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Heavy Metal Distribution Characteristics, Water Quality Evaluation, and Health Risk Evaluation of Surface Water in Abandoned Multi-Year Pyrite Mine Area

Yiwen Jiao [1,2], Yitian Liu [1,2], Wei Wang [1,2,*], Yujiao Li [1,2], Wentong Chang [1,2], Ao Zhou [1,2] and Ronglong Mu [1,2]

[1] School of Water and Environment, Chang'an University, No. 126 Yanta Road, Xi'an 710054, China
[2] Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region, Chang'an University, Ministry of Education, No. 126 Yanta Road, Xi'an 710054, China
* Correspondence: wangweichd@chd.edu.cn

Abstract: Acid mine drainage (AMD) is a major anthropogenic source of heavy metal discharge worldwide. However, little research has been carried out on the development of AMD in abandoned pyrite mines and the heavy metal contamination of mine surface water. The aim of this study was to investigate and assess heavy metal pollution in three streams within an abandoned pyrite mine area in southeastern Shaanxi Province, China. Surface water pollution was assessed using the pollution index assessment method and the health risk assessment model. The results showed that the combined heavy metal pollution indices of the surveyed rivers were Tielu Creek (4699.227), Jiancao Creek (228.840), and Daoban Creek (68.106). After multivariate statistical analysis, it was found that the tailings slag and mine chamber in the abandoned mine area were the main causes of AMD, and AMD posed a serious risk of heavy metal pollution to the surrounding waters. The risk of carcinogenicity of heavy metals is also quite high in the surface water of mining area. Therefore, there is an urgent need to ecologically manage heavy metal pollution from abandoned mine sites, and this study provides insights into understanding heavy metal pollution in the aquatic environment of abandoned mine sites.

Keywords: acid-mine drainage (AMD); heavy metals; water quality index; human health risk; multivariate statistical analysis

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1. Introduction

A great deal of rivers are contaminated by heavy metal pollution from modern industrial growth, affecting aquatic biological structure, function, water resource utilization, and biological health [1–5]. Heavy metals are particular non-biodegradable pollutants that are released into aquatic ecosystems, enter the water and sediment phases, accumulate in organisms, and cause a number of serious diseases and disorders, even at low concentrations [6–9], such as neurological, cardiovascular, respiratory, and reproductive issues [10]. The main source of heavy metal contamination of river water bodies, heavy metal enrichment of river sediments, and severe harm to aquatic creatures is unregulated mining activity [11–13], particularly in the majority of developing nations such as India, Peru, Ghana, etc. [14–19]. In the course of mining operations, pyrite oxidation combines with oxygen and water to create metal ions and sulfuric acids. This material then reacts with the rocks, surface water, and groundwater to create acid mine drainage (AMD), which is water with a pH of 2 to 8 [20–22]. With AMD, large amounts of acid and high levels of heavy metals are created, which has long-lasting negative effects on the soil, water systems, and other species [23,24]. Almost all major global mining countries have serious AMD problems; even when the mining process is stopped, AMD may continue to form for hundreds or even thousands of years [25]. Lefcort et al. showed that even 70 years after the closure of a mine, the effects of increased heavy metal pollution from mining activities on river community ecosystems persisted [26]. Heavy metal mining leaves slags, pits, and other waste that react with air and water to form AMD. These are transported by surface runoff and spread to the surrounding area, causing severe heavy metal pollution in rivers and soil, seriously threatening water security for local residents and crop growth, which is a problem that has attracted global attention [27,28].

Heavy metal contamination from mining activities is also common in China. Acidic wastewater generated by the mine accelerates the solubility of heavy metals, which allows them to travel long distances and damage nearby rivers, nearby soil, and even groundwater [29]. In the Dabaoshan Mining District of China, extensive mining activities have been carried out over the past 40 years, and downstream of the mining district shallow aquifers are contaminated with a variety of heavy metals from the discharge of acidic mine effluents [30]. A study by Peng et al. investigating the Hejiacun uranium mine in Hunan, China, showed that AMD water and surface water at the mine site were potential sources of heavy metal pollution in the surrounding environment [31]. The Dabao Mountain polysulfide mine in China has produced a large amount of overburden and accumulated a large amount of waste rock, and the mine wastes without proper treatment have led to the generation of large amounts of acidic wastewater, and simultaneously released a large amount of toxic and harmful heavy metal ions, resulting in heavy pollution of the surrounding rice fields and ponds. Pollution from the Hengshi River in the mine area has spread downstream to the town of Xinjiang, causing the deaths of numerous aquatic organisms in the water body [32]. Mining activities and mine remnants are the main causes of environmental problems downstream of mines. However, most current studies have focused on mines with ongoing production activities and their downstream heavy metal pollution, with fewer investigations on the environmental impacts of closed mines.

In this study, a total of three streams in the abandoned pyrite mine of southeast Shaanxi were investigated and analyzed. Due to careless mining practices, antiquated technology, and a lack of environmental protection awareness, waste ore slag was dumped into mining caves as they were being dug, abandoned mining caves and waste slag were piled up with the slope, and waste slag was discharged directly into nearby rivers, where it was oxygenated in the air, turned into "sulfur water", and caused some river sections to fall below water quality standards and the riverbed to turn yellowish-brown. Jiancao Creek, Daoban Creek, and Tielu Creek, three streams in the study area, join to form the Baishi River, a tributary of the upper Han River that runs through the city. Heavy metal pollution in the rivers poses a serious threat to the local ecological environment and the health of the local population. In this study, we attempted to understand the pollution pathways and extent of acid mine drainage generated from multi-year abandoned mines on the surrounding surface water environment, and to analyze the main pollution factors and their composition in river water bodies. By obtaining water samples from nearby rivers, we were able to determine the distribution of surface water contamination caused by abandoned tailings. We also examined how rainfall affected the concentrations and transport of pollutants in rivers by collecting water samples both before and after rain. Determining the pollution level of water bodies in the study area was carried out using the Nemerow index method. The non-carcinogenic risk of water bodies was evaluated using the health risk index calculation, and the pollution sources and spatial variations in the distribution of pollution were analyzed using Pearson correlation analysis, principal component analysis, and cluster analysis.

2. Materials and Methods

2.1. Study Area

This study was conducted in Baihe County, southeastern Shaanxi Province, China. Baihe County has a continental monsoonal humid climate with an average temperature of 12.2–16.5 °C and an average rainfall of 787.4 mm. It has a distinguished ecological status and is located in the South–North Water Transfer Central Line's water quality impact area. The mineral resources in Baihe County are abundant, with 23 deposits of gold, silver, copper, iron, lead, zinc, and other metals dispersed throughout the area's mountains and waterways. In the 1960s, Baihe County began the mining and beneficiation of iron sulfide ore resources and other production activities.

2.2. Sample Collection and Preparation

For the purpose of investigating the distribution of heavy metals in the water body, samples were taken on March 2022, from Jiancao Creek, Daoban Creek, and Tielu Creek at 17 water points representing the surface water quality of the abandoned mine area, labeled J1–J7 (Figure 1a), D1–D5 (Figure 1b), and T1–T5 (Figure 1c). Water samples were taken from upstream, downstream, and from each tributary of each river confluence. At the time of sample collection, the instruments were thoroughly cleansed with river water to prevent dissolved trace metal elements in the water samples from being contaminated by other substances. Water samples were taken using a water sampler at every point of sampling, allowed to settle for five minutes, and then filtered through a 0.45 μm acetate membrane and stored in fully rinsed polyethylene bottles. One liter of water was then taken from every site of sampling for laboratory analysis. Fifteen water samples were taken before the rain and 17 samples were taken after the rain because of the flow interruption at sampling points D5 and J5 before the rain.

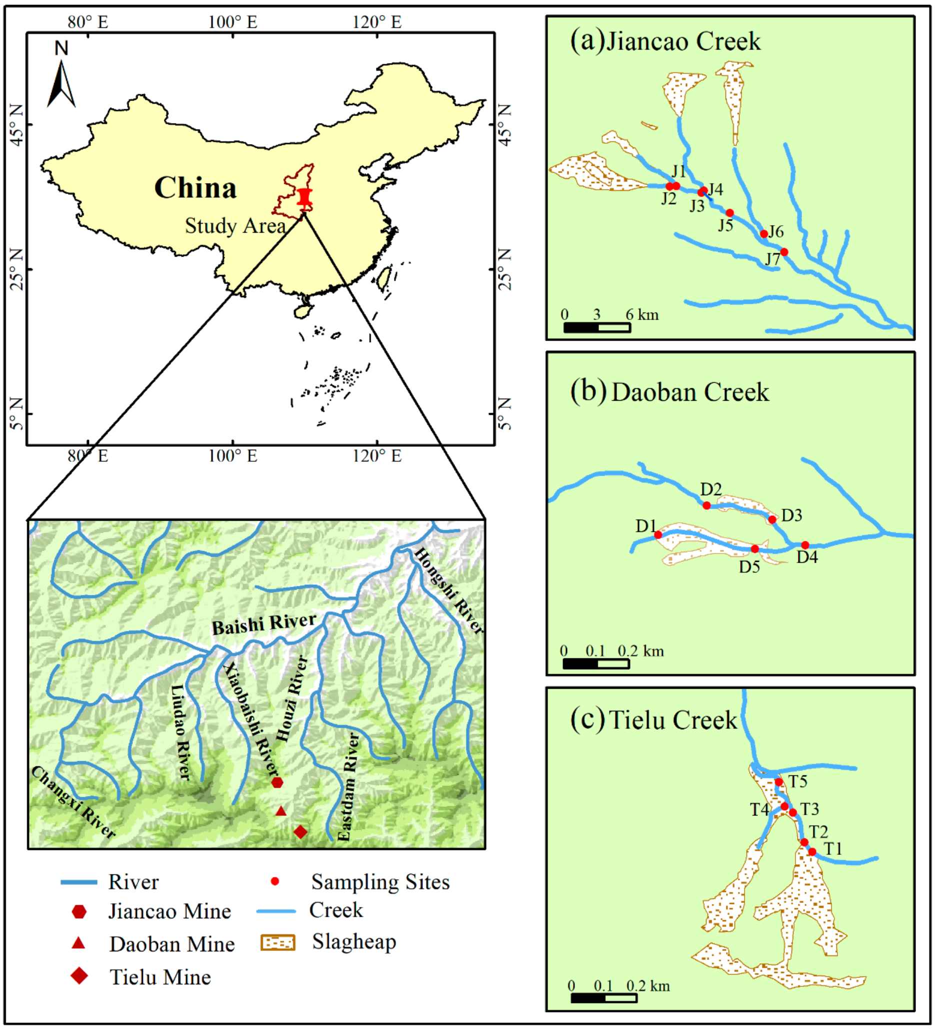

Figure 1. Location map and sampling sites map of abandoned mine sites in southeast Shaanxi.

