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Spatial-temporal variations and multi-statistical analysis of contaminants in the waters affected by acid mining drainage in Karst area: A case of coal-mining area in Zhijin County

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Abstract: Due to the adverse effects of coal mining activities in Karst areas, it's necessary to monitor the contaminants, analyze their fate in the transport and identify the sources. Therefore, concentrations of contaminants were measured in both groundwater and surface water samples collected from coal-mining area in Karst, located in Zhijin County, Guizhou Province (China). The analysis of spatial-temporal variations of contaminants indicates that (1) the concentrations of metal elements (except Ba) and SO_4^{2-} tend to decrease along the water flow direction while the concentrations of Ba and nitrate still show an upward trend and (2) the concentrations of metal elements and SO_4^{2-} in Stream1 and Stream3, are higher in wet season than dry season. Further, the results of multi-statistical analysis which combined Pearson correlation coefficients (PCC) with the principal component analysis (PCA), identify five factors for the data structure of contaminants. What's more, the assessment of the water quality was evaluated by Nemerow index method to better understand the status. The results indicate that over 60% of water samples were divided into Grade IV and Grade V.

Keywords: Spatial-temporal variations; Multi-statistical analysis; Pearson correlation coefficients; Principal component analysis; Nemerow index method

Introduction

Assessment and treatment methods of water pollution are of great importance in environmental research since more than two billion people worldwide are confronting with water scarcity issues (Oki et al. 2006). Particularly, pollution of water environment in karst areas has currently become one of the most predominant environmental problems due to (1) the unique and vulnerable dualistic hydrological system which is easy to be polluted and destroyed but hard to be remediated, and (2) the negative impacts of coal mining activities on water environment (Li et al. 2018). Also, during coal mining processes, acid mining drainage (AMD) occurs when metal sulfides (such as pyrite, etc.) are exposed to the air and subsequently oxidized by oxygen and water in the medium of microorganisms. The discharge of AMD can induce low

pH as well as highly concentrated metals (Alpers and Blowes 1994), which are usually non-degradable and significantly toxic to aquatic organisms and human beings (Weimin et al. 2016). Given the severe damage on global watersheds and ecosystems (Blowes et al. 2014; Lottermoser 2010; McCarthy and Terence 2011; Szulczewski 2015), it is vital to control the water pollution and protect ecological environment via identifying the main pollution factors and analyzing their fate in the mining karst area.

Zhijin County in Guizhou Province, China, is a typical karst area with abundant coal resources. By the end of 2013, the identified anthracite deposits have reached 12.9 billion tons, which is the largest anthracite producing area in Guizhou Province. In this mining region, resources in groundwater are abundant, and the entire water supply area is mainly supported by Zhijin River belonging to the Pearl River water system. Here the drinking water mainly comes from karst groundwater, while irrigation water comes from the surface water bodies surrounding farmland. However, many studies have shown that the high-strength and long-term mining of coal mines in Zhijin County has considerable influence on the water bodies (Li et al. 2017; Shi et al. 2016). Moreover, under the unique karst hydrogeological conditions, frequent human activities (e.g., mining activities, agricultural activities and urbanization) have caused multiple pollution to the water bodies with a wide variety of pollutants and complex variations. Therefore, simple mathematical statistical methods are insufficient to conduct a comprehensive and systematic analysis of water pollutants.

Geochemical analysis combined with multiple statistical analysis could better explain the relationship between contaminants (Chen et al. 2016; Cui et al. 2020). One classical approach is to use the Piper diagram to reveal the overall chemical properties of water bodies to analyze the formation of water chemical components (An et al. 2012; Cui et al. 2020). Another widely applied method is the Pearson correlation coefficients (PCC), which can reflect the linear relationship between variables (Abulimiti et al. 2017), and hence qualitatively as well as quantitatively analyze the correlation between pollution factors. Moreover, principal component analysis (PCA) is usually used in source attribution by treating the research area as receptor and subsequently identifying the main components (i.e. possible pollution source) with their degree of influence via dimensionality reduction (Zhuo et al. 2020). It should be noted that PCA is one of the most widely used methods to extract key information for pollutant source research (Gao et al. 2018; Huifen et al. 2020; Yang et al. 2020). In addition, assessment of water quality can more intuitively describe the status of the water environment. Recently, water quality index methods such as Horton index method, Brown index (NSF) method, Nemerow index method, CCME water quality index method, similar index method, Pesce-Wunderlin subjective and objective index method, have been widely employed and practically verified in evaluation of water quality (Lumb et al. 2011; Wu and Li 2014), where the Nemerow index method owns simple structure and strong practicability by highlighting the maximum value as well as involving extreme value (Zheng et al.).

