

Hydro-geochemical and isotopic characterization of the deep groundwater from coal bearing in Mining district, Northern Anhui Province, China

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Abstract

Hydro-geochemistry and isotopes were used to understand the geochemical character and origin of the groundwater from coal bearing aquifer in Northern Anhui province, China. Twenty three groundwater samples were collected, and the isotopic composition δD , $\delta^{18}O$ and major ions were analyzed, conventional graphical and multivariate statistical approach was completed and the result showed: three groups of groundwater could be divided from the rectangular field, the Ca-Mg-Cl, Na-Cl-SO₄ and Na-HCO₃ type water; the feldspar weathering is dominating weathering process, whereas, the sulfuric acid is the weathering agent along with the carbonic acid; the groundwater mainly supplied from the meteoric water for all the plots are below the local meteoric water line and global meteoric water line, the values of δD are drifted obviously, what could be caused by the exchange reaction of δD between groundwater and alkyl.

Key words: environmental isotopic, groundwater, hydro-geochemical, Northern Anhui province, principal component analysis

INTRODUCTION

Groundwater, especially deep groundwater plays a key role for the development of society and economy. Thus, so many studies focused on the hydro-geochemical process, groundwater quality, rock-water interaction and the anthropogenic influences on the groundwater system [1–3]. However, for the difficulty of groundwater sample collection, only a few studies have been devoted to the hydro-geochemical characteristic in deep groundwater (depth > 400 m). The previous studies revealed that the approaches such as conventional graphical and multivariate analysis of the hydro-geochemical data, combining with the isotopic characterization of the groundwater, could obtain the hydro-geochemical process (dissolution, mixing, weathering and ion exchange) and understand the origin of groundwater [3,4].

Deep groundwater investigations, such as major ions, rare earth element, as well as isotopic studies, have been carried out in the Northern Anhui Province, China [5–7], which has abundant coal resources. However, these studies were focused on the discrimination of water sources, for coal mining safely. The study about the hydro-geochemical process, groundwater quality assessment and isotopic composition is limited. The purpose of this study is to identify the groundwater characteristic of coal bearing aquifer, using hydro-chemical and isotopic data. The major targets are to (1) define the geochemical characteristic of coal bearing aquifer system, (2) assessment the groundwater quality and find out the suitability of groundwater for irrigation and drinking purpose, (3) identify the origin of coal bearing groundwater. The results can be used as a basis for making sustainable groundwater development schemes and tracing the origin of deep groundwater.

MATERIALS AND METHODS

Geological and hydrological setting

The Huaibei mining area is located at Northern Anhui Province, China, which constituted by about thirty couples mine (Figure 1). The basement of coal mine in the district is composed by Archean and Proterozoic metamorphic rock, with cover strata are stable sedimentation between late-Proterozoic and Permian. The previous study revealed that the groundwater system in the district could be subdivided into four aquifers from shallow to deep, along with diversify of the aquifer rock [8]. The characteristics of each aquifer synthesized according to previous work are list in Table 1.

In detail, the coal bearing aquifer was mainly constituted by the sandstone, with little cranny and poor permeability. In nature, the coal bearing aquifer are mainly of the storage from groundwater, whereas the recharge and discharge conditions are limited. The mode of discharge in Permian sandstone aquifer is constituted by the water inrush and water burst, along with the coal mine exploitation. The four aquifers with varied hydrodynamic conditions are considered different hydraulic conditions. In special, the Quaternary aquifer is an 'open' system because of mining, and the coal bearing aquifer is relatively 'closed'. The limestone aquifer (including Taiyuan Fm and the Ordovician limestone aquifer) are also closed systems, although there groundwater flows rapidly [7].

The Qianyingzi coal mine, Baishan coal mine and Wolonghu coal mine are all independent hydro-geological units for there special tectonic setting (Figure 2). In detail, the Baishan coal mine is located at synclinal basin, with the Permian as the axis. Qianyingzi coal mine is surrounded by Nanping fault and Sunan anticline, whereas Wolonghu coal mine is separated by the Huangyin fault (Figure 2). Thus, the water runoff in coal bearing aquifer between the three coal mines is limited.