Lab analysis was carried out after pre-treatment. Water samples for trace metal content assays were acidified with concentrated nitric acid to pH ≤ 2 and all examples were kept at roughly 4 °C prior to detection. The pH, Fe, Mn, Cu, Zn, As, Cd, Se, and sulfate levels in the water samples were all measured. Utilizing an inductively coupled plasma mass spectrometer (ICP-MS) to determine the mass concentrations of heavy metals and metalloids in the lab, quality control was carried out using reference materials provided by the National Standards Center, and the results were found to meet the standards.

2.3. Nemerow Composite Pollution Index Method

A common composite multifactor pollution index called the Nemerow Composite Pollution Index is often used to evaluate heavy metal pollution of water bodies and to objectively reflect the pollution levels of water bodies [33]. The calculation formula includes both a single pollution index and a multi-factor integrated pollution index. Based on the results of the two pollution indices, it is possible to reflect the degree of pollution to individual heavy metal elements as well as identify the primary factor, primary periods, and primary areas of water contaminants. It can also reflect the integrated pollution of multiple heavy metals, which can more accurately reflect the proportion of pollutants in water bodies and highlight the influence of pollutants on the environment [34,35].

Single-factor pollution index:

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

Multi-factor integrated pollution index:

$$Pn = \sqrt{\frac{\max(P_i)^2 + ave(P_i)^2}{2}} \tag{2}$$

where C_i represents the measured concentration of heavy metal i; this study adopts the Chinese surface water environmental quality standard III water standard, and Bi represents the corresponding surface water environmental quality standard III water quality standard value of heavy metals; max(P_i) represents the maximum value of the single-factor pollution index of heavy metals; and ave(P_i) represents the average value of the single-factor pollution index of heavy metals. Table 1 shows the assessment standards of the single-factor pollution index (P_i) and multi-factor integrated pollution index (P_n).

Table 1. Assessment standards of single-factor pollution index and multi-factor comprehensive pollution index.

P_i	Pollution Level	P_n	Pollution Evaluation
$P_i \leq 1$	Cleaning	$P_n \leq 0.7$	Non-polluting
$1 < P_i \leq 2$	Light pollution	$0.7 < P_n \leq 1$	Low pollution
$2 < P_i \leq 3$	Moderate pollution	$1 < P_n \leq 2$	Moderate pollution
$P_i > 3$	Severe pollution	$P_n > 2$	Strong pollution

2.4. Health Risk Assessment Methods

Two modes, direct human intake of water and skin absorption, are taken into account when analyzing trace element levels in the water according to U.S. Environmental Protection Agency (EPA) risk standards. The hazard quotient (HQ) and hazard index (HI) are widely employed in the assessment of aquatic animal risk. The non-carcinogenic risk under various exposure pathways is evaluated using HQ, and the overall potential non-carcinogenic risk of each heavy metal element is evaluated using HI. When HQ and HI are greater than 1, the potential health risk posed by a particular pathway or element must be taken into account [36]. The following equations were employed to calculate the daily dosage of direct ingestion ($ADD_{ingestion}$) and skin absorption (ADD_{dermal}) through water, as well as the cancerous and non-cancerous hazards of trace metals to humans, following the pertinent USEPA documents [37]:

$$ADD_{ingestion} = (C_w \times IR \times EF \times ED) / (BW \times AT) \tag{3}$$

$$ADD_{dermal} = (C_w \times SA \times K_p \times ET \times EF \times ED \times 10^{-3})/(BW \times AT) \quad (4)$$

$$HQ = ADD/RfD \quad (5)$$

$$RfD_{dermal} = RfD \times ABS_{GI} \quad (6)$$

$$HI = \sum HQ \quad (7)$$

The physical significance of the parameters in the formula is shown in Table 2. K_p is the dermal permeability coefficient in water (cm/h, Table 3), *RfD* is the corresponding reference dose (μgkg^{-1}day^{-1}, Table 3), and ABS_{GI} is the gastrointestinal absorption factor (Table 3). The parameter values were taken from Refs. [3,38–40].

Table 2. The health risk model calculation parameters.

Parameters	Physical Meaning	Units	Adult	Child
$ADD_{ingestion}$	daily dose consumed through direct water intake			
ADD_{dermal}	daily dosage absorbed by the skin		/	/
C_w	average heavy metal element concentration in every water sample	μg/L	/	/
BW	average body weight	kg	70	15
IR	ingestion rate	L/day	2	0.64
EF	exposure frequency	days/year	350	350
ED	exposure duration	years	30	6
AT	average time	days	25,550	2190
SA	exposed skin area	cm^2	18,000	6600
ET	exposure time	1 h/day	0.58	1
K_p	dermal permeability coefficient	cm/h		

Table 3. Dermal permeability coefficient, Gastrointestinal absorption factor, and Reference dose for trace metals in the Jiancao Creek, Daoban Creek, and Tielu Creek.

	Kp **cm/h**	ABS_{GI}	$RfD_{ingestion}$ **μg/kg/Day**	RfD_{dermal}
Fe	0.001	0.014	700	140
Mn	0.001	0.06	24	0.96
Cu	0.001	0.57	40	8
Zn	0.006	0.01	300	60
Cd	0.001	0.57	0.5	0.025
As	0.001	0.01	0.3	0.285
Se	0.001	0.05	5	2.2

2.5. Multivariate Statistical Analysis

To identify the associations between the variables and investigate their statistical significance, multivariate statistical techniques were applied [41,42]. In this study, correlation analysis, principal component analysis, and cluster analysis were carried out to compare the spatial differences of water quality parameters among water sampling sites in order to investigate the potential sources of trace metal elements by reducing the dimensionality of the data set and the spatial distribution characteristics. In this research, SPSS (IBM SPSS Statistics 26, Armonk, NY, USA) was used for data analysis to determine the source of contamination.

3. Results and Discussion

3.1. Spatial Distribution Characteristics of Trace Metal Concentration

It is efficient to identify specific pollution exceedances in a water body and confirm the degree to which pollutants are exceeding the standards by comparing them to relevant water quality standards [43,44]. Table 4 displays the surface water environmental quality standards for China, the WHO (2011) Drinking water Guidelines, and the USEPA (2011) Drinking water Guidelines, along with the water bodies, pH, sulfuric acid concentration, and trace metal element content of the rivers in the area of the abandoned pyrite mine. As can be seen from Table 4, the trace metal elements Fe, Mn, Zn, Cu, Cd, As, and Se in the water bodies all exceed the water quality standards of the waters to varying degrees. Surface water in the mining region has dissolved trace metal concentrations in the following order: Fe > Mn > Zn > Cu > As > Cd > Se. Among them, the heavy metal Fe element exceeds the standard by the largest margin, and the average value of Fe content in the Daoban Creek, Jiancao Creek, and Tielu Creek is 171.6 times, 320 times, and 6590 times the standard of Fe concentration in Class III waters, respectively. The water bodies in the research region have also undergone substantial acidification, with the pH of the Jiancao Creek and Tielu Creek's waters ranging from 2 to 3. The table also shows that sulfuric acid concentrations are also exceeded. The water samples from the three rivers showed low pH, high sulfate concentration, and high trace metal concentration, reflecting the same correlation among water pH, sulfuric acid concentration, and trace metal content. This may be due to the fact that the oxidation of iron sulfide produces large amounts of hydrogen ions and sulfuric acid, while low pH facilitates the dissolution of trace metals in the water column, and acidic water improves the diffusion of trace metals in the water, which leads to the pollution of rivers [45]. According to the box line diagrams (Figures 2 and 3), Tielu Creek and Jiancao Creek have significantly higher sulfuric acid and trace metal concentrations than the Daoban Creek. Upon further investigation, it was discovered that the waste rock floor space and stockpile on Daoban Creek are relatively smaller than those on the other two rivers, suggesting that the pollution level may be related to waste rock pile stockpiles. This illustrates that precipitation and riverine leaching from mine waste rock heaps may be the main sources of trace metal pollution of the study area's water bodies. In the Supplementary Materials, we consider the effects of precipitation on surface water pollution. As shown in Figure S1, there is no significant change in ion concentrations in the two batches of water samples before and after rainfall, possibly because while rain brings clean water to dilute trace elements in the river, it also washes away the remains of abandoned mines, which in turn causes more pollutants to enter the river.

