

Water rock interaction in deep groundwater aquifers of coal mining area: qualitative and quantitative approaches based on hydrochemistry

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Present study indicates that groundwater from three aquifer systems have different concentrations of major ions. This implies that kinds and degrees of water rock interactions in them are different with each other. Relationships between major ions or their ratios (e.g. Gibbs diagrams, $\text{Na}^+\text{-Cl}^-$ relationships), as well as statistical analyses (correlation and factor analyses) suggested that water rock interaction is the main mechanism controlling the groundwater chemistry. EPA Unmix model has identified two sources responsible for the hydrochemistry of the groundwater, sulfate-carbonate (source 1) and silicate-chloride (source 2) sources. Groundwater from the limestone and coal bearing sandstone aquifer systems are mainly contributed by source 1 and 2, respectively. As to the groundwater from the loose layer aquifer system, the contributions of the source 1 and 2 are 4: 6, respectively, and the result is consistent with previous exploitation.

[Keywords: Groundwater, water-rock interaction, hydrochemistry, statistical analysis, quantitative analysis]

Introduction

Hydro-geochemistry had attracted a series of studies because its unique role in water source identification, which is considered to be important for water disaster treatment in coal mines after water inrush because the first task is identifying the source of water. And therefore, large numbers of studies have been carried out¹⁻⁸. However, the mechanism about water-rock interaction in the groundwater system has not been well understood, which is considered to be the basis for applying of the hydrochemistry of groundwater for water source identification. Without a right understanding about the water-rock interaction, only the data can be applied by mathematical or statistical methods, no one can explain why? And therefore, the truth that the model for water source identification we established in one coal mine cannot be migrated to another coal mine easily.

In this study, twenty-two groundwater samples from three representative aquifer systems in the Wolonghu coal mine, northern Anhui Province, China have been collected and analyzed for their major ion concentrations, and qualitative and quantitative methods have been applied for the inversion of water rock interactions in the aquifer systems, which can

provide information for understanding the hydro-geochemical processes, and then, the water hazard controlling.

Materials and Methods

The Wolonghu coal mine is located 25 km southwest to the Suixi County, northern Anhui Province, China (Fig. 1) with a length of 8-9 km from south to north, and the width is 3-4 km from east to west, the total area is 28.9 km². Previous investigations revealed that the groundwater system in the mine can be divided into three major aquifer systems from shallow to deep: loose layer aquifer system (LA), coal bearing sandstone aquifer system (CA), and the underlying limestone aquifer system (TA).

The depth of LA is up to 234 m, and the host rocks are mainly composed of clay, sandstone, and conglomerate, silicate and carbonate minerals are the main mineral phases. Total thickness of CA is approximately 240 m, and the water storage is medium, the main rock type is sandstone, silicate minerals are dominant in the aquifer. The TA is mainly composed of limestone and also rich with water because of its karstic characteristics.

A total of twenty-two water samples (ten from LA, seven from CA and five from TA) have been collected in the allay. All of the water samples were filtered through 0.45 μm pore-size membrane and collected into 2 L polyethylene bottles that had been cleaned in the laboratory by using deionized water for three times. Analytical processes were conducted in the Engineering and Technology Research Center of Coal Exploration in Anhui Province, China, following the methods below: ($\text{Na}^+ + \text{K}^+$), Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Cl^- were analyzed by Ion Chromatography, and alkalinity (including HCO_3^- and CO_3^{2-}) was analyzed

by acid–base titration.

For data treatment, descriptive statistics were firstly processed by Excel for calculating the min, max, mean concentrations of each major ion from different aquifer systems. And then, traditional (including Gibbs diagrams, relationship between major ions)⁹⁻¹¹ and statistical methods (correlation analysis and factor analysis)¹²⁻¹⁵ have been applied to the data for getting the qualitative information about water rock interactions, and then the EPA Unmix model has been applied for obtaining the quantitative information¹⁶⁻¹⁸.