In this study, the spatial-temporal variations and multivariate statistical analysis of water pollutant in the karst coal mining areas of Zhijin County have been explored. Nemerow index of different water bodies was calculated and water quality was graded by referring to "Groundwater Quality Standard" (GB/T 14848-2017) and "Surface Water Quality Standard" (GB 3838-2002).

Materials and method

Site selection

The study site is located in the Midwest of Guizhou Province, Southwest China which extends from 105° 39' 00" to 105° 46' 30" in the east and from 26° 34' 30"–26° 41' 45" in the north (Fig. 1). As one of the most complete karst development areas, Zhijin country is approximately 2868 km², about 60% of which is covered by carbonate rocks. From the west to the northeast, the nature of the land has changed from mining to housing. The land use types in the study area are mainly cultivated land, forest land and residential land.

The county has a subtropical monsoon climate, with mean annual temperature 14.1 °C and mean annual precipitation 1436 mm. Under the control of topography and synclinal structures, the groundwater flows from the southwest to the northeast and eventually converges in Zhijin River valley, which then expose to the surface in the form of karst springs, which is the indispensable drinkingwater supply of Zhijin County. And the irrigation system is composed mainly of surface water.

Fig.1 Sampling sites in Zhijin County, China(Li et al. 2021)

Sampling

According to the ground-surface water systems, a total of 39 water samples were collected in August 2016 (wet season) and January 2017 (dry season), of which 14 were groundwater samples, numbered G1-G14; 25 were surface water samples, numbered R1-R25. The detailed distribution of sampling points is shown in Figure 1. The containers used for sampling were soaked in 5% HNO_3 for at least 24 hours and then washed with tap water and deionized water for 3 times to be dried for later use. A portable water quality parameter meter (Germany, Multi 3430) was used on site to measure the pH value, water

temperature (T), oxidation-reduction potential (Eh), electrical conductivity (EC), and dissolved oxygen (DO) of the water samples. The concentration of HCO_3^- was titrated by 0.01mol/L HCl. The water samples were filtered by a 0.45 μm cellulose acetate filter membrane and stored in two 50mL polyethylene bottles. One for the analysis of cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Mn, Pb, Cu, Zn, Cd, etc.) was acidified to $\text{pH} < 2$ with ultrapure HNO_3 and the other one was used for anions without adding any reagent. The samples were sealed with Parafilm sealing film and stored at low temperature (4°C) in the dark until analysis.

Analytical methods

Major cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) of all water samples and the Mn of surface water samples were determined by flame atomic absorption spectrophotometer (AAS, ICE3500, Thermo Fisher, USA), while the Mn of groundwater were analyzed by inductively coupled plasmamass spectrometry (ICP-MS; X-Series II, Thermo Fisher, USA) due to the relatively low concentrations. The anions (Cl^- , SO_4^{2-} and NO_3^-) of all water samples were determined by ion chromatography (IC, ICS-1100, Dionex, USA). All water samples were analyzed in the College of Resource and Environmental Engineering, Guizhou University, and the errors of anion and cation test analysis are $\pm 2\%$ (Eq.1).

$$\text{CBE} = \left[\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right] \times 100\% \quad \text{Eq. 1}$$

Multi-statistical analysis of data

The multi-statistical analysis of data was operated through the software Origin9.0.

Nemerow Index Method

According to the "Groundwater Quality Standards" and "Surface Water Environmental Quality Standards", Nemerow index were (Eq.2-Eq.3):

$$F = \sqrt{\frac{F_{\max}^2 + \bar{F}^2}{2}} \quad (2)$$

$$\bar{F} = \frac{1}{n} \sum_{i=1}^n F_i \quad (3)$$

in the formula, F is the comprehensive evaluation index; $\bar{F}$ is the score value of each single component; F_i is the score value of each single component; $F_{\max}$ is the maximum value of the single component score; n is the number of items.

