Zn^{2+} and Cd^{2+} into the environment. The released heavy metals either co-precipitate or adsorb into the early-formed iron oxides/hydroxides or metasomatize with carbonate rocks to form precipitates, thus reducing harm to the environment [6,30]. Galena has greater resistance to weathering than sphalerite, because during weathering of galena, insoluble anglesite ($PbSO_4$) is formed and adheres to the mineral surface, preventing further oxidation. However, coexistence with pyrite greatly enhances the dissolution of galena, and Pb^{2+} released in a carbonate environment metasomatizes with Ca^{2+} in the surrounding rock to form insoluble cerussite [28,29,31]. Studies have shown that smithsonite has a much higher ability to migrate in supergene fluids than cerussite, which is largely retained in situ after formation [32]. In contrast, Zn readily migrates with fluids [32].

Migration of mineralization-related elements such as S, Fe, As, Cd, Pb, Zn, etc., in the ore-tailings-sediment system are somewhat correlated due to interactions, synergistic release, adsorption, and precipitation, and the regulation of carbonate rocks and secondary minerals (iron oxide/hydroxide). To a certain extent, these processes reduce the harmful effects of deposit mining on the environment. In addition to the release and migration of heavy metals due to chemical weathering, physical migration also affects heavy metal concentrations in the sediment, resulting in a high-concentration area of heavy metals downstream of the mine site (Figure 6). These results are consistent with those of Jian (2010), whose research results indicate that the impact of the mine on sediment extends up to 200 km downstream [33].

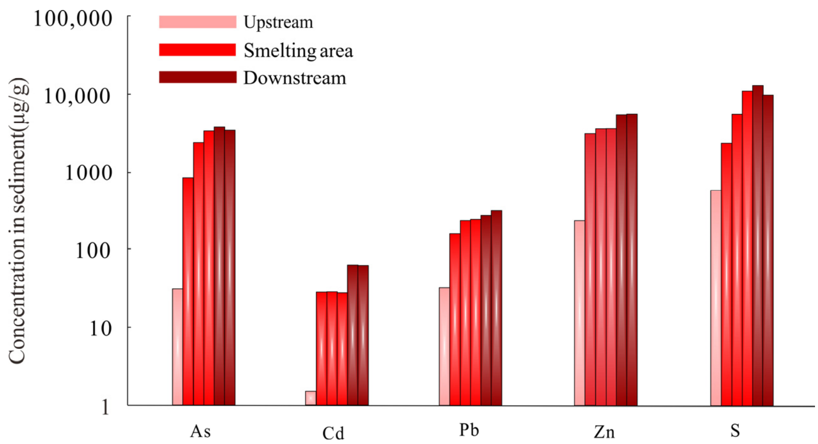

Figure 6. Migration characteristics of different elements in stream sediment. Logarithmic coordinates. The color from light to dark indicates the concentration characteristics of heavy metals in the upstream, midstream, and downstream in order.

3.4. Risk Assessment for Soil and Crops in Mining Area

Soil is the end receptor of geochemical processes such as atmospheric deposition and weathering of ore/tailings, and its environmental quality directly affects the safe production of crops and human health. Heavy metal concentrations in soil in the study area are shown in Table 4. It is apparent that mining and smelting in the study area have resulted in serious contamination in the soil. According to the risk screening values of GB 15618-2018 "Soil Environmental Quality Risk Control Standard for Soil Contamination on Agricultural Land [34]", the dryland soils in the study area are seriously contaminated with heavy metals, with exceedance rates for metals such as As, Cd, and Zn of >90% and an exceedance rate for Pb of 70.97%. However, overall acidification is not high; the soil samples were mainly neutral to alkaline, which promotes fixation of heavy metals. Exceedances for heavy metals in paddy fields were greater than for dryland. The soil pH was slightly acidic, which is conducive to mobilization of heavy metals, increasing risks. However, due to a limited planting area, the sample quantity for the paddy fields was not statistically significant and the results are usable only for reference. The high concentrations of heavy metals in the topsoil near the mine site are mainly influenced by contributions from the mining activities, including atmospheric deposition and river transport. The surface water environmental quality is good and its contribution of heavy metals to the soil was much lower than that of the atmosphere. Thus, contamination with heavy metals of the cultivated soils was mainly due to atmospheric deposition.

Table 4. Characteristics of heavy metals content in topsoil (µg/g).

Paddy Field (*n* = 3)	**As**	**Cd**	**Pb**	**Zn**	**pH**
Min	49.3	1.92	61.5	222	5.68
Mean	61	4.04	138.50	420	-
Max	67.2	5.41	196	548	6.2
Exceedance rate	100%	100%	66.67%	100%	-
Dryland (*n* = 62)	**As**	**Cd**	**Pb**	**Zn**	**pH**
Min	23.3	0.15	28	67.9	4.47
Mean	685	12.53	569	1562	-
Max	5273	108	5003	14,715	8.48
Exceedance rate	90.32%	98.39%	70.97%	93.55%	-

The heavy metal concentrations in corn and rice samples from the study area are shown in Table 5. According to the provisions of GB 2762-2017 "National Standard for Food Safety Maximum Levels of Contaminants in Foods [35]", heavy metals in corn do not exceed these standards and are safely edible, consistent with the results of Lu et al. (2017) [36]. In contrast, the Cd concentrations in rice were all higher than the national standard. Although the sample quantity is small, the potential for high risk cannot be ignored.

