



# Article Assessment of the Impact of Abandoned Mine Water on Groundwater Environment

Yuxiang Liu<sup>1</sup>, Guanqun Ma<sup>1,\*</sup>, Yu Han<sup>1</sup>, Yubo Wang<sup>1</sup>, Cui Tang<sup>1</sup>, Ning Tian<sup>1</sup>, Xiaoshan Tang<sup>1</sup>, Lulu Jiang<sup>1</sup>, Hanyue Zuo<sup>1</sup>, Yuexing Zhang<sup>2</sup>, Shanlin Wang<sup>2</sup>, Ao Wang<sup>2</sup>, Deqiang Mao<sup>2</sup> and Shiliang Liu<sup>2</sup>

- <sup>1</sup> 801 Institute of Hydrogeology and Engineering Geology, Shandong Provincial Bureau of Geology & Mineral Resources, Jinan 250014, China; wang0756@163.com (Y.W.)
- <sup>2</sup> School of Civil Engineering, Shandong University, Jinan 250061, China; zhangyuexing11@mail.edu.sdu.cn (Y.Z.)
- \* Correspondence: 18615691518@163.com

Abstract: The assessment of the impact of abandoned mine water on the underwater environment is critical for protecting and restoring the groundwater environment. Taking the abandoned coal mining area in the west of Zhangqiu District as the engineering background and comprehensively considering the regional groundwater chemical characteristics data during the wet and dry seasons, the main characteristics of the ions, hydrochemical types, and ion correlations of the abandoned mine water with the regional groundwater components were analyzed using mathematical statistics, correlation analysis, and Piper diagrams. An impact assessment was conducted on the water quality index values of the groundwater monitoring point. Furthermore, this research establishes an evaluation method of abandoned mine water in a regional groundwater environment based on the improved Nemero index method and matter element theory. Overall, the groundwater pH is weakly alkaline in Zhangqiu District. The groundwater Ca<sup>2+</sup> is the dominant cation, while HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are the dominant anions. The main ion concentration during the dry season is slightly greater than during the wet season. The main hydrochemical type of groundwater during the wet and dry seasons is HCO<sub>3</sub>-Ca. In addition, there is a correlation between NO<sub>3</sub><sup>-</sup> and F<sup>-</sup>, which may be caused by human activities. The groundwater environment is classified as level IV and severely polluted.

Keywords: abandoned mine water; hydrogeochemistry; matter element theory; groundwater environment

# 1. Introduction

Due to factors such as coal resource depletion, resource integration, and the shutdown of outdated production facilities, many coal mines in China have been or are on the verge of closure. After the closure of a mine, the discharge of mine water stops, and the groundwater level quickly rises [1–4]. The abandoned mine water carries pollutants from the tunnel through mining-induced fractures, faults, and poor sealing of drill holes into other aquifers, leading to cross-layer pollution [5–7]. Groundwater pollution has become a major environmental problem in abandoned mining areas. As the number of abandoned mines are set to increase, groundwater pollution incidents caused by abandoned mines are set to increase. Therefore, it is critical to investigate the groundwater hydrochemical characteristics in the abandoned coal mining area and evaluate their impact on the groundwater environment.

Numerous studies have been conducted on groundwater pollution in abandoned mines. To prevent the surface from being flooded by sewage due to the rise in the ground-water level in abandoned mines, in addition to establishing a hydrology monitoring network in the abandoned mine areas, key goaf areas should also be filled to prevent surface collapse [8]. It has been established that before a mine is abandoned, all water stop holes without grouting should be grouted and sealed, interconnected alleys and wells filled,



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and a specialized drainage system constructed to ensure that the water table is below the local elevation of the ground [9–11]. Moreover, Pauwels et al. [12] used the isotopic tracer method to study the effects of the interaction between abandoned mines and agriculture on the chemical characteristics of groundwater and found that arsenic is the most sensitive element of all polluting species. Plummer et al. [13] developed NETPATH and PHREQE software version 2.0 and investigated the inverse problem of groundwater quality changes and pollution prediction simulation in abandoned mines.

Hu and Zhou et al. [14,15] systematically analyzed the characteristics of environmental geology disasters such as water pollution, surface collapse, and water inrush from adjacent mines caused by abandoned mines. Gao [16], Isabelle et al. [17], Emdadul et al. [18], Okolo et al. [19], and Zhang et al. [20] analyzed the changes in water quality of underground and surface water in abandoned mines and surrounding areas, studied the water environmental effects caused by mine closures, and proposed groundwater resource risk management measures. Chen [21] simulated and predicted the migration patterns and development trends of Hg and nitrates in shallow groundwater by constructing a numerical simulation model for groundwater and a solute transport simulation model. Wang [22] clarified the basic characteristics of the Yushenfu coal mining area groundwater environment and identified the main factors affecting the groundwater caused by the closure of the mine. They determined the transport law and water quality evolution law of pit water after the closure of the mine and proposed preventative measures for water environment pollution after the mine closure. Sun et al. [23] determined the main characteristics of mine water in typical mining areas in China and discussed in detail several scientific issues related to the formation and evolution of mine water quality in China. Li [24] established a risk assessment index system and evaluation model for groundwater pollution in abandoned mines from three perspectives: pollution source risk indicators, pollution channel risk indicators, and pollution receptor harmfulness indicators. Li also developed a risk assessment system software and proposed risk management measures. Ma [25] combined the characteristics of the regional groundwater flow field, analyzed the evolution process of the groundwater flow field in the Fengfeng mining area during different periods, and reasonably selected the initial flow field based on the drainage data of the mining area. They simulated the impact of mine abandonment on the regional groundwater flow field.