Table 1. Score table of each assessment factor

Level	I	II	III	IV	V
F _i	0	1	3	6	10

Table 2. Score table of Nemerow index

Class	Grade I	Grade II	Grade III	Grade IV	Grade V
F	<0.80	0.80~2.50	2.50~4.25	4.25~7.20	>7.20

Results and analysis

Water chemistry

According to the analysis results, the water samples in the study area can be divided into three categories: acid mine drainage (AMD), water samples with direct hydraulic connection with AMD (named AAMD), and water samples without direct hydraulic connection with AMD (named UAMD).

Table 3. Concentrations of water quality variables in AMD

Parameter	Unit	Wet season				Dry season			
		Mean	Min.	Max.	CV.	Mean	Min.	Max.	CV.
T	°C	20.9	19.2	22.4	0.057	9.8	8.3	13.0	0.160
pH		3.86	2.87	6.16	0.289	5.11	2.82	7.61	0.421
DO	mg/L	7.19	6.86	7.41	0.028	8.96	8.09	9.63	0.074
Eh	mv	402.89	253.00	548.00	0.214	344.67	118.00	558.00	0.489
Ec	μs/cm	1651.67	556.00	2460.00	0.382	2330.00	828.00	3860.00	0.419
K	mg/L	2.69	1.06	4.75	0.438	1.62	0.33	3.51	0.659
Ca	mg/L	132.02	17.35	276.20	0.522	226.06	77.02	496.30	0.554
Na	mg/L	85.41	2.08	171.48	0.774	159.77	5.66	404.83	0.946
Mg	mg/L	44.69	12.19	98.99	0.580	75.33	23.95	181.30	0.677
F ⁻	mg/L	0.75	0.13	1.35	0.562	0.92	0.16	1.41	0.467
Cl	mg/L	1.84	0.51	3.08	0.478	1.75	0.29	5.10	0.877
NO ₃	mg/L	4.56	2.62	7.43	0.389	2.11	0.78	3.04	0.337
SO ₄	mg/L	1022.43	266.24	1756.54	0.477	1184.26	271.74	1968.01	0.465
HCO ₃	mg/L	15.61	45.19	2.90	0.000	40.97	0.00	220.58	1.839

Table 4. Concentrations of water quality variables in AAMD

Parameter	Unit	Wet season				Dry season			
		Mean	Min.	Max.	CV.	Mean	Min.	Max.	CV.
T	°C	17.2	15.6	18.1	0.043	14.6	9.0	16.0	0.132
pH		7.52	6.70	8.10	0.054	7.37	6.27	8.17	0.060

DO	mg/L	6.85	2.10	8.16	0.236	6.49	1.01	8.95	0.337
Eh	mv	271.79	220.00	339.00	0.132	379.43	217.00	492.00	0.221
Ec	μs/cm	370.43	217.00	546.00	0.257	411.21	196.00	538.00	0.244
K	mg/L	1.52	0.69	4.14	0.686	0.48	0.18	1.18	0.542
Ca	mg/L	66.59	46.35	94.39	0.255	70.37	42.43	101.18	0.249
Na	mg/L	3.81	0.53	10.87	0.774	6.47	0.74	15.68	0.735
Mg	mg/L	7.11	1.20	12.54	0.452	10.06	0.92	24.59	0.526
F ⁻	mg/L	0.23	0.06	0.78	0.905	0.26	0.17	0.49	0.356
Cl	mg/L	2.84	0.76	10.53	0.998	1.66	0.35	4.66	0.770
NO ₃	mg/L	11.52	5.89	27.00	0.606	7.19	2.06	10.82	0.385
SO ₄	mg/L	58.55	17.72	106.72	0.470	69.82	12.17	144.33	0.515
HCO ₃	mg/L	142.18	87.78	212.87	0.246	157.17	110.29	214.10	0.185
TDS	mg/L	282.59	171.21	425.78	0.271	316.03	167.76	393.93	0.205

