Meteorological and Environmental Research 2024, 15(1): 75 – 82

Quantitative Evaluation of Heavy Metal Pollution and Its Influencing Factors in Water Bodies of Karst Areas

Dijin MU, Shizhen XIAO *

School of Karst Science, Guizhou Normal University, Guiyang 550001, China

Abstract At present, there is relatively little research on the synergistic effects of heavy metals in soil, sediment, and bedrock on heavy metal pollution in water bodies. In this paper, heavy metals in soil, sediment, bedrock, and water of a typical karst watershed in southwest China were investigated. The results indicated that the average values of heavy metals in soil and sediment were relatively higher than those in bedrock except for Ni and As. During the research period, As and Cd were the main heavy metal elements polluting the soil and sediment in the study area, while water bodies were mainly polluted by Ni, As, and Cd. The pollution assessment indicated that there were instances of poor or very poor water quality in the study area during the study period; the soil as a whole was slightly polluted by Cd and As; sediment was subject to moderate Cd pollution and mild As pollution. Analysis of geochemical form for heavy metals showed that heavy metals in soil and sediment were mainly in residual form, and the proportions of exchangeable As and Cd were relatively high. Multiple statistical analysis showed that heavy metals in sediment, soil, and bedrock explained 23.8%, 16.8%, and 16.2% of the changes in heavy metals of water, respectively. The research results can provide scientific basis for the prevention and control of heavy metal pollution in water bodies.

Key words Water body; Sediment; Soil; Bedrock; Speciation forms; Pollution; Influence factor

DOI 10.19547/j.issn2152 – 3940.2024.01.014

With the development of industries such as mining, metallurgy, and electroplating, serious heavy metal pollution has been caused worldwide[1 – 3]. Heavy metals have toxicity and persistence, and can be transferred and enriched into human bodies through direct exposure or indirect food chain, ultimately posing a risk to human health[4 – 5]. For example, long-term exposure to Cd may lead to kidney damage and have adverse effects on the lungs, cardiovascular system, and musculoskeletal system[6]. China is one of the world's largest producers and consumers of metals[7], and the continuous development of industry has caused serious pollution of soil, water bodies, and sediments in many places[8 – 9]. Therefore, it is necessary to conduct comprehensive pollution assessments in areas with intensive industrial activities.

Research has shown that in terrestrial ecosystems, the excess infiltration or saturation-excess runoff generated by precipitation separates heavy metals from the soil surface in dissolved or particulate form and deposits them in rivers or lakes, achieving the migration of heavy metals[10]. Extensive research on the sources of heavy metals in water bodies has been conducted, and sources include surface runoff[11], sewage discharge[12], atmospheric deposition[13], and sediment activation[14]. However, due to the distribution of heavy metals in soil[15], the properties of heavy metals[16], and the characteristics of riparian zones[17], the entry of heavy metals from soil into water bodies is highly uncertain. In addition, there are few studies that quantify the impact of heavy metals in bedrock on water bodies.

Based on this, a typical karst watershed was selected as the research area to study the quantitative effects of 9 heavy metals (Cr, Mn, Ni, Cu, Zn, As, Cd, Sb, and Pb) in soil, sediment, and bedrock on heavy metals in the watershed water. This study aims to: ① evaluate the degree of heavy metal pollution in water, soil, and sediment in the study area through water quality index (*WQI*) and geo-accumulation index (I_{geo}); ②study the availability of heavy metals in soil, sediment, and bedrock through sequential extraction method; ③ use multivariate statistical analysis to quantify the contribution of heavy metals in soil, sediment, and bedrock to heavy metals in water bodies. The research results can provide scientific basis for the prevention and control of heavy metal pollution in water bodies.

1 Materials and methods

1.1 Research area The research area is a typical karst basin in southwest China, with mainly exposed strata from the Carboniferous and Permian periods. The lithology is mainly limestone, with a small amount of quartz sandstone interbedded with shale. The karst landform is very developed[18]. The soil types in the research area include paddy soil, lime soil, yellow lime soil, coarse bone soil, red soil, *etc.* It is dominant by agricultural activities in the middle and lower reaches of the watershed, and a large amount of industry has been developed in the upstream. The research area belongs to the subtropical monsoon humid climate zone, with an average annual temperature of 16.5 ℃ and an average annual rainfall of 1 313 m.

1.2 Sample collection and analysis According to field and

Received: December 6, 2023 Accepted: January 29, 2024

Supported by Guizhou Provincial Key Technology R&D Program (2202023QKHZC).

* Corresponding author.

historical data investigations, no entrance to the underground river was found in the southern tributaries and middle reaches of the study area. Therefore, river water samples were collected at 12 sampling points using a water sampler in November 2022 (Fig. 1), loaded into a 100 ml of polyethylene bottle, and acidified with concentrated nitric acid. A grapple-type of mud collector was used to collect 0 – 5 cm of sediment of the river bottom. After discarding any debris, it was packed in a polyethylene bag for sealed storage. According to the *Technical Specification for Soil Environmental Monitoring* (HJT 166 – 2004), soil sampling is the process of collecting 5 soil samples from the surface layer of 0 – 10 cm in each sampling unit and combining them into a mixed soil sample. A geological hammer was used to collect bedrock with soil and river development. Except for rock samples, all samples were stored in portable ice boxes.

