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The Impact of Molybdenum Mining on Cd Pollution along Wenyu Stream in Qinling Mountains, Northwest China

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Abstract: Mining has brought many environmental problems to the surrounding soil, water, and air, with toxic elements contaminating surface water, threatening ecological balance and human health. This study selected the Wenyu watershed downstream from a large molybdenum mine in the Qinling Mountains as the study area, aiming to explore the impact of molybdenum mining on surface water quality. The content characteristics of Cd, Pb, Cu, Cr and Hg in surface water, sediment, and rock samples were analyzed by field sampling and chemical testing. The results showed only obvious Cd pollution. The pollution status and ecological risk level of surface water and sediment samples in the Wenyu Stream watershed were evaluated using the single pollution index method, geo-accumulation index method, and Hakanson potential ecological risk assessment method. Finally, the sources of Cd pollution and the impact of mining on Cd distribution in the Wenyu Stream were comprehensively discussed. The research results showed that Cd content in the Wenyu Stream was significantly affected by mining activity and the coefficient of variation of Cd content reached 99.44%. Among 22 surface water samples, 21 samples met the Class II water standard, indicating a clean overall water quality of the Wenyu Stream, and only one sample exceeded the Class II water standard with a mild pollution level. All 15 sediment samples were polluted to varying degrees and the most severely polluted sample had reached a moderate to strong pollution level. Most of the samples were at a moderate pollution level. The potential ecological hazard indexes of Cd content were at medium to very strong risk level, indicating that the overall sediment in the main ditch of the Wenyu Stream was under a strong ecological risk level. The main sources of Cd pollution, including acid mine drainage, regional geological background, sediment release, and atmospheric dry and wet deposition, were discussed.

Keywords: molybdenum mining; cadmium pollution; surface water; sediment

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1. Introduction

Mining resources exploration has made great contributions to the development of the local economy and has brought a series of favorable conditions for local employment, taxation, etc. However, unreasonable and unscientific mining resource development has also caused a series of ecological environment deterioration problems, such as vegetation damage, landscape damage, groundwater level decline, water pollution, and heavy metal pollution in crops [1–4]. The problem of heavy metal pollution in surface water has always been the focus of many studies because it is related to the daily life of residents living near the river, such as drinking water quality, crop irrigation, and food safety. Predecessors have investigated the total amount of heavy metal elements in the sediments of Taiyu River and Taiyu Reservoir in Tongguan gold mining area and discussed the pollution degree of heavy metal elements in the river sediments concerning the gold mining activities [5].

Some studies also showed that the contents of Hg, Pb, Cd, As, Cr, Cu, and Zn in the sediments of the Xiyu river were adjacent to the Taiyu River and evaluated the pollution of the Xiyu River sediment affected by gold mining activities. The results indicated that Hg and Pb were the main pollution elements. Meanwhile, the elements with strong potential ecological hazards in the whole Xiyu River were revealed to be Hg and Pb through the evaluation of the potential ecological hazard index method [6]. Another study analyzed the content of heavy metal elements in the river water and sediment of typical rivers in the Xiaoqinling gold mining area and four rivers, with seven heavy metal elements in the mining area exceeding the national standard limit. The main occurrence form of heavy metal elements in rivers was the sedimentary state, and the adsorption and desorption of sediment were the main controlling factors for the changes of heavy metal elements in river sediment and river water along the river [7]. In southern China, the mining drainage water from Dabaoshan polymetallic mine in Guangdong Province has a long-term impact on the Hengshi River. Many studies have studied the spatial distribution of the concentration of six heavy metal elements (Mn, Cu, Zn, As, Cd, and Pb) in the suspended solids of the river. The results showed that the suspended solids in the Hengshi River were seriously polluted by heavy metals from Dabaoshan mining drainage water, and the concentration of heavy metals gradually decreased along the flow path, which was significantly positively correlated with the content of suspended solids [8]. Subsequently, 60 water samples were collected in the Dabaoshan mining area by 1 km square grid cells, and the distribution characteristics of 10 toxic elements, including Cr, Cd, Co, Ni, Cu, Zn, As, Sb, Hg, and Pb, were obtained through chemical testing. It was found that the most serious pollution was Cd, followed by Zn, Cu, Pb, Cr, Ni, and Hg. According to the analysis of the concentration center distribution of elements, the pollution sources are mainly pit soil, tailings, waste rock piles, and civilian mining sites [9]. Many previous studies on heavy metal pollution of rivers in mining areas in China have played a strong role in promoting the prevention and control of river pollution and achieved fruitful results. However, for the research on heavy metal pollution of rivers in the mining area, most predecessors used sediment to deduce the pollution of river water, while few studies have comprehensively evaluated water pollution by directly testing river water samples and studying the content characteristics of heavy metal elements in sediment, rock, and ore samples [10,11].

Cadmium (Cd) is a toxic heavy metal element which has the characteristics of high toxicity, difficult degradation, and easy residue and is one of the “five toxins” in the environment. Mining, beneficiation and metallurgy, sewage irrigation, and other activities will lead to the entry of Cd into the environment, which will not only affect the quality of water and soil, cause harm to the ecological environment, but also directly affect the quality and safety of agricultural products and threaten people’s health through the food chain [12]. In recent years, heavy metal pollution incidents have occurred frequently, causing serious harm to people’s production and life and local water environment ecology. Among them, the cadmium pollution incident in Longjiang, Guangxi province, in January 2012, had a significant social impact [13]. Since the 1920s, with the development of the global electrolysis industry, the annual production of Cd has significantly increased, and the environmental pollution problems caused by Cd have also emerged [14]. The most famous public nuisance event caused by Cd pollution is the Itai-itai disease event in the Jinzū River of Toyama Prefecture, Japan [15]. In addition, according to relevant research reports, the “cancer village” in Longling village, Hua County, Shaanxi Province, may also be related to Cd pollution [16]. Therefore, studying the pollution characteristics of representative harmful heavy metal element Cd is of great significance for river pollution prevention and control work.

Qinling Mountains is an important water conservation area for the South–North Water Transfer Project. In the journey of carrying out ecological civilization construction, its important position is increasingly prominent [17,18]. As a unique resource treasure trove and national-level ecological environment protection zone in recent years, Shaanxi Province has issued a series of ecological environment protection policies and regulations for the Qinling Mountains [19,20]. A previous study had discussed the overlying water and sediment in a reservoir downstream of a molybdenum mining area, but a comprehensive analysis of the pollution of surface water and sediment in streams or rivers has not yet been conducted [21]. In order to explore the impact of molybdenum mining activities on surface water quality, Wenyu Stream, within the influence range of a large molybdenum mine exploration in the Qinling Mountains, was selected as the study area. On the basis of analyzing the Cd, Pb, Cu, Cr and Hg contents in surface water, sediment, and surrounding rocks, only Cd exceeded the limit given by Soil Environmental Quality—Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018) and Environmental Quality Standard for Surface Water (GB 3838-2002) [22,23]. Then, the single pollution index method was used to evaluate the pollution status of Cd in surface water in Wenyu Stream. The geoaccumulation index and potential ecological risk evaluation were applied to study the pollution status and ecological risk degree of Cd in sediment and to explore the source of Cd in river water. This manuscript aims to provide a scientific basis for the sustainable development of the mining industry and the prevention and control of water and soil environmental pollution in the region.