Table 5. Concentrations of water quality variables in UAMD

Parameter	Unit	Wet season				Dry season			
		Mean	Min.	Max.	CV.	Mean	Min.	Max.	CV.
T	°C	19.2	16.9	22.3	0.073	11.8	8.7	15.0	0.140
pH		7.43	5.08	8.16	0.096	7.54	6.32	8.37	0.064
DO	mg/L	6.95	2.48	7.77	0.183	7.81	4.48	9.20	0.197
Eh	mv	218.13	-44.00	292.00	0.388	273.13	133.00	443.00	0.382
Ec	μs/cm	708.00	412.00	1554.00	0.473	836.94	443.00	2350.00	0.683
K	mg/L	2.15	1.28	3.68	0.315	2.10	0.54	5.90	0.733
Ca	mg/L	84.38	59.08	122.83	0.188	87.91	31.72	176.22	0.371
Na	mg/L	46.52	5.81	188.86	1.131	82.19	7.69	516.64	1.614
Mg	mg/L	14.23	3.25	32.73	0.576	14.03	7.36	54.72	0.812
F ⁻	mg/L	0.33	0.19	1.11	0.698	0.42	0.21	1.29	0.655
Cl	mg/L	2.60	1.00	5.59	0.454	3.28	0.71	10.17	0.697
NO ₃	mg/L	6.73	1.58	9.70	0.314	4.98	1.09	10.98	0.496
SO ₄	mg/L	259.51	74.25	656.96	0.688	219.22	61.10	685.76	0.837
HCO ₃	mg/L	129.62	0.00	263.34	0.453	208.01	108.13	808.80	0.796
TDS	mg/L	538.10	313.72	1221.72	0.483	616.72	323.23	1973.96	0.699

For AMD, pH values were relatively low with the ranges of 2.87-6.16 and 2.82-7.61 in the wet and the dry season respectively. And the pH values in the wet season were significantly lower than that in the dry season. In addition, compared with other sampling points, the pH at site R1 is relatively high (6.16 and 7.45 during the wet and dry seasons respectively). This may be owing to the effluent from this site flowed through the wind shaft rather than the coal mine. The pH values of UAMD were generally at a neutral value with the ranges of 6.7-8.1 and 6.3-8.2 in the wet and the dry season respectively. For AAMD, the pH values ranged from 5.1 to 8.2 in the wet season and from 6.3 to 8.4 in the dry season, showing the same seasonality as the pH values of AMD that the pH values in the wet season were lower than the dry season.

As shown in Table 4 and Table 5, the average total dissolved solids(TDS) of AAMD in the study area during in the wet and the dry season were 539.00 mg/L and 616.74 mg/L, which were in the same order of magnitude as the TDS of other rivers affected by AMD (Dabrowski et al. 2016) but higher than the TDS of world rivers (97 mg/L) (Meybeck 2003). For UAMD, the average values of UAMD in the study area during the wet and the dry seasons were 282.59 mg/L and 316.03 mg/L, respectively, which were lower than the limits of class II in “Groundwater Quality Standards” (500 mg/L).

Fig. 2 Piper diagram

Piper diagrams help in the segregation of analytical data necessary for developing an understanding of the chemistry of water, which are used to assess the composition of cations and anions. It can be seen from the Piper diagram that there was no significant difference between wet and dry seasons. For AMD, the cations were mainly distributed in the Ca·Mg region, and the anions tended to SO_4^{2-} end members, which means the hydrochemical type of AMD was $\text{SO}_4\text{-Ca}\cdot\text{Mg}$ type. And the hydrochemical type of UAMD in the study area was $\text{HCO}_3\text{-Ca}$ type. For AAMD, the cations distributed widely that while most points distributed in the Ca·Mg area, some points tended to Na+K end-members and the anions distributed in the $\text{HCO}_3\cdot\text{SO}_4$ area. Therefore, the hydrochemical type of AAMD was composed of $\text{SO}_4\text{-Ca}\cdot\text{Mg}$ type, $\text{HCO}_3\text{-}$

Ca·Mg type and SO₄-Na type. Research has shown hydrochemical ions mainly came from the weathering of carbonate rocks by H₂CO₃ and H₂SO₄ (Han 2009).

Spatial-temporal variations of metal elements, sulfate and nitrate nitrogen

In the three kinds of water samples, the concentrations of metal elements (except Ba) and sulfate followed the order: AMD>AAMD>UAMD, while the concentrations of metal Ba and nitrate nitrogen followed the opposite order: AMD<AAMD<UAMD (Fig.3). The order of the concentrations of metal elements and sulfate may be directly related to AMD with low pH and highly concentrated metals. Metal and sulfate concentrations were generally highest at AMD samples and decreased further downstream where AAMD samples sited due to the inflowing water. But the metal and sulfate concentrations of AAMD samples were still higher than that of UAMD without direct hydraulic connection with AMD. The metal and sulfate concentrations of UAMD were relatively low that lower than the acceptable limits of class III in "Groundwater Quality Standards". It's worth noting that compared with other sampling sites in UAMD, the concentrations of metals such as Mn, Co, Ni, Cu, As, etc. at the G4 were higher, with multiple maximum values, which may be owing to that the G4 site was close to the coal mine and was affected by the mining industry.