Several models of assessment have been established. Zhu et al. [26] established an abandoned mine groundwater risk assessment model based on pressure-state-response. Feng et al. [27] presented a framework and quantitative method for groundwater environmental risk analysis at different phases of the mine life cycle composed of the groundwater system destruction risk and social-economic-ecological vulnerability assessment. Irina et al. [28], Azzeddine et al. [29], Jiang et al. [30], Yang et al. [31], Zhang et al. [32], and Zhang [33] conducted hydrogeochemical studies to identify the specific features and potentially toxic elements associated with the mining district by assessing the groundwater vulnerability. Patrick and Christopher [34] presented the robustness of 'first-flush' empirical models for describing and predicting mine water behavior. Suvarna et al. [35], Baran et al. [36], and Chen [37] established groundwater quality assessments using multivariate statistical approaches. Anthony and Smart [38] and Zhang et al. [39] investigated the open-pit mine geological environment and the effect of mining on socioeconomic and health conditions. Moreover, Wu and Li [40], Sun et al. [41], Du et al. [42], and Zhu et al. [43] analyzed the progress and development directions of groundwater pollution prevention and control technology in coal mine sites. They proposed water pollution prevention and comprehensive utilization measures.

The abovementioned research results have important theoretical and practical significance for the assessment of the impact of abandoned water on groundwater and groundwater environmental protection. However, there are still two shortcomings. Current research often focuses on the mechanism of rising water tables in abandoned mines while neglecting the evaluation of regional groundwater pollution in abandoned mining areas during different periods. Furthermore, the evaluation of abandoned water in regional groundwater systems focuses on establishing indicator systems for pollution sources, channels, and receptors while ignoring the evolution analysis of regional groundwater quality indexes.

Therefore, this research comprehensively considered the regional groundwater hydrochemical characteristics during the wet and dry seasons, the main characteristics of the ions, hydrochemical types, and ion correlations of abandoned mine water with the groundwater components, using the abandoned coal mine area in the western part of Zhangqiu District. Furthermore, this study proposes an evaluation method of the impact of abandoned mine water on the groundwater system using the improved Inner Mongolia Index method and matter element theory.

#### 2. Materials and Methodology

#### 2.1. Study Area

The western coal mining area of Zhangqiu District is within the Jidong coal field, where there are over 90 coal mines of various sizes, such as the Bucun Coal Mine, Lifu Coal Mine, Shengjing Coal Mine, Yushan Coal Mine, Mintai Coal Mine, and Dongxuma Coal Mine. Since 2003, the western coal mining area of Zhangqiu District has gradually shut down, and by June 2016 the coal mines in the area were fully closed. The Shengjing groundwater drinking water source area provides water for urban residents' daily life and public services. It is located in the western coal mining area of Zhangqiu District, which contains 6 drinking water plants and 41 karst groundwater production wells, and its total mining output reaches 125,000 m<sup>3</sup> per day.

## 2.2. Methodology

## 2.2.1. Sampling and Groundwater Hydrochemical Composition Testing

Generally, the wet season in the research area is from June to September, with relatively high rainfall, usually exceeding 100 mm per month. The dry season is from October to May of the following year, with less precipitation, usually less than 50 mm or no precipitation per month. For example, rain only occurred over 9 days in August 2021, totaling 101.13 mm. Sampling and water quality testing were conducted at 20 groundwater monitoring points on 10 September 2021 (wet season) and 22 March 2022 (dry season) in the abandoned mining areas of Zhangqiu District. There was no rainfall during the sampling procedure. The laboratory test results show the main hydrochemical components of the groundwater, including K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, TDS, and pH.

In polyethylene plastic bottles, two samples were taken from each location at each sampling time, one 1 L and one 500 mL. The 1 L water sample was used to analyze  $Cl^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ , and other components. The 500 mL sample was acidified with nitric acid and used for measuring K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>. Before collecting the water sample, the sample bottles were rinsed 2–3 times with the water in the sampling location. During the sampling process, it was ensured that there were no bubbles in the sample bottle. After sampling, the sample was sealed for storage, and the sample was refrigerated during transportation. There were 40 groundwater hydrochemical data from 20 sets of groundwater chemical testing points during the wet and dry seasons in the abandoned mining areas in total.

The Shandong Geological and Mineral Engineering Survey Institute laboratory tested the groundwater samples. The pH and total dissolved solids (TDS) of the water samples were tested on-site using the portable water quality parameter instrument HQ40D (Hach, Loveland, CO, USA) and recorded.

The content of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> was determined by ion chromatography. The measuring instrument DionexICS-6000 produced by Thermofly in the United States has an ion detection limit of 0.01 mg/L with a measurement error of less than 0.1%. The HCO<sub>3</sub><sup>-</sup> content was determined by using the acid–base titration method, with a detection limit of 1.0 mg/L. Ion chromatography was used to test SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>; the corresponding limit of detection was 0.09, 0.02, and 0.2 mg/L; and the instrument used was the ICS-2100 (America, DIONEX). After the test was completed, the error of charge

balance was calculated, and the calculation results showed that the errors were all within  $\pm$ 5%, indicating that the water chemistry data were reliable.

#### 2.2.2. Analysis Method for Groundwater Hydrochemical Characteristics

After the data were collected, statistical analysis of the hydrochemical components was conducted first using SPSS software, indicating the main ion characteristics during the wet and dry seasons. Secondly, a Piper diagram was drawn according to the percentage of the main ion content at the water sample point, reflecting the hydrochemical types of the aquifer. Using AqQA software, a Piper three-line map of regional groundwater was drawn to represent the hydrochemical types of groundwater during the wet and dry seasons and to analyze the evolution of groundwater chemical components. Then, considering the correlation between the changes in the main ion content in the groundwater, the correlation between the main ion characteristics was analyzed.