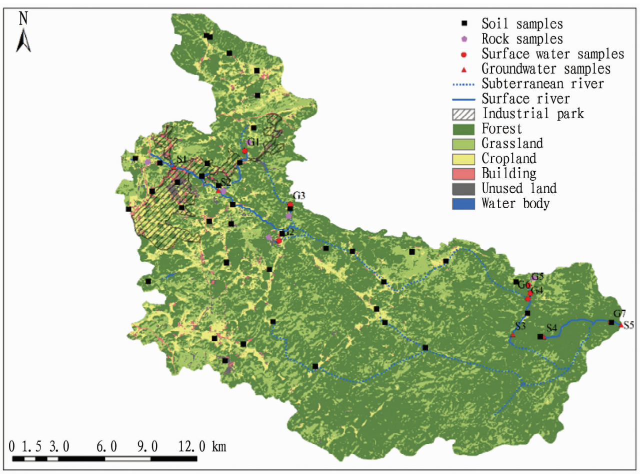


Fig. 1 Situation of research area and sampling point

The pH of water was measured in situ using a multi-parameter water quality analyzer (Ponsel, France) with a measurement accuracy of 0.01. The concentrations of 9 heavy metals (Cr, Mn, Ni, Cu, Zn, As, Cd, Sb, Pb) in water samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific, USA) under standard operating conditions. The detection limits for these metals were 0.11, 0.12, 0.06, 0.08, 0.67, 0.12, 0.05, 0.15, and 0.09, respectively μg/L. After removing plant residues and stones from soil and sediment samples, they were placed in a cool place of the laboratory for natural air drying. After grinding, they passed through a 0.15 mm of nylon sieve, and then were packed in a clean polyethylene bottle for sealed storage and future use. The rock sample was first crushed. After grinding with a ball mill, it passed through a 0.15 mm of nylon sieve, and then was packed in a clean polyethylene bottle for sealed storage and future use. The pH values of soil and sediment were measured using a pH meter at a solid – liquid ratio of 1 : 2.5 (w/v)[19], with a measurement accuracy of 0.01. Soil, sediment, and rock samples were digested with aqua regia according to the protocol provided by HJ 803 – 2016, and metal concentrations in the samples were analyzed using ICP-MS. The detection limits for using this method were 2, 0.7, 2, 0.5, 7, 0.6, 0.07, 0.3, and 2 mg/kg, respectively. The metal forms of soil, sediment, and rock samples were extracted using sequential extraction method[20]. By this fractionation method, metal elements were divided into exchangeable state (F1), carbonate bound state (F2), iron manganese oxide bound state (F3), organic matter bound state (F4), and residual state (F5) in sequence. Metal concentrations of all extracted samples were measured using ICP-MS.

Quality assurance and control used reagent blank controls, duplicate samples, and standard substances (soil standard substance GBW07404a and sediment standard substance GBW07310, Hebei, China, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences). The response value of the internal standard during the sample testing process was between 70% and 120% of the standard curve response value, and the recovery rate of the added standard was between 70% and 110%.

1.3 Assessment of heavy metal pollution Based on aggregation function, the *WQI* model allows for the conversion of a wide range of water quality data into individual values or indices, and enables a more comprehensive evaluation of water quality (surface water and groundwater) according to local water quality standards. I_{geo} evaluates environmental pollution by comparing pollutant concentrations with local environmental background values, which is suitable for heavy metal pollution assessment in soil and sediment[21 – 22]. In this study, the calculation formulas for *WQI* and I_{geo} are as below.

$$WQI = \sum \left[W_i \times \left(\frac{C_i}{S_i} \right) \times 100 \right] \tag{1}$$

$$I_{geoi} = \log_2 [C_n / (k \times B_n)] \tag{2}$$

where $W_i = w_i / \sum w_i$ is relative weight of each parameter on the overall water quality; w_i shows assigning different weight levels of 1 (minimum impact on water quality) to 5 (maximum impact on water quality) to each parameter based on their relative importance to human health and drinking water; $\sum w_i$ is the sum of the weights of all elements; C_i is the concentration of each heavy metal; S_i is drinking water limit for each heavy metal element[23]. *WQI* is composed of 5 categories shown in Table 1. C_n is actual measured concentration of heavy metals (mg/kg); B_n is background value of heavy metals (mg/kg)[24]; k is the coefficient chosen due to differences in rocks in different regions that may cause changes in environmental background values, typically taken as 1.5. I_{geo} is composed of 7 categories shown in Table 1.

1.4 Multivariate statistical analysis Multivariate statistical analysis method was used to analyze the characteristics and influencing factors of heavy metal pollution in the watershed. Firstly, Pearson correlation analysis was used to test the relationship between heavy metal concentration in water and heavy metal concentration in soil, sediment, and rock. In order to systematically analyze the impact of heavy metals in various media on the concentration of heavy metals in water, this paper used redundancy analysis (RDA) to quantify the contribution of heavy metals in each media to heavy metals in water. Then, gradient boosting machine (GBM) analysis was used to quantitatively evaluate the relative impact of each medium on heavy metals in water. In addition, Mantel testing was used to further verify the significance of the impact of heavy metals in various media on metals in water bodies.

Table 1 Classes of I_{geo} and *WQI*

I_{geo}	Sediment and soil quality	*WQI*	Water quality
$I_{geo} \leqslant 0$	Mildly uncontaminated	$WQI < 50$	Excellent
$0 < I_{geo} \leqslant 1$	Uncontaminated to moderately contaminated	$50 \leqslant WQI < 100$	Good
$1 < I_{geo} \leqslant 2$	Moderately contaminated	$100 \leqslant WQI < 200$	Poor
$2 < I_{geo} \leqslant 3$	Moderately to heavily contaminated	$200 \leqslant WQI < 300$	Very poor
$3 < I_{geo} \leqslant 4$	Heavily contaminated	$300 \leqslant WQI$	Undrinkable
$4 < I_{geo} \leqslant 5$	Heavily to extremely contaminated		
$5 < I_{geo}$	Extremely contaminated		