2. Materials and Methods

2.1. Study Area

Wenyu Stream originates from the valley of the southeast slope of the Qinling Mountains, about 5 km northwest of Jindui town in the southeast of Shaanxi province. The stream is formed by several mountain streams with a total length of about 33 km from north to south. The mining and mineral processing area is 26 km away from the Luohe River downstream of the Wenyu Stream (Figure 1). The stream bed in the valley at the upper reaches of the stream is narrow, with a rapid and small flow. Only a small amount of sand and gravel are deposited at the bottom of the stream bed. Bedrocks are exposed in some sections, and farmland is rarely distributed on both banks. The terrain from the middle reaches of the stream to the downstream banks is relatively flat, the stream bed is becoming wider, the flow is slowing down, the flow is gradually increasing due to the continuous inflow of branch streams, and the sediment at the bottom of the stream bed is gradually increasing. The middle and upper reaches of Wenyu Stream are a large-scale molybdenum open-pit mining and beneficiation area. The stream is about 7 km long from north to south. Mining facilities, such as open-pit mining, waste piles, tailings pond, and concentrator, are distributed on the terraces on the east and west sides of the ditch. The study area is situated within the monsoon humid climate zone at the southern edge of the warm temperate zone, featuring distinct climatic patterns in mountainous regions. The mean annual temperature within this mining locale averages 11.5 °C. Precipitation levels typically range around 770 mm annually, with a significant portion of this precipitation concentrated between July and October, constituting approximately 60% of the total. Throughout the year, the prevailing wind direction is predominantly northwest-east, with an annual average wind speed of approximately 1.5 m/s [24]. The fault structure in the study area is the Yanmen sag fault, with strike of 70° to 90°, dip of 62° to 72° and width of 200 m to 300 m. The exposed strata are mainly volcanic rocks of the Middle Proterozoic Xionger group, including metamorphic andesitic porphyrite and tuffaceous slate. In the southeast of the study area, some quartzite of the Mesoproterozoic Daokou group is unconformably covered in the Xionger group. The intrusive rocks are mainly Yanshanian granite porphyry [25]. The main minerals in the large molybdenum mining area are molybdenite and pyrite, accompanied by sphalerite and chalcopyrite. The mine has been explored for over five decades since 1966.

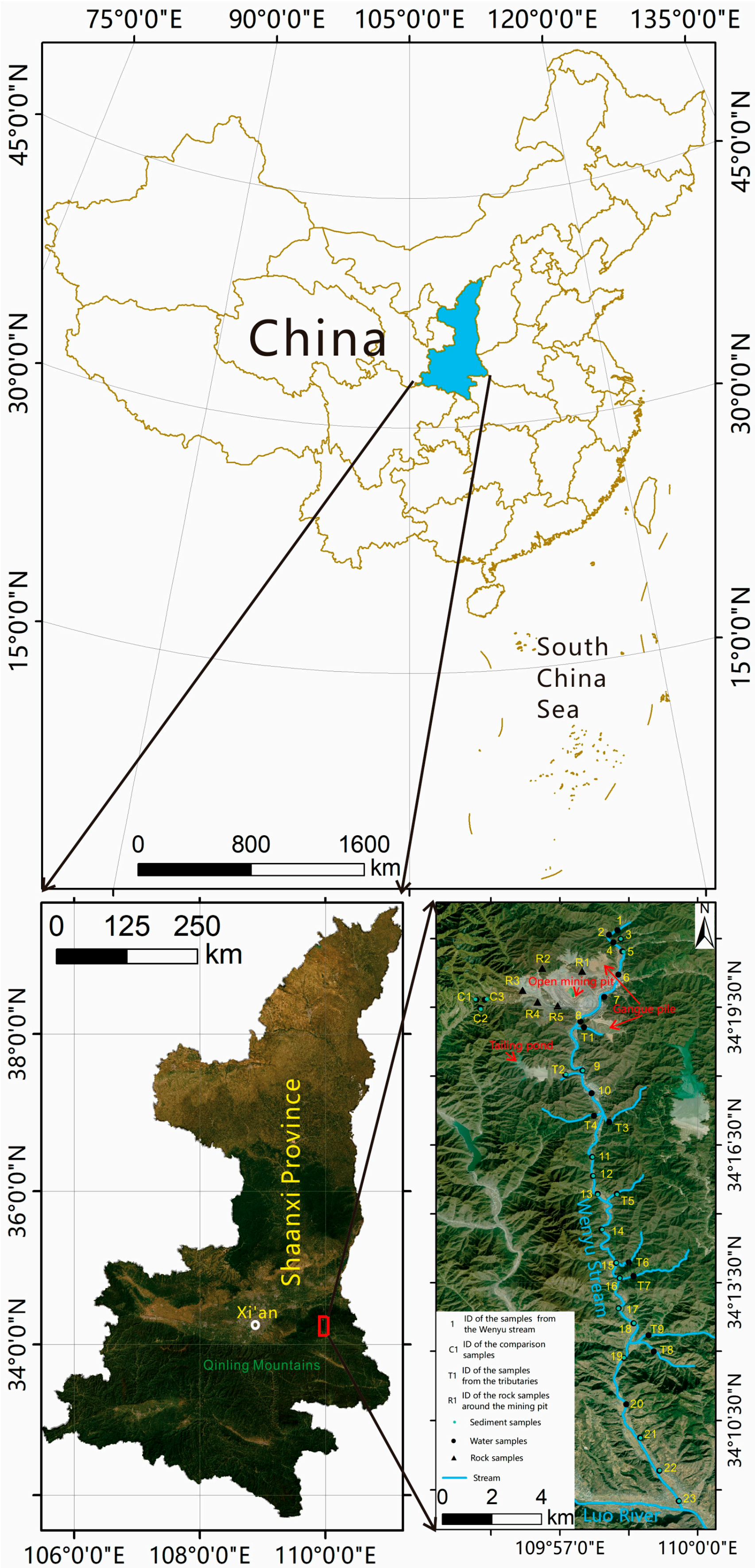

Figure 1. The map of the study area.

2.2. Methods

In this study, surface water and sediment samples were collected from north to south at an average density of one sample per kilometer in the Wenyu Stream Basin and within a process of about 26 km that may be affected by mining activities. Water samples and sediment samples upstream of the tributary inlet of Wenyu Stream were also collected. A total of 32 water samples and 17 sediment samples were collected in the field work from July to August in the year of 2022 (Figure 1). In order to compare and evaluate the impact of Molybdenum Mining on the enrichment of toxic elements in streams and the source of pollutants, three water and sediment samples were collected as the contrast samples at the ridge where there was no mining activity at the source of the Wenyu Stream (sampling points of C1, C2, and C3 in Figure 1) and five surrounding rock samples were collected around the open pit (Figure 1, sampling points of R1 to R5).