2.2.3. Method of Evaluating the Impact of Abandoned Mine Groundwater on Regional Groundwater Environment

Matter element analysis studies the laws and methods of solving incompatible problems. It is an interdisciplinary subject of noetic science, systems science, and mathematics. Moreover, it is widely used in decision making, management, evaluation, and other areas of the natural and social sciences. N is an object, c a feature of a thing, and v the value of the feature. Here, the ordered triplet R = (N, c, v) was used as the basic element to describe things, abbreviated as matter element [44]. A thing has multiple features. If a thing N is described by n features such as  $c_1, c_2, \ldots, c_n$  and corresponding values  $v_1, v_2, \ldots, v_n$ , it can be expressed as

$$R(N, c, v) = \begin{bmatrix} N & c_1 & v_1 \\ & c_2 & v_2 \\ & \vdots & \vdots \\ & & c_n & v_n \end{bmatrix}$$
(1)

where *R* is an n-dimensional matter element,  $c_i$  is the feature of the matter element, and  $v_i$  is the value corresponding to the feature of the matter element.

Based on the above analysis and matter element theory and combined with the Nemero index method, the evaluation of the impact of abandoned mine water on the regional groundwater environment was carried out as follows:

## (1) Determine the matter element to evaluate

To evaluate the features of something based on the actual situation, the measured values of multiple feature values need to be verified and the corresponding matter element matrix established:

$$R_0(P_0, c, v) = \begin{bmatrix} P_0 & c_1 & v_1 \\ & c_2 & v_2 \\ & \vdots & \vdots \\ & & c_n & v_n \end{bmatrix}$$
(2)

where  $P_0$  is the matter element to be evaluated;  $c_i$  is the feature of the matter element; and  $v_i$  is the raw data of the *i*-th matter element feature.

Based on the "Quality Standard for Groundwater" [45] and the measured data of water quality index in the research area, five evaluation indicators were ultimately selected:  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $NO_3^-$ , and TDS.

The measured data from the Xishan well in Bucun Village in the research area were used throughout the study as the evaluation sample, as shown in Table 1.

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5 of 13

**Table 1.** The evaluation groundwater sample (mg/L).

Ca <sup>2+</sup>	$SO_4^{2-}$	$\mathbf{F}^{-}$	$NO_3^-$	TDS
132	139	0.188	30.3	650.516

## (2) Determine the classical domain and joint domain

Based on the hierarchical division of factors, the classical domain is determined as

$$R_{j}(N_{j}, c, v_{ji}) = \begin{bmatrix} N_{j} & c_{1} & v_{j1} \\ & c_{2} & v_{j2} \\ & \vdots & \vdots \\ & c_{n} & v_{jn} \end{bmatrix} = \begin{bmatrix} N_{j} & c_{1} & < a_{j1}, b_{j1} > \\ & c_{2} & < a_{j2}, b_{j2} > \\ & \vdots & \vdots \\ & c_{n} & < a_{jn}, b_{jn} > \end{bmatrix}$$
(3)

The joint domain is

$$R_{p}(N,c,v_{pi}) = \begin{bmatrix} N_{p} & c_{1} & v_{p1} \\ & c_{2} & v_{p2} \\ & \vdots & \vdots \\ & c_{n} & v_{pn} \end{bmatrix} = \begin{bmatrix} N_{p} & c_{1} & < a_{p1}, b_{p1} > \\ & c_{2} & < a_{p2}, b_{p2} > \\ & \vdots & \vdots \\ & c_{n} & < a_{pn}, b_{pn} > \end{bmatrix}$$
(4)

where  $N_j$  is the *j* levels divided;  $c_i$  (i = 1, 2, ..., n) is the feature of level  $N_j$ ; classical domain  $v_{ji}$  is the range of values prescribed by  $N_j$  regarding the feature  $c_i$ ;  $N_p$  is the total number of levels; and  $v_{vi}$  is the range of values taken by  $N_p$  regarding  $c_i$ .

The grade classification of water bodies was based on the "Quality Standard for Groundwater" [45]. The water quality was divided into five levels: I–V. In the "Quality Standard for Groundwater", only the lower limit concentration is prescribed for Class V water, and the upper limit concentration is not specified for Class V water. However, there are extensive data exceeding the standard in the measured sample data. Therefore, based on the measured data, the upper limit standard for Class V water was divided, and the final standard concentrations for each level are shown in Table 2.

Table 2. Criteria for groundwater quality evaluation (mg/L).

	Ι	II	III	IV	V
Ca <sup>2+</sup>	$\leq 150$	$\leq$ 300	$\leq 450$	$\leq$ 550	$\leq 650$
$SO_4^{2-}$	$\leq$ 50	$\leq 150$	$\leq 250$	$\leq$ 350	$\leq 450$
$F^-$	$\leq 1$	$\leq 1$	$\leq 1$	$\leq 2$	$\leq 3$
NO <sub>3</sub> <sup>-</sup>	$\leq 2$	$\leq 5$	$\leq 20$	$\leq 30$	$\leq 40$
TDS	$\leq$ 300	$\leq$ 500	$\leq 1000$	$\leq 2000$	$\leq$ 3000