Table 4. Statistical tables for analysis of river water parameters and quality standards for surface water and drinking water (units in mg/L for trace elements).

Creek			pH	SO_4^{2-}	Fe	Mn	Cu	Zn	As	Cd	Se
	China [a]		6–9	250	0.3	0.1	1	1	0.05	0.005	0.01
	WHO [b]		6.5–8.5	250	0.3	0.4	2	3	0.01	0.003	0.01
	USEPA [c]	MCLG					1.3			0.05	0.05
		MCL					1.3		0.05	0.05	0.05
Jiancao Creek	Mean		2.72	1299.27	96.1	3.88	0.73	1.35	0.005	0.06	0.0017
	Var		0.03	8.0×10^5	1.2×10^4	2.08	0.21	0.89	4×10^{-5}	0	1.14×10^{-7}
	Min		2.41	570.8	3.19	1.39	0.26	0.26	<0.0003	<0.05	<0.0004
	Max		2.99	3684	358.8	6.2	1.8	3.57	0.02	0.06	0.002
Daoban Creek	Mean		5.55	5.15	7.92	2.40	0.20	0.44	0.15	/	0.01
	Var		5.15	4.51×10^4	4.46×10^3	0.71	0.08	0.24	0.11	/	0.00
	Min		2.4	0.2	<0.03	<0.01	<0.05	<0.05	<0.0003	<0.05	<0.0004
	Max		7.92	656.7	197.2	1.96	0.77	1.45	0.875	<0.05	0.026
Tielu Creek	Mean		2.21	7.7×10^3	1977	21.48	6.73	862.18	0.13	0.1	4×10^{-3}
	Var		0.01	1.7×10^7	5.3×10^5	78.38	5.07	6.5×10^6	7×10^{-3}	0.019	3.7×10^{-7}
	Min		2	0.205	1010	9.06	3.78	3.39	0.041	0.14	3×10^{-3}
	Max		2.4	1.4×10^4	3428	36.75	11.1	8526	0.27	3.6×10^{-2}	4.5×10^{-2}

Note(s): [a] Chinese Surface water environmental quality III water standards (GB 3838-2002). [b] WHO (2011) drinking water guidelines. [c] US EPA (2003) drinking water standards.

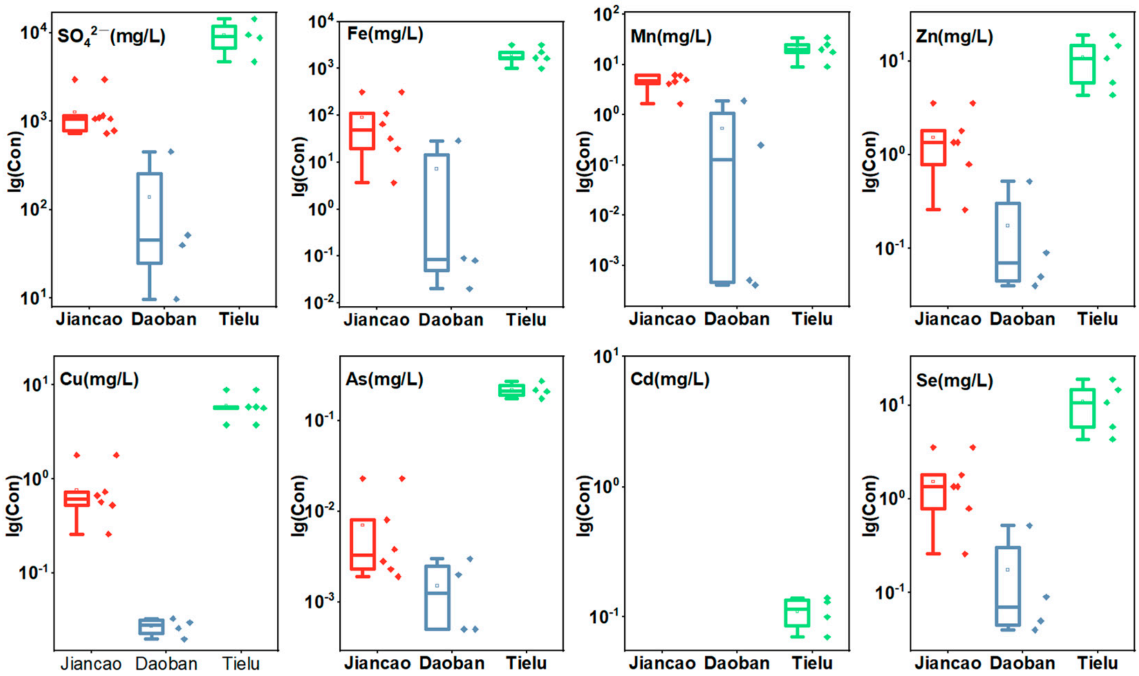

Figure 2. Box line diagram of sulfuric acid and trace metal concentrations in water samples before rain in the study area.

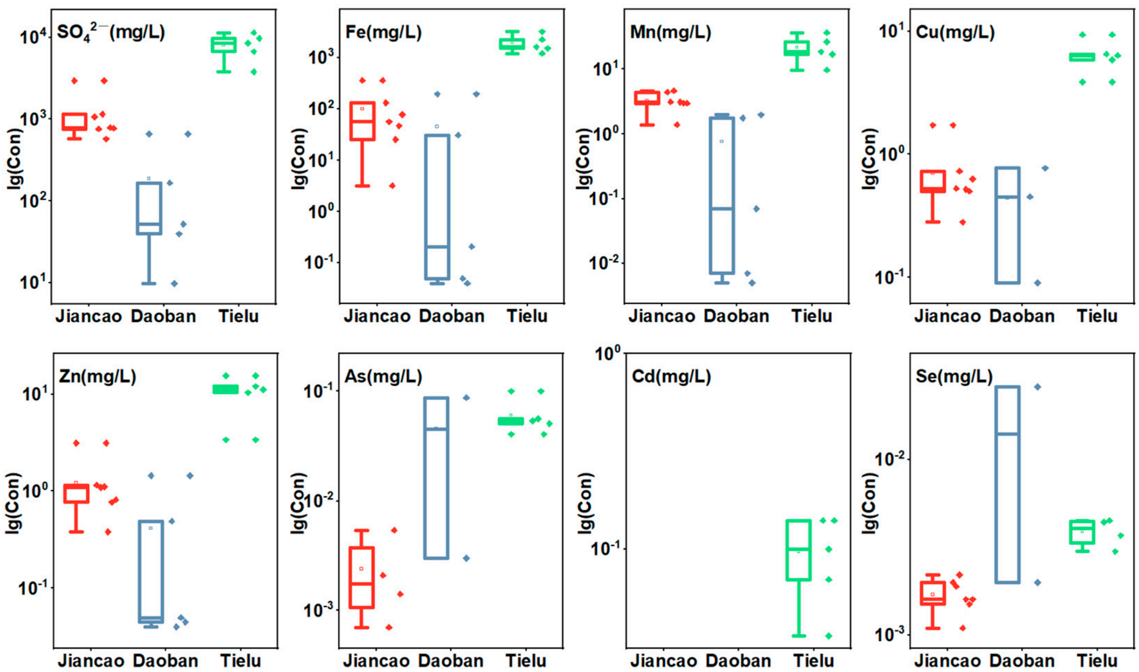

Figure 3. Box line diagram of sulfuric acid and trace metal concentrations in water samples after rain in the study area.

To better understand the spatial distribution of water chemical characteristics, it is helpful to analyze both the characteristics of collected water samples and the locations where they were sampled. This analysis can help identify sources of pollution and trends in spatial variation [46,47]. The variation of sulfuric acid concentration and trace metal concentration with sampling points in the three rivers in the study area are shown in Figure 4. The concentrations of sulfuric acid and Fe, Mn, and Zn ions in the river water samples of the research zone were large and were the main pollution factors, while the concentrations of As, Cd, and Se were low, even down to the detection limit at some sampling points. The concentrations of sulfuric acids, Fe, Mn, and Zn reached their maximum values at sampling points J6, D5, and T4 of the three rivers, respectively. The riverbeds of these three sampling points were directly covered in slag, and the water bodies were severely polluted by trace metals from leaching waste rock piles. The dissolved trace metal content in the water bodies was significantly increased, reflecting the vulnerability of the water body environment. Because of the processes of movement, dilution, deposition, and reaction of the river water, the concentration of pollutants reduces where tributaries of rivers such as J7, D5, and T5 meet [48]. Of all the water samples, the sampling points with serious exceedances of sulfuric acids and trace metal standards are mostly located in the streams and ditches behind the slag as well as in the streams and ditches adjacent to the mine chambers. As a result, the abandoned slag leachate and the mine chambers gushing water are the direct causes of excessive heavy metal content in surface water.