When collecting water samples, 500 mL clean polyethylene bottles were used to collect surface water samples, and small shovels were used to collect fine sediment at the bottom of the streambed. The sediment samples were put into cloth bags with plastic bags inside. The sediment samples were dried at room temperature, ground with a mortar, and sieved through a 200 mesh sieve for analysis and testing. Rock samples were processed to 200 mesh by coarse crushing, medium crushing, and shrinkage fine grinding for analysis and testing. A certain amount of sediment powder was weighed, an appropriate amount of aqua regia was added, and the mixture was heated on a heating plate to boil slightly for 2 h for digestion. After digestion, the solution was cooled, filtered with qualitative filter paper, and collected. The volume was fixed to a certain scale. A certain amount of rock powder was weighed and added into a tetrafluoroethylene crucible, distilled water was added to infiltrate, then an appropriate amount of perchloric acid was added, and it was heated on the electric heating plate to dissolve. The solution was removed when it was nearly evaporated to dryness, an appropriate amount of hydrofluoric acid and distilled water was added after cooling, and then evaporate to dryness. Finally, the crucible was removed, an appropriate amount of perchloric acid was added, and then it was heated until the white smoke of perchloric acid disappeared. After evaporation, an appropriate amount of hydrochloric acid and a small amount of distilled water were added, and then it was heated until the solution is transparent. The solution was cooled and then fixed to a certain scale. The analysis of Cd in water sample, sediment, and rock was completed by Xi'an Geological Survey Center of China Geological Survey. All testing steps were carried out in strict accordance with the Technical Code for China Geological Survey—Technical Requirements for Analysis of Ecological Geochemical Evaluation Samples (DD2005-03) [26]. The pH values of the water samples were measured in the laboratory with Rex phs-3c pH meter (Shanghai Inesa Scientific Instrumental Co., Ltd., Shanghai, China), the measurement resolution was 0.01 pH, and the accuracy was about ± 0.01 pH. The Cd in the water sample was determined by an inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Fisher Scientific Inc., Waltham, MA, USA). Before determination, the water samples were acidified with 1% superior pure nitric acid to pH < 2. The contents of Cd in sediment samples were mainly determined by an induced coupled plasma atomic emission spectrometer (ICP-AES) (Thermo Fisher Scientific Inc., Waltham, MM, USA). Rock samples were determined by an atomic fluorescence spectrometer (AFS-2202E) (Beijing Haiguang Instrument Co., Ltd., Beijing, China).

The relative deviation limits of Cd, Pb, Cu, Cr, and Hg in the two standards of Soil Environmental Quality—Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018) and Environmental Quality Standard for Surface Water (GB 3838-2002) should be within 20%, and 10% of the duplicate samples of each batch of tests should be randomly selected for retest. In this study, 3 water samples and 2 sediment samples were selected as duplicate samples. The quality of sample test results shall be evaluated according to the relative deviation:

$$\mathrm{RD} = \frac{|A - B|}{(A + B)} \times 100\% \quad (1)$$

where RD is the relative deviation, A is the measured values, and B is the measured values of the duplicate samples.

The water quality in this study was evaluated using the single pollution index method. In accordance with the objectives of watershed classification for Wenyu Stream, which serves as a primary drinking water source protection area, the water quality of Wenyu Stream must meet the Class II surface water standard [27]. The Cd single pollution indexes of surface water and sediment were calculated by the following formula [28]:

$$P_{Ci} = (C_i - C_0)/C_0 \quad (2)$$

where P_{Ci} is the single pollution index of Cd element, C_i represents the measured concentration of Cd content (surface water in mg/L, sediment in mg/kg), C_0 is the limit value of Cd content in surface water quality standard Class II (mg/L) or the Cd content of the background from the contrast area (mg/kg) [23]. The single-exceedance factors can generally be divided into five levels to represent the range of pollution levels (Table 1).

Table 1. The relationship between single pollution index and the pollution degree level.

Pollution Level	No Pollution	Light Pollution	Moderate Pollution	Heavy Pollution	Extreme Pollution
The single pollution index (P_{Ci})	$P_{Ci} \leq 0$	$0 < P_{Ci} \leq 1$	$1 < P_{Ci} \leq 4$	$4 < P_{Ci} \leq 10$	$10 < P_{Ci}$

In order to comprehensively analyze the impact of pollutants on surface water/sediment, the Nemerow pollution index method was used to evaluate Cd, Pb, Cu, Cr, and Hg in surface water/sediment. Nemerow pollution index method reflects the comprehensive effect of various pollutants on surface water/sediment and highlights the impact of high-concentration pollutants on the environmental quality of surface water/sediment. The calculation formula is:

$$P_{Ni} = \sqrt{\frac{P_{imean}^2 + P_{imax}^2}{2}}$$

where P_{Ni} is the Nemerow pollution index of sample i, P_{imean} is the average value of all the single pollution indexes of sample i, P_{imax} is the max value of all the single pollution indexes of sample i. The Nemerow pollution index can generally be divided into five levels to represent the range of pollution levels [22,23] (Table 2).

Table 2. The relationship between the Nemerow pollution index and the pollution degree level.

Pollution Level	No Pollution	Light Pollution	Moderate Pollution	Heavy Pollution	Extreme Pollution
The Nemerow pollution index (P_{Ni})	$P_{Ni} \leq 1$	$1 < P_{Ni} \leq 2$	$2 < P_{Ni} \leq 3$	$3 < P_{Ni} \leq 5$	$5 < P_{Ni}$

The sediment is an important component of the riverbed structure, and the sediment not only serves as a repository for heavy metal pollutants but also as a potential secondary pollution source with potential impacts on water quality in the aquatic-sediment system [29]. The content of heavy metal elements in riverbed sediments is an important reference index for determining the quality of the water environment [30]. In this study, the geoaccumulation index method was used to evaluate 16 sediment samples collected in Wenyu Stream watershed. The geoaccumulation index method was proposed by Müller from the Institute of Sedimentology at Heidelberg University in 1969. It is a quantitative evaluation method for studying the degree of heavy metal pollution in sediments in water environments, and it is currently one of the most widely used methods for evaluating modern sediments with heavy metal pollution [31,32]. The specific calculation formula is provided below:

$$I_{geo} = \log_2\left(\frac{C_n}{kB_n}\right) \quad (3)$$

where B_n is the geochemical background, which is the average Cd content of three sediment samples from the contrast area (0.74 mg/kg), C_n is the measured content of pollutants in sediments (mg/kg), k is a constant generally taken to be 1.5 indicating that the background may vary due to differences in sedimentary characteristics and litho-geological features. The geoaccumulation indexes can generally be divided into seven levels [33] to indicate the range of pollution degrees (Table 3).

Table 3. Geoaccumulation index and pollution classification.

Pollution Level	No Pollution	No to Moderate Pollution	Moderate Pollution	Moderate to Severe Pollution	Severe Pollution	Severe to Extreme Pollution	Extreme Pollution
Index range	$I_{geo} \leq 0$	$0 < I_{geo} \leq 1$	$1 < I_{geo} \leq 2$	$2 < I_{geo} \leq 3$	$3 < I_{geo} \leq 4$	$4 < I_{geo} \leq 5$	$5 < I_{geo}$
Level	0	1	2	3	4	5	6

The ecological risk of Cd in river sediments was evaluated using the Potential Ecological Risk Index (PERI) method. PERI is a method developed by Swedish scholar Hakanson in 1980 for evaluating the pollution and ecological hazards of heavy metal elements in sediments and soils [34]. The advantage of this method is that it takes into account the concentration effect, ecological effect, and toxicity effect of heavy metal elements, which allows for both the calculation of an individual pollutant's potential ecological risk index ($E^i{}_r$), which measures the level of ecological risk caused by a single pollutant, as well as the calculation of the comprehensive ecological impact of multiple pollutants through a composite potential ecological risk index. In this study, we primarily used $E^i{}_r$ to evaluate the samples of riverbed sediment from the main channel of Wenyu Stream, and the formula used in the calculation is provided below:

$$E_r^i = T_r^i \times \left(\frac{E_s^i}{C_n^i}\right) \quad (4)$$

where $E^i{}_r$ is the potential ecological hazard index of a Cd element, $T^i{}_r$ is the toxicity response coefficient of Cd element, $E^i{}_s$ is the measured Cd content of sediment sample (mg/kg), and $C^i{}_n$ is the Cd background reference of sediment samples, in units of mg/kg. Based on previous research [35], the toxicity response coefficient $T^i{}_r$ for Cd in this study was set to 30, while the background reference $C^i{}_n$ was adopted as the average of the Cd content in three bottom sediment samples from the contrast area, which was 0.74 mg/kg. The relationship between the classification of single pollutant potential ecological hazard index and ecological risk level is shown in Table 4.