## (3) Determine the incidence function

The incidence function represents the value of a matter element taken as a point on the real axis. The degree where the matter element meets the required value range has been reached, and its value is the relevancy degree. The relevancy degree  $K_j(v_i)$  of each evaluation index  $v_i$  with respect to each evaluation level j can be expressed as

$$K_{j}(v_{i}) = \begin{cases} -\frac{\rho(v_{i}, v_{ji})}{|a_{ji} - b_{ji}|}, v_{i} \in v_{ji} \\ \frac{\rho(v_{i}, v_{ji})}{\rho(v_{i}, v_{pi}) - \rho(v_{i}, v_{ji})}, v_{i} \notin v_{ji} \end{cases}$$
(5)

where 
$$\rho(v_i, v_{ji}) = \left| v_i - \frac{(a_{ji}+b_{ji})}{2} \right| - \frac{(b_{ji}-a_{ji})}{2} = \begin{cases} a_{ji} - v_i, v_i \le (a_{ji}+b_{ji})/2 \\ v_i - b_{ji}, v_i > (a_{ji}+b_{ji})/2 \end{cases}$$
,  $\rho(v_i, v_{pi}) = \left| v_i - \frac{(a_{pi}+b_{pi})}{2} \right| - \frac{(b_{pi}-a_{pi})}{2} = \begin{cases} a_{pi} - v_i, v_i \le (a_{pi}+b_{pi})/2 \\ v_i - b_{pi}, v_i > (a_{pi}+b_{pi})/2 \end{cases}$ 

## (4) Determine the weight

Because different indicators have different impacts on the degree of water pollution, it is necessary to calculate the weight of each indicator. After calculating the weights, the pollution index was calculated for each monitoring well evaluation indicator. Normalization processing was performed according to the standard value of water quality concentration specified in the "Quality Standard for Groundwater" [45]. The calculation process was as follows:

$$C_{0i} = (C_{i1} + C_{i2} + C_{i3} + C_{i4} + C_{i5})/5$$
(6)

$$w_i = \frac{c_i}{C_{0i}} \tag{7}$$

$$\overline{w_i} = \frac{w_i}{\sum\limits_{i=1}^{m} w_i}$$
(8)

where  $C_{i1}$ ,  $C_{i2}$ , and  $C_{i5}$  are the standard concentration values at all levels corresponding to the *i* index in the "Quality Standard for Groundwater",  $C_i$  is the measured concentration,  $w_i$  is the pollution concentration, and *m* is the number of evaluation factors.

(5) Determine the synthetic relation degree of the matter element  $P_0$  to be evaluated for each level *j* 

The synthetic relation degree  $K_j(P_0)$  is the weighted value of the relevancy degree  $K_j(v_i)$  of each evaluation indicator of the unit to be evaluated with respect to the evaluation level *j*, namely:

$$K_j(P_0) = \sum_{i=0}^n w_i \cdot K_j(v_i) \tag{9}$$

where  $w_i$  is the weight of the i-th feature, and  $K_j(P_0)$  is the synthetic relation degree of the unit  $P_0$  to be evaluated, which belongs to the *j*-th level.

(6) Evaluate the  $P_0$  level of the matter element to be evaluated

The  $K_i$  is used to judge the level of the evaluated matter element.

$$K_j = \max\{K_j(P_0)\}\tag{10}$$

where *j* = 1,2, . . . , *m*;

The level of unit  $P_0$  to be evaluated is level *j*, which means that the water quality of the evaluated matter element is at level *j*.

## 3. Results and Discussion

- 3.1. Hydrochemical Characteristics
- 3.1.1. Characteristics of Major Ions

The statistical results of the groundwater hydrochemistry during the wet and dry seasons in the abandoned coal mining area of Zhangqiu are shown in Table 3. Overall, there is essentially no significant difference in the chemical composition of the groundwater between the wet and dry seasons. The main cation in the groundwater is  $Ca^{2+}$ , with an average of 160.01 mg/L and 156.017 mg/L during the wet and dry seasons, respectively.  $HCO_3^-$  is the main anion, with an average of 304.27 mg/L and 301.15 mg/L in the wet and dry seasons, respectively. The average pH of the groundwater in the study area during the wet and dry seasons is 7.49 and 7.587, respectively, showing weak alkalinity overall, which varies little throughout the year. The TDS value of the groundwater during the wet

season ranges from 381.966 to 3122.08 mg/L, with an average of 3122.08 mg/L. According to the TDS classification method for fresh and saline water [45], freshwater accounts for 89.8% of the karst groundwater samples, and saline accounts for 10.2%. The order of ion concentration in the groundwater of the abandoned coal mining area is not affected by the wet and dry seasons. The order of cation concentration is  $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ , and the order of anion concentration is  $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^- > F^-$ . However, the main ion concentrations during the dry season are slightly higher than those during the wet season, mainly due to the dilution effect of water volume on ion concentration during the wet season.

Time Interval	Statistical Value	K+	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl-	$SO_4^{2-}$	HCO <sub>3</sub> -	$\mathbf{F}^{-}$	$NO_3^-$	TDS	nH
		 ρ/(mg·L <sup>-</sup> )									pii	
Wet season	Maximum	15.7	91	583	211	49.8	1763	456	0.559	45.4	3122.08	7.87
	Minimum	0.49	5.52	3.53	0.64	9.03	77.1	152	0.172	0.693	381.966	7.23
	Average	2.383	12.708	156.017	40.842	16.982	294.525	301.15	0.3	21.535	3122.08	7.587
	Standard deviation Variation	3.164	19.514	109.334	41.384	10.464	360.448	62.809	0.093	11.333	559.289	0.169
	coefficient (VC)	1.328	1.536	0.701	1.013	0.616	1.224	0.209	0.308	0.526	0.67	0.022
	Maximum	4.7	40.3	587	226	57.4	1959	527.29	0.577	58.2	3443.343	8
Dry season	Minimum	0.4	1.81	87.5	17.3	10.3	55.2	214.46	0.121	0.597	460.499	7.1
	Average	1.04	8.41	160.01	43.46	19.55	297.01	304.27	0.27	20.72	868.64	7.49
	Standard deviation Variation	0.86	7.91	108.01	44.76	12.23	408.3	60.77	0.11	14.01	630.69	0.17
	coefficient (VC)	0.83	0.94	0.68	1.03	0.63	1.37	0.2	0.42	0.68	0.73	0.02

Table 3. Statistical results of groundwater hydrochemistry.