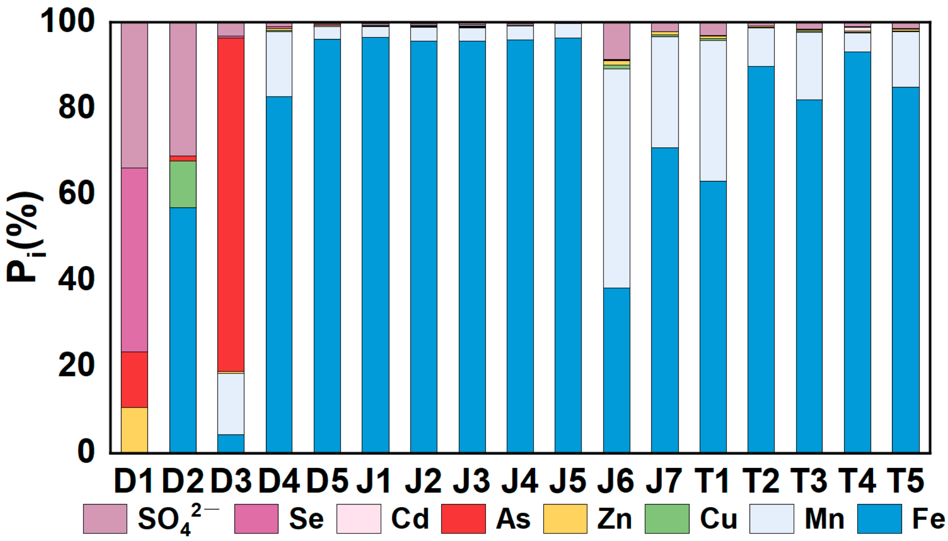

Figure 4. Single-factor pollution index percentage stacked histogram.

3.2. Heavy Metal Pollution Index of Surface Water in the Study Area

The Nemerow pollution index eliminates the variations in the magnitude of trace metal concentrations, making it simple to compare pollution levels and improving the clarity of assessment results. The single-factor pollution index was calculated using the trace metal concentrations in the Daoban Creek, Tielu Creek, and Jiancao Creek water bodies to determine the main trace metal pollutants and the severity of their harm. This index was combined with the multi-factor integrated pollution index to accurately reflect the level of pollution in the water bodies while emphasizing the contribution of the more harmful heavy metal pollutants. Equation (1) was used to determine the Nemerow single-factor contamination index for each element of pollution in the three streams. The Jiancao Creek's trace metal contamination levels are Fe > Mn > Cd > Zn > Cu > As > Se. Fe (320.336) and Mn (38.769) have Nemerow merely indices (P_i) greater than 3, indicating that there is heavy contamination; Cd (1.846) and Zn (1.354) have light contamination and Cu (0.728), As (0.079), and Se (0.092) have no contamination. Each trace metal element in the Daoban Creek has a pollution level of Fe > Mn > As > Se > Zn > Cu > Cd. The Nemerow single-factor pollution index (P_i) of Fe (171.64), Mn (11.8), and As (3.51) is greater than 3, indicating that the pollution level of these three trace elements is strong; the pollution index of Cu (0.244), Zn (0.51), Cd (0), and Se (0.78) is less than 1, and the concentration is low and at a clean level. Each trace metal in the Tielu Creek has a pollution level of Fe > Mn > Cd > Cu > Zn > As > Se. Fe (6590), Mn (214.76), Cd (17.872), Zn (10.077), and Cu (6.732) are the heavy metal elements with the highest levels of pollution in the Tielu Creek water body. Meanwhile, Se (0.156) has a pollution index below 1 and is in a clean state and As (2.3594) has a moderate pollution level. Therefore, it can be concluded from the P_i value that Fe and Mn are the main heavy metal elements responsible for polluting water bodies in the study area. Their pollution levels are both shown to be high, which poses a threat to the environment of the water bodies. Sulfuric acid pollution is a problem that needs to be addressed in addition to trace metal pollution because Jiancao Creek and Tielu Creek have moderate sulfate pollution levels.

The bar chart of the single-factor pollution index of Nemerow in the study area is shown in Figure 4. As can be seen from the figure, the main contamination factor in the study area is Fe, especially in the Jiancao Creek and the Tielu Creek, where the contamination by the heavy element Fe is dominant. This is consistent with the spatial distribution characteristics of trace metals above, and the reason for the occurrence of this phenomenon is related to the AMD generated by waste rock piles and abandoned mine caverns in the study area. It is noteworthy that the pollution of As and Se in Daoban Creek is serious, which may be due to the distribution of villages and farmlands around Daoban Creek, and trace metals from the accumulation of crop fertilizers, pesticides, and domestic wastes entering the water body of Daoban Creek with surface runoff, so the pollution of As and Se in Daoban Creek is concerning.

The histogram of the integrated pollution index (P_n) of Nemerow in the study area is shown in Figure 5. The integrated pollution index of water samples taken from the remaining sampling points, with the exception of D1 and D2, is greater than 2, indicating a serious level of pollution. According to Equation (2), the integrated pollution indexes of the three streams and ditches were calculated. Tielu Creek had the highest combined pollution index (4699.227), followed by Jiancao Creek (228.840), and Daoban Creek (68.106), and all three creeks had P_n values greater than 2. All three rivers are in a serious state of pollution, with poor water quality and significant pollution threats to the water safety of residents in downstream villages, according to the integrated pollution index judgment guidelines. Compared with the Nemerow single-factor pollution index, the Nemerow composite pollution index expands the influence of high concentrations of heavy metals, and in these mine spoils the Nemerow integrated index is chiefly influenced by the value of the single-factor pollution index for iron, and the heavy metal pollution is mainly iron.

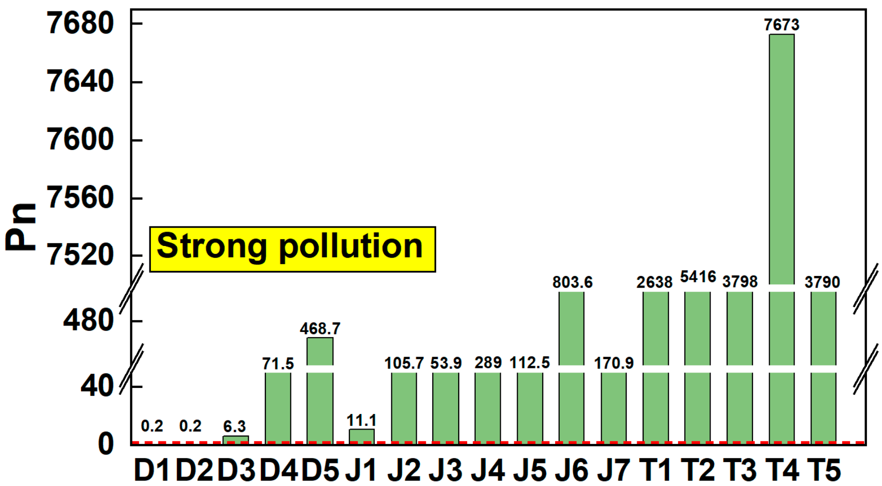

Figure 5. Composite pollution index histogram.

3.3. Health Risk Evaluation

The non-carcinogenic risk of surface water in the study area was assessed using *HI* and *HQ*. These values are listed in Table 4 along with the *HQ* and *HI* calculation results of trace metal elements for grown-ups and children through direct intake and dermal absorption. The $HQ_{ingestion}$ and HQ_{dermal} values of Fe and Mn are greater than 1 for both adults and children in the study area, indicating that these two trace elements are the main ions of greater hazard and a carcinogenic risk to human health in the study area. Along with Fe and Mn, the $HQ_{ingestion}$ and HQ_{dermal} values were higher than 1 for Cd in Jiancao Creek; As in Daoban Creek; and Zn, Cd, and As in Tielu Creek, reflecting spatial differences in non-carcinogenic risks among the rivers in the study area. Cu element in Tielu Creek had a HQ_{dermal} value less than 1 and $HQ_{ingestion}$ value greater than 1, indicating the possibility of negative health effects and carcinogenesis from daily consumption of this element in people. According to Table 5, children generally have higher *HQ* and *HI* values than adults, which is related to their level of physical fitness and drinking habits. This shows that children are more vulnerable to trace elements than adults in the same environment. The following is a list of the different trace elements' non-carcinogenic risk coefficients in the study area, ranked from largest to smallest for both adults and children: Fe > Mn > Zn > As > Cd > Cu > Se.

Table 5. Hazard quotient for trace metals in the Jiancao Creek, Daoban Creek, and Tielu Creek.