In order to better understand the temporal and spatial distribution characteristics of contaminants in water bodies, the spatial-temporal variations of contaminants in three main streams named Stream1, Stream2 and Stream3 (the water flow directions in Stream1, Stream2 and Stream3 were: R1-R2-R3-R4-R5-R22-R23-R24-R25; R8-R9-R13-R14-R22-R23-R24-R25 and R15-R16-R18-R24-R25, respectively) were drawn (Figure 4(a)-(c)).

Fig.3 Boxplot of concentrations of contaminants in AMD, AAMD and UAMD

*TE indicates the total concentration of Cr, Co, Ni, Cu, Zn, Cd, Sb, Pb and As

Spatial-temporal variations of metal elements and sulfates

In Stream1, Stream2 and Stream3, the concentrations of metal elements (except Ba) and SO_4^{2-} decreased along the water flow direction, which were mainly due to the dilution effect of inflowing water. However, the ochre deposits found on the river bank indicated that during the transport of highly concentrated Fe, Mn

or other metal elements, various colloids and secondary minerals may be formed and precipitated, which could provoke rapid decreases of metal concentrations by absorption or coprecipitation (Caraballo et al. 2019; Carbone et al. 2013; Lee et al. 2002; Liu et al. 2017; Lozano et al. 2020; Lozano et al. 2018; Sánchez-España et al. 2011). On the contrary, the concentration of Ba increased. It's because the precipitation of BaSO_4 decreased with the decrease of SO_4^{2-} concentration.

In Stream1 and Stream3, the concentrations of metal elements and SO_4^{2-} were seasonally different that the concentrations of metal elements and SO_4^{2-} were higher in wet season. Some studies have similar phenomena (Li 2018) which is because the increase of flow in wet season results in the increase discharge of AMD which releases protons and metals. However, the concentrations of metal elements and SO_4^{2-} in Stream 2 showed the opposite seasonal trend, which may be due to the relatively larger increase of the flow resulting the dilution of metal elements and SO_4^{2-} .

Spatial-temporal variations of nitrate

Contrary to the distribution characteristics of metal elements and sulfates, the concentration of nitrate increased along the flow (see Figure 4(a)-(c)). This may be because along the direction of the water flow, the nature of the study area has changed from mining-based to residential-based, which was affected by local agricultural activities and urban sewage. Studies have shown that nitrate in groundwater in this area is mainly affected by local agricultural activities and the process of urbanization.

(a) Spatial-temporal variations of contaminants in Stream1

(b) Spatial-temporal variations of contaminants in Stream2

(c) Spatial-temporal variations of contaminants in Stream3

Fig.4 (a)-(c) Spatial-temporal variations of contaminants in Stream1, Stream2 and Stream3

*TE indicates the total concentration of Cr, Co, Ni, Cu, Zn, Cd, Sb, Pb and As

Multivariate statistical analysis of pollutants

The sources of contaminants in the water environment are complex, and the content is easily disturbed by external factors such as human activities. Therefore, a strong correlation between different contaminants means great possibility that they are derived from the same source. The Pearson correlation coefficient describes the contaminants concentrations (Table 6 and Table 7). Significant correlations between Co, Mn,

Ni, Cu, Zn and Cd in UAMD shows that these elements may have the same source. And the significant correlations between SO_4^{2-} , Co, Mn, Ni, and Zn indicates that these elements are derived from the same source, most likely related to the mining activities. PCA investigates five principal components, explaining 79.47% of the total variance. As shown in Table 8, for UAMD, PC1 accounts for 33.06% of the total variance and is characterized by the strong loading of Mn (0.90), Co (0.97), Ni (0.96), and Zn (0.87), and moderate loading of SO_4^{2-} (0.66), Cu (0.66), and Cd (0.58). Combined with the significant correlations between these elements, the loading of PC1 may be due to the groundwater-rock interactions and mining activities. PC2 contributes 18.05% of the total variance with strong loading of NO_3^- (0.924) and $\text{NO}_2\text{-N}$ (0.832), which is generally related to the agricultural activities and urbanization processes. PC3, PC4, and PC5 accounting for 12.46%, 8.21% and 7.69 % of the total variance, respectively, are characterized by with loading of Cd (0.66) and Sb (0.80), Cr (0.86), and $\text{NH}_4\text{-N}$ (0.77), respectively, which may be attributed to the utilization of fertilizers for farmland and chemical behavior.