The variation coefficient (VC) is an indicator that reflects data variability. The VC values of Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> in the groundwater of the study area during the wet and dry seasons are relatively high, which indicates that the concentrations of these two ions exhibit prominent variance characteristics and unstable spatial distribution. In addition, the VC of pH in the groundwater is very small, with values of 0.02 and 0.022 during the wet and dry seasons, respectively, indicating that the pH value of karst groundwater in the study area is relatively stable and the spatial variability is minimal.

#### 3.1.2. Hydrochemical Type

As shown in Figure 1, the projective points in the Piper diagram during the wet and dry seasons are relatively concentrated, and the difference is not apparent. In the triangle diagram, the dominant anions are mainly  $HCO_3^-$  and  $SO_4^{2-}$ , while the dominant cations are mainly  $Ca^{2+}$ , followed by Na<sup>+</sup> and Mg<sup>2+</sup>. Moreover, the distribution is located in zone one, indicating that the content of alkaline earth metal ions is greater than that of alkaline metal ions. According to the Shukarev classification method [46], there are three hydrochemical types during the wet season:  $HCO_3$ -Ca,  $SO_4$ -Na, and  $SO_4$ -Ca, accounting for 70%, 5%, and 25% of the total water sample types, respectively. During the dry season, there are three hydrochemical types:  $HCO_3$ -Ca,  $HCO_3$ ·SO<sub>4</sub>-Ca, and  $SO_4$ -Ca, accounting for 60%, 15%, and 25% of the total water sample types, respectively. This is basically consistent with the hydrochemical type classification results obtained from the Piper diagram. The three hydrochemical types in the wet season are the same as those in the Shukarev classification. While there are only two types in the dry season in the Piper diagram, the main types are  $HCO_3$ -Ca, accounting for 65% of the total water sample types, then  $SO_4$ -Ca, accounting for 35% of the total water sample types.



Figure 1. Piper diagram of groundwater hydrochemical type.

## 3.1.3. Ion Correlation Analysis

The changes in groundwater ions often correlate to a certain extent and play an indispensable role in groundwater research. The relative relation matrix of the main hydrochemical components of the groundwater was obtained using SPSS software, as shown in Table 4. The TDS has an obvious correlation with  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and  $HCO_3^-$  during the wet season, with correlation coefficients of 0.987, 0.988, 0.787, 0.930, and 0.765, respectively. This indicates that these chemical components contribute significantly to TDS, especially because the correlation coefficients of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_4^{2-}$  exceed 0.9. There is a significant positive correlation between  $SO_4^{2-}$  and  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Na^+$ , indicating that these three substances have the same origin, most likely related to the dissolution of gypsum. In addition, the correlation between  $Ca^{2+}$  and  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and  $HCO_3^-$  is pronounced, which may be related to the dissolution of certain minerals. Moreover, there is a correlation between  $NO_3^-$  and  $F^-$ , which may be caused by human activities.

Terr					Dry Sea	son				
1011	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	$SO_4^{2-}$	HCO <sub>3</sub> <sup>-</sup>	$F^-$	$NO_3^-$	TDS
K <sup>+</sup>	1									
Na <sup>+</sup>	0.975 **	1								
Ca <sup>2+</sup>	-0.093	0.066	1							
Mg <sup>2+</sup>	0.025	0.152	0.969 **	1						
Čĺ−	0.063	0.273	0.808 **	0.691 **	1					
$SO_4^{2-}$	0.407	0.531 *	0.863 **	0.917 **	0.718 **	1				
$HCO_3^-$	-0.357	-0.253	0.816 **	0.743 **	0.595 **	0.528 *	1			
$F^-$	-0.152	-0.261	0.126	0.233	-0.394	0.084	0.26	1		
$NO_3^-$	0.15	-0.467 *	-0.467 *	-0.579 **	0.105	-0.403	-0.520 *	-0.789 **	1	
TDS	0.053	0.202	0.987 **	0.988 **	0.787 **	0.930 **	0.765 **	0.136	-0.487 *	1
Terr		Wet season								
Ion	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	$SO_4^{2-}$	HCO <sub>3</sub> <sup>-</sup>	$F^-$	NO <sub>3</sub> -	TDS
K+	1									
Na <sup>+</sup>	0.950 **	1								
Ca <sup>2+</sup>	0.958 **	0.936 **	1							
Mg <sup>2+</sup>	0.981 **	0.901 **	0.975 **	1						
CĨ-	0.722 **	0.890 **	0.768 **	0.656 **	1					
$SO_4^{2-}$	0.980 **	0.915 **	0.986 **	0.998 **	0.689 **	1				
HCO <sub>3</sub> -	0.866 **	0.909 **	0.909 **	0.848 **	0.815 **	0.864 **	1			
F <sup>-</sup>	0.12	-0.105	0.21	0.28	-0.344	0.26	-0.008	1		
$NO_3^-$	-0.44	-0.218	-0.368	-0.505 *	0.15	-0.471 *	-0.262	-0.666 **	1	
TDS	0.979 **	0.939 **	0.995 **	0.989 **	0.744 **	0.995 **	0.903 **	0.21	-0.411	1

 Table 4. Relative correlation coefficients of main hydrochemical components of groundwater.

Note: \* Significantly correlated at the 0.05 level; \*\* Significantly correlated at 0.01 level.