	Creek	$HQ_{ingestion}$ Adult	Child	HQ_{dermal} Adult	Child	*HI* Adult	Child
Fe	Jiancao Creek	3.76	5.62	7.01	2.07	1.08	2.63
	Daoban Creek	1.44	2.15	2.69	7.92	4.13	1.01×10^{1}
	Tielu Creek	7.74×10^{1}	1.16×10^{2}	1.44×10^{2}	4.26×10^{2}	2.22×10^{2}	5.41×10^{2}
Mn	Jiancao Creek	4.43	6.61	9.63	2.84×10^{1}	1.41×10^{1}	3.50×10^{1}
	Daoban Creek	1.36	2.03	2.95	8.70	4.31	1.07
	Tielu Creek	2.45×10^{1}	3.66×10^{1}	5.33×10^{1}	1.57×10^{2}	7.79×10^{1}	1.94×10^{2}
Cu	Jiancao Creek	5.00×10^{-1}	7.47×10^{-1}	2.29×10^{-2}	6.75×10^{-2}	5.23×10^{-1}	8.14×10^{-1}
	Daoban Creek	2.99×10^{-1}	4.47×10^{-1}	1.37×10^{-1}	4.04×10^{-2}	3.13×10^{-1}	4.87×10^{-1}
	Tielu Creek	4.61	6.88	2.11×10^{-1}	6.23×10^{-1}	4.82	7.51
Zn	Jiancao Creek	1.23×10^{-1}	1.84×10^{-1}	1.93×10^{-1}	5.70×10^{-1}	3.16×10^{-1}	7.54×10^{-1}
	Daoban Creek	4.03×10^{-2}	6.02×10^{-2}	6.32×10^{-2}	1.86×10^{-1}	1.03×10^{-1}	2.47×10^{-1}
	Tielu Creek	7.87×10^{1}	1.18×10^{2}	1.23×10^{2}	3.64×10^{2}	2.02×10^{2}	4.81×10^{2}
Cd	Jiancao Creek	3.29	4.91	6.86	2.03×10^{1}	1.02×10^{1}	2.52×10^{1}
	Daoban Creek	/	/	/	/	/	/
	Tielu Creek	5.48	8.18	1.14×10^{1}	3.38×10^{1}	1.69×10^{1}	4.19×10^{1}
As	Jiancao Creek	4.57×10^{-1}	6.82×10^{-1}	2.51×10^{-1}	7.40×10^{-1}	7.08×10^{-1}	1.42
	Daoban Creek	1.35×10^{1}	2.01×10^{1}	7.39	2.18×10^{1}	2.08×10^{1}	4.19×10^{1}
	Tielu Creek	1.19×10^{1}	1.77×10^{1}	6.52	1.92×10^{1}	1.84×10^{1}	3.70×10^{1}
Se	Jiancao Creek	9.32×10^{-3}	1.39×10^{-2}	1.11×10^{-2}	3.26×10^{-1}	2.04×10^{-1}	4.65×10^{-1}
	Daoban Creek	4.71×10^{-2}	7.04×10^{-2}	5.59×10^{-2}	1.65×10^{-1}	1.03×10^{-1}	2.35×10^{-1}
	Tielu Creek	2.19×10^{-2}	3.27×10^{-2}	2.60×10^{-2}	7.67×10^{-2}	4.79×10^{-2}	1.09×10^{-1}

Excessive human intake of iron will be toxic to human tissue, leading to tissue damage and organ failure [49]; manganese in the body will produce neurotoxicity, inducing Parkinson's disease [50]; excessive intracellular zinc content will promote apoptosis, leading to cellular nervous system decline, which may induce the onset of Alzheimer's disease; arsenic may cause potential carcinogenic effects on the body's blood vessels and bladder, etc., resulting in lesions [51,52]; cadmium has adverse effects on the renal system, which is the cause of immune deficiency and bone damage [53]; copper in the human body, once the content is excessive, will lead to abnormal changes in the metabolism of human tissue form [54]. Excessive intake of selenium over a long period of time can be toxic to the human body, causing pallor, mental fatigue, gastrointestinal disorders, indigestion, and other serious consequences. In general, it is necessary to take some actions to decrease the entry of trace elements into water bodies in the surface waters of the study area to protect human health and aquatic ecosystems. Additionally, since the concentrations of Fe and Mn are significantly high, special precautions should be taken to prevent these two elements from entering rivers.

3.4. Multivariate Statistical Analysis

3.4.1. Correlation Analysis

The data set was subjected to correlation analysis in order to describe the relationship between trace metals in the form of a mathematical language and learn more about the origins of the chosen heavy metal elements [55]. Correlation analysis has been widely used to investigate the relationship between heavy metal element variables in water [56,57]. Figure 6 displays the correlation analysis for the pH, trace metal concentration, and sulfuric acid content in the study area. This indicates that the lower the pH, the higher the concentration of trace metals and sulfuric acid. Metal sulfides (such as pyrite, arsenopyrite, and chalcopyrite) produce a high concentration of sulfate ions and hydrogen ions when oxidation occurs. The acidic water also accelerates the oxidation dissolution of heavy metals into minerals [45,58]. Additionally, pH and arsenic showed a positive correlation at the significance level of $p < 0.01$, and an increase in pH resulted in the dissolved release of As, which is consistent with the findings of Mirazimi et al.'s study [59]. Trace elements with high correlation coefficients in the water column may have similar hydrochemical characteristics in the investigated area [56]. A significant correlation between trace metal elements implies that these elements are homologous or have a certain correlation. Fe, Mn, Cu, and Cd heavy metals were discovered to have a strong positive correlation that ranged from 0.707 to 0.986. Sulfuric acid and Fe, Mn, Cu, and Cd also showed strong positive correlations ($p < 0.05$). The source of heavy elements and sulfuric acid may be related to the oxidation of sulfides, and these contaminants may have come from the waste piles of abandoned sulfur iron ore mines.

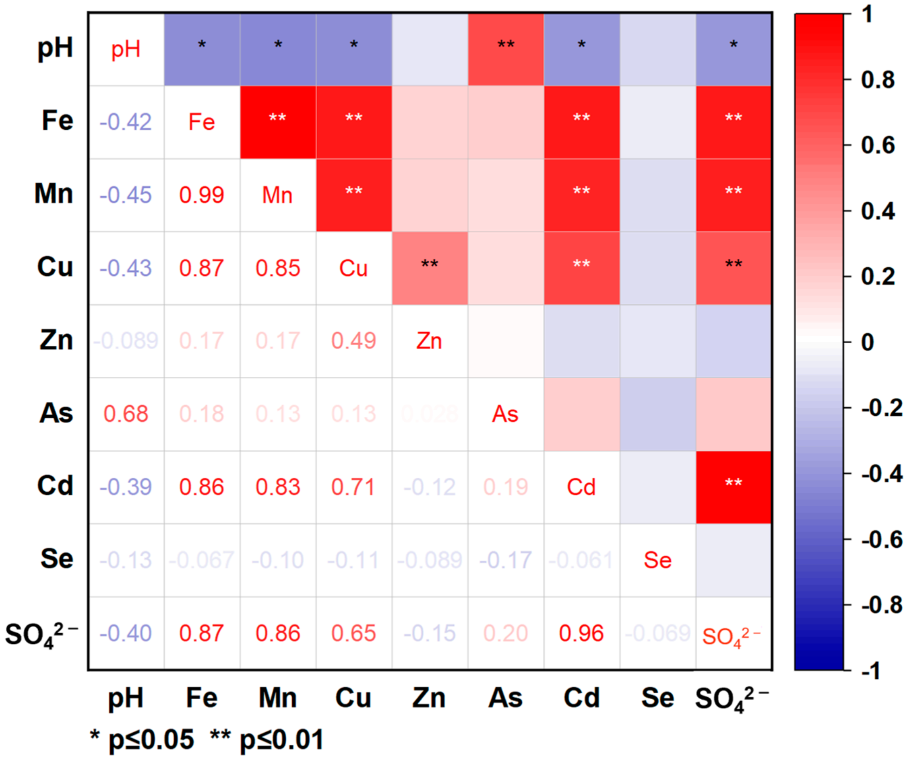

Figure 6. Heat map of correlation of physicochemical parameters in surface waters of the study area.

3.4.2. Principal Component Analysis

By analyzing the principal components, the main sources of pollution can be obtained [60]. The principal component analysis uses the maximum variance method to rotate the factors, and the validity of the results of the principal component analysis is judged by the KMO and Burtlett's sphericity test, which is a measure of sampling adequacy with a value between 0 and 1. A smaller value close to 0 indicates that it is not appropriate to perform PCA, a value greater than 0.6 is considered satisfactory, and a value close to 1 improves the reliability of PCA. The results of the principal component analysis were valid if KMO > 0.5 or Burtlett < 0.001 [61]. For the water bodies in Daoban Creek, Jiancao Creek, and Tielu Creek, the principal components of factor analysis were used to extract the key factors that explained the origins, make-up, and contribution of the seven trace metals present in the water. KMO and Burtlett were 0.646 and 0.000, respectively, indicating statistical significance. Table 6 shows that the cumulative contribution rate of the three factors is 85.186%, of which the variance contribution rate of factor 1 is 52.388%, the variance contribution rate of factor 2 is 16.960%, and the variance contribution rate of factor 3 is 15.838%. Therefore, the water quality of rivers in mining areas is affected by three main factors (Figure 7).

Table 6. Principal component analysis of trace elements in surface water of abandoned sulfur and iron mine area.

Variable	Factor 1	Factor 2	Factor 3
Fe	0.979	0.091	0.074
Mn	0.965	0.106	0.067
Cu	0.862	0.447	0.065
Zn	0.083	0.972	0.036
As	0.147	−0.126	0.749
Cd	0.928	−0.217	0.096
Se	0.011	−0.176	−0.773
Eigenvalues	3.667	1.187	1.109
Variance (%)	52.388	16.960	15.838
Cumulative (%)	52.388	69.349	85.186

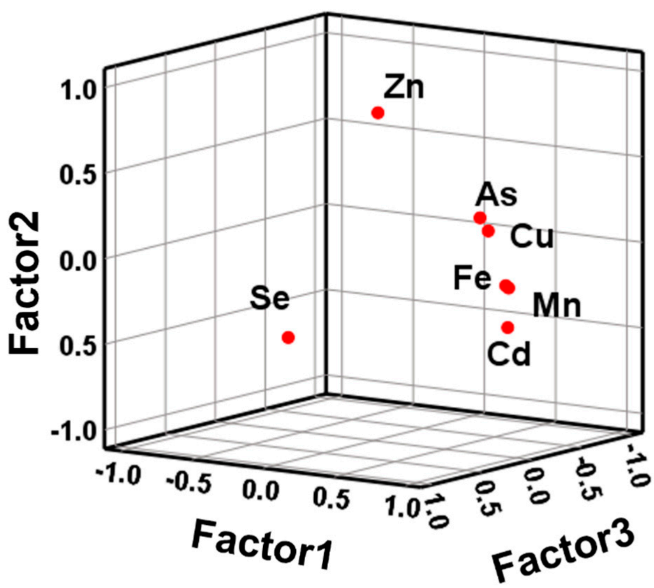

Figure 7. Loadings of heavy metals in surface water from abandoned sulfur and iron ore mines.