Table 5. Characteristics of heavy metals in crops (µg/g).

Rice (*n* = 3)	**As**	**Cd**	**Pb**	**Zn**	**Corn (*n* = 62)**	**As**	**Cd**	**Pb**	**Zn**
Min	0.25	0.26	0.078	19.1	Min	0.03	0.0075	0.07	19.9
Mean	0.27	0.60	0.09	21.03	Mean	0.10	0.02	0.09	31.10
Max	0.3	1.13	0.1	24.8	Max	0.32	0.085	0.2	46.2
Exceedance rate	-	100%	0%	-	Exceedance rate	0%	0%	0%	-

The differences in risks between the crops are not only by differences in absorption, but also by the terrain and landforms in the study area, the areas of cultivation, and the degree to which they are influenced by the supergene media. Nandan County is located at the southeast edge of the Yunnan-Guizhou Plateau. After crustal uplift, the riverbed was elevated, resulting in a relative lowering of the groundwater level and a difference in hydraulic head. Because the river channel is relatively narrow, the river flow is rapid and the area was dominated by downcutting. These conditions are not conducive to sediment deposition or the formation of a floodplain. Therefore, the study area is mainly planted with dryland crops, and paddy crops are sparsely distributed. The dryland crops are mainly planted on the slopes of both banks of the river, which are less affected by surface water and sediment. Corn is also covered in leaves and has little contact with the atmosphere; thus, it is less affected by atmospheric deposition. Therefore, despite the high risk associated with heavy metals in the soil, absorption of heavy metals by corn is low, and the edible portions are safe. Paddy fields are scattered in karst depressions on both sides of the river where irrigation is easy. Irrigation with river water carries a large amount of sediment with high concentrations of heavy metals. These metals are more bioavailable under acidic pH conditions, which results in unsafe concentrations in rice.

3.5. Comprehensive Environmental Response and Pollution Prevention Suggestions

3.5.1. Mechanism of Heavy Metal Migration and Transformation

Ore and tailings exposed to the surface will undergo strong oxidation under epigenetic conditions. The dissolution of major minerals such as marmatite, galena, pyrite, and pyrrhotite can cause the release of large amounts of heavy metals, and cause acidification of surrounding rivers and soils. The reaction is as follows [8]:

$$\text{Pyrite: } FeS_{2(s)} + 15/4O_2 + 7/2H_2O \rightarrow 2SO_4{}^{2-} + Fe(OH)_3 + 4H^+$$

$$\text{Pyrrhotite: } Fe_{(1-x)}S_{(s)} + (2 - x/2)O_2 + xH_2O \rightarrow (1 - x)Fe^{2+} + SO_4{}^{2-} + 2xH^+$$

$$\text{Marmatite: } (Zn_{(1-x)}Fe_x)S_{(s)} + 2O_2 \rightarrow (1 - x)Zn^{2+} + xFe^{2+} + SO_4{}^{2-}$$

$$\text{Galena: } PbS + O_2 \rightarrow Pb^{2+} + SO_4{}^{2-}$$

$$\text{Arsenopyrite: } 4FeAsS(s) + 11O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4H_3AsO_3 + 4SO_4{}^{2-}$$

Generally, the released heavy metals migrate as cations with high biological activity and risk. However, under the background of karst, metal cations will combine with $CO_3{}^{2-}$ to form precipitation, and the H^+ released by the weathering of sulfide minerals will also be buffered to a certain extent by $CO_3{}^{2-}$-$HCO_3{}^-$, as shown below [37]. Therefore, lime addition is also used in many mining areas to reduce the ecological hazards of sulfide deposit mining. In addition to co-precipitation with carbonate ions, metal cations can also be adsorbed by clay minerals such as illite and kaolinite, as well as iron and manganese oxides. Therefore, heavy metals in water mainly accumulate in sediments as particulate, which is consistent with the research results of this paper. It is worth noting that the buffering effect of carbonate rocks on heavy metals is limited, and serious acidification and heavy metals pollution can still occur in ore districts with long mining time, high grade and large scale.