Table 4. The relationship between the potential ecological hazard index of a single pollutant and the degree of ecological risk.

Ecological Risk Degree	Slight	Medium	Strong	Very Strong	Extremely Strong
Index range	<40	$40 \leq E_r{}^i < 80$	$80 \leq E_r{}^i < 160$	$160 \leq E_r{}^i < 320$	$320 \leq E_r{}^i$

3. Results

3.1. The Test Quality of the Five Elements in Surface Water and Sediment Samples

In this study, three surface water samples and two sediment samples were randomly selected for duplicate sample testing, and the test results are shown in Table 5. The relative deviation of Cd, Pb, Cu, Cr, and Hg in surface water samples is between 0.00% and 7.69%, meeting the requirement of less than 20% relative deviation for parallel sample testing specified in the Environmental Quality Standard for Surface Water (GB 3838-2002) [23]. The relative deviation of Cd, Pb, Cu, Cr, and Hg in the sediment samples is between 2.05% and 5.43%, which also meets the requirement of parallel sample testing with a relative deviation of less than 20% specified in the Soil Environmental Quality Risk Control Standard for Soil Continuity of Agricultural Land (GB 15618-2018) [22].

Table 5. The test quality of the elements in surface water and sediment samples.

Elements			Cd	Cu	Pb	Cr	Hg
Water samples	15	Results (mg/L)	0.00200	0.01300	0.00100	0.00100	0.00005
		Duplicate results (mg/L)	0.00190	0.00140	0.00090	0.00110	0.00005
		RD (%)	2.56	3.70	5.26	4.76	0.00
	20	Results (mg/L)	0.00200	0.00900	0.00100	0.00100	0.00005
		Duplicate results (mg/L)	0.00210	0.01030	0.00110	0.00090	0.00005
		RD (%)	2.44	6.74	4.76	5.26	0.00
	T1	Results (mg/L)	0.00600	0.08700	0.00100	0.00100	0.00005
		Duplicate results (mg/L)	0.00700	0.08900	0.00110	0.00105	0.00005
		RD (%)	7.69	1.14	4.76	2.44	0.00
Sediment samples	3	Results (mg/kg)	3.78000	82.70000	620.00000	93.70000	1.28000
		Duplicate results (mg/kg)	3.95000	87.10000	646.00000	98.50000	1.17000
		RD (%)	2.20	2.95	2.05	2.50	4.49
	5	Results (mg/kg)	1.76000	50.50000	221.00000	66.70000	0.13800
		Duplicate results (mg/kg)	1.89000	56.30000	236.00000	63.20000	0.13100
		RD (%)	3.56	5.43	3.28	2.69	2.60

3.2. The Cd Exceedance in the Surface Water of the Wenyu Stream

The statistical results of Cd content in 35 water samples from the Wenyu Stream and contrast area are shown in Figure 1. Figure 2a showed that the Cd contents of 14 samples from total 23 samples in the main ditch of the Wenyu Stream were significantly higher than those in the contrast areas which were not influenced by mining activities. Moreover, the average Cd content in the main ditch of Wenyu Stream was twice as high as that in the contrast area, with the highest value being 10 times higher. The results indicated that the cumulative effect caused by Cd contamination in Wenyu Stream was significant due to mining activities. Among the nine samples in the tributary ditches of the Wenyu Stream, six samples did not exceed the contrast areas named T4, T5, T6, T7, T8, and T9. Samples from T1, T2, and T3 were two, four, and six times higher in Cd content than the contrast areas, respectively. Additionally, from a statistical perspective, the coefficient of variation for Cd content reaches 99.44%, and the Cd content presents an uneven distribution from upstream to downstream indicating that Cd pollution in the Wenyu Stream was significantly influenced by mining activities (Table 6). The intensive human activities in the study area mainly include mining, transportation, ore processing, and storage of surrounding rock wastes and tailings.

According to the Cd limit of Class II water from the Environmental Quality Standards for Surface Water Standard (GB3838-2002), 22 of the 23 samples in the main ditch of the Wenyu Stream met the standards of Class I and Class II water accounting for 95.65%, indicating the overall water quality of Wenyu Stream was clear. The Class I water samples accounted for 52.17%, including samples 1, 2, 3, 4, 5, 6, 7, 8, 18, 21, 22, and 23 in Figure 1b. The Class II water samples accounted for 43.48%, including samples 9, 11, 12, 13, 14, 15, 16, 17, 19, and 20 in Figure 2b. The sample of Class V water accounted for 6.25%, including sample 10 in Figure 2b. The water quality of six water samples from the nine tributaries of Wenyu Stream were Class I water, which were samples T4, T5, T6, T7, T8, and T9, respectively. Sampling point T1 was Class II water and sampling points T2 and T3 were Class V water.

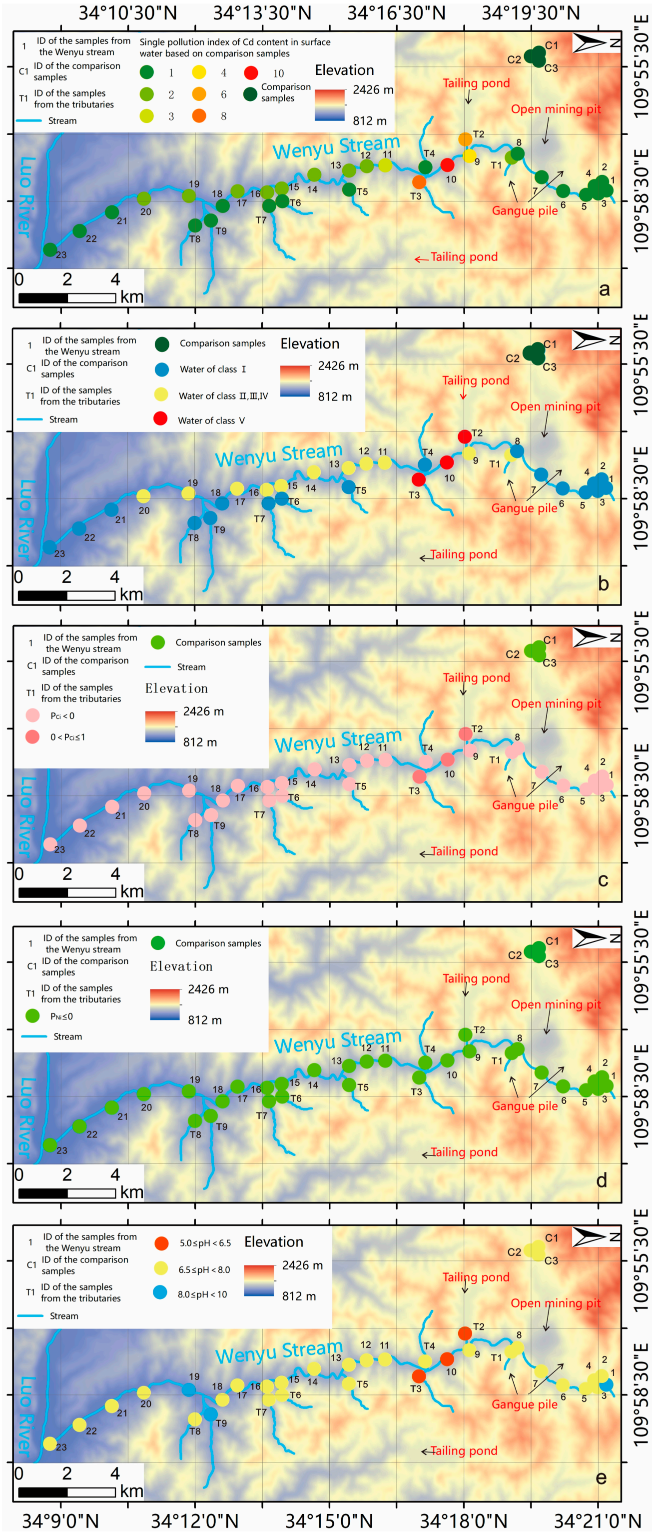

Figure 2. The evaluation maps of the surface water in Wenyu Stream. (**a**). The single pollution indexes of Cd content in surface water based on comparison samples. (**b**). The water quality classes divided according to the Environmental Quality Standards for Surface Water Standard (GB3838-2002). (**c**). The single pollution indexes of Cd content in surface water based on Class II water limit issued by the Environmental Quality Standards for Surface Water Standard (GB3838-2002). (**d**). The Nemerow pollution indexes of Cd, Pb, Cu, Cr, and Hg contents in surface water based on Class II water limit issued by the Environmental Quality Standards for Surface Water Standard (GB3838-2002). (**e**). The water pH of the surface water samples.