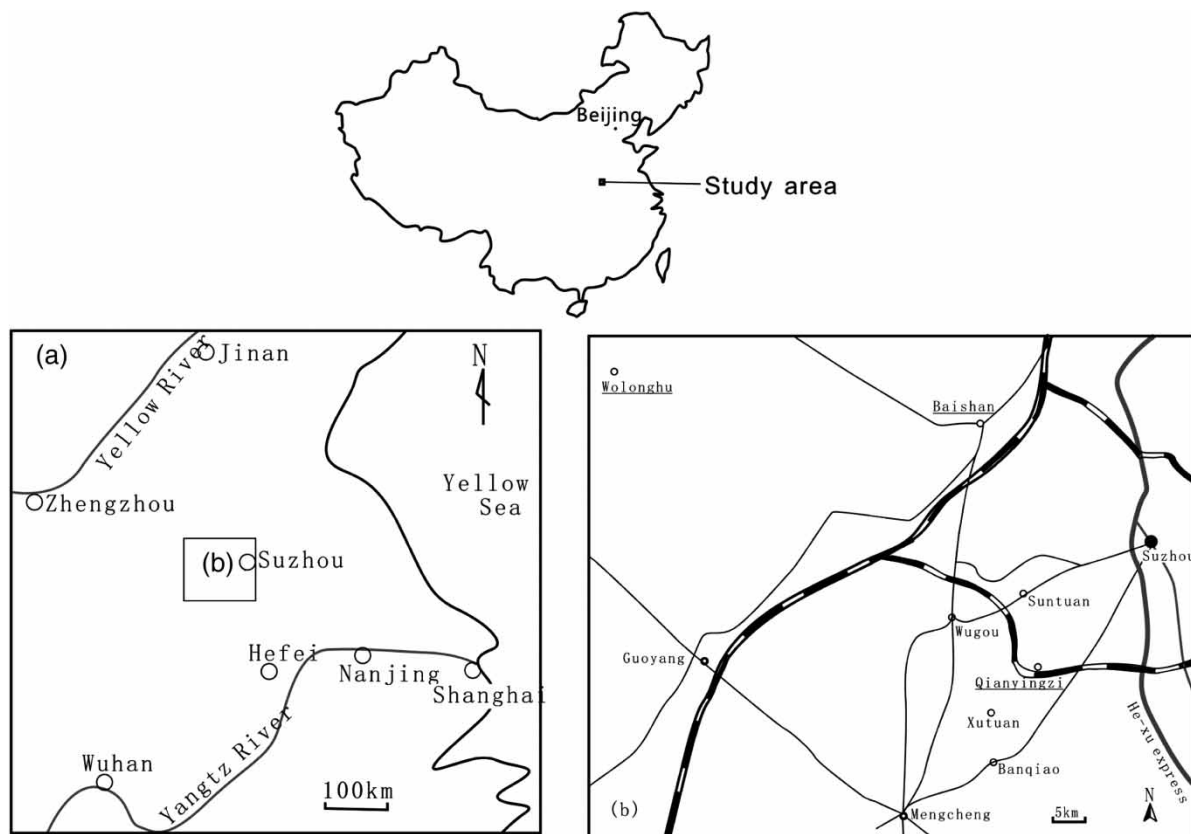
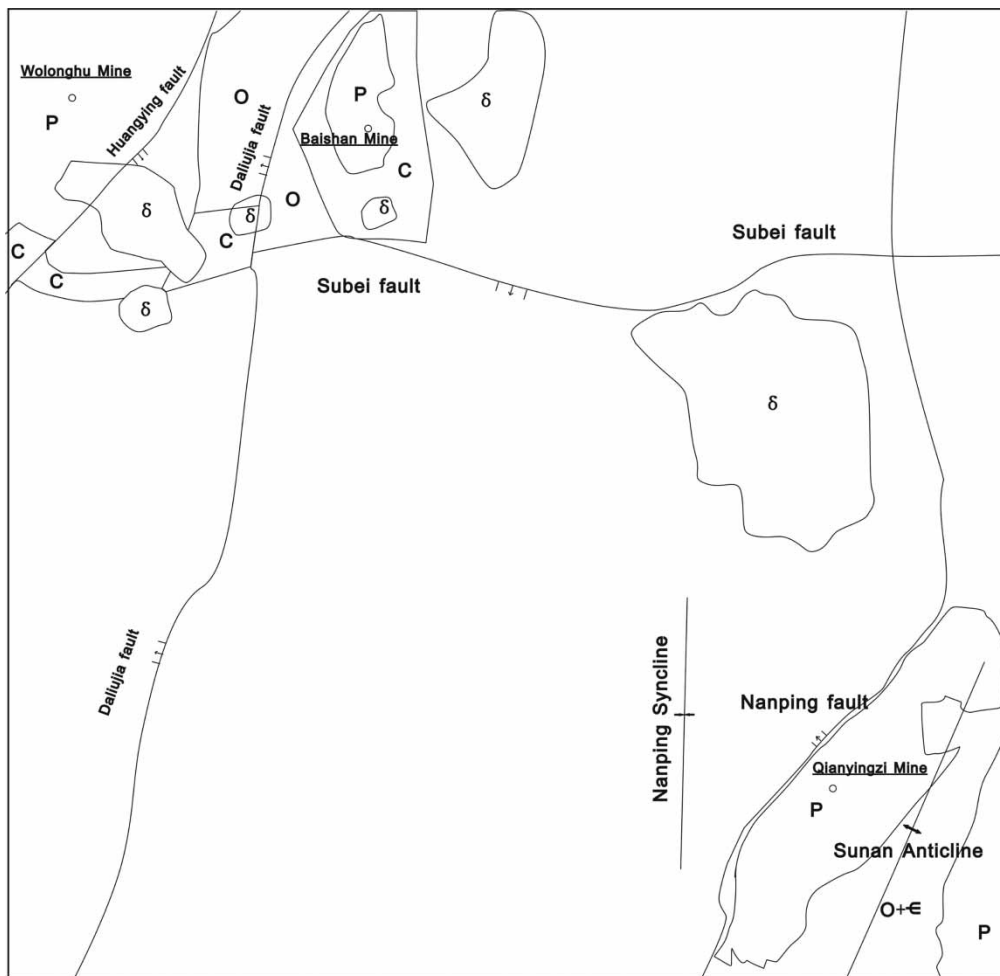


Figure 1 | Location of study area in Northern Anhui Province, China.