# 3.2. Evaluation of Abandoned Mine Water on Regional Groundwater Environment

The matter elements to be evaluated, and the classical and joint domains, were calculated as follows.

The matter elements to be evaluated:

$$R_1(P_1, c, v) = \begin{bmatrix} P_1 & Ca^{2+} & 132 \\ & SO_4^{2-} & 139 \\ & F^- & 0.188 \\ & NO_3^- & 30.3 \\ & TDS & 650.516 \end{bmatrix}$$
(11)

The classical domain:

$$R_{j}(N_{j}, c, v_{ji}) = \begin{bmatrix} I & II & III & IV & V \\ Ca^{2+} & <0,150 > & <150,300 > & <300,450 > & <450,550 > & <550,650 > \\ SO_{4}^{2-} & <0,50 > & <50,150 > & <150,250 > & <250,350 > & <350,450 > \\ F^{-} & <0,1 > & <0,1 > & <0,1 > & <1,2 > & <2,3 > \\ NO_{3}^{-} & <0,2 > & <2,5 > & <5,20 > & <20,30 > & <30,40 > \\ TDS & <0,300 > & <300,500 > & <500,1000 > & <1000,2000 > & <2000,3000 > \end{bmatrix}$$
(12)

The joint domain:

$$R_{p}(N,c,v_{pi}) = \begin{bmatrix} N_{p} & Ca^{2+} & <0,650 > \\ & SO_{4}^{2-} & <0,450 > \\ & F^{-} & <0,3 > \\ & NO_{3}^{-} & <0,40 > \\ & TDS & <0,3000 > \end{bmatrix}$$
(13)

The relevancy degree was obtained from the following equation:

$$K_{j}(v_{i})_{5\times5} = \begin{bmatrix} 0.12 & -0.12 & -0.56 & -0.707 & -0.76 \\ -0.39 & 0.11 & -0.073 & -0.444 & -0.603 \\ 0.188 & 0.188 & 0.188 & -0.812 & -0.906 \\ -0.744 & -0.723 & -0.515 & -0.03 & 0.03 \\ -0.35 & -0.188 & 0.301 & -0.349 & -0.675 \end{bmatrix}$$
(14)  
$$K_{j}(v_{i})_{5\times5} = \begin{bmatrix} 0.12 & -0.12 & -0.56 & -0.707 & -0.76 \\ -0.39 & 0.11 & -0.073 & -0.444 & -0.603 \\ 0.188 & 0.188 & 0.188 & -0.812 & -0.906 \\ -0.744 & -0.723 & -0.515 & -0.03 & 0.03 \\ -0.35 & -0.188 & 0.301 & -0.349 & -0.675 \end{bmatrix}$$
(15)

Because the different indicators were considered to have different impacts on water pollution, the weight of each indicator was calculated as

$$\overline{W_i} = \begin{bmatrix} Ca^{2+} & 0.104\\ SO_4^{2-} & 0.184\\ F^- & 0.039\\ NO_3^- & 0.516\\ TDS & 0.158 \end{bmatrix}$$
(16)

The synthetical relational degree of the matter element to be evaluated for each level was ensured to be

$$K_i(P_1)_{1\times 5} = [-0.491 - 0.388 - 0.282 - 0.257 - 0.316]$$
(17)

It can be concluded that the synthetical relational degree of Class IV water is the highest, and the final evaluation of the water environment of this sample shows that it belongs to Class IV, indicating that the groundwater in this area is severely polluted and no longer suitable for residents to use for daily living.

Overall, this research provides a global reference for the assessment of the impact of abandoned mine water on the groundwater environment. Generally, due to the dilution effect of water volume on ion concentration during the wet season, the main ion concentrations during the dry season are slightly higher than those during the wet season. In addition, the method of evaluating the impact of abandoned mine groundwater on regional groundwater environments is suitable for further application.

#### 4. Conclusions

- (1) The order of ion concentration in the groundwater of the abandoned coal mining area is not affected by the wet and dry seasons. The pH of the groundwater is weakly alkaline overall. The order of cation concentration is  $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ , and the order of anion concentration is  $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^- > F^-$ . However, the main ion concentration during the dry season is slightly higher than during the wet season. The ion concentration of Na<sup>+</sup> and  $SO_4^{2-}$  exhibits obvious variance characteristics, while the pH varies little between seasons.
- (2) TDS has an obvious correlation with  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ , and  $HCO_3^-$  during the wet season, with correlation coefficients of 0.987, 0.988, 0.787, 0.930, and 0.765, respectively. This indicates that these chemical components contribute significantly to TDS, especially because the correlation coefficients of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_4^{2-}$  exceed 0.9.
- (3) There are three hydrochemical types of groundwater during the wet season: HCO<sub>3</sub>-Ca, SO<sub>4</sub>-Ca, and SO<sub>4</sub>-Na, accounting for 70%, 25%, and 5% of the total water sample types, respectively. There are two hydrochemical types of groundwater during the

dry season: HCO<sub>3</sub>-Ca and SO<sub>4</sub>-Ca, accounting for 65% and 35% of the total water sample types, respectively.

(4) A method of assessing the impact of abandoned mine water on the groundwater environment was established based on the improved Nemero index method and matter element theory. The comprehensive evaluation of water quality indicators at the groundwater monitoring point shows that the groundwater environment is severely polluted at level IV.