2 Results

2.1 Characteristics of heavy metal concentration in the research area The soil pH in the study area ranged from 4.4 to 7.8 (with an average of 5.8), and the soil was mainly acidic (Table 2). Table 2 listed the characteristics of heavy metals in soil, bedrock, and sediment. The average concentrations of heavy metals in soil were Mn (624.8 ppm), Zn (77.9 ppm), Cr (59.7 ppm), As (41.9 ppm), Pb (31.4 ppm), Ni (14.0 ppm), Cu (12.0 ppm), Cd (1.9 ppm), and Sb (1.2 ppm), respectively. The average concentrations of heavy metals in the bedrock were As (127.4 ppm), Ni (34.9 ppm), Mn (19.0 ppm), Cr (14.0 ppm), Zn (12.1 ppm), Cu (4.4 ppm), Pb (4.2 ppm), Cd (1.5 ppm), and Sb (0.1 ppm), respectively. Compared with the heavy metal content in bedrock, most heavy metals in soil exhibited significant enrichment, especially Mn (32.95 times) and Sb (13.12 times). It was worth noting that the content of As in rocks was higher than that in soil. The concentration of most heavy metals in sediment was similar to that in soil, and it exhibited similar patterns compared with heavy metals in bedrock. However, Cd in sediment showed significant enrichment, with a concentration 5.6 times higher than that in soil and 7.1 times higher than that in bedrock. The analysis of coefficient of variation showed that the spatial differences of Cr, Cu, and As in soil were relatively small; except for Zn, Cd, and Sb, the spatial differences of other heavy metals in rocks were relatively small; the spatial differences of heavy metals in sediments were significant.

Table 2 pH and heavy metal conditions of soil, bedrock, and sediment ppm

Item		pH	Cr	Mn	Ni	Cu	Zn	As	Cd	Sb	Pb
Soil	Minimum	4.10	24.60	22.50	2.50	4.60	23.40	17.50	0.10	0.70	11.80
	Maximum	8.02	126.70	3 559.80	40.30	29.20	196.00	74.70	6.60	4.90	101.70
	Mean	5.74	59.70	624.80	14.00	12.00	77.90	41.90	1.90	1.20	31.40
	Median	5.51	57.60	182.30	11.20	10.60	71.40	40.20	1.40	1.00	28.20
	SD	0.86	21.30	861.20	9.10	4.80	40.80	14.50	1.60	0.70	16.70
	CV//%	14.40	35.60	137.80	65.10	40.30	52.30	34.70	86.10	59.10	53.10
Rock	Minimum	–	6.80	9.30	32.70	4.00	4.40	90.50	0.60	0	2.80
	Maximum	–	21.70	28.70	38.00	4.90	41.80	160.40	3.10	0.20	5.80
	Mean	–	14.00	19.00	34.90	4.40	12.10	127.40	1.50	0.10	4.20
	SD	–	5.90	6.40	1.90	0.40	14.70	23.30	0.90	0.10	1.30
	CV//%	–	41.80	33.80	5.40	8.80	122.20	18.30	58.90	95.90	30.40
Sediment	Minimum	7.29	15.90	52.90	5.20	2.60	28.40	7.30	0.90	0.10	6.90
	Maximum	8.57	104.90	1 567.20	44.10	38.70	252.00	83.00	46.60	2.20	70.30
	Mean	8.03	43.30	609.70	17.00	11.70	106.50	38.30	10.60	0.80	25.50
	SD	8.12	31.00	462.30	12.80	11.50	90.00	25.10	15.40	0.80	22.90
	CV//%	5.20	71.60	75.80	75.10	98.70	84.40	65.60	144.90	105.00	89.70
	Soil background of Guizhou	–	95.90	794.00	39.10	32.00	99.50	20.00	0.70	2.20	35.20
	Soil standard value	–	250.00	–	190.00	100.00	300.00	40.00	0.60	–	100.00
	Compared with soil background value//%	–	4.88	26.83	2.44	0	26.83	97.56	75.61	4.88	26.83
	Compared with soil standard value//%	–	0	–	0	0	0	78.05	92.68	–	2.44

Note: *SD* is standard deviation; *CV* is coefficient of variation.

Compared with the regional soil background value, the content of As (2.1 times) and Cd (2.8 times) in soil samples was higher, while the average concentration of other heavy metals was lower than the background value. In addition, the concentrations of As in 97.56% of soil samples and Cd in 75.61% of soil samples were higher than the regional background values. The average total concentrations of As and Cd in soil samples were 1.01 and 3.12 times of the standard values of the corresponding metals in the *Soil Environmental Quality – Risk Control Standard for Soil Contamination of Agricultural Land* (GB 15618 – 2018). 78.05%

of As and 92.68% of Cd in soil exceeded the standard, indicating that the study area was mainly polluted by As and Cd.

Table 3 pH and heavy metal situations of water body ppb

Item	pH	Cr	Mn	Ni	Cu	Zn	As	Cd	Sb	Pb
Minimum	7.40	0.60	0.40	469.50	59.30	6.00	9.00	0.80	0.10	0.70
Maximum	8.30	3.00	145.70	1 726.00	213.50	46.40	178.00	9.60	1.50	4.30
Mean	7.80	1.50	22.60	957.10	119.50	23.60	38.50	3.00	0.60	1.70
SD	0.30	0.70	44.60	380.60	46.30	9.70	47.30	3.00	0.50	1.00
CV//%	4.20	48.10	197.80	39.80	38.80	41.20	122.80	101.60	82.50	56.20
Water body standards	6.50 - 8.50	50.00	80.00	70.00	2 000.00	3 000.00	10.00	3.00	20.00	10.00
Water body/standard	-	0	0.30	13.70	0.10	0	3.80	1.00	0	0.20
Comparison with water body standards//%	0	0	16.67	100.00	0	0	83.33	33.33	0	0

Note: *SD* is standard deviation; *CV* is coefficient of variation.