Table 1 | Hydrological characteristics of aquifer in the Huaibei mining area

Aquifer	Rock type	Thickness (m)	Depth (m)	Water type
Quaternary	Orange-deep yellow mudstone, sandstone and conglomerate	20–57	220–280	Cl-SO ₄ -Ca,Na
Coal bearing*	Mudstone, siltstone, sandstone and coal seams, and a small amount of limestone	37–128	280–400	SO ₄ -HCO ₃ -Na
Taiyuan Fm	Black limestone, mudstone, siltstone and thin coal seam	129–130	400–530	Cl-HCO ₃ -Na
Ordovician limestone	Thick layer of light gray limestone	<136	530–680	HCO ₃ -Na,Ca

Note: Synthesized from Gui and Chen [8].

**Figure 2** | Simply geological map of the study area.

Sampling and analysis

Our study focused on the groundwater from the coal bearing aquifer that sandstone is dominant, thus, the water samples were collected from typical Coal Mine of the Huaibei mining area, Northern Anhui province, such as Qianyingzi Coal Mine, Baishan Coal Mine and Wolonghu Coal Mine (Figures 1 and 2), where water runoff in coal bearing aquifer is limited. In addition, the published hydro-geochemical information of these Coal Mines is absence, these hydro-geochemical data and deduction could be as

basis for the sustainable development of groundwater, and then enrich the information about the water-rock interactions. In total twenty three water samples were collected via drainage holes in alleys. All water samples were collected from the main coal seam in Permian, with the depth between 486.8 to 601.2 m.

Water samples were filtered through 0.45 μm pore-size membrane and collected into polyethylene bottles that had been cleaned using trace element clean procedures. All the twenty three samples were analyzed for major ions, and ten samples were selected to determine the isotopic composition of oxygen and deuterium.

Major ions were analyzed in the analysis testing center of department of coal geology of Anhui province, China. The K^+ and Na^+ were analyzed by atomic absorption spectrometry, SO_4^{2-} and Cl^- by ion chromatography, Ca^{2+} and Mg^{2+} by EDTA titration and alkaline by acid-based titration. The isotopic compositions were analyzed in the laboratory of Institute of Karst Geology, Chinese Academy of Geological Sciences. $\text{CO}_2\text{-H}_2\text{O}$ equilibrium method was introduced to process the ^{18}O specimen, and uranium reduction process method was introduced for preparation of the δD specimen. $\delta^{18}\text{O}$ and δD were analyzed by mass spectrometry. The isotopic data are reported with respect to standard mean ocean water (SMOW), and $\delta^{18}\text{O}$ and δD have an overall precision of 0.2 and 2 ‰, respectively.

The piper diagram and calculates about carbonate equilibrium, total dissolved solids (TDS), density, conductivity and hardness were accomplished by software Aqqa, the statistical of samples data were completed by the SPSS (version 17).

RESULTS AND DISCUSSION

Major ion chemistry

The analytical result of groundwater samples are listed in Table 2. The chemical characteristics of groundwater are discussed based on the chemical data. The chemical data for sandstone water show that $\text{Na}^+ + \text{K}^+$ and HCO_3^- are the dominant element (Table 2, Figure 3). In general, the pH values of groundwater varied from 7.9 to 8.9, with an average value 8.4, which indicates water is alkaline in nature. The amount of TDS of groundwater ranges from 686 to 5165 mg/L, with an average of 1,894 mg/L. The electrical conductivity average value were 1917 $\mu\text{S}/\text{cm}$ in the study area, which calculated by the software Aqqa. The ionic balance of chemical data was also checked, and the result showed that the % difference of Anion-Cation balance ranging from 0.03 to 4.24, with average value 1.47, all the data could be satisfied the desire to analysis. The mineral saturations are supersaturated for Calcite and Aragonite, with the values of mineral saturation between 0.66 to 1.40 and 0.49 to 1.23, with the average 1.00 and 1.84, respectively.

The geochemical data of groundwater were plotted on a Piper diagram (Figure 3), some information could be printed. The major cations in groundwater are $\text{Na}^+ + \text{K}^+$ for most of the samples, except two samples from Wolonghu coal mining, which characterized by the high concentrations in Ca^{2+} and Mg^{2+} . The major anions are SO_4^{2-} and HCO_3^- , with the low degree of content of Cl^- . Almost all the ground water could be described the $\text{SO}_4\text{-HCO}_3\text{-Na-K}$ type. These water samples could be divided two types in detail, the $\text{Na} + \text{K-HCO}_3$ and Ca-Mg-SO_4 type.

The rectangular field of the plot describes the primary character of the water including the permanent and temporary hardness domain, and eight sub-fields could be divided from the rectangular field, each of which represents a water type and hardness domain [3]. The geochemical data of groundwater were plotted on the rectangular field diagram (Figure 4). Three groups of groundwater samples could be divided from the diagram, the first groups could be characterized by alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions, which represent Ca-Mg-Cl type of water. Such water has permanent hardness and does not deposit residual sodium carbonate in irrigation use.