For AAMD, the Pearson matrix shows that many metals are significantly correlated. The significant correlations between Mn, Co, Ni, Cu, Zn, Cd and SO_4^{2-} indicate that these elements are derived from the same source. PCA investigates five principal components, explaining 75.06% of the total variance. As shown in Table 9, PC1 accounts for 33.52% of the total variance and is characterized by the strong loading of Mn (0.80), Co (0.96), Ni (0.94), Cu (0.95), and Zn (0.91), and moderate loading of SO_4^{2-} (0.54). Taking the low pH values of water samples, the hydrologically geographical characteristics of the study sites, and the significant correlations between these elements into consideration, the loading of PC1 may be due to the AMD occurred during mining activities. And according to the survey, about $1.825 \times 10^7 \text{m}^3$ of mine wastewater is discharges in Zhijin County every year(Li 2018).PC2 contributes 14.13% of the total variance with the loading of NO_3^- (0.76), which is generally related to the agricultural activities and domestic sewage. PC3, PC4, and PC5 accounting for 11.54%, 9.05% and 6.82 % of the total variance, respectively, are characterized by with loading of Cr (0.86), Cd (0.58), Sb (0.63), As (0.86), and $\text{NH}_4\text{-N}$ (0.86), respectively, which may be attributed to the utilization of fertilizers for farmland and chemical behavior.

Table 6. Results of PCC in UAMD

Items	F	Cl	HCO ₃ ⁻	NO ₃ ⁻	NH ₄ -N	NO ₂ -N	SO ₄ ²⁻	Cr	Mn	Co	Ni	Cu	Zn	Cd	Sb	Ba	Pb	As
F	1.000	-0.262	-0.258	-0.282	-0.087	-0.324	-0.178	-0.025	-0.096	-0.151	-0.190	-0.246	-0.095	-0.216	-0.027	-0.157	-0.017	0.110
Cl		1.000	0.618*	0.929*	-0.021	0.573*	0.229	-0.010	-0.054	-0.080	0.057	-0.207	-0.253	-0.159	-0.250	0.365	-0.279	-0.250
HCO ₃ ⁻			1.000	0.548*	0.043	0.171	0.232	0.417*	-0.227	-0.235	-0.089	-0.091	-0.237	-0.116	0.158	0.398*	0.180	-0.418
NO ₃ ⁻				1.000	0.026	0.727*	0.198	-0.140	-0.112	-0.110	0.030	-0.163	-0.319	-0.168	-0.150	0.425*	-0.425	-0.277
NH ₄ -N					1.000	-0.085	0.103	0.104	-0.052	-0.033	-0.042	-0.143	-0.063	-0.024	-0.071	0.209	-0.101	-0.057
NO ₂ -N						1.000	0.114	-0.230	-0.055	-0.021	0.082	-0.034	-0.224	-0.204	-0.170	0.027	-0.354	-0.193
SO ₄ ²⁻							1.000	0.336	0.460*	0.534*	0.644*	0.323	0.384*	0.050	-0.283	0.105	-0.132	-0.176
Cr								1.000	0.176	0.052	0.047	0.020	0.275	0.010	-0.003	0.355	0.552*	-0.158
Mn									1.000	0.893*	0.844*	0.498*	0.809*	0.514*	-0.043	-0.066	0.030	0.129
Co										1.000	0.959*	0.614*	0.877*	0.572*	-0.068	-0.109	-0.026	0.164
Ni											1.000	0.595*	0.779*	0.479*	-0.099	-0.064	-0.086	0.033
Cu												1.000	0.615*	0.697*	0.271	-0.211	0.278	0.249
Zn													1.000	0.638*	0.145	-0.184	0.238	0.353
Cd														1.000	0.302	-0.072	0.234	0.431*
Sb															1.000	-0.099	0.328	0.263
Ba																1.000	-0.184	-0.253
Pb																	1.000	-0.037
As																		1.000