The pH value of the water in the watershed ranged from 7.4 to 8.3, with a coefficient of variation of 4.2%, indicating that the water in the watershed was weakly alkaline and the spatial differences were small (Table 3). The average concentration of heavy metals in the watershed water was Ni (957.1 ppb), Cu (119.5 ppb), As (38.5 ppb), Zn (23.6 ppb), Mn (22.6 ppb), Cd (3.0 ppb), Pb (1.7 ppb), Cr (1.5 ppb), and Sb (0.6 ppb). The average concentrations of Ni and As were 13.7 and 3.0 times of the standard values of the World Health Organization, respectively, and they were the main heavy metal pollutants in the watershed water (100% and 83.33%). In addition, 33.3% of the water in the watershed was also polluted by Cd, which should be noted. The coefficient of variation of heavy metals in the watershed was between 38.8% and 197.8%, with particularly significant spatial differences in Mn, As, and Cd, which may be greatly influenced by human activities.

2.2 Evaluation of heavy metal pollution in the research area Based on the standard limits and relative weights of each parameter, the *WQI* for each sampling point was calculated using formula (1) (Fig. 2). The *WQI* values of the rivers in the study area ranged from 61.1 to 290.8. Within the study area, the *WQI* values of G3, G4, G6, and S4 water samples were relatively high (>100), with values of 290.8, 168.6, 108.9, and 162.8, respectively. According to the classification of *WQI*, the water quality of G3 was very poor, while the water quality of G4, G6, and S4 was poor, and the water quality of the other water samples was good. Obviously, G3 may be affected by human activities, leading to severe heavy metal pollution in the water, which directly affected the downstream water quality.

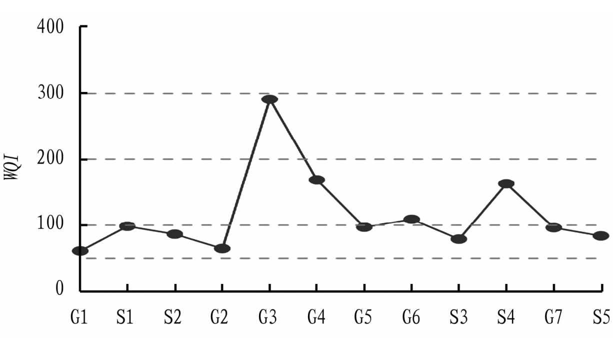


Fig.2 Distribution of *WQI* in water bodies of the research area

The average I_{geo} values of heavy metals in soil samples were Mn (-2.40), Ni (-2.35), Cu (-2.10), Sb (-1.59), Cr (-1.35), Zn (-1.12), Pb (-0.90), Cd (0.29), and As (0.40) in order (Table 3). The overall soil quality in the study area was good. Except for the average values of Cd and As showing mild pollution, other heavy metals all showed no pollution. Further analysis of all soil samples in the study area showed that Cr (100%), Ni (100%), and Cu (100%) were all pollution-free, while Cd (9.8%) had moderate pollution, which should be noted. The average I_{geo} values of heavy metals in sediment samples were Sb (-2.68), Cu (-2.54), Ni (-2.08), Cr (-1.87), Pb (-1.53), Mn (-1.26), Zn (-0.82), As (0.12), and Cd (1.88) in order (Table 4). This indicated that the sediment in the study area generally exhibited moderate Cd pollution and mild As pollution, especially some sediments in rivers had severe (9.1%) or serious (9.1%) Cd pollution.

2.3 Geochemical morphological characteristics of heavy metals Nine soil samples, seven sediment samples, and five bedrock samples were selected based on land use types and bedrock layers for continuous extraction of heavy metal element forms. The analysis on the morphological characteristics of heavy metal elements in various media in the study area (Fig. 3) showed that the geochemical morphological characteristics of heavy metals in soil and sediment were relatively similar. In soil samples, Cr, Ni, Cu, Zn, and Sb were mainly in residual form. In sediments, the residual state was the main carrier of Cr, Cu, Zn, and Sb. In addition, the exchangeable states of As and Cd in soil and sediment were relatively high. The geochemical forms of metals in bedrock were significantly different from those in soil and sediment. Ni, Cu, and As in bedrock were mainly in iron manganese oxide bound states.

2.4 Influencing factors of heavy metals in water bodies The correlation analysis results showed that there was a significantly positive correlation between Cr, Ni, Cu in water and Cr, Ni, Cu in soil, with correlation coefficients of 0.605 ($P=0.037$), 0.598 ($P=0.040$), and 0.648 ($P=0.023$), respectively. There was a significantly positive correlation between Mn, Sb, and Pb in water and Mn, Sb, and Pb in sediment, with correlation coefficients of 0.666 ($P=0.001$), 0.648 ($P=0.001$), and 0.634 ($P=0.001$), respectively. There was a correlation between Ni in water and Ni in bedrock ($R=0.435$, $P=0.038$). These results

Table 4 I_{geo} means of different heavy metals and proportions of risk levels in the research area %