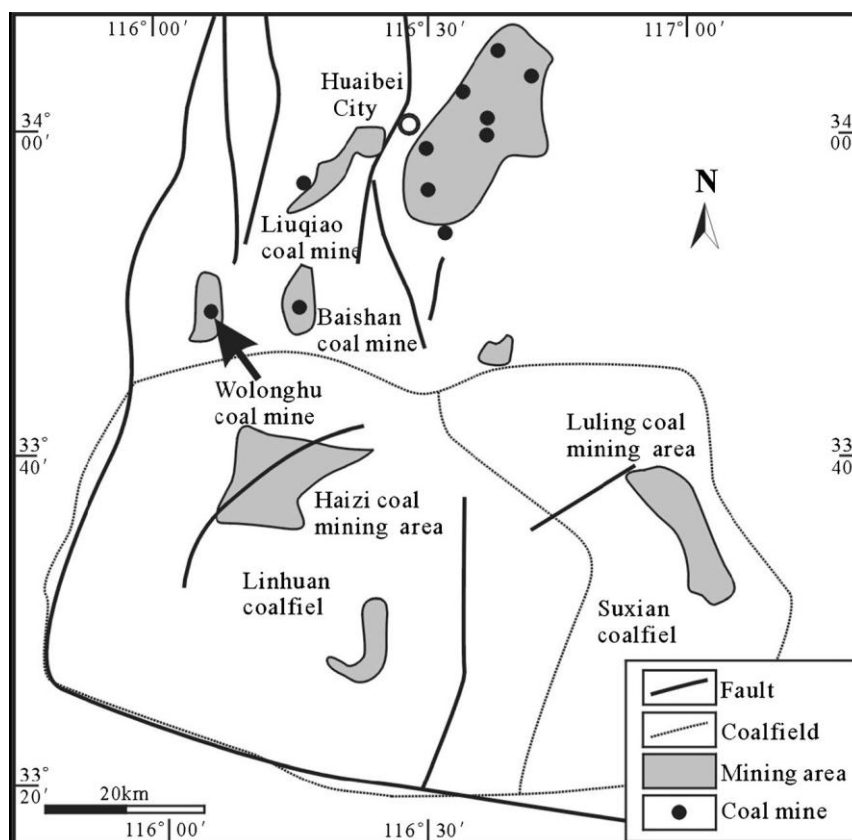


Fig. 1—Location of the study area.

Results and Discussions

Concentrations of major ions:

All of the analytical results are synthesized in Table 1. As can be seen from the table, the water samples from the LA possess the lowest mean ($\text{Na}^+ + \text{K}^+$) (377 mg/l) and Cl^- (148 mg/l) concentrations; CA groundwater samples have the highest mean ($\text{Na}^+ + \text{K}^+$) (640 mg/l) and HCO_3^- (1203 mg/L) and lowest mean Ca^{2+} (5 mg/l), Mg^{2+} (3 mg/l) and SO_4^{2-} (8 mg/l) concentrations, whereas TA groundwater samples

shows the highest mean Ca^{2+} (400 mg/l), Mg^{2+} (200 mg/l), Cl^- (375 mg/l), and SO_4^{2-} (2176 mg/l) concentrations relative to other aquifers.

Classification of hydro-chemical types for groundwater is important because of the dominant anion species of water change systematically from HCO_3^- , SO_4^{2-} to Cl^- as groundwater flows from the recharge zone to the discharge zone¹⁹. Classification of water in this study is based on the concentration of cations and anions by using Aquachem and Piper

diagram, and the result is shown in Fig. 2. The result indicates that the groundwater samples from the CA are Na-HCO₃ and Na-HCO₃-Cl types, whereas the samples from the LA are classified to be Na-HCO₃-

SO₄-Cl, Na-Mg-HCO₃-SO₄ and Na-HCO₃-SO₄ types. Moreover, the TA samples include Na-Ca-Mg-SO₄ and Ca-Mg-Na-SO₄ types.