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#### References

- Yoginder, P.; Chugh, B.K.S.; Chet, S. Sustainable and responsible mining through sound mine closure. *Int. J. Coal Sci. Technol.* 2023, 10, 14.
- 2. Pan, Y.; Liu, Y.; Zeng, X.K.; Wu, J.C. Numerical simulation of groundwater flow field evolution in abandoned mine in the east Xuzhou. *Hydrogeol. Eng. Geol.* 2017, 44, 52–56.
- 3. Chen, Z.H.; Xu, H.; Liao, M.Y.; Zhu, K.Y. Study on prediction of groundwater enrichment region after closure of typical coal mines. *Groundwater* **2022**, *2*, 1–3.
- 4. Zhai, X.R.; Wu, J.W.; Wang, G.T.; Bi, Y.S.; Hu, J. MODFLOW-based groundwater rebound forecast in abandoned coal mine. *Coal Geol. Explor.* 2018, 46, 27–32.
- 5. Cai, X.J.; Han, R.G.; Meng, L.; Yang, J.W. Safe and warning water level control of closed pit groundwater in Zhaogezhuang Mine. *Coal Eng.* **2020**, *52*, 116–121.
- Wang, H.; Lv, Y.Y. Study on pollution characteristics and control measures of water pollution caused by coal mining. *Environ. Sci.* Manag. 2019, 44, 68–73.
- Wu, J.W.; Zeng, X.K. Numerical Simulation of Groundwater Pollution in Abandoned Mines; China Water Power Press: Beijing, China, 2015; pp. 90–105.
- State Administration of Work Safety. Technical Specification for Monitoring Network Layout of Groundwater Pollution in Abandoned Mines; China Coal Industry Publish House: Beijing, China, 2016; pp. 280–285.
- 9. Khalil, A.; Hanich, L.; Hakkou, R.; Lepage, M. GIS-based environmental database for assessing the mine pollution: A case study of an abandoned mine site in Morocco. *J. Geochem. Explor.* **2014**, *144*, 468–477. [CrossRef]
- Khalil, K.; Hanich, L.; Bannari, A.; Zouhri, L.; Pourret, O.; Hakkou, R. Assessment of soil contamination around an abandoned mine in a semi-arid environment using geochemistry and geostatistics: Pre-work of geochemical process modeling with numerical models. J. Geochem. Explor. 2013, 125, 117–129. [CrossRef]
- 11. Ding, G.T.; Liu, Y.X.; Sun, Z.G.; Han, Y.; Zhang, X.B.; Liu, Y.X.; Wei, S.M.; Cao, G.M.; Jiang, L.L. Emergency disposal of groundwater contamination curtain grouting in an abandoned mining area in North China. *Acta Geol. Sin.* **2019**, *1*, 291–300.
- 12. Pauwels, H.; Pettenati, M.; Greffie, C. The combined effect of abandoned mines and agriculture on groundwater chemistry. *J. Contam. Hydrol.* **2010**, *115*, 64–78. [CrossRef]
- 13. Plummer, L.N.; Prestemon, E.C.; Parkhurst, D.L. An Interactive Code (NETPATH) for Modeling Net Geochemical Reactions along a Flow Path, version 2.0; US Geological Survey: Lakewood, CO, USA, 1991.
- 14. Zhou, J.J.; Hu, W.Y.; Hou, D.Y. Numerical simulation of groundwater rebound process and water table value in abandoned mines. *Coal Geol. Explor.* **2011**, *4*, 28–31.
- 15. Zhou, J.J.; Hu, W.Y.; Liu, D.Y. Analysis on Water Content Medium Field Features and Water Flow Motion Features in Abandoned Mine. *Coal Sci. Technol.* **2011**, *1*, 107–110.
- Gao, B. Groundwater Chemical Characteristics of Jiawang Coal Field in Response to Mine Closure. Master's Thesis, China University of Mining and Technology, Xuzhou, China, 2014; pp. 45–55.
- 17. Isabelle, C.; Cyrille, B.; Jannes, K.; Mustapha, B.; Pascal, B.; Pascal, B. Aseismic mining subsidence in an abandoned mine: Influence factors and consequences for post-mining risk management. *Pure Appl. Geophys.* **2019**, *176*, 801–825.