Item		Cr	Mn	Ni	Cu	Zn	As	Cd	Sb	Pb
Soil	Mean	-1.35	2.40	-2.35	2.10	-1.12	0.40	0.29	1.59	-0.90
	Non-pollution	100.00	75.60	100.00	100.00	92.70	19.50	39.00	97.60	90.20
	Slight pollution	0	19.50	0	0	7.30	68.30	29.30	2.40	9.80
	Intermediate pollution	0	4.90	0	0	0	12.20	22.00	0	0
	Moderate pollution	0	0	0	0	0	0	9.80	0	0
	Heavy pollution	0	0	0	0	0	0	0	0	0
	Severe pollution	0	0	0	0	0	0	0	0	0
	Serious pollution	0	0	0	0	0	0	0	0	0
Sediment	Mean	-0.34	-0.51	-0.60	-0.55	-0.18	0.33	0.44	-0.53	-0.14
	Non-pollution	100.00	81.80	100.00	100.00	63.60	36.40	27.30	100.00	90.90
	Slight pollution	0	18.20	0	0	36.40	54.50	18.20	0	9.10
	Intermediate pollution	0	0	0	0	0	18.20	27.30	0	0
	Moderate pollution	0	0	0	0	0	0	9.10	0	0
	Heavy pollution	0	0	0	0	0	0	9.10	0	0
	Severe pollution	0	0	0	0	0	0	9.10	0	0
	Serious pollution	0	0	0	0	0	0	9.10	0	0

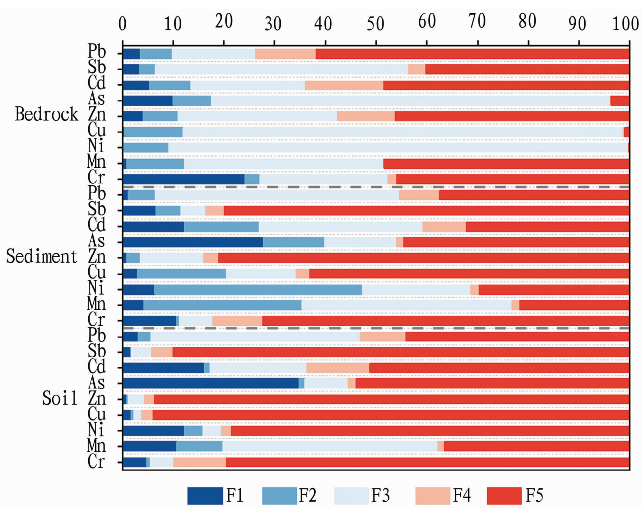


Fig. 3 Geochemical forms of various metals in soil, sediment, and bedrock

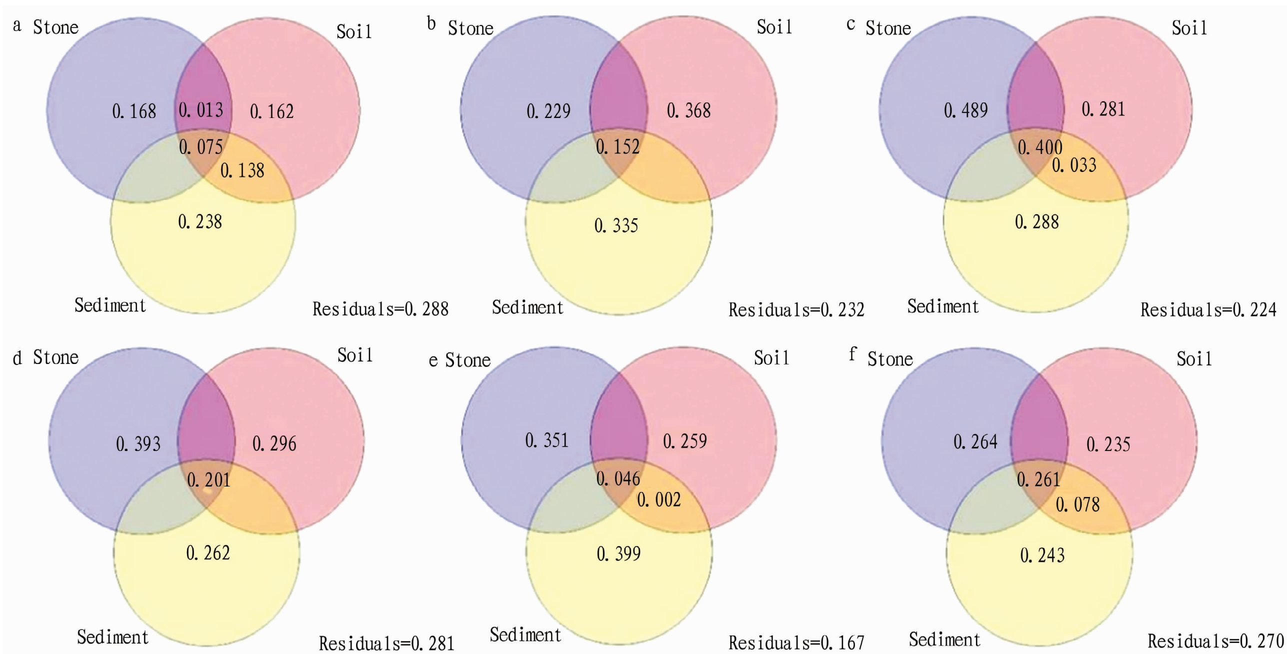
indicated that the concentration of heavy metals in water was influenced by soil, sediment, and bedrock. Further use of RDA indicated (Fig. 4) that metals in sediment, soil, and bedrock jointly explained 79.3% of the changes in heavy metal values in water. Among them, heavy metals in sediment (23.8%) had the highest explanatory power, and it was worth noting that heavy metals in sediment and soil jointly accounted for 13.8% of the heavy metal changes in water bodies. In addition, the different geochemical forms of heavy metals in sediments, soil, and bedrock had varying interpretations of heavy metals in water bodies. For example, soil (36.8%) and sediment (33.5%) had higher interpretations in the exchangeable state, while bedrock had the highest interpretation in the carbonate bound state (48.9%).