Table 2 | Major solute composition (in mg/L) and other relations parameter from coal bearing aquifer in Northern Anhui province, China

Sample No	K ⁺ + Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	Hardness	Alkalinity	PH	TDS	δD	δ ¹⁸ O
QYZ1	652.33	4.75	3.84	181.67	375.79	738.59	115.78	27.68	798.75	8.54	1714	- 58.5	- 8.58
QYZ2	582.45	3.17	3.36	282.21	4.53	817.06	129.4	21.75	885.81	8.9	1425	- 64.8	- 8.59
QYZ3	1178.38	24.54	4.8	199.31	1687.97	736.28		81.05	603.79	8.05	3675	- 68.5	- 8.59
QYZ4	1718.35	26.13	11.53	149.93	2837.57	687.81	70.38	112.68	681.4	8.55	5165	- 64.8	- 8.58
QYZ5	543.67	6.33	3.84	188.73	125.13	853.99	70.38	31.63	817.67	8.31	1377	- 64	- 8.36
QYZ6	471.82	5.54	3.84	146.4	21.4	860.91	72.65	29.65	827.14	8.65	1164	- 67.8	- 8.75
QYZ7	524.29	16.63	19.2	407.44	8.64	817.06		120.59	670.04	8.02	1394	- 64.2	- 8.7
QYZ8	949.88	102.13	87.37	287.5	1899.53	290.82	34.05	614.81	296.27	8.36	3516	- 66.9	- 8.78
BSH17	504.23	44.34	30.73	146.4	513.27	634.72	43.13	237.23	592.44	8.38	1601	- 61.7	- 8.76
BSH18	479.62	41.96	28.8	153.54	504.62	565.48	36.32	223.39	524.3	8.36	1539		
BSH23	494.27	31.02	28.69	143.84	510.38	698.78		195.59	573.05	8.17	1569		
BSH24	492.59	31.02	26.81	145.55	495.15	701.26		187.85	575.08	8.23	1557		
BSH25	498.87	39.55	28.22	147.26	499.68	611.65		214.96	745.87	8.11	1531		
WLH20	537.74	5.43	5.64	183.22	5.76	1060.57	80.43	36.79	1003.85	8.67	1359		
WLH21	553.89	4.65	3.29	190.07	9.47	958.97	136.49	25.18	1014.01	8.89	1221		
WLH14	714.4	6.2	1.88	169.53	4.53	1499.17	116.99	23.24	1424.48	8.6	1775		
WLH15	708.68	7.76	1.41	178.09	2.47	1476.86	114.56	25.18	1402.13	8.46	1762		
WLH1	593.4	4.75	5.28	190.49	8.64	1036.33	118.05	33.61	1046.7	8.43	1449	- 66.9	- 8.77
WLH2	589.77	3.96	2.88	159.79	6.17	1006.32	118.05	21.75	1022.09	8.63	1425		
WLH4	175.58	284.22	204.51	261.05	1350.87	191.57		1551.85	157.1	8	2385		
WLH5	189.34	276.3	204.51	262.81	1354.58	196.19		1532.08	160.89	7.9	2396		
WLH6	783.33	4.75	2.88	192.26	20.99	1384.85	179.35	23.72	1434.72	8.36	1886		
WLH12	156.68	40.38	30.25	125.23	211.97	205.42		225.36	168.46	8.2	686		