$$HCO_3{}^- + H^+ \rightarrow H_2O + CO_2$$

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3{}^-$$

$$Zn^{2+} + HCO_3{}^- \rightarrow H^+ + ZnCO_3 \text{ (Smithsonite)}$$

$$Pb^{2+} + HCO_3{}^- \rightarrow H^+ + PbCO_3 \text{ (Cerussite)}$$

According to the previous results, in addition to the heavy metals released by chemical dissolution, smelting is also one of the important ways for heavy metal emissions. The heavy metals discharged from smelting undergo high-temperature oxidation and are mostly emitted into the environment in the form of oxides. The reaction process is shown below. Therefore, although the annual flux density of heavy metals in the atmosphere is relatively high, their activity is low and they are less harmful to crops. However, long-term accumulation in the soil can affect soil functions and lead to ecological imbalances.

$$2ZnS + 3\,O_2 \text{ (high-temperature)} \rightarrow 2ZnO + 2SO_2$$

$$2PbS + 3\,O_2 \text{ (high-temperature)} \rightarrow 2PbO + 2SO_2$$

3.5.2. Potential Risk Assessment

Based on the above investigation results and mechanism, the atmosphere is the most sensitive to mining activities within the mining area, while the pollution downstream of the mining area is mainly concentrated in sediments.

Atmospheric heavy metals have a high proportion of vertical deposition and the risk receptors are mainly soil and human. (1) Soils: the accumulation of heavy metals in soil is long-term, cumulative, concealment, latency, and irreversibility, which have adverse effects on the physical and chemical properties of soil and microbial structure [1]. The further intensification of pollution will also pose a threat to the survival of biological communities [38]. (2) Humans: atmospheric particulates enter the human trachea, lungs, and even the blood system through the respiratory pathway, leading to cardiovascular and other diseases [39]. Nandan County has been reported that human lead poisoning in smelting areas, and developmental delays and immune deficiencies are common in children. It can be seen that heavy metals ingested through respiration, although they are trace elements, are extremely harmful to human health. Therefore, it is important to control emissions and deposition of atmospheric heavy metals in the mine area to maintain a safe soil environment and protect human health.

The stream sediment receives high concentrations of heavy metals from the ore and tailings. However, due to the influence of the mountainous area, the anthropogenic disturbance of the water is relatively low, making the sediment in the mining area either carried away by the current and deposited downstream, or deposited in the river bottom, less harmful. Sediments with high heavy metals concentration pose a great threat to the downstream floodplain because, in open areas, downcutting gradually decreases and erosion increases. With the development of floodplains, sediments will gradually accumulate on convex banks. Under specific conditions (e.g., low pH), accumulated heavy metals will be activated and released, leading to high-risk secondary pollution, endangering soil, crops, and even human beings along the food chain. Therefore, risk abatement in the downstream area should focus on the river sediment.

3.5.3. Suggestions on Prevention and Control of Pollution

In view of the above environmental results, the following suggestions are provided for risk management and control in the study area:

(1) The area of concentrated mining activities is mainly contaminated through atmospheric deposition, of which smelting emissions are the main source, supplemented by dust from transportation. Therefore, it is necessary to control atmospheric heavy metal deposition within the mine area. Rainfall has a significant impact on the concentration and flux of atmospheric deposition. Therefore, the smelting operation should be properly adjusted in the rainy season to prevent flux increases due to the driving force of rainfall, and the mining and transportation plan can be improved to minimize dust emissions.

(2) Downstream of the mining area, the main focus should be on sediment management. Through the ore district, the river is fast flowing and downcutting the surrounding geology. The middle and lower reaches are more prone to lateral erosion and sedimentation as the flow velocity decreases and the river channel widens. Therefore, special attention should be paid to the risk of secondary pollution caused by heavy metals in sediment where the tributaries converge into the main river, river convex banks, and floodplains. There are differential hazards to corn and rice crops. Consequently, we recommend adjusting the planting structure accordingly, gradually converting paddy fields to dryland crops to reduce the risks associated with paddy soils and irrigation, and planting mainly dryland crops that are safe for consumption.

4. Conclusions

1. The heavy metals pollution caused by atmospheric deposition in the mine area is relatively high. The annual deposition flux density of Cd is two-times higher than the relevant standards. Influenced by climate and topography, heavy metals contamination from atmospheric deposition migrates about 25 km along the wind direction and then decreases. About 90% of the heavy metals migrate in the form of vertical deposition in the mine area.
2. Effluent drainage from the ore district contains individual heavy metals exceeding the standards, but the water quality of the river is less affected by the mining activities. After treatment, only As slightly exceeded the standard at the river bend, the pH of

the water was neutral–alkaline, and the concentrations of soluble heavy metal ions were low.

3. Weathering and migration of ore and tailings contribute to high concentrations of heavy metals in river sediments, mainly downstream of the mine. Risks associated with migration of sulfide particles are high, while heavy metals migrating in chemical form are more stable after co-precipitated with carbonates or adsorbed by secondary iron oxides.
4. The soil in the mine area is greatly affected by mining activities. The surface soil is significantly enriched in heavy metals and greatly exceeds the standards. It is mainly influenced by atmospheric deposition. The risks of the soil environment to various crops differ. Cd in rice greatly exceeds the standard, while corn does not exhibit heavy metals exceedances and can be safely consumed.

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