In order to further evaluate the impact of specific factors on heavy metal changes in water bodies, GBM and Mantel significance tests were conducted on heavy metals and their geochemical forms in all media. In GBM (Table 5), Cr, Ni, and Cu in water were mostly affected by the corresponding heavy metals in sediment, while the remaining metals were mainly affected by the exchangeable and carbonate bound states of the corresponding metals in sediment and soil. The Mantel test further proved that metals in sediment and soil had a significant impact on metal changes in water bodies (Fig. 5).

3 Discussion

3.1 Characteristics of heavy metal pollution in the research area The water body in the research area was mainly polluted by As and Cd, and the spatial differences of As and Cd in the water body were significant. According to the survey, the metal industry developed in the upper reaches of the research area will generate a large amount of waste residue and liquid, which contain Cd and As[25-26]. It may enter the groundwater of the watershed through rainwater leaching or direct input. Research has shown that acidic wastewater entering karst areas is buffered by carbonate rocks, and metals in acidic wastewater are adsorbed and co precipitated by some secondary minerals[27-28]. Therefore, sediments were also contaminated by As and Cd in this paper, and the contaminated areas were consistent with the water bodies. In addition, As and Cd were also the main elements that pollute the local soil. Previous studies have shown that long-term exposure to the environment with high concentration of As may cause skin cancer, lung cancer, bladder cancer, kidney cancer, liver cancer and other diseases[29], and long-term exposure to the environment with high Cd may damage respiratory organs, renal function, immune dysfunction, metabolic disorder, bone loss, endocrine disorders and other symptoms[30]. Therefore, further attention needed to be paid to As and Cd in the research area.

3.2 Migration of heavy metals in the research area The enrichment of heavy metals in soil relative to bedrock is consistent with previous studies[31]. This is because the weathering rate of carbonate rocks is relatively high, and heavy metal elements in carbonate rocks are rapidly released and enriched in the soil[32]. This may be one of the reasons for the high background values of heavy metals in soil of karst areas, and the soil in karst areas is more susceptible to heavy metal pollution. Research has shown that heavy metals in soil are closely bound to soil colloids and organic matter, and enter the environment in the form of particulate matter through water erosion, leading to sedimentation. Therefore, heavy metals in sediments are usually similar or enriched in their surrounding soil[33].



Note: a. Total heavy metal content; b. Exchangeable state; c. Carbonate bound state; d. Iron manganese oxide bound state; e. Organic bound state; f. Residual state.

Fig. 4 RDA analysis

Table 5 Relative effects of different parameters on heavy metals in water bodies %

Parameter	Cr	Mn	Ni	Cu	Zn	As	Cd	Sb	Pb
Bedrock	–	–	17.00	–	–	2.00	–	–	5.00
Soil	3.00	18.00	–	–	–	–	12.00	–	17.00
Sediment	22.00	–	38.00	24.00	–	19.00	–	–	4.00
Bedrock F1	–	–	–	–	–	–	–	–	–
Bedrock F2	–	13.00	–	–	11.00	–	–	–	–
Bedrock F3	–	–	–	–	–	–	–	–	–
Bedrock F4	–	–	–	13.00	–	–	–	–	–
Bedrock F5	–	–	–	–	–	–	–	–	–
Soil F1	14.00	7.00	11.00	13.00	–	1.00	–	–	52.00
Soil F2	22.00	14.00	–	–	–	13.00	11.00	29.00	–
Soil F3	–	23.00	–	–	–	–	–	–	–
Soil F4	–	–	–	3.00	5.00	11.00	–	26.00	–
Soil F5	–	–	–	–	–	–	–	–	9.00
Sediment F1	16.00	9.00	10.00	20.00	3.00	7.00	47.00	13.00	4.00
Sediment F2	4.00	–	–	12.00	9.00	18.00	19.00	12.00	–
Sediment F3	10.00	5.00	–	15.00	–	–	–	15.00	–
Sediment F4	–	11.00	–	–	33.00	29.00	–	5.00	9.00
Sediment F5	–	–	24.00	–	39.00	–	11.00	–	–

In this paper, the average pH value of the soil was 5.8, which was higher than the pH value of the surface soil in areas such as Quaternary (5.58), clastic rocks (5.25), and acidic igneous rocks (5.00)[34]. Research has found that the higher pH value in karst areas was mainly controlled by Ca^{2+} in the surface soil[35]. It also found that pH is the most important factor affecting soil metal availability. Lower pH increases the availability of heavy metals in surface soil, thereby promoting the migration of heavy metals from the soil to other media[7]. In addition, due to the buffering effect of widely distributed carbonate minerals in the watershed, the water samples in the research area were all alkaline, which was beneficial for some metals (such as Cd, Pb, Zn, *etc.*)

in the water to form insoluble substances and then settle[36-37]. Therefore, a portion of heavy metals entering the water were enriched in sediment, indicating that heavy metals of sediment had a high degree of interpretability for metals in the water. In addition, hydrochemical characteristics can affect the geochemical behavior of heavy metals in water by affecting the adsorption and desorption of sediments, thereby affecting the characteristics of the water environment[14]. Therefore, higher metal concentrations in sediment may pose a risk to water bodies.