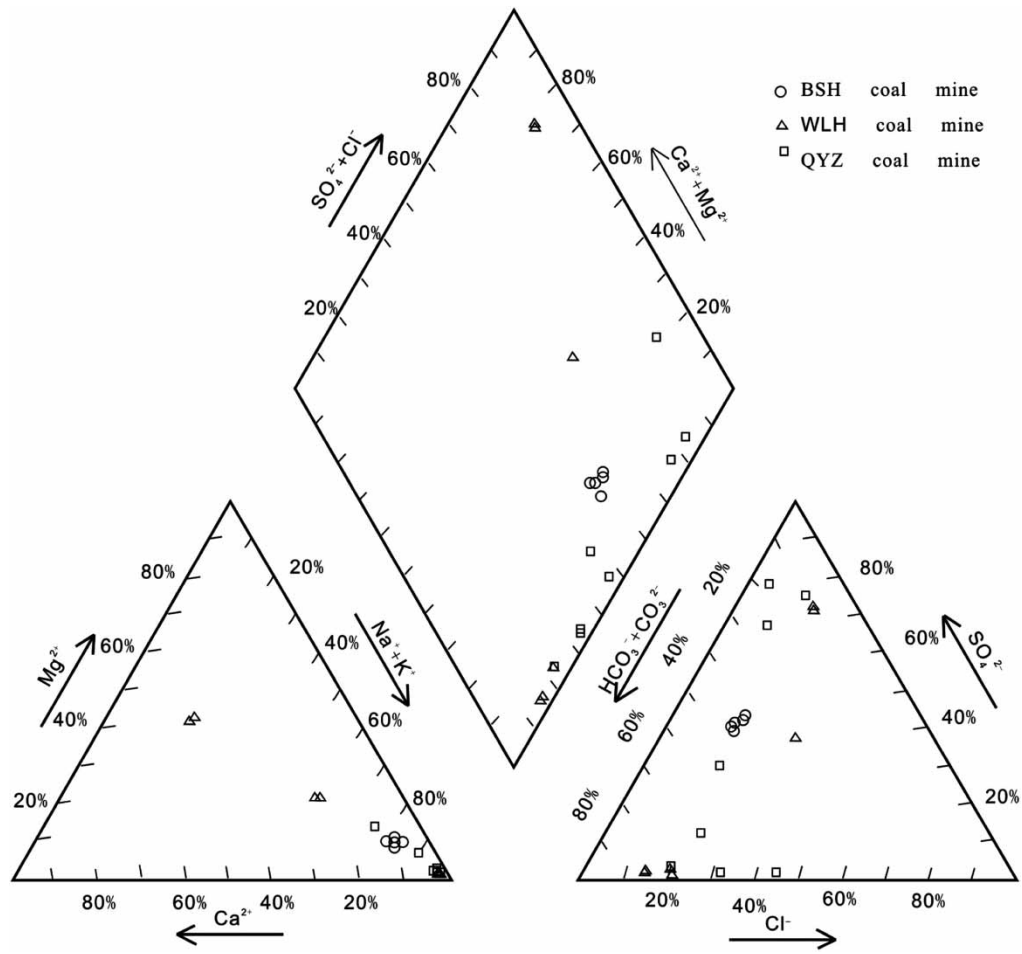


Figure 3 | Piper diagram of groundwater from coal bearing aquifer in Northern Anhui province, China.

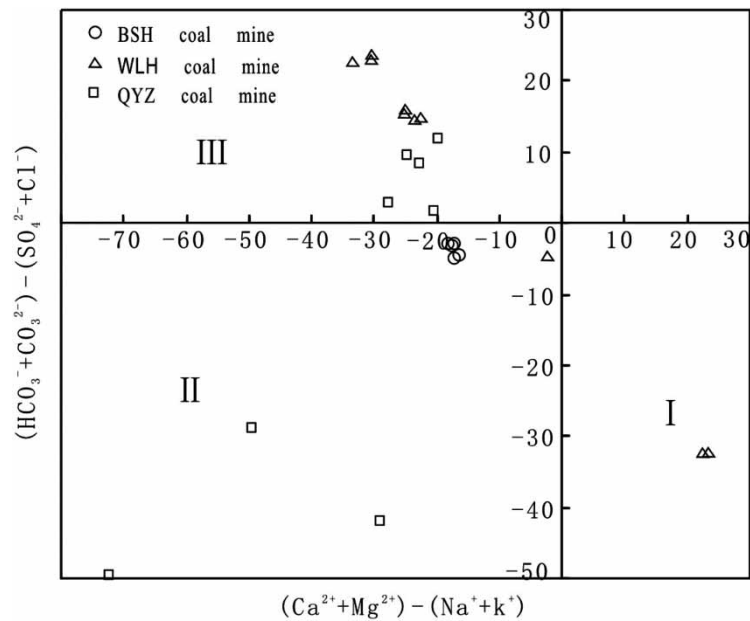


Figure 4 | Diagram demonstrating geochemical classifications of groundwater from coal bearing aquifer in Northern Anhui province, China.

The second groups could be described alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions, which represent Na-Cl-SO₄ type of water. And such water always creates salinity problems in irrigation and drinking. The third group is dominated in the study area, with twelve samples plotted in the sub-field. Alkali metals exceed alkaline earth and weak acidic anions exceed strong acidic anions, which represent Na-HCO₃ type water. And such water could cause foaming problems for depositing residual sodium carbonate in irrigation use.

Water-rock interaction

In order to identify the hydro-geochemical characterization and the mechanisms in the aquifer region of the study area, various conventional graphical plots had been completed. The possible identified processes are explained below in detail. The chloro-alkaline index (CAI) was used to define the ionic exchanges between water and the aquifer rocks and assess the chemical evolution [9]. The CAI was calculated using the following Equation (All values are expressed in meq/l):

$$CAI = r \frac{Cl^- - (K^+ + Na^+)}{Cl^-}$$

The ratio is positive when the sodium and potassium contents are low, indicating the interchangeable cations released from minerals are limited. The groundwater has been slightly in contact with the wall rock of aquifer. Otherwise, the ratio is negative when the sodium and potassium contents are high, that may be caused by the interchangeable cations yield from the minerals easily. This phenomenon of base exchanges is most generally known with the aluminosilicated clays formed by layers or sheets whose cohesion is ensured by the existence of interlayer cations and water [2]. The values of CAI are plotted in Figure 5, all the values are negative revealed that there is a reverse ion exchange, thus, the groundwater has exchanged Ca and Mg ions against the Na and K ions of the aquifer rocks [10].

The plot of Ca²⁺ + Mg²⁺ versus SO₄²⁻ + HCO₃⁻ will be close to the 1:1 line if the dissolution of calcite, dolomite and gypsum are the dominant reactions in a system. Ion exchange tends to shift the points to right due to an excess of SO₄²⁻ + HCO₃⁻ [11]. If reverse ion exchange is the process, it will shift the points to the left due to a large excess of Ca²⁺ + Mg²⁺ over SO₄²⁻ + HCO₃⁻. The plot of Ca²⁺ + Mg²⁺ versus SO₄²⁻ + HCO₃⁻ (Figure 6(a)) shows that almost all the groundwater sample below the 1:1 line which indicate ion exchange is obviously. In addition, all the sample points are placed below the 1:1 line, what combined with the high concentrations of Na⁺ + K⁺, indicating the silicate weathering in the hydro-geochemical process.