Aquifer	N	Na ⁺ +K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
LA	10	299-495 (377)	29.5-70.5 (52.0)	37.0-80.2 (56.6)	125-185 (148)	247-415 (319)	561-1157 (803)	0-0 (0)
CA	7	538-783 (640)	3.96-7.76 (5.36)	1.41-5.64 (3.32)	170-196 (186)	2.47-21.0 (8.29)	959-1499 (1203)	80.4-179 (123)
TA	5	423-567 (505)	316-439 (400)	178-245 (200)	351-392 (375)	1824-2288 (2176)	131-289 (174)	0-0 (0)

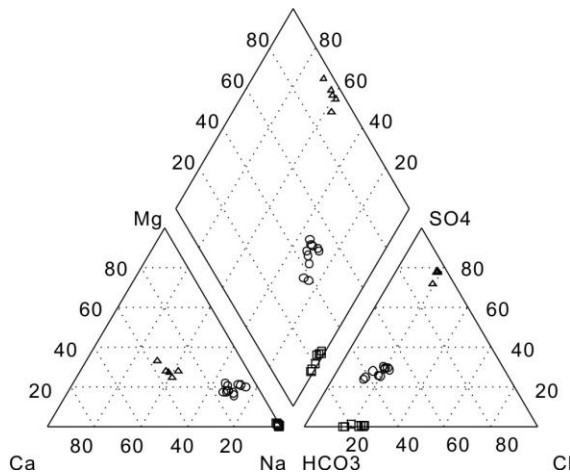


Fig.2—Piper diagram (Circle - LA, Square - CA, Triangle - TA).

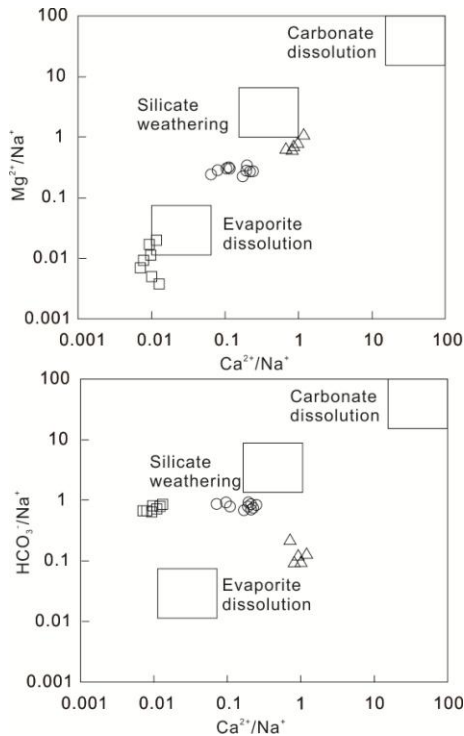


Fig.3—Na⁺ normalized Ca²⁺-Mg²⁺ and Ca²⁺-HCO₃⁻ diagrams (Circle - LA, Square - CA, Triangle - TA).

Qualitative analysis – traditional methods:

Gibbs diagram²⁰ was firstly applied for understanding the relationships between the chemical components of water and their aquifer rocks. Gibbs diagram consists of three distinct fields namely precipitation dominance, evaporation dominance and rock dominance. In this study, Gibbs ratio I values (Cl⁻/(Cl⁻+HCO₃⁻), meq/l) are 0.17 to 0.30 for LA, 0.16-0.25 for CA and 0.68-0.83 for TA, respectively, whereas Gibbs ratio II values ((Na⁺+K⁺)/(Na⁺+K⁺+Ca²⁺), meq/l) are 0.66-0.72 for LA, 0.97-0.99 for CA and 0.30-0.42 for TA, respectively. Such results indicate that water-rock interactions are the main mechanism controlling the groundwater chemistry in this study. Including either weathering of silicate minerals and dissolution of carbonates or evaporates.

Such a consideration can be further demonstrated by the relationship between Na⁺ normalized Ca²⁺, Mg²⁺ and HCO₃⁻. As can be seen from Fig. 3, weathering of silicate and dissolution of evaporate are considered to be the main processes controlling the chemistry of groundwater from the CA and LA, however, dissolution of carbonate and evaporate are important for controlling the chemistry of groundwater from the TA.