*indicates significant correlation

Table 7. Results of PCC in AAMD

Items	F	Cl	HCO ₃ ⁻	NO ₃ ⁻	NH ₄ -N	NO ₂ -N	SO ₄ ²⁻	Cr	Mn	Co	Ni	Cu	Zn	Cd	Sb	Ba	Pb	As
F	1.000	0.078	0.699*	-0.019	-0.121	0.177	0.258	0.602*	-0.045	-0.093	-0.111	-0.108	-0.137	-0.058	0.134	-0.083	-0.039	0.319
Cl		1.000	0.031	-0.093	0.016	0.087	-0.031	0.088	0.165	0.068	0.098	-0.061	-0.058	-0.090	0.731*	-0.011	0.104	0.627*
HCO ₃ ⁻			1.000	-0.186	-0.160	-0.125	0.292	0.892*	-0.240	-0.282	-0.295	-0.231	-0.244	-0.052	0.182	-0.162	0.091	0.392*
NO ₃ ⁻				1.000	0.114	0.480*	-0.486	-0.196	-0.349	-0.180	-0.212	-0.017	0.007	-0.024	-0.190	0.251	0.055	0.081
NH ₄ -N					1.000	0.443*	0.316	-0.311	0.341	0.159	0.187	0.011	-0.101	-0.214	-0.189	-0.031	-0.315	-0.040
NO ₂ -N						1.000	-0.178	-0.309	-0.071	-0.143	-0.164	-0.186	-0.162	-0.327	-0.133	0.537*	-0.271	0.181
SO ₄ ²⁻							1.000	0.173	0.777*	0.575*	0.572*	0.399*	0.248	0.199	-0.148	-0.481	-0.258	-0.188
Cr								1.000	-0.257	-0.223	-0.200	-0.127	-0.119	0.106	0.193	-0.133	0.388*	0.262
Mn									1.000	0.880*	0.886*	0.646*	0.539*	0.343	-0.050	-0.315	-0.261	-0.196
Co										1.000	0.989*	0.902*	0.845*	0.624*	-0.005	-0.231	-0.214	-0.148
Ni											1.000	0.866*	0.809*	0.606*	-0.005	-0.239	-0.158	-0.176
Cu												1.000	0.970*	0.758*	-0.047	-0.162	-0.080	-0.132
Zn													1.000	0.785*	-0.024	-0.007	0.005	-0.094
Cd														1.000	0.037	-0.087	0.060	-0.125
Sb															1.000	-0.065	0.030	0.819*
Ba																1.000	0.236	0.066
Pb																	1.000	-0.057
As																		1.000

*indicates significant correlation

Table 8. Results of the principal component analysis in UAMD

Variable	PC1	PC2	PC3	PC4	PC5
NO ₃	-0.058	0.924	-0.078	-0.087	0.183
SO ₄ ²⁻	0.661	0.206	-0.4	0.212	0.139
NH ₄ -N	-0.021	-0.146	-0.071	-0.075	0.774
NO ₂ -N	0.003	0.832	-0.117	-0.198	-0.189
Cr	0.149	-0.130	-0.077	0.864	0.251
Mn	0.900	-0.069	0.014	0.028	-0.003
Co	0.973	-0.048	0.029	-0.075	-0.023
Ni	0.961	0.101	-0.059	-0.043	-0.034
Cu	0.664	0.01	0.473	0.088	-0.238
Zn	0.865	-0.273	0.240	0.105	-0.046
Cd	0.579	-0.118	0.661	-0.034	0.048
Sb	-0.108	-0.035	0.801	0.155	-0.093
Ba	-0.084	0.401	-0.014	0.318	0.697
Pb	-0.016	-0.357	0.317	0.740	-0.280
As	0.147	-0.343	0.549	-0.43	0.039
Eigenvalues	4.709	2.708	1.868	1.233	1.153
Proportion to the total variance%	33.057	18.051	12.455	8.221	7.686
Cumulative percent%	33.057	51.108	63.563	71.784	79.47