Factor 1 mainly has a high positive load with Fe, Mn, Cu, and Cd (all > 0.8). The pollution of Fe, Mn, Cu, and Cd mainly comes from mining, electroplating, and heavy metal processing industries. In our research, the source of heavy metals is related to the historical conditions of mining in Baihe County. The river water quality is most adversely impacted by the mine wastewater because the study area is located in an area where abandoned non-ferrous metal mining operations once operated.

The correlation between factor 2 and Zn is large, which may be influenced by human activities, and the heavy metal Zn may originate from the waste generated in human activities [62]. It is assumed that the source of zinc is closely related to the rainwater leaching of domestic pollution waste because the study area is close to the town of Qiazi and there is a problem with domestic waste piling up and improper disposal, which affects the water quality of the river.

Factor 3 has a high correlation with As. Sources of arsenic pollution include agricultural activities such as pesticides and fertilizers [63]. The high concentration of arsenic is mostly concentrated in the Daoban Creek, and upon investigation of the environment at the time of sampling, it was discovered that the area was contaminated by agricultural surface sources brought by the nearby farmland, and that the arsenic elements contained in the pesticides and fertilizers used entered the river through surface runoff by rainwater drenching. It is therefore assumed that the source of arsenic is closely related to human agricultural activities.

3.4.3. Cluster Analysis

The purpose of hierarchical cluster analysis is to find groups of similar items and variables (sample points) and group them together. When applied to a set of variables, cluster analysis orders and categorizes the variables into groups that are as identical as possible based on their correlations [64]. The cluster analysis is therefore based on the spatial similarity of the ionic components in the water samples [65]. In this study, samples were classified using hierarchical clustering of mean linkages (between groups), and a dendrogram of the two statistically significant clusters was drawn at $(D_{link}/D_{max}) \times 100 < 25$. The dendrograms resulting from the analysis show the ranking of the variables (sampled points) in similar clusters, while the distance between the points on the horizontal axis represents the proximity order (Figure 8). In addition, on the plots, we can see how each variable fits into successive clusters as they are formed, as well as determine when clusters are formed. The sampling points form two main clusters. As a result, we can see that the water samples from Jiancao Creek and Daoban Creek are grouped together, while the water samples from Tielu Creek are in a different group. Combined with the above analysis, Tielu Creek has the highest trace metal pollution index and the most severe level of pollution. The pollution levels in Jiancao Creek and Daoban Creek are also relatively low, so the two clustering results primarily reflect the extent of trace metal pollution. Based on the average trace metal concentration of each cluster, clusters 2 and 1 can be classified as trace metal pollution areas and moderate pollution areas, respectively.

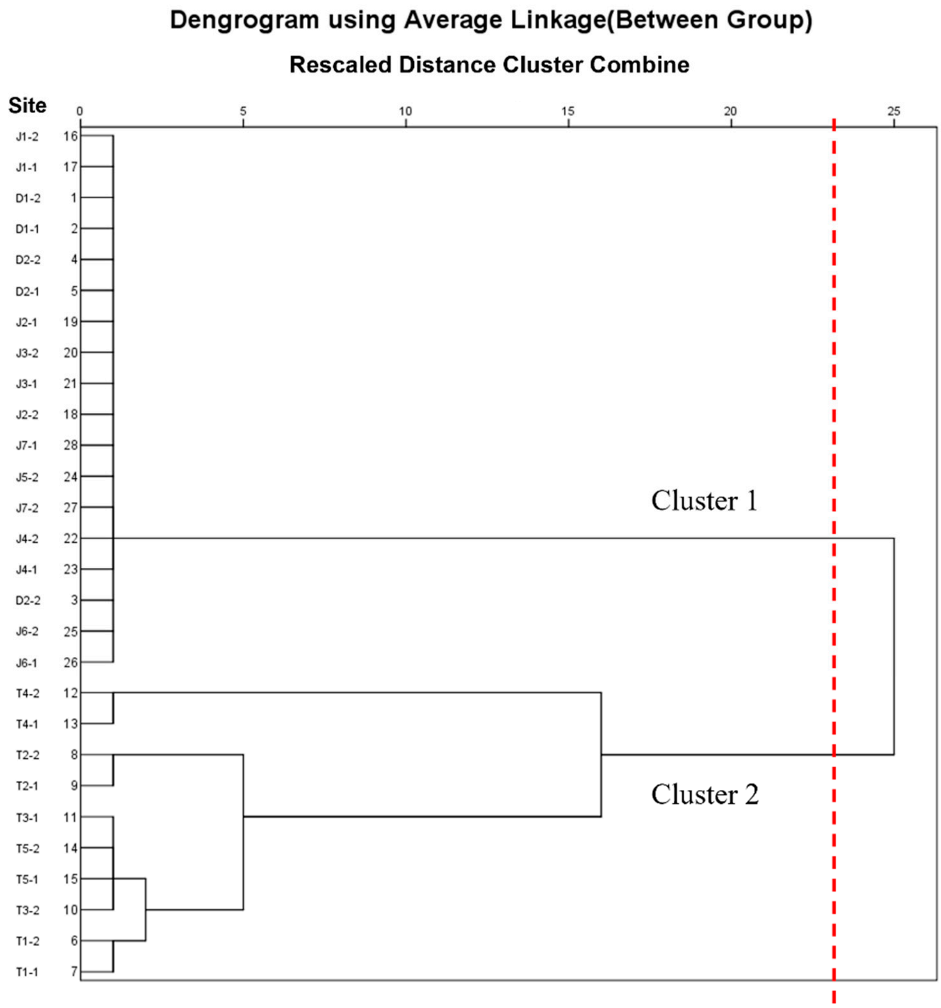

Figure 8. Dendrogram of water samples of surface water of abandoned pyrite mine based on clustering classification. Note(s): The red line intersects the cluster tree at two points, meaning that there are three statistically significant clusters on the tree.

4. Conclusions

In this study, the spatial distribution and pollution characteristics of trace metals (Fe, Mn, Cu, Zn, As, Cd, Se) and sulfuric acid in the surface waters of abandoned mining areas in Baihe County were investigated. Using the Nemerow index, water body contamination levels were assessed, and the non-carcinogenic risk was determined using *HI*. Additionally, a variety of statistical analysis techniques were used to investigate the relationships between heavy metals and pinpoint their sources. The key findings were as follows:

The trace metals such as Fe, Mn, Zn, Cu, Cd, As, and Se in the water bodies showed different degrees of ecological and environmental risks, among which Fe and Mn showed the most significant degree of contamination and the highest single-factor pollution index in Nemerow. Tielu Creek had the worst heavy metal pollution of the three rivers studied, and Tielu Creek had the highest integrated Nemerow pollution index. According to the pollution index and hazard index findings, the water bodies in the study area are unsuitable for use as drinking water or for daily activities and pose a high risk for ecological and cancer-causing hazards. According to the results of the multivariate statistical analysis, the main source of iron and manganese in water bodies was AMD from closed mines; waste rock pile leaching pollution was the main source of pollution in this study area, and crop fertilizers, pesticides, and household waste were the main sources of arsenic and zinc.

The findings of this study suggest that AMD is still being produced by long-abandoned pyrite mines, which endanger nearby water bodies with pollution. This study brings insight into the understanding of the hazards of AMD generated by abandoned mines, as well as the scientific treatment and ecological restoration of the remaining mine sites after mine closure. However, this study does not investigate the impact of AMD on soil, which will be improved in future studies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15173138/s1, Figure S1: Changes in sulfate and heavy metal concentrations in water samples before and after rain in the study area [66].