Some other methods can also be used for identifying the water rock interactions in the groundwater, such as relationship between Na⁺ and Cl⁻, and (Ca²⁺+Mg²⁺) versus (HCO₃⁻+SO₄²⁻)²¹ in Fig. 4. All of the groundwater samples in this study have higher Na⁺ concentrations relative to Cl⁻, especially the CA samples, indicating that the weathering of silicate minerals are responsible for the Na⁺ in the groundwater because dissolution of halite will generate Na⁺/Cl⁻ equal to 1:1. It can also be demonstrated by the relationship between (Ca²⁺+Mg²⁺) and (HCO₃⁻+SO₄²⁻), that higher (HCO₃⁻+SO₄²⁻) is observed relative to (Ca²⁺+Mg²⁺) because

weathering of silicate minerals can generate additional HCO_3^- . Moreover, the high $\text{Na}^+/\text{Ca}^{2+}$ ratios (> 2) of CA and LA groundwater samples (86.4-143 and 4.13-10.5, respectively) suggest that weathering of silicate minerals are significant in the CA and LA, whereas the low $\text{Na}^+/\text{Ca}^{2+}$ ratios (0.84-1.41) of the TA samples implying that weathering of silicate minerals is not obvious in the TA.

The study of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios of groundwater samples herein suggests the dissolution of calcite and dolomite. If the ratio of $\text{Ca}^{2+}/\text{Mg}^{2+} = 1$, dissolution of dolomite should occur and, the ratio higher than 1 is indicative of contribution from calcite. Much higher ratio (> 2) indicates weathering of silicate minerals. Two samples from the CA have $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios > 2 , indicating that weathering of silicate minerals; all of the five samples from the TA have $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratios between 1 and 2, suggesting that calcite dissolution is important in controlling the groundwater chemistry of TA.

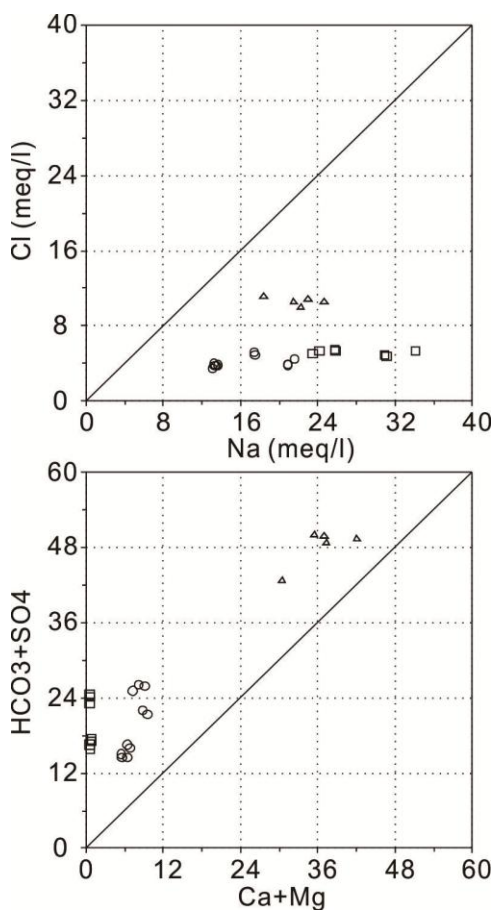


Fig.4— Na^+/Cl^- and $(\text{Ca}^{2+}+\text{Mg}^{2+})$ versus $(\text{HCO}_3^-+\text{SO}_4^{2-})$ diagrams (Circle - LA, Square - CA, Triangle - TA).

Qualitative analysis – statistical methods:

Statistical methods, especially the correlation and factor analyses, have long been applied for geochemical data for understanding the relationships between chemical variables¹²⁻¹⁵.