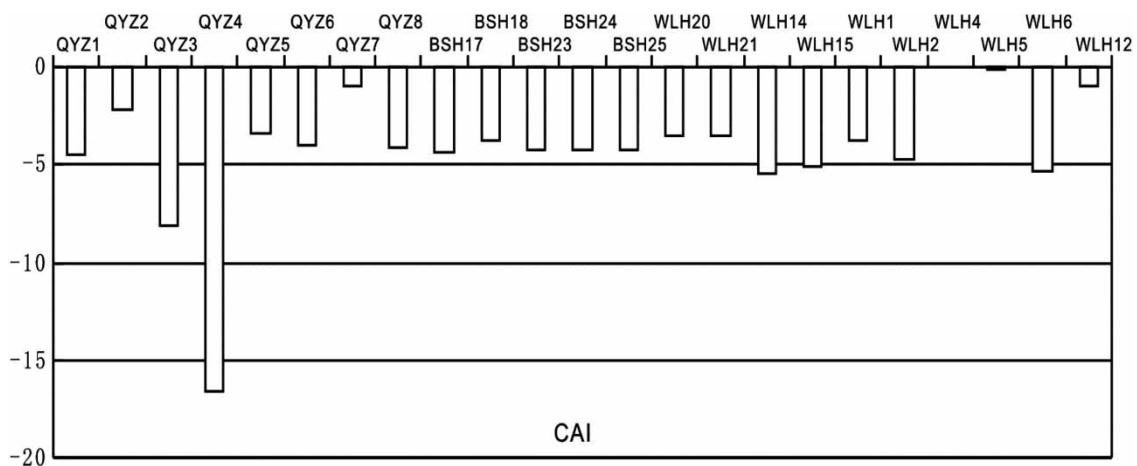


Figure 5 | Diagram of Chloro Alkaline Index (CAI) for the groundwater from coal bearing in Northern Anhui province, China.

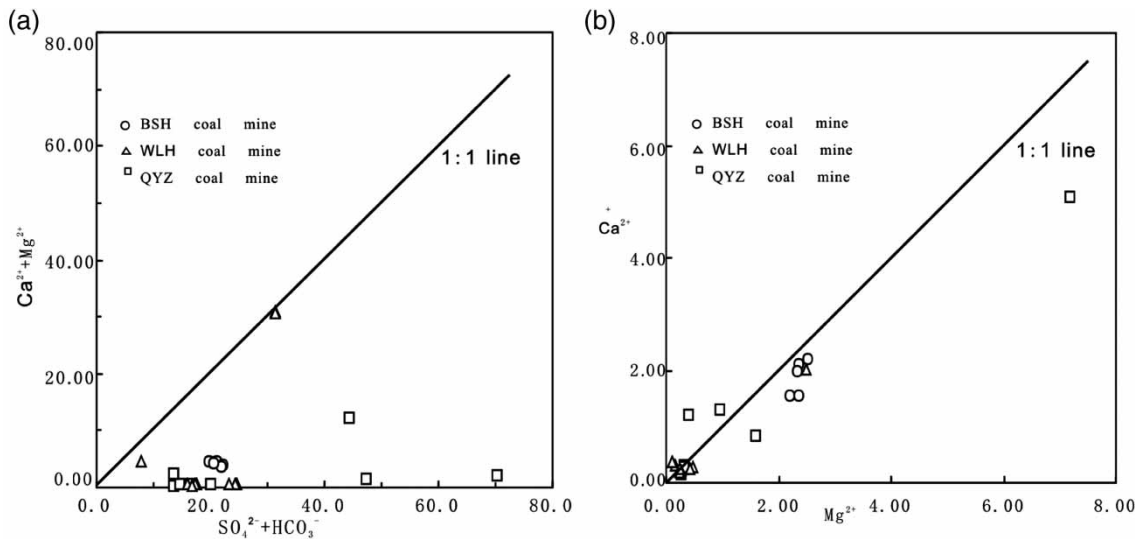


Figure 6 | The scatter diagrams of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$, Ca^{2+} versus Mg^{2+} of groundwater from coal bearing aquifer in Northern Anhui province, China.

The plot of Ca^{2+} versus Mg^{2+} of the groundwater suggests the dominance of the dissolution of calcite and dolomite that present in the Coal bearing formation (Figure 6(b)). If the points near to the 1:1 line, dissolution of dolomite should occur, whereas a high ratio is indicative of great calcite contribution. Most of the samples near to the line 1:1, and some samples above the line 1:1, what should be indicated that the dissolution of dolomite is exited, whereas the calcite weathering is dominant. The view what combined with the calculating result of the mineral saturations, the result calcite in groundwater were dominant would be acceptable.

Factor analysis

The previous studies have revealed that the obtained matrix of hydro-geochemical data was subjected to multivariate analytical technique, which was an efficient way of displaying complex relationships among many variables and their roles [12]. In order to understand the character and relation between the hydro-geochemical data, the multivariate methods of statistical analysis were applied, such as correlation matrix and Principal Component Analysis (PCA). The correlation matrix and PCA of the results is present in Table 3 and 4.