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References

1. Ya'ni, G. Research Progress of Heavy Metal Pollution in River. *Chin. Agric. Sci. Bull.* **2012**, *28*, 262–265.
2. Li, W.; Qian, H.; Xu, P.; Zhang, Q.; Chen, J.; Hou, K.; Ren, W.; Qu, W.; Chen, Y. Distribution Characteristics, Source Identification and Risk Assessment of Heavy Metals in Surface Sediments of the Yellow River, China. *Catena* **2022**, *216*, 106376. [CrossRef]
3. Cui, L.; Wang, X.; Li, J.; Gao, X.; Zhang, J.; Liu, Z.; Liu, Z. Ecological and Health Risk Assessments and Water Quality Criteria of Heavy Metals in the Haihe River. *Environ. Pollut.* **2021**, *290*, 117971. [CrossRef] [PubMed]
4. Zhelev, Z.M.; Arnaudova, D.N.; Popgeorgiev, G.S.; Tsonev, S.V. In Situ Assessment of Health Status and Heavy Metal Bioaccumulation of Adult *Pelophylax ridibundus* (Anura: Ranidae) Individuals Inhabiting Polluted Area in Southern Bulgaria. *Ecol. Indic.* **2020**, *115*, 106413. [CrossRef]
5. Bhuyan, M.S.; Haider, S.M.B.; Meraj, G.; Bakar, M.A.; Islam, M.T.; Kunda, M.; Siddique, M.A.B.; Ali, M.M.; Mustary, S.; Mojumder, I.A.; et al. Assessment of Heavy Metal Contamination in Beach Sediments of Eastern St. Martin's Island, Bangladesh: Implications for Environmental and Human Health Risks. *Water* **2023**, *15*, 2494. [CrossRef]
6. Singovszka, E.; Balintova, M.; Junakova, N. The Impact of Heavy Metals in Water from Abandoned Mine on Human Health. *SN Appl. Sci.* **2020**, *2*, 934. [CrossRef]
7. Munir, N.; Jahangeer, M.; Bouyahya, A.; El Omari, N.; Ghchime, R.; Balahbib, A.; Aboulaghras, S.; Mahmood, Z.; Akram, M.; Ali Shah, S.M.; et al. Heavy Metal Contamination of Natural Foods Is a Serious Health Issue: A Review. *Sustainability* **2022**, *14*, 161. [CrossRef]
8. Ali, H.; Khan, E. Trophic Transfer, Bioaccumulation, and Biomagnification of Non-Essential Hazardous Heavy Metals and Metalloids in Food Chains/Webs-Concepts and Implications for Wildlife and Human Health. *Hum. Ecol. Risk Assess.* **2019**, *25*, 1353–1376. [CrossRef]
9. Kumari, P.; Chowdhury, A.; Maiti, S.K. Assessment of Heavy Metal in the Water, Sediment, and Two Edible Fish Species of Jamshedpur Urban Agglomeration, India with Special Emphasis on Human Health Risk. *Hum. Ecol. Risk Assess. Int. J.* **2018**, *24*, 1477–1500. [CrossRef]
10. Sharma, S.; Nagpal, A.K.; Kaur, I. Appraisal of Heavy Metal Contents in Groundwater and Associated Health Hazards Posed to Human Population of Ropar Wetland, Punjab, India and Its Environs. *Chemosphere* **2019**, *227*, 179–190. [CrossRef]
11. Gerson, J.R.; Topp, S.N.; Vega, C.M.; Gardner, J.R.; Yang, X.; Fernandez, L.E.; Bernhardt, E.S.; Pavelsky, T.M. Pavelsky Artificial Lake Expansion Amplifies Mercury Pollution from Gold Mining. *Sci. Adv.* **2020**, *6*, eabd4953. [CrossRef] [PubMed]
12. Lin, C.Y.; Ali, B.N.M.; Tair, R.; Musta, B.; Abdullah, M.H.; Cleophas, F.; Isidore, F.; Nadzir, M.S.M.; Roselee, M.H.; Yusoff, I. Distance Impacts Toxic Metals Pollution in Mining Affected River Sediments. *Environ. Res.* **2022**, *214*, 113757. [CrossRef] [PubMed]
13. Liu, Y.; Wang, P.; Gojenko, B.; Yu, J.; Wei, L.; Luo, D.; Xiao, T. A Review of Water Pollution Arising from Agriculture and Mining Activities in Central Asia: Facts, Causes and Effects. *Environ. Pollut.* **2021**, *291*, 118209. [CrossRef] [PubMed]
14. Kumar, V.; Sharma, A.; Kumar, R.; Bhardwaj, R.; Kumar Thukral, A.; Rodrigo-Comino, J. Assessment of Heavy-Metal Pollution in Three Different Indian Water Bodies by Combination of Multivariate Analysis and Water Pollution Indices. *Hum. Ecol. Risk Assess.* **2020**, *26*, 1–16. [CrossRef]
15. Sun, Z.; Xie, X.; Wang, P.; Hu, Y.; Cheng, H. Heavy Metal Pollution Caused by Small-Scale Metal Ore Mining Activities: A Case Study from a Polymetallic Mine in South China. *Sci. Total Environ.* **2018**, *639*, 217–227. [CrossRef]

16. Li, Z.; Ma, Z.; van der Kuijp, T.J.; Yuan, Z.; Huang, L. A Review of Soil Heavy Metal Pollution from Mines in China: Pollution and Health Risk Assessment. *Sci. Total Environ.* **2014**, *468*, 843–853. [CrossRef]
17. Islam, M.S.; Ahmed, M.K.; Raknuzzaman, M.; Habibullah-Al-Mamun, M.; Islam, M.K. Heavy Metal Pollution in Surface Water and Sediment: A Preliminary Assessment of an Urban River in a Developing Country. *Ecol. Indic.* **2015**, *48*, 282–291. [CrossRef]
18. Ali, M.M.; Ali, M.L.; Islam, M.S.; Rahman, M.Z. Preliminary Assessment of Heavy Metals in Water and Sediment of Karnaphuli River, Bangladesh. *Environ. Nanotechnol. Monit. Manag.* **2016**, *5*, 27–35. [CrossRef]
19. Adamovic, D.; Ishiyama, D.; Dordievski, S.; Ogawa, Y.; Stevanovic, Z.; Kawaraya, H.; Sato, H.; Obradovic, L.; Marinkovic, V.; Petrovic, J.; et al. Estimation and Comparison of the Environmental Impacts of Acid Mine Drainage-Bearing River Water in the Bor and Majdanpek Porphyry Copper Mining Areas in Eastern Serbia. *Resour. Geol.* **2021**, *71*, 123–143. [CrossRef]
20. Skousen, J.; Zipper, C.E.; Rose, A.; Ziemkiewicz, P.F.; Nairn, R.; McDonald, L.M.; Kleinmann, R.L. Review of Passive Systems for Acid Mine Drainage Treatment. *Mine Water Environ.* **2017**, *36*, 133–153. [CrossRef]
21. Nordstrom, D.K. Hydrogeochemical Processes Governing the Origin, Transport and Fate of Major and Trace Elements from Mine Wastes and Mineralized Rock to Surface Waters. *Appl. Geochem.* **2011**, *26*, 1777–1791. [CrossRef]
22. Skousen, J.G.; Ziemkiewicz, P.F.; McDonald, L.M. Acid Mine Drainage Formation, Control and Treatment: Approaches and Strategies. *Extr. Ind. Soc.* **2019**, *6*, 241–249. [CrossRef]
23. Jiao, Y.; Zhang, C.; Su, P.; Tang, Y.; Huang, Z.; Ma, T. A Review of Acid Mine Drainage: Formation Mechanism, Treatment Technology, Typical Engineering Cases and Resource Utilization. *Process Saf. Environ.* **2023**, *170*, 1240–1260. [CrossRef]
24. Shi, A.; Shao, Y.; Zhao, K.; Fu, W. Long-Term Effect of E-Waste Dismantling Activities on the Heavy Metals Pollution in Paddy Soils of Southeastern China. *Sci. Total Environ.* **2020**, *705*, 135971. [CrossRef]
25. Park, I.; Tabelin, C.B.; Jeon, S.; Li, X.; Seno, K.; Ito, M.; Hiroyoshi, N. A Review of Recent Strategies for Acid Mine Drainage Prevention and Mine Tailings Recycling. *Chemosphere* **2019**, *219*, 588–606. [CrossRef] [PubMed]
26. Lefcort, H.; Vancura, J.; Edward, L. Lider 75 Years after Mining Ends Stream Insect Diversity Is Still Affected by Heavy Metals. *Ecotoxicology* **2010**, *19*, 1416–1425. [CrossRef]
27. Wang, Z.; Xu, Y.; Zhang, Z.; Zhang, Y. Review: Acid Mine Drainage (AMD) in Abandoned Coal Mines of Shanxi, China. *Water* **2020**, *13*, 8. [CrossRef]
28. Zhang, J.; Li, X.; Guo, L.; Deng, Z.; Wang, D.; Liu, L. Assessment of Heavy Metal Pollution and Water Quality Characteristics of the Reservoir Control Reaches in the Middle Han River, China. *Sci. Total Environ.* **2021**, *799*, 149472. [CrossRef] [PubMed]
29. Hammarstrom, J.M.; Seal, R.R.; Meier, A.L.; Jackson, J.C. Weathering of Sulfidic Shale and Copper Mine Waste: Secondary Minerals and Metal Cycling in Great Smoky Mountains National Park, Tennessee, and North Carolina, USA. *Environ. Geol.* **2003**, *45*, 23. [CrossRef]
30. Wang, Y.; Dong, R.; Zhou, Y.; Luo, X. Characteristics of Groundwater Discharge to River and Related Heavy Metal Transportation in a Mountain Mining Area of Dabaoshan, Southern China. *Sci. Total Environ.* **2019**, *679*, 346–358. [CrossRef] [PubMed]
31. Peng, B.; Tang, X.; Yu, C.; Xie, S.; Xiao, M.; Song, Z.; Tu, X. Heavy Metal Geochemistry of the Acid Mine Drainage Discharged from the Hejiacun Uranium Mine in Central Hunan, China. *Environ. Geol.* **2009**, *57*, 421–434. [CrossRef]
32. Shu, X.-H.; Zhang, Q.; Lu, G.-N.; Yi, X.-Y.; Dang, Z. Pollution Characteristics and Assessment of Sulfide Tailings from the Dabaoshan Mine, China. *Int. Biodeterior. Biodegrad.* **2018**, *128*, 122–128. [CrossRef]
33. Zhang, W.J.; Xin, C.L.; Yu, S.; Liu, Q.; Zeng, P. Spatial and temporal distribution and pollution evaluation of dissolved heavy metals in Liujiang River Basin. *Environ. Sci.* **2021**, *42*, 4234–4245. [CrossRef]
34. Yangming, N.; Faneng, Y. Water quality evaluation based on improved Nemerow pollution index method and grey clustering method. *J. Cent. China Norm. Univ. (Nat. Sci.)* **2020**, *54*, 149–155. [CrossRef]
35. Guo, H. Application of different water quality evaluation methods in Qinghe River water quality evaluation. *Yangtze River* **2012**, *43*, 132–134. [CrossRef]
36. Huanhuan, Q.I.; Bai, G.A.; Zhanxue, S.U. Concentration properties and health risk assessment of heavy metals in Lhasa River, Tibet. *J. Water Resour. Water Eng.* **2022**, *33*, 1–7.
37. Tong, S.; Li, H.; Tudi, M.; Yuan, X.; Yang, L. Comparison of Characteristics, Water Quality and Health Risk Assessment of Trace Elements in Surface Water and Groundwater in China. *Ecotoxicol. Environ. Saf.* **2021**, *219*, 112283. [CrossRef]
38. Wu, B.; Zhao, D.Y.; Jia, H.Y.; Zhang, Y.; Zhang, X.X.; Cheng, S.P. Preliminary Risk Assessment of Trace Metal Pollution in Surface Water from Yangtze River in Nanjing Section, China. *Bull. Environ. Contam. Toxicol.* **2009**, *82*, 405–409. [CrossRef]
39. Wang, J.; Gao, B.; Yin, S.; Xu, D.; Liu, L.; Li, Y. Simultaneous Health Risk Assessment of Potentially Toxic Elements in Soils and Sediments of the Guishui River Basin, Beijing. *Int. J. Environ. Res. Public Health* **2019**, *16*, 4539. [CrossRef]
40. Emenike, P.C.; Neris, J.B.; Tenebe, I.T.; Nnaji, C.C.; Jarvis, P. Estimation of Some Trace Metal Pollutants in River Atuwara Southwestern Nigeria and Spatio-Temporal Human Health Risks Assessment. *Chemosphere* **2020**, *239*, 124770. [CrossRef]
41. Li, M.; Liu, Z.; Zhang, M.; Chen, Y. A Workflow for Spatio-Seasonal Hydro-Chemical Analysis Using Multivariate Statistical Techniques. *Water Res.* **2021**, *188*, 116550. [CrossRef] [PubMed]
42. Paliy, O.; Shankar, V. Application of Multivariate Statistical Techniques in Microbial Ecology. *Mol. Ecol.* **2016**, *25*, 1032–1057. [CrossRef] [PubMed]
43. Huang, X.; Sillanpää, M.; Gjessing, E.T.; Peräniemi, S.; Vogt, R.D. Environmental Impact of Mining Activities on the Surface Water Quality in Tibet: Gyama Valley. *Sci. Total Environ.* **2010**, *408*, 4177–4184. [CrossRef] [PubMed]