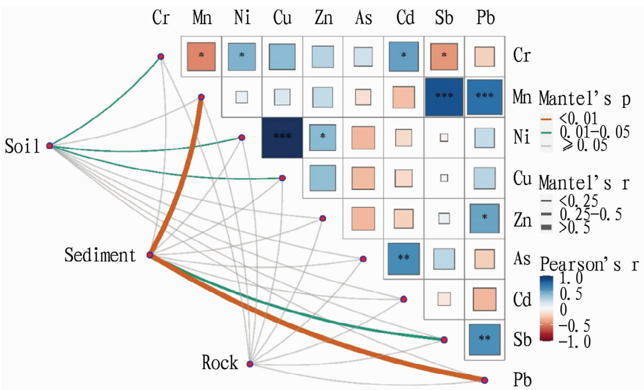


Fig. 5 Mantel significance test of heavy metals in different media on heavy metals in water bodies

In this paper, heavy metals in soil and sediment were mainly in the residual state, while heavy metals in bedrock were mainly in Iron manganese oxide bound state and residual state. The geochemical morphological characteristics of heavy metals in the study area slowed down the migration of heavy metals to some extent and reduced the load of metals in the water. However, the proportions of exchangeable states of As and Cd in soil and sediment were relatively high, which posed certain risks and required further attention to these two metals.

4 Conclusions

With the development of industry, the world has been exposed to a wide range of heavy metal pollution sources, posing a serious threat to human health. However, there is limited research on the synergistic effects of heavy metals in soil, sediment, and bedrock on heavy metal pollution in water bodies. Therefore, this paper investigated heavy metals in soil, sediment, bedrock, and water body of a typical karst watershed in the southwest region. The results indicated that the heavy metal concentrations in the soil and sediment of the research area were similar. Except for Ni and As, the average values of other metals were higher than those in the bedrock. During the research period, the soil and sediment in the study area were mainly polluted by As and Cd, while the water body was mainly polluted by Ni, As and Cd. *WQI* analysis showed that the water quality in the research area was affected by heavy metal pollution during the study period, resulting in both poor and very poor conditions. I_{geo} analysis showed that the overall soil in the research area was subject to mild Cd and As pollution, while sediment was subject to moderate Cd and mild As pollution. Analysis on geochemical forms of heavy metals showed that heavy metals in soil and sediment were mainly in residual state, and the proportion of exchangeable As and Cd was relatively high. Multiple statistical analysis showed that heavy metals in sediment, soil, and bedrock explained the changes in heavy metals in water by 23.8, 16.8, and 16.2, respectively. In addition, soil (36.8) and sediment (33.5) had higher interpretability in the exchangeable state. The research results can understand the pollution situation of local soil, sediment, and water, providing scientific basis for the prevention and control of heavy metal pollution in water bodies.

References

[1] PAVANELLI DD, DOMINGUES DF, HOCH PG, et al. Transient alterations in streamwater quality induced by pollution incidents: Interim losses calculations and compensation alternatives based on habitat equivalency analysis[J]. Environmental Management, 2022, 69(3): 576-587.

[2] LIANG J, FENG CT, ZENG GM, et al. Spatial distribution and source identification of heavy metals in surface soils in a typical coal mine city, Lianyuan, China[J]. Environmental Pollution, 2017, 225: 681-690.

[3] MISHRA S, KUMAR A, SHUKLA P. Estimation of heavy metal contamination in the Hindon River, India: An environmetric approach[J]. Applied Water Science, 2021, 11(1):2.

[4] LIU YZ, XIAO TF, BAVEYE PC, et al. Potential health risk in areas with high naturally-occurring cadmium background in southwestern China [J]. Ecotoxicology and Environmental Safety, 2015, 112: 122-131.

[5] HUANG W, SONG BA, LIANG J, et al. Microplastics and associated contaminants in the aquatic environment: A review on their ecotoxicological effects, trophic transfer, and potential impacts to human health[J]. Journal of Hazardous Materials, 2021, 405: 39.

[6] WEI R, WANG X, TANG W, et al. Bioaccumulations and potential human health risks assessment of heavy metals in ppk-expressing transgenic rice[J]. Science of the Total Environment 2020, 710: 136496.

[7] ZHONG X, CHEN ZW, LI YY, et al. Factors influencing heavy metal availability and risk assessment of soils at typical metal mines in Eastern China[J]. Journal of Hazardous Materials 2020, 400: 11.

[8] LIU M, HE Y, BAUMANN Z, et al. The impact of the Three Gorges Dam on the fate of metal contaminants across the river-ocean continuum [J]. Water Research, 2020, 185: 13.

[9] LUO MK, YU H, LIU Q, et al. Effect of river-lake connectivity on heavy metal diffusion and source identification of heavy metals in the middle and lower reaches of the Yangtze River[J]. Journal of Hazardous Materials, 2021, 416: 13.

[10] REICHENBERGER S, BACH M, SKITSCHAK A, et al. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness: A review[J]. Science of the Total Environment, 2007, 384(1-3): 1-35.

[11] LE GALL M, AYRAULT S, EVRARD O, et al. Investigating the metal contamination of sediment transported by the 2016 Seine River flood (Paris, France)[J]. Environmental Pollution 2018, 240: 125-139.

[12] LI XC, BING JP, ZHANG JH, et al. Ecological risk assessment and sources identification of heavy metals in surface sediments of a river-reservoir system[J]. Science of the Total Environment, 2022, 842: 11.

[13] BAIN DJ, HILLMAN AL, ABBOTT MB, et al. Metal ratio mixing models clarify metal contamination sources to lake sediments in Yunnan, China[J]. Science of the Total Environment, 2022, 820: 10.

[14] HU J, ZHU CB, LONG YC, et al. Interaction analysis of hydrochemical factors and dissolved heavymetals in the karst Caohai Wetland based on PHREEQC, cooccurrence network and redundancy analyses[J]. Science of the Total Environment, 2021, 770: 13.

[15] MAILLARD P, PINHEIRO SANTOS NA. A spatial-statistical approach

for modeling the effect of non-point source pollution on different water quality parameters in the Velhas river watershed Brazil[J]. Journal of Environmental Management, 2008, 86(1): 158 – 170.