Table 3 | Correlation matrix of parameter for groundwater form coal bearing aquifer in Northern Anhui province, China ($n = 23$)

	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	Hardness	Alkalinity	PH	TDS
Na^+	1.00										
Ca^{2+}	-0.36	1.00									
Mg^{2+}	-0.39	1.00	1.00								
Cl^-	-0.07	0.33	0.36	1.00							
SO_4^{2-}	0.57	0.48	0.45	0.08	1.00						
HCO_3^-	0.28	-0.66	-0.67	-0.16	-0.54	1.00					
CO_3^{2-}	0.24	-0.49	-0.50	-0.12	-0.43	0.74	1.00				
Hardness	-0.38	1.00	1.00	0.35	0.46	-0.67	-0.50	1.00			
Alkalinity	0.27	-0.66	-0.67	-0.18	-0.55	0.98	0.82	-0.67	1.00		
PH	0.24	-0.58	-0.58	-0.23	-0.35	0.52	0.78	-0.58	0.59	1.00	
TDS	0.80	0.26	0.22	0.12	0.93	-0.20	-0.15	0.24	-0.21	-0.16	1.00

Table 4 | Variance explained and component matrixes for groundwater from coal bearing aquifer in Northern Anhui province, China

Component	PC1	PC2	PC3
Alkalinity	0.95	- 0.58	- 0.14
HCO ₃ ⁻	0.92	- 0.58	- 0.14
CO ₃ ²⁻	0.89	- 0.40	- 0.09
PH	0.77	- 0.54	- 0.06
Mg ²⁺	- 0.77	0.96	0.07
Hardness	- 0.77	0.95	0.08
Ca ²⁺	- 0.77	0.95	0.10
Cl ⁻	- 0.13	0.60	0.05
TDS	- 0.22	0.23	0.98
SO ₄ ²⁻	- 0.55	0.39	0.89
Na ⁺ + K ⁺	0.32	- 0.35	0.88
Initial Eigen value	5.82	2.45	1.21
Percentage of variance	52.93%	22.31%	10.99%
Cumulative % of varince	52.93%	75.24%	86.23%

It can be seen from Table 3, that strong positive correlations between cations was observed for Ca²⁺ – Mg²⁺, with the correlation matrix nearing to 1, what could be indicated that dissolution of dolomite should occur in the hydro-geochemical process. The positive correlations exist between SO₄²⁻ and Na⁺ + K⁺, Mg²⁺ and Ca²⁺, with the correlation matrix 0.57, 0.45 and 0.48, what also showed the sulfuric acid is the weathering reactions.

The Principle Component Analysis was conducted for obtaining the detailed statistical information. The rotated PCA loading are given in Table 4. Three Principal Components emerged with more than 86.23% of cumulative variance. Factor 1 accounts 52.93% variance in the data. The variable present in this factor are HCO₃⁻, CO₃²⁻, PH and alkalinity, which indicates the water in natural with slight carbonic acid weathering reaction. Factor 2 accounts for 22.31% of total variance, with the high loading for Mg²⁺, Ca²⁺, Cl⁻ and hardness, attributed from the calcite and dolomite weathering. Factor 3 account 10.99% of variance, indicated the process of feldspar weathering by the sulfuric acid. The plot of score between PC1 and PC2 (Figure 7) were also supported this view.

In summary, the different hydro-geochemical processes like weathering, ion-exchange and dissolution could be identified by the multivariate analytical technique, and the results are accord with the frontal information.

Isotopic composition of groundwater

The results of the stable isotope analysis for groundwater in coal bearing aquifer are plotted in Figure 8. The stable isotope values for groundwater samples were listed in Table 2. It can be seen, the value of δD varied between -68.5 to -58.5, with an average of -64.81‰ (n = 10), and the δ¹⁸O ranging from -8.78 to -8.36, with an average of -8.65‰ (n = 10), respectively. More information about the environmental isotopic are required to be compared with the feature of groundwater samples. The local meteoric water line (LMWL), local surface water line (LSWL) and global meteoric water line (GMWL) about the relation between δD and δ¹⁸O were gathered. The LMWL was defined from the measured data of the stable isotopes, which described by δD = 7.9*δ¹⁸O + 8.2 [13], the GMWL was defined by Craig (1961), δD = 8*δ¹⁸O + 10.56 [14], and the LSWL is printed the δD = 6.74*δ¹⁸O - 3.33 [15]. All the lines and the isotopic message of the

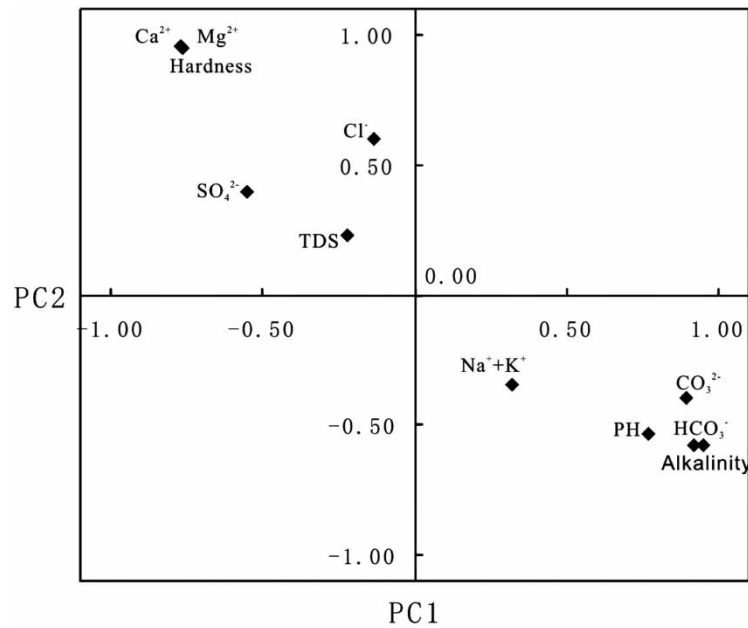


Figure 7 | Plots of the Score between Principle Component 1 and Principle Component 2.