- Emdadul, H.; Selim, R.; Raquib, A. Assessing the vulnerability of groundwater due to open pit coal mining using DRASTIC model: A case study of Phulbari Coal Mine, Bangladesh. *Geosci. J.* 2018, 22, 359–371.
- Okolo, C.C.; Oyedotun, T.D.T.; Akamigbo, F.O.R. Open cast mining: Threat to water quality in rural community of Enyigba in south-eastern Nigeria. *Appl. Water Sci.* 2018, *8*, 204. [CrossRef]
- Zhang, Q.X.; Zhou, J.W.; Lin, S.H.; Wei, D.; Zhang, L.M.; Yuan, L. Characteristics and causes of groundwater pollution after Hongshan-Zhaili mine closure in Zibo. Saf. Environ. Eng. 2015, 22, 23–28.
- Chen, S. Numerical Simulation of Groundwater Pollution and Water and Soil Pollution Evaluation and Analysis in Mining Area of Suzhou in Mining. Master's Thesis, Hefei University of Technology, Hefei, China, 2020; pp. 25–36.
- 22. Wang, H.M. Evolution of Groundwater Environment in the Closed Mines of Yushenfu Mining Area. Doctor's Thesis, China Coal Research Institute, Beijing, China, 2022; pp. 77–80.
- Sun, Y.J.; Xu, Z.M.; Li, X.; Zhang, L.; Chen, G.; Zhao, X.M.; Gao, Y.T.; Liu, Q.; Zhang, S.G.; Wang, W.J.; et al. Mine water drainage pollution in China's coal mining areas and the construction of prevention and control technical system. *Coal Geol. Explor.* 2021, *5*, 1–16.
- Li, T. Study on Groundwater Pollution Risk Assessment of Abandoned Coal Mine. Doctor's Thesis, China University of Mining and Technology, Xuzhou, China, 2014; pp. 66–103.
- 25. Ma, L. Study on Process and Mechanism of Water Rebound Impact on the Regional Groundwater Flow Field in Abandoned Mines. Master's Thesis, China University of Geosciences, Beijing, China, 2016; pp. 29–33.
- 26. Zhu, M.T.; Li, B.; Liu, G. Groundwater risk assessment of abandoned mines based on pressure-state-response—The example of an abandoned mine in southwest China. *Energy Rep.* 2022, 10728–10740. [CrossRef]
- Feng, H.B.B.; Zhou, J.W.; Chai, B.; Zhou, A.G.; Li, J.Z.; Zhu, H.H.; Chen, H.N.; Su, D.H. Groundwater environmental risk assessment of abandoned coal mine in each phase of the mine life cycle: A case study of Hongshan coal mine, North China. *Environ. Sci. Pollut. Res.* 2020, 27, 42001–42021. [CrossRef]
- 28. Irina, T.; Aleksei, K.; Alexander, Z.; Igor, C. Chemical composition of groundwater in abandoned coal mines: Evidence of hydrogeochemical evolution. *Appl. Geochem.* **2022**, *137*, 105210.
- Azzeddine, K.; Talbi, E.H.; Abdessalam, A.; Khalid, B.; Isabel, M.H.R.A.; Mohamed, A. Groundwater vulnerability and potentially toxic elements associated with the iron mining district of Ouixane (Northeast of Morocco). Water 2023, 15, 118.
- Jiang, B.B.; Ji, K.M.; Xu, D.J.; Cao, Z.G.; Wen, S.K.; Song, K.; Ma, L. Effects of coal gangue on the hydrochemical components under different types of site karst water in closed mines. *Water* 2022, 14, 3110. [CrossRef]
- Yang, Q.; Cao, Y.J.; Zhang, Y.; Chen, J.Y.; Wang, S.Z.; Tian, D. Hydrochemical characteristics and its cause analysis of groundwater and mine water in closed Lead Zinc Mining Area. *Ecol. Environ. Sci.* 2023, 32, 361–371.
- Zhang, Q.X.; Zhou, J.W.; Kang, F.X.; Lin, S.H.; Wei, D.; Zhang, L.M.; Yuan, L. Hydrodynamic analysis and isotope tracing for probing into groundwater pollution of Zibo Mining Area. *Environ. Sci. Technol.* 2016, 39, 116–121.
- Zhang, W.F. Hydrogeochemical Changes of Closed Pit Simulation System in Coal Mine. Master's Thesis, China University of Mining and Technology, Xuzhou, China, 2017; pp. 25–35.
- 34. Patrick, M.; Christopher, P. Assessing the long-term evolution of mine water quality in abandoned underground mine workings using first-flush based models. *Sci. Total Environ.* **2022**, *846*, 157390.
- Suvarna, B.; Sunitha, V.; Sudharshan, R.Y.; Muralidhara, R.B.; Kadam, A.K.; Ramakrishna, M.R. Groundwater quality assessment using multivariate statistical approach and geospatial modelling around cement industrial corridor, South India. *Int. J. Environ. Sci. Technol.* 2023, 20, 5051–5070. [CrossRef]
- Baran, A.H.; Nalbantcilar, T.M.; Koktan, N. Pollution and health risk assessment of heavy metals in waters around mine sites of Elazig (Eastern Turkey). J. Mountain Sci. 2023, 20, 1293–1306. [CrossRef]
- Chen, Y.Z. Karst Spring Water Pollution by Abandoned Coal Mines—A Case of Longdong Spring Pollution. Master's Thesis, China University of Mining and Technology, Xuzhou, China, 2019; pp. 32–41.
- Anthony, C.; Obiora, S.C. Effect of Lead–Zinc mining on socio-economic and health conditions of Enyigba and Ishiagu Lead–zinc Mining Districts of Southeastern Nigeria. *Min. Metall. Explor.* 2023, 40, 691–701.
- 39. Zhang, P.; Zhang, J.P.; Wang, J. Research on open-pit coal mine geological environment problems and governance program. *Coal Technol.* **2016**, *12*, 320–321.
- 40. Wu, Q.; Li, S.Y. Positive and negative environmental effects of closed mines and its countermeasures. *J. China Coal Soc.* **2018**, 43, 21–32.
- 41. Sun, W.J.; Ren, S.L.; Wu, Q.; Dong, D.L.; Gan, X.Y. Water pollution's prevention and comprehensive utilization of abandoned coal mines in China under the new normal life. *J. China Coal Soc.* **2022**, *47*, 2161–2169.
- 42. Du, M.Z.; Li, H.J.; Li, W.; Qiu, H.; Jiang, P.; Wang, D.H. Study progress and development directions of the prevention and control technology of ground water pollution in coal mine sites. *Met. Mine* **2020**, *9*, 1–14.
- 43. Zhu, Y.N.; Wang, S.S.; Song, B.L.; Zhang, Y.; Yu, X.L. Summary of mechanism and treatment of mine groundwater pollution. *Technol. Innov. Appl.* **2023**, *13*, 36–39.
- 44. Cai, W. Matter-Element Model and Its Application; Science and Technology Press: Beijing, China, 1994; pp. 56-67.

- 45. *GB/T14848-2017*; Standard for Groundwater Quality. State Administration of Quality Supervision, Inspection and Quarantine of the China. Standardization Administration of China: Beijing, China, 2017; pp. 2–4.
- 46. Zhu, X.Y.; Qian, X.X. Groundwater Hydrology; China Environmental Science Press: Beijing, China, 2005; pp. 42–46.

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