Table 6. Statistical characteristics of Cd, Pb, Cu, Cr, and Hg content in surface water of the Wenyu Stream.

Elements	Mode (mg/L)	Mean (mg/L)	Median (mg/L)	Range (mg/L)	Range/Mode	Range/Average	Standard Deviation (mg/L)	Coefficient of Variation (%)	Limits (mg/kg) [23]	Average Single Pollution Index
Cd	0.001	0.001	0.001	0.001–0.01	9.000	4.299	0.002	99.440	0.005	0.960
Pb	0.001	0.001	0.001	0.001–0.001	0.000	0.000	0.000	0.000	0.010	0.000
Cu	0.001	0.021	0.008	0.001–0.280	86.000	4.151	0.019	93.800	1.000	−0.984
Cr	0.001	0.001	0.001	0.001–0.001	0.000	0.000	0.000	0.000	0.050	−0.980
Hg	0.00005	0.00005	0.00005	0.00005–0.00005	0.000	0.000	0.000	0.000	0.00005	0.000

As shown in Figure 2c, the Cd single pollution index of sample 10 in the main ditch of the Wenyu Stream was 1, attributed to mild pollution, and the other 22 samples were not beyond the limit. Among the nine water samples in the tributary ditches of Wenyu Stream, seven samples from T1, T4, T5, T6, T7, T8, and T9 were unpolluted by Cd content. Samples T2 and T3 were attributed to mild pollution. The Nemerow pollution indexes of the surface water samples shown in Figure 2d were all below 1. Concerning the position of the over-limit sample 10 in Figure 2b,e, this point was located near the mineral processing production area, approximately 2.0 km away from the mining area. Additionally, a large tailing pond is located on the west bank, about 1 km upstream. The T2 sample at this location was Class V water. Therefore, the abnormal Cd content of sample 10 may be related to the drainage water from the tailings pond.

3.3. The Cd Accumulation Degree of Stream Sediment

From the statistical results of Cd contents in sediment samples (Table 7), the range of Cd contents was 7.06, with significant variations, and the coefficient of variation was 43.93%. Moreover, the Cd concentration in each sample from upstream to downstream exhibits an asymmetrical distribution, indicating a significant disturbance by human activities. The results of the geoaccumulation index analysis showed that all 15 sediment samples from the main ditch of Wenyu Stream exhibit varying degrees of pollution, with point numbers 15 and 16 having the highest levels of pollution, reaching moderate to severe levels (Figure 3a). The least pollution level included point numbers 5, 13, and 22, ranging from not polluted to moderate pollution. Most points fall within moderate levels of pollution. The T2 and T5 sediment samples in two tributary ditches of Wenyu Stream also reached moderate levels of pollution (Figure 3c). The Cd content in sediment from the entire watershed, both individually and averagely, was significantly higher than that in the contrast area. This reflects the impact of external heavy metal element inputs on Wenyu Stream, leading to the accumulation and enrichment effects of Cd in the river water. As shown in Figure 3b, only tree Nemerow pollution indexes of the sediment samples were between 1 and 2, indicating light pollution. Previous studies analyzed and evaluated the heavy metal pollution of sediments in the middle and upper reaches of the Beijiang River in northern Guangdong Province by testing eight elements of Cu, Pb, Zn, Cd, Ni, Cr, As, and Hg using the geoaccumulation index. The results showed that the pollution of toxic elements in the main stream of the Beijiang River was more serious than that in the tributaries due to long-term accumulation, and the main sources of pollution were the existence of multiple mining and smelting enterprises near the river [36]. In addition, the contents of toxic elements in tailings and river sediments downstream of six tailings ponds in southern China were compared and analyzed. The study found that the contents of Cu, Pb, Zn, Cd, Ni, Cr, As, Hg, and Sb in river sediments downstream of some tailings ponds were higher than those in tailings, indicating that the accumulation effect of elements could cause the content of toxic elements in sediments to be higher than that in pollution sources [37]. These results demonstrate that mining activities are significant contributors to the accumulation and exceedance of heavy metals in river sediments near mining areas, and studying sediment pollution and enrichment characteristics is crucial for reflecting river water pollution conditions.

Table 7. Statistical characteristics of Cd, Pb, Cu, Cr, and Hg content in sediment samples from the Wenyu Stream.

Elements	Mean (mg/kg)	Median (mg/kg)	Range (mg/kg)	Range/Average	Standard Deviation	Coefficient of Variation(%)	Limits [22] (mg/kg)	Average Single Pollution Index
Cd	3.71	3.41	1.760–7.660	1.90	1.63	43.930	4.000	1.559
Pb	178.100	138.000	23.100–564.000	3.037	141.579	79.494	1000.000	−0.771
Cu	57.988	49.200	16.600–151.000	2.318	36.226	62.471	200.000	−0.673
Cr	63.759	64.600	29.600–98.400	1.097	19.464	30.528	1300.000	−0.949
Hg	0.144	0.094	0.023–0.776	5.211	0.119	82.563	6.000	−0.955