[16] WANG SF, JIA YF, WANG SY, *et al.* Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China[J]. Journal of Environmental Sciences, 2010, 22(1): 23 – 31.

[17] WANG XL, MANNAERTS CM, YANG ST, *et al.* Evaluation of soil nitrogen emissions from riparian zones coupling simple process-oriented models with remote sensing data[J]. Science of the Total Environment, 2010, 408(16): 3310 – 3318.

[18] LI JY, JI CM, YAN GQ, *et al.* Characteristics and assessment on water resources of huanghou karst underground drainage at dushan in south Guizhou Province[J]. Carsologica Sinica, 1999(3): 39 – 49.

[19] ZHANG YM, LI S, CHEN Z, *et al.* A systemic ecological risk assessment based on spatial distribution and source apportionment in the abandoned lead acid battery plant zone, China[J]. Journal of Hazardous Materials, 2018, 354: 170 – 179.

[20] NKINAHAMIRA F, SUANON F, CHI QQ, *et al.* Occurrence, geochemical fractionation, and environmental risk assessment of major and trace elements in sewage sludge[J]. Journal of Environmental Management, 2019, 249: 9.

[21] MULLER GJG. Index of geoaccumulation in sediments of the Rhine River[J]. 1969, 2: 108 – 118.

[22] FERREIRA SLC, DA SILVA JB, DOS SANTOS IF, *et al.* Use of pollution indices and ecological risk in the assessment of contamination from chemical elements in soils and sediments: Practical aspects[J]. Trends in Environmental Analytical Chemistry, 2022, 35: 6.

[23] World Health Organization. WHO guidelines for drinking-water quality: fourth edition incorporating the first and second addenda[S]. Geneva, 2022.

[24] China National Environmental Monitoring Centre. Background values of soil elements in China[M]. Beijing: China Environmental Science Press, 1990.

[25] XIONG J, HAN ZW, WU P, *et al.* Spatial distribution characteristics, contamination evaluation and health risk assessment of arsenic and antimony in soil around an antimony smelter of Dushan County[J]. Acta Scientiae Circumstantiae, 2020, 40(2): 655 – 664.

[26] WANG L, YANG AJ, DENG QJ, *et al.* Distribution characteristics of heavy metals in soil – *Polygonum capitatum* system at Dushan antimony deposit, Guizhou Province[J]. Chinese Journal of Ecology, 2017, 36(12): 3545 – 3552.

[27] XIA YF, GAO T, LIU YH, *et al.* Zinc isotope revealing zinc's sources and transport processes in karst region[J]. Science of the Total Environment, 2020, 724: 11.

[28] REN YY, CAO XX, WU P, *et al.* Experimental insights into the formation of secondary minerals in acid mine drainage-polluted karst rivers and their effects on element migration[J]. Science of the Total Environment, 2023, 858: 13.

[29] NAUJOKAS MF, ANDERSON B, AHSAN H, *et al.* The broad scope of health effects from chronic arsenic exposure: Update on a worldwide public health problem[J]. Environmental Health Perspectives, 2013, 121(3): 295 – 302.

[30] LI ZM, LIANG Y, HU HW, *et al.* Speciation, transportation, and pathways of cadmium in soil-rice systems: A review on the environmental implications and remediation approaches for food safety[J]. Environment International, 2021, 156: 13.

[31] WEI W, LING SX, WU XY, *et al.* Geochemical accumulation and source tracing of heavy metals in arable soils from a black shale catchment, southwestern China[J]. Science of the Total Environment, 2023, 857: 10.

[32] QU SY, WU WH, NEL W, *et al.* The behavior of metals/metalloids during natural weathering: A systematic study of the mono-lithological watersheds in the upper Pearl River Basin, China[J]. Science of the Total Environment, 2020, 708: 10.

[33] OUYANG W, WANG YD, LIN CY, *et al.* Heavy metal loss from agricultural watershed to aquatic system: A scientometrics review[J]. Science of the Total Environment, 2018, 637: 208 – 220.

[34] LI C, ZHANG CS, YU T, *et al.* Use of artificial neural network to evaluate cadmium contamination in farmland soils in a karst area with naturally high background values[J]. Environmental Pollution, 2022, 304: 10.

[35] MAHAR A, WANG P, ALI A, *et al.* Impact of CaO, fly ash, sulfur and Na2S on the mobilization and phytoavailability of Cd, Cu and Pb in contaminated soil[J]. Ecotoxicology and Environmental Safety, 2016, 134: 116 – 123.

[36] GAO HY, XU ZM, WANG K, *et al.* Evaluation of the impact of karst depression-type impoundments on the underlying karst water systems in the Gejiu mining district, southern Yunnan, China[J]. Bulletin of Engineering Geology and the Environment, 2019, 78(7): 4673 – 4688.

[37] HU J, ZHU C, LONG Y, *et al.* Interaction analysis of hydrochemical factors and dissolved heavy metals in the karst Caohai Wetland based on PHREEQC, cooccurrence network and redundancy analyses[J]. Science of the Total Environment, 2021, 770: 145361.

Acknowledgement

Meteorological and Environmental Research [ISSN: 2152 – 3940] is a comprehensive meteorological and environmental scientific journal, and contains strong technicality and high orientation in China, being published bimonthly in Rhode Island, USA. It has been included by UPD, Chemical Abstracts, CABI, Cambridge Scientific Abstracts, EBSCO, AGRIS, EA, Chinese Science and Technology Periodical Database, Library of Congress (United States), and CNKI.

Fortunately, for the contributions of all authors and readers to *Meteorological and Environmental Research*, it has been published successfully for fourteen years. And we, all members of the editor office of *Meteorological and Environmental Research*, appreciate all help and assistance from you in the publication of our journal.