Table 9. Results of the principal component analysis in AAMD

Variable	PC1	PC2	PC3	PC4	PC5
NO ₃	-0.107	0.764	-0.192	-0.187	-0.007
SO ₄ ²⁻	0.540	-0.569	-0.022	-0.235	0.368
NH ₄ -N	0.054	0.121	-0.116	0.017	0.860
NO ₂ -N	-0.059	-0.156	-0.571	-0.161	0.267
Cr	-0.137	-0.129	0.802	0.011	0.252
Mn	0.798	-0.378	-0.199	-0.113	0.217
Co	0.962	-0.164	-0.121	-0.025	0.067
Ni	0.941	-0.220	-0.099	-0.042	0.091
Cu	0.950	-0.020	0.003	0.000	-0.054
Zn	0.907	0.125	0.092	0.134	-0.156
Cd	0.386	0.272	0.239	0.578	-0.177
Sb	-0.06	-0.164	0.139	0.635	0.097
Ba	-0.134	0.819	0.108	-0.061	0.188
Pb	-0.083	-0.059	0.758	0.005	-0.165
As	-0.087	-0.083	-0.103	0.858	-0.060
Eigenvalues	5.028	2.119	1.731	1.358	1.023
Proportion to the total variance%	33.518	14.128	11.543	9.054	6.820
Cumulative percent%	33.518	47.646	59.189	68.243	75.063

3.4 The assessment of water quality

Based on the "Groundwater Quality Standards" and "Surface Water Quality Standards", pH, F^- , Cl^- , SO_4^{2-} , NH_4-N , NO_2-N , Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sb and other factors were analyzed for water quality assessment, and the Nemerow indexes of AMD, AAMD and UAMD were calculated, respectively (Fig.5).

Fig.5 Results of Nemerow method

According to Fig.5, for UAMD, 19 of the 28 water samples, accounting about 68%, are divided into Grade IV, mainly related to NH_4-N . For AAMD and AMD, 19 and 14 of the 50 water samples, accounting 66%, are divided into Grade IV and Grade V, respectively, mainly related to pH, NH_4-N , Mn, Cu, and Zn. Compared to the UAMD, the water quality of AMD and AAMD are significantly affected by the metal elements. Therefore, the water quality of AAMD is mainly controlled by the mining activities while the water quality of UAMD is mainly controlled by the agricultural activities and urbanization.

Conclusion

(1) In the three kinds of water samples, the order of concentrations of metal elements (except Ba) and sulfate was: $AMD > AAMD > UAMD$, while the concentrations of metal Ba and nitrate nitrogen show the opposite concentration order: $AMD < AAMD < UAMD$.

(2) On the spatial scale, the concentrations of metal elements (except Ba) and SO_4^{2-} showed an overall decreasing trend along the flow direction, and the concentrations of metal elements Ba and nitrate nitrogen showed an upward trend along the flow direction.

(3) On the temporal scale, in Stream1 and Stream3, the concentrations of metal elements (except Ba) and SO_4^{2-} in the water samples were significantly affected by the season, which were higher in wet season than dry season. This may be due to the increase in AMD during the wet season, which intensified the release of heavy metals. However, in Stream2, the concentrations of metal elements (except Ba) and SO_4^{2-} showed

opposite seasonal trends, which may be due to the relatively larger increase in the flow rate of Stream2 during the wet season, which diluted the concentrations of metal elements and SO_4^{2-} instead.

(4) PCC and PCA analysis indicate that water pollution was mainly affected by mining industry activities, agricultural activities and urbanization. The Nemerow index shows that in UAMD water samples, 68% are divided into Grade IV, mainly related to $\text{NH}_4\text{-N}$; in AMD and AAMD water samples, 66% are divided into Grade IV and Grade V, mainly related to pH, $\text{NH}_4\text{-N}$, Mn, Cu, and Zn. Therefore, the water quality of AAMD water quality is mainly affected by mining activities, while the water quality of UAMD is mainly affected by agricultural activities and urbanization.

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Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

Sampling sites in Zhijin County, China(Li et al. 2021). Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Piper diagram

Figure 3

Boxplot of concentrations of contaminants in AMD, AAMD and UAMD *TE indicates the total concentration of Cr, Co, Ni, Cu, Zn, Cd, Sb, Pb and As

(a) Spatial-temporal variations of contaminants in Stream1

(b) Spatial-temporal variations of contaminants in Stream2

(c) Spatial-temporal variations of contaminants in Stream3

Figure 4

(a)-(c) Spatial-temporal variations of contaminants in Stream1, Stream2 and Stream3 *TE indicates the total concentration of Cr, Co, Ni, Cu, Zn, Cd, Sb, Pb and As

Figure 5

Results of Nemerow method