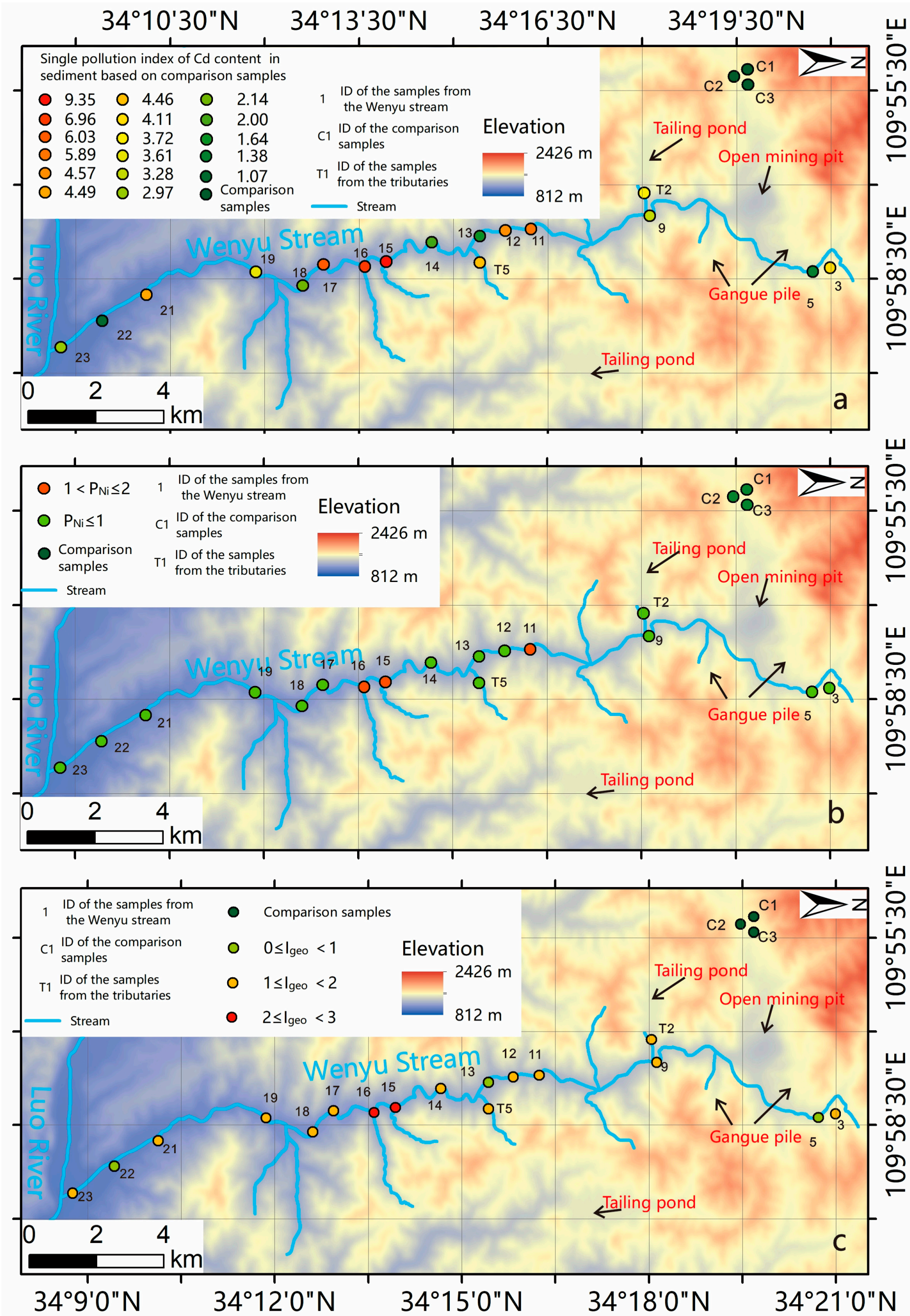

Figure 3. The evaluation maps of the sediment in the Wenyu Stream. (**a**). The single pollution indexes of Cd content in sediment based on comparison samples. (**b**). The Nemerow pollution indexes of Cd, Pb, Cu, Cr, and Hg contents in sediment based on the Soil Environmental Quality–Risk Control Standard for Soil Contamination of Agricultural Land (GB 15618-2018). (**c**). The geoaccumulation indexes of Cd content in sediment.).

3.4. Potential Ecological Risk of Cd Content in Sediment

According to the results of the potential ecological risk index, the potential ecological risk index ($E^i{}_r$) for Cd in each sample were obtained. As shown in Figure 4, the $E^i{}_r$ values for Cd in 15 sediment samples in the main ditch of the Wenyu Stream range from moderate to very high-risk levels, indicating that the overall level of sediment pollution in the main ditch of the Wenyu Stream reached a high level of ecological risk. According to the classification principle in Table 4, samples with strong ecological risk levels accounted for 40.00%, strong ecological risk levels accounted for 46.67%, and samples with moderate ecological risk levels accounted for 13.33%. The Cd potential risks in T2 and T5 samples from two tributaries of the Wenyu Stream were strong and very strong. Therefore, it can be inferred that the contamination of Cd in sediment in the Wenyu Stream has seriously threatened the ecological security of the study area. On the one hand, the accumulation effect caused by mining activities was significant because the content of Cd in the sediment of the Wenyu Stream was high and significantly higher than the contrast area. On the other hand, it is also closely related to the high toxicity response coefficient of Cd element. Several common Cd-containing compounds in nature, such as CdS and CdO, have certain toxicity and are one of the main elements harmful to human health [38,39]. The results of this study are consistent with previous soil heavy metal pollution survey results conducted in the Lalin River Basin in northeastern China [40].

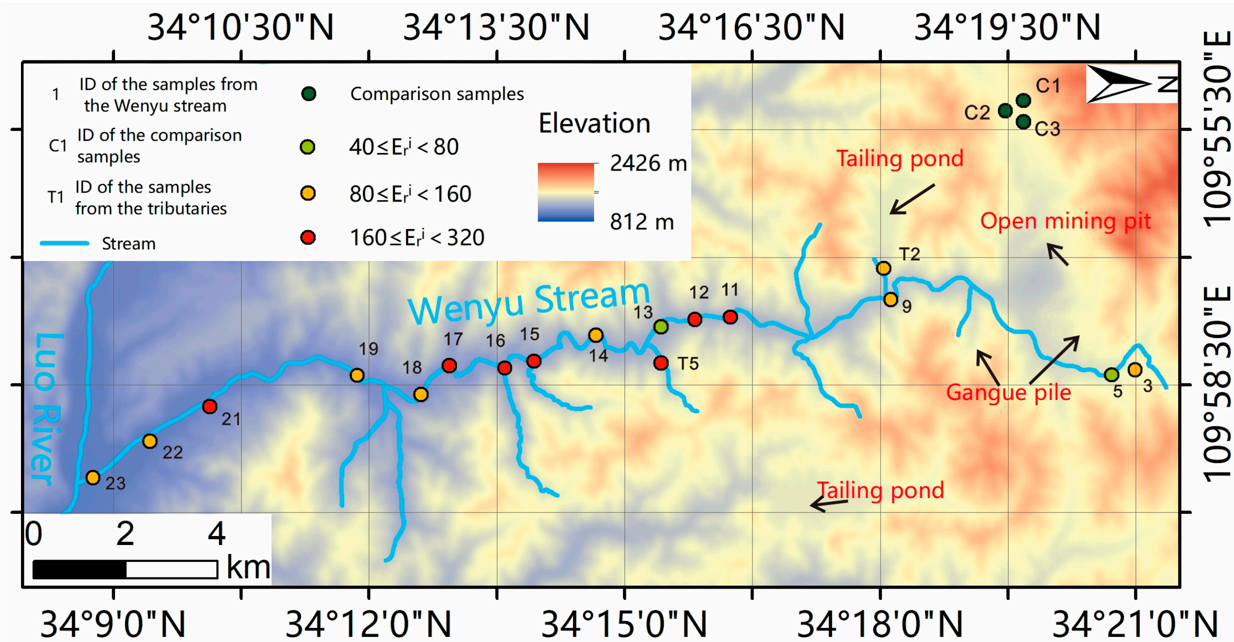

Figure 4. The potential ecological risk maps of the sediment in the Wenyu Stream.

It is worth noting that the average value of the sediment in the contrast area was selected as the background reference ($C^i{}_n$) in the evaluation of the potential ecological risk index of Cd in this study. This indicator implicitly ignored the influence of natural geological background factors on sediment Cd content in the study area and only considered the impact of mining activities, which conformed to the overall exploration ideas of this article. If both effects need to be considered simultaneously, the element indicator for background reference $C^i{}_n$ could be selected as the highest value of heavy metal elements in sediment before global industrialization [41–43]. Furthermore, if it is determined that riverbed sediment mainly comes from upstream and soil erosion on both sides of the river, then the background value of heavy metal elements in soils in the province where the research area is located can be used [44,45]. Different backgrounds have a significant impact on calculating potential ecological hazard indices. Using the background value of heavy metal elements in the research area as a reference value can better reflect the degree of pollution caused by human activities [46,47], which is the basis for selecting the nearby control area sediment average as the background reference value for $C^i{}_n$ in this study.