44. Chen, M.; Li, F.; Tao, M.; Hu, L.; Shi, Y.; Liu, Y. Distribution and Ecological Risks of Heavy Metals in River Sediments and Overlying Water in Typical Mining Areas of China. *Mar. Pollut. Bull.* **2019**, *146*, 893–899. [CrossRef] [PubMed]
45. Candeias, C.; Ávila, P.F.; Da Silva, E.F.; Ferreira, A.; Durães, N.; Teixeira, J.P. Water–Rock Interaction and Geochemical Processes in Surface Waters Influenced by Tailings Impoundments: Impact and Threats to the Ecosystems and Human Health in Rural Communities (Panasqueira Mine, Central Portugal). *Water Air Soil Poll.* **2015**, *226*, 23. [CrossRef]
46. Wu, J.; Lu, J.; Zhang, C.; Zhang, Y.; Lin, Y.; Xu, J. Pollution, Sources, and Risks of Heavy Metals in Coastal Waters of China. *Hum. Ecol. Risk Assess. Int. J.* **2020**, *26*, 2011–2026. [CrossRef]
47. El-Sorogy, A.S.; Youssef, M.; Al-Hashim, M.H. Water Quality Assessment and Environmental Impact of Heavy Metals in the Red Sea Coastal Seawater of Yanbu, Saudi Arabia. *Water* **2023**, *15*, 201. [CrossRef]
48. NAbdel-Ghani, N.T.; Elchaghaby, G.A. Influence of Operating Conditions on the Removal of Cu, Zn, Cd and Pb Ions from Wastewater by Adsorption. *Int. J. Environ. Sci. Technol.* **2007**, *4*, 451–456. [CrossRef]
49. D'Mello, S.R.; Mark, C. Kindy Overdosing on Iron: Elevated Iron and Degenerative Brain Disorders. *Exp. Biol. Med.* **2020**, *245*, 1444–1473. [CrossRef]
50. Polito, L.; Greco, A.; Seripa, D. Genetic Profile, Environmental Exposure, and Their Interaction in Parkinson's Disease. *Park. Dis.* **2016**, *2016*, 6465793. [CrossRef]
51. Liang, C.-P.; Chen, J.-S.; Chien, Y.-C.; Chen, C.-F. Spatial Analysis of the Risk to Human Health from Exposure to Arsenic Contaminated Groundwater: A Kriging Approach. *Sci. Total Environ.* **2018**, *627*, 1048–1057. [CrossRef]
52. Sohrabi, N.; Kalantari, N.; Amiri, V.; Saha, N.; Berndtsson, R.; Bhattacharya, P.; Ahmad, A. A Probabilistic-Deterministic Analysis of Human Health Risk Related to the Exposure to Potentially Toxic Elements in Groundwater of Urmia Coastal Aquifer (NW of Iran) with a Special Focus on Arsenic Speciation and Temporal Variation. *Stoch. Environ. Res. Risk Assess.* **2021**, *35*, 1509–1528. [CrossRef]
53. Godt, J.; Scheidig, F.; Grosse-Siestrup, C.; Esche, V.; Brandenburg, P.; Reich, A.; David, A. Groneberg The Toxicity of Cadmium and Resulting Hazards for Human Health. *J. Occup. Med. Toxicol.* **2006**, *1*, 22. [CrossRef] [PubMed]
54. Ipek, Y.; Kocak, B.; Moussavi-Harami, R.; Zand-Moghadam, H.; Mahboubi, A.; Tohidi, M.R. Spatial Dispersion Hot Spots of Contamination and Human Health Risk Assessments of PTEs in Surface Sediments of Streams around Porphyry Copper Mine, Iran. *Environ. Geochem. Health* **2023**, *45*, 3907–3931. [CrossRef]
55. Shakhari, S.; Verma, A.K.; Ghosh, D.; Bhar, K.K.; Banerjee, I. Diverse Water Quality Data Pattern Study of the Indian River Ganga: Correlation and Cluster Analysis. In Proceedings of the 2019 17th International Conference on ICT and Knowledge Engineering (ICT & KE), Bangkok, Thailand, 20–22 November 2019; pp. 93–99.
56. Wang, J.; Liu, G.; Liu, H.; Paul, K.S. Lam Multivariate Statistical Evaluation of Dissolved Trace Elements and a Water Quality Assessment in the Middle Reaches of Huaihe River, Anhui, China. *Sci. Total Environ.* **2017**, *583*, 421–431. [CrossRef] [PubMed]
57. Mitryasova, O.; Pohrebennyk, V.; Cygnar, M.; Sopilnyak, I. Environmental Natural Water Quality Assessment by Method of Correlation Analysis. *Int. Multidiscip. Sci. GeoConference SGEM* **2016**, *2*, 317–324.
58. Nordstrom, D.K.; Ball, J.W. Toxic Element Composition of Acid Mine Waters from Sulfide Ore Deposits. *Mine Water Cong.* **1985**, *2*, 749–757.
59. Mirazimi, M.; Fan, J.; Liu, W. Kinetics of Arsenic and Sulfur Release from Amorphous Arsenic Trisulfide. *Hydrometallurgy* **2021**, *200*, 105555. [CrossRef]
60. Hao, R.X.; Li, S.M.; Li, J.B.; Zhang, Q.K.; Liu, F. Water Quality Assessment for Wastewater Reclamation Using Principal Component Analysis. *J. Environ. Inform.* **2013**, *21*, 45–54. [CrossRef]
61. Bhardwaj, R.; Gupta, A.; Garg, J.K. Evaluation of Heavy Metal Contamination Using Environmetrics and Indexing Approach for River Yamuna, Delhi Stretch, India. *Water Sci.* **2017**, *31*, 52–66. [CrossRef]
62. Wang, Q.L.; Song, Y.T.; Wang, C.W.; Xu, R.T.; Peng, M.; Zhou, Y.L.; Han, W. Source identification and spatial distribution of soil heavy metals in Western Yunnan. *China Environ. Sci.* **2021**, *41*, 3693–3703. [CrossRef]
63. Manli, C. Study on the Transfer Rule of Hg, As, Se for Weihe River in Xi'an. Bachelor's Thesis, Chang'an University, Xi'an, China, 2016.
64. Grande, J.A.; Borrego, J.; De La Torre, M.L.; Sáinz, A. Application of Cluster Analysis to the Geochemistry Zonation of the Estuary Waters in the Tinto and Odiel Rivers (Huelva, Spain). *Environ. Geochem. Health* **2003**, *25*, 233–246. [CrossRef] [PubMed]
65. GShenbagalakshmi, G.; Shenbagarajan, A.; Thavasi, S.; Nayagam, M.G.; Venkatesh, R. Determination of Water Quality Indicator Using Deep Hierarchical Cluster Analysis. *Urban Clim.* **2023**, *49*, 101468. [CrossRef]
66. Sarmiento, A.M.; Nieto, J.M.; Olías, M.; Cánovas, C.R. Hydrochemical Characteristics and Seasonal Influence on the Pollution by Acid Mine Drainage in the Odiel River Basin (SW Spain). *Appl. Geochem.* **2009**, *24*, 697–714. [CrossRef]