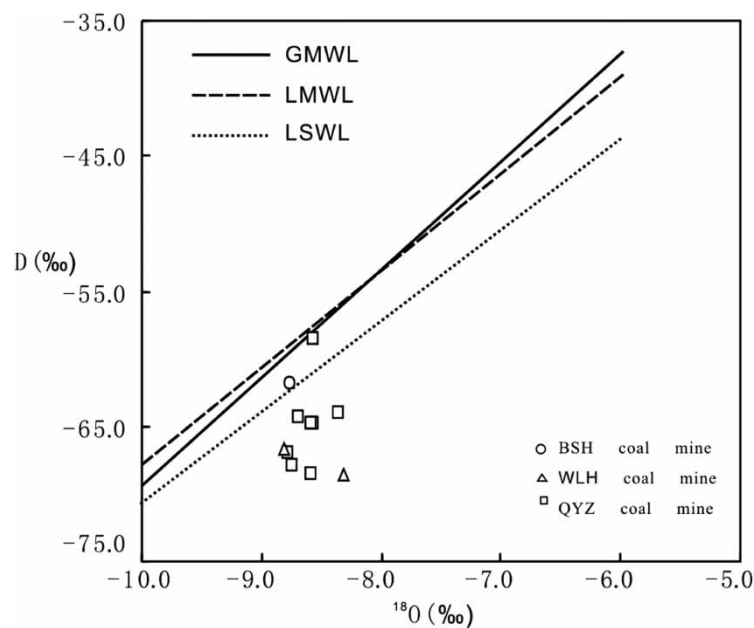


Figure 8 | Diagram between $\delta^{18}\text{O}$ and δD of groundwater from coal bearing aquifer in Northern Anhui province, China.

groundwater samples are plotted in Figure 6. It can be concluded that the LSWL are below the LMWL and GMWL, what indicated that the surface water was shaped through the evaporation [16].

Almost all the groundwater samples are plotted below the LMWL and GMWL, except one groundwater sample be on the GMWL, what combined with the feature two samples among the LMWL and LSWL, indicating that the coal bearing aquifer groundwater be supplied from the meteoric water, with varied degree evaporation or not. In addition, the $\delta^{18}\text{O}$ and δD are slightly variety, and the relationship between $\delta^{18}\text{O}$ and δD in the groundwater form coal bearing aquifer could be defined as $\delta\text{D} = 5.77 * \delta^{18}\text{O} - 14.9$. Further more; the values of δD are variety obviously, whereas the $\delta^{18}\text{O}$ are stabilization reversely. The plots for δD upward movement with a direction vertical or approximate

to vertical, and all the plots are not exceed the LMWL, what revealed that the δD have been drifted obviously.

The variety of $\delta^{18}O$ and δD could be caused by such factors as evaporation, reservoir temperature, residence time and rock-water interaction [17]. The sight presented in Figure 8 could be interpreted by the coal bearing aquifer being reducing environment, where exchange reaction of δD between groundwater and alkyl is more markedly, whereas the exchange of $\delta^{18}O$ have been equilibrium. And the deduction could be supported by the previous study [15].

CONCLUSIONS

The concentration of major ions and isotopic in groundwater from coal bearing aquifer, Northern Anhui province, China had been analyzed, combined with the conventional graphical and multivariate statistical approach, a series of conclusion could be obtained:

1. All the twenty three water samples could be divided two types through the Piper Diagram: $Na-HCO_3$ and $Ca-Mg-SO_4$, the water is alkaline in nature with the average PH values 8.4. Three groups of groundwater could be divided form the rectangular field, the $Ca-Mg-Cl$, $Na-Cl-SO_4$ and $Na-HCO_3$ type water, the $Na-Cl-SO_4$ and $Na-HCO_3$ type groundwater could be created salinity or foaming problems in irrigation, and the $Ca-Mg-Cl$ type water without any hazard.
2. The reverse ion exchanges were observed for all the CAIs are negative. The feldspar weathering contributing the Na and K ions to groundwater, which is a dominating weathering process. In corresponding, the sulfuric acid is the weathering agent along with the carbonic acid. Though the calcite and dolomite weathering are exited obviously, but the degree is limited.
3. The stable isotope values for groundwater were found to vary between -68.5 and -58.5 in $\delta^{18}O$ with an average of -64.81‰ and from -8.78 to -8.36 in δD with an average of -8.65‰ , respectively. Most of the groundwater samples are plotted below the LMWL and GMWL, what reflected the coal bearing aquifer groundwater mainly supplied from the meteoric water. The values of δD are drifted obviously, moving to the LMWL with a direction vertical, what could be caused by the exchange reaction of δD between groundwater and alkyl.

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