3.5. The Cd Content of Surrounding Rock

As shown in Table 8, the average Cd content in five rock samples collected from the surrounding area of the large open-pit molybdenum mine is 4.10 times the Cd background in Shaanxi Province and 4.90 times the Cd background in the Guanzhong Basin, indicating a high natural geological background for Cd within a certain range of the molybdenum mine upstream of the Wenyu Stream. Previous studies on the geochemical region of southern Shaanxi Province have also shown that chalcophile elements, tungsten-molybdenum group elements, such as Mo, Cr, V, Cu, Zn, Cd, and Ti, usually occur in high concentrations and have enriched features. In particular, Cd is highly concentrated in some areas, with local concentrations even exceeding five times the background average, forming an excess of microelements [47], which is similar to the findings of this study.

Table 8. The Cd contents in surrounding rock samples and soil Cd background in Shaanxi Province and the Guanzhong Basin.

ID	Cd Content (mg/kg)	Mean (mg/kg)	The Cd Background of Shaanxi Province (mg/kg) [47]	The Cd Background of Soils of Guanzhong Basin (mg/kg) [48]
R1	0.20	0.58	0.14	0.118
R2	0.24			
R3	0.36			
R4	0.11			
R5	2.00			

4. Discussion

This study evaluated the surface water and sediment Cd content in the Wenyu Stream, which is downstream of a large molybdenum mine in the Qinling Mountains. After determining the main pollution problems, the potential sources of pollution were investigated and analyzed. The results can provide targeted countermeasures for subsequent treatment and restoration. Currently, two levels of source apportionment were discussed in previous studies: The first level involves qualitative identification of the main sources of pollutants in environmental media, known as source identification. The second level involves quantitative calculation of the contribution of various sources of pollution, known as source apportionment [49]. Many researchers referred to both levels as source apportionment [50]. This study focused on source identification for pollution in the Wenyu Stream to provide technical references for pollution control at the source of the mining area.

4.1. Acid Mine Drainage Source of Cadmium in the Wenyu Stream

As shown in Figure 2, both T2 and T3 samples located in the drainage ditches of the tailings pond leachate discharge canal and the mineral processing drainage canal, respectively, have Cd content exceeding Class II water limit and reaching Class V water. Sample 10, located between them, was the most heavily polluted point in the main ditch of the Wenyu Stream. In addition, pH testing results of water samples show that the pH values of T2 and T3 points are 6.00 and 6.13, respectively. This indicates that both the tailings pond upstream of T2 and the mineral processing plant upstream of T3 discharge Cd-contaminated acid drainage water into the main ditch of the Wenyu Stream. According to previous studies, acid mine drainage mainly forms in three ways [51]: ① In the process of ore processing, if acid reagent is used for mineral processing, the wastewater discharged is acid water, ② During mine production, a large number of waste rocks and tailings containing sulfide minerals are stacked in the open air, which are easily oxidized to form metal ions and sulfate ions. In rainy weather, they will be dissolved in water and slowly enriched to form acidic wastewater through leaching, ③ During the mining of the deposit, a large amount of groundwater seeps into the working face, which is in long-term contact with rocks and minerals containing sulfur and heavy metals, and partially dissolves to form acid mine water. Obviously, the acidic wastewater at T2 and T3 points in this study conforms to the first two production methods mentioned above. Combined with previous research results, the unprocessed metallurgical wastewater of Dabaoshan multimetal mine in northern Guangdong Province was directly discharged into Hengshi River, causing serious harm to the environment along the the Hengshi River Basin [52]. The acid and polluted wastewater discharged by Dexing Copper Mine in Jiangxi Province contaminated the Le'an River and caused harm to animals, plants, and farmland along the riverbanks [53]. The results of previous research have shown that acidic wastewater generated by mining activities and its illegal discharge are another important cause of Cd pollution in the Wenyu Stream [54].

4.2. The Surrounding Rock Source of Cd in the Wenyu Stream

According to the test results of rock samples, the Cd content distribution is extremely uneven, with the highest value exceeding 18 times the lowest value. The rock sample with the highest Cd content is a pit surrounding rock rich in pyrite. In addition, Cd is often distributed in sulfide ores, such as sphalerite and others associated with large-scale molybdenum mines [55]. This phenomenon is related to the properties of Cd's copper affinity and sulfur affinity as well as its similar geochemical behavior to Zn [56,57]. As a trace heavy metal element in rocks, the average abundance of Cd is 0.2 mg/kg in the crust [42]. Under strong oxidizing conditions, Cd can form oxide minerals, such as CdO and $CdCO_3$, and can also be oxidized into $CdSO_4$ in aqueous solutions [42]. In weak oxidizing environments, the mineral sphalerite containing Cd can be rapidly oxidized and dissolved, producing cadmium sulfide (CdS) [58]. The large-scale molybdenum mine upstream of the Wenyu Stream has been operating for over 50 years. Long-term mining, mineral processing, transportation, and other mining activities have changed the original occurrence environment of Cd, which is released from minerals and rocks, migrated and transformed in the supergene geological environment, and finally accumulated and enriched, causing river pollution.

4.3. Sediment Sources of Cd in the Wenyu Stream

River pollution caused by heavy metal adsorption and release in sediment-water systems is one of the hot issues in research. Most of the heavy metal pollutants will be adsorbed by suspended particles after entering the river watershed, and the suspended particles will be accelerated to sink by gravity in the water body, when particles accelerate to sink to a state where gravity and resistance are equal, they will sink at a stable settling speed [59]. Generally, the flow of river water body is relatively stable, that is, the handling effect of hydrodynamic force is gentle. However, the Wenyu Stream is formed by the convergence of mountain streams, and the frequent agitation of the river makes the load of sediment particles exceed its carrying capacity. At the same time, sediment particles are prone to generate intermolecular forces with heavy metal pollutant molecules [60–62]. For example, cadmium ions will generate electrostatic adsorption with coarse and fine sediment particles, which will combine through chemical bonds and accelerate the settlement of pollutants [63–65]. The flow velocity at the bottom of the river water body is slow, and the sediment at the bottom is less affected by hydraulic transport. Less heavy metal pollutants in the sediment re-enter the water body due to river impact and transport. Therefore, the existing form of heavy metal pollutants after sedimentation is greatly affected by the water environment.

The pH is the main factor affecting the adsorption and desorption of heavy metals in the water environment. H^+ ions will desorb metal ions from the sediment and re-enter the water environment through ion competition [65]. Previous studies on the release kinetics of heavy metals in Guangzhou urban water polluted sediments under acidic conditions can be divided into two stages. The first stage is the rapid desorption of heavy metals on the sediment surface after the deposition of particulate suspended solids, and the second stage is the slow diffusion of heavy metals from the internal pores of the sediment to the external solution [42]. The first stage is the release process after sedimentation of sediment particles mentioned above. In the second stage, there is a concentration difference between the surface interstitial water of sediment and the overlying water (river water) [59]. As the free water in the sediment void, interstitial water connects the sediment with the overlying water. Through ion exchange, molecular diffusion, and biological disturbance, interstitial water diffuses and migrates to the river with interstitial water as the intermediate medium, thus affecting the water quality of the river. A total of eight toxic elements, including Cu, Pb, Zn, Cd, Ni, Cr, as and Hg, have been tested and analyzed in 25 sediment samples from the main stream of the Zhongbei River and its tributaries in the northern mountainous area of Guangdong Province. They used the geoaccumulation index method to analyze and evaluate the heavy metal pollution in the sediment of the area. The study found that the concentration of heavy metals in the main stream was more serious than that in the branch ditch due to the large amount of pollutants in the main stream. The pollution of this degree was due to the existence of multiple mining yards and smelters in the area. Other scholars' research found that the content of heavy metals in river sediments downstream of tailings pond is higher than that in tailings, indicating that the cumulative effect of heavy metals [41] will lead to the content of heavy metals in sediments higher than that in pollution sources. In the study on the release law of elements in the river sediment of Harbin reach of the Songhua River in Northeast China, it was found that different temperatures, pH values, water disturbance levels, and salt concentrations will have different degrees of influence on the release of heavy metals [43].

After the development of molybdenum ore in the study area, Cd, Zn, and other heavy metal ions were released after entering the downstream Wenyu Stream watershed. Comparing the times of exceeding the background value of Cd content in river water in Figure 2a with the times of exceeding the background value of Cd content in sediment in Figure 3a, it was found that the times of exceeding the standard of Cd content in river sediment samples are 4.18 times that of the Wenyu Stream water samples. Meanwhile, comparing the Nemerow indexes between the surface water in Figure 2d and the sediment in Figure 3b, the Nemerow indexes of pollutants in sediment were larger, indicating the sediment was in the stage of pollutant enrichment. The Nemerow index of pollutants in sediment is larger, indicating that the sediment is in the stage of pollutant enrichment. After the release of heavy metal ions through different ways in the development into the river, on the one hand, with the continuous migration, transformation, and accumulation of river water flow from the downstream of tailings pond to the upstream of the river, the pH, and water quality structure of the water body are gradually changed, and the function of the river water body is reduced. On the other hand, when it infiltrates into the groundwater, the suspended solids become sediments and are transferred to the river sediment, which changes the water quality to a certain extent. Exchangeable heavy metal ions may also be released into the river water and have an impact again. Previous studies on the treatment of river sediment pollution in Guangdong Province have shown that the treatment of heavy metal elements in river sediment can be carried out by physical remediation methods with the help of engineering technology, such as artificial dredging, chemical remediation methods with chemical remediation agents applied to the sediment, or biological remediation methods with the use of surrounding microorganisms and plant communities [44]. In order to deal with the relationship between China's rapid economic development and environmental and ecological protection in mining areas, relevant functional staff must pay more attention to the treatment of river sediment pollution, understand the types of heavy metal pollutants in sediment and treatment methods, so as to effectively control and repair the ecological health of rivers.

4.4. The Atmospheric Dust Fall Sources of Cd in the Wenyu Stream

In addition, the effects of atmospheric dry and wet deposition on the input of Cd elements into rivers also occupy a significant proportion. On the one hand, mining activities in densely populated areas generate a large amount of dust through heavy machinery operation. On the other hand, the surface rocks and minerals exposed to air undergo geological weathering processes that produce dust particles containing heavy metal ions and sulfate ions. These particles are eventually transported directly into rivers via wind or leached into surface runoff during rainfall, ultimately entering rivers. Predecessors have observed atmospheric dust fall in another mining area 20 km east of the study area and found that the cumulative multiple of the atmospheric dust content in the mining area relative to the background value of soil Cd in the area has reached 1.67, which indicates that the dust from mining activities is also a way of causing heavy metal pollution in the mining area [66–68]. Based on Figure 2, it can be inferred that water samples 8, 9, 10, and 11, within a 1–5 km radius of the upper reaches of the Wenyu Stream, where open-pit mines and dumpsites are prone to generating high levels of dust, may have Cd concentrations exceeding background values by factors of 0, 3, 9, and 2, respectively, while downstream sites have the highest concentration ratios exceeding background values by up to 1. According to relevant studies, the enrichment of Cr, Co, Mn, Ni, As, Cd, Cu, Pb, Zn, Tl, and rare earth elements in sediments of Beijing's Beiyun River is similar to that of metal elements in atmospheric particulate matter. It can be inferred that heavy metal elements in atmospheric particulate matter have a significant contribution rate to heavy metal elements in the sediments of the Beiyun River, mainly through rainfall into rivers [69], which is similar to the viewpoint presented in this study. Another study has found that the spatial distribution of air dust pollution is consistent with the distribution of pollution sources [70]. Meanwhile, three aspects of atmospheric dry-and-wet deposition, human activities, and parent rock weathering in the Gongnaisi River Basin in Xinjiang Uygur Autonomous Region have impacts on the enrichment of heavy metal elements in the river [71,72]. These studies indicate that the effects of atmospheric dry and wet deposition generated by mining activities may be another important cause of riverine Cd contamination. In future research, we will carry out atmospheric dust fall observation in the mining area to provide data support for the comprehensive discussion of mine environmental problems in the study area.

5. Conclusions

In conclusion, this study aimed to explore the effects of mineral exploitation on river water quality in the Wenyu Stream downstream of a large molybdenum mining area in Qinling Mountains. The results showed that Cd pollution was a significant problem in the Wenyu Stream due to mining activities.

The analysis of surface water, sediment, rock, and ore samples by ground sampling and chemical testing revealed that 14 out of 23 sampling points had significantly higher Cd contents than those in the contrast area, which was not affected by mining activities. The variation coefficient of Cd content reached 99.44%, indicating that the Cd contents in the Wenyu Stream are highly variable and significantly influenced by mining activities. Only one point exceeded the Class II water quality limit, and the pollution exceeding multiple was 1 with slight pollution. The results of geoaccumulation index analysis showed that the 15 sediment samples from the main ditch of the Wenyu Stream had different degrees of pollution: The most seriously polluted samples 15 and 16 reached the moderate to strong pollution level. Samples 5, 13, and 22 with the lightest pollution were no pollution to moderate pollution. Most of the samples were moderately polluted. The potential ecological risk indexes of Cd in 15 sediment samples from the main ditch of the Wenyu Stream were in the range of medium risk to very strong risk, indicating the sediment in the main ditch of the Wenyu Stream is suffering strong ecological risk.

Acid mine drainage, original geological background, sediment release, and atmospheric dust fall were identified as the primary sources of Cd pollution in the Wenyu

Stream watershed. Acid mine drainage is a common form of pollution caused by mining activities, which can lead to the release of heavy metals into rivers and streams. Original geological background also plays a crucial role in determining the levels of heavy metal concentrations in soils and water bodies. Sediment release is another important source of heavy metal pollution, as it can transport pollutants from mines to nearby waterways. Finally, atmospheric dust fall can also contribute to heavy metal pollution through its interaction with rain and wind.

To address these issues, it is essential to implement effective monitoring and management strategies for heavy metal pollution in rivers and streams caused by mineral exploitation. This includes reducing emissions from mines, improving waste disposal practices, and promoting sustainable development in mining areas. For example, mining companies could adopt more environmentally friendly technologies, such as hydrometallurgy and leaching techniques, to reduce their environmental impact. Additionally, governments could impose stricter regulations and penalties on polluting industries to encourage them to adopt cleaner production methods.

Furthermore, public education and awareness-raising campaigns are crucial for promoting sustainable development in mining areas. By educating local communities about the impacts of heavy metal pollution on aquatic ecosystems and human health, we can encourage people to take action to protect their environment. This could include supporting initiatives, such as rainwater harvesting and wastewater treatment plants, to reduce the amount of pollutants released into rivers and streams.

In conclusion, this study highlights the importance of protecting wetlands and riparian areas from heavy metal pollution caused by mineral exploitation. By understanding the sources and effects of pollution, we can develop effective strategies to mitigate its impact on aquatic ecosystems and promote sustainable development in mining areas. It is essential that we work together to find solutions to this pressing environmental issue before it is too late.

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