Correlations between dissolved species can reveal the origin of solutes and the process that generated the observed water compositions. Degree of a linear association between any two of the water chemical parameters, as measured by the simple correlation coefficient, is presented in Table 2. The results show high correlations (significant at $\alpha=0.01$) between some pairs of parameters: Ca^{2+} - Mg^{2+} - Cl^- - SO_4^{2-} - HCO_3^- , whereas Na^+/K^+ shows moderate correlation with HCO_3^- (significant at $\alpha=0.05$). Such results suggest that the geochemical variations of these groundwater samples are related to two main factors: one is dissolution of Ca-Mg chloride, sulfate and carbonate minerals, another is weathering of silicate minerals.

As to the factor analysis, two factors with eigenvalue higher than one after varimax rotation have been obtained. The first one has high positive loadings of Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} , which accounts for 63.8% of variance information, whereas the second factor has high positive loadings of Na^+/K^+ and HCO_3^- and accounts for 22.9% variance information (Table 3). Such information suggests that dissolution of Ca-Mg chloride and sulfate minerals, and weathering of silicate minerals are responsible for the groundwater chemical variations. It can also be observed in Table 3 that HCO_3^- has high negative loading in factor one, which might be an indication of the exchange of HCO_3^- in water by Cl^- and SO_4^{2-} during groundwater discharge, because dissolution ability of carbonate minerals in water is weaker than sulfate and chloride minerals with similar conditions.

Quantitative analysis:

The EPA Unmix model, which was firstly applied for environmental studies, especially the air quality data, has been successfully applied in hydrochemical studies¹⁶⁻¹⁸. In this study, two sources have been identified and the results are shown in Fig. 5 and 6. These two sources have $\text{Min Rsq} = 0.98$, indicating that more than 98% of the variance information can be explained by the modeling and it is higher than the minimum requirement of the model ($\text{Min Rsq} = 0.8$). Moreover, the Min Sig/Noise is 8.67, also higher than the minimum requirement ($\text{Min Sig/Noise} > 2$). Therefore, it can be considered that the modeling is efficient²².

The detailed explanations about these two sources are as follows: Source 1 has the highest loadings of Ca^{2+} , Mg^{2+} and SO_4^{2-} , and moderate loading of Cl^- , the contributions of source 1 for these major ions are 100%, 88%, 100% and 52% (Fig. 5). Therefore, this source can be explained to be sulfate source, to a lesser extent, the carbonate source (related to Ca^{2+} and Mg^{2+}). Source 2 has the highest loadings of $\text{Na}^+ + \text{K}^+$ and HCO_3^- , and moderate loading of Cl^- , the contributions of source 2 for these major ions are 73%, 97% and 48% (Fig. 5). Therefore, this source can be explained to be silicate source, to a lesser extent, the chloride source (related to $\text{Na}^+ + \text{K}^+$).

Other information can be obtained from Fig. 6 is that groundwater samples from different aquifer systems have variable contributions from these two sources: source 1 has the highest contributions for the

groundwater samples from the TA (>90%), but lowest contributions for the samples from the CA (<10%). As to the samples from the LA, near 40% of the major ions are contributed by source 1. However, source 2 has >90%, <10% and near 60% contributions for the samples from the CA, TA and LA, respectively. In consideration with the truth that the major ions of these groundwater samples are mainly controlled by water-rock interactions, these different contributions might be an indication of the variations of the wall rock compositions of different aquifers: TA is mainly composed of carbonate rocks (calcite), whereas silicate minerals are dominant in the CA (sandstones). As to the LA, carbonate and silicate minerals are all exist with ratios near 4: 6. This consideration is similar to the previous exploitation by drilling (see in the Materials and Methods).

Table 2—Pearson correlation matrix (*and**mean significant at 0.05 and 0.01 levels).

	$\text{Na}^+ + \text{K}^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
$\text{Na}^+ + \text{K}^+$	1.000					
Ca^{2+}	-0.063	1.000				
Mg^{2+}	-0.174	0.962**	1.000			
Cl^-	0.216	0.942**	0.866**	1.000		
SO_4^{2-}	-0.057	0.996**	0.972**	0.936**	1.000	
HCO_3^-	0.520*	-0.841**	-0.818**	-0.692**	-0.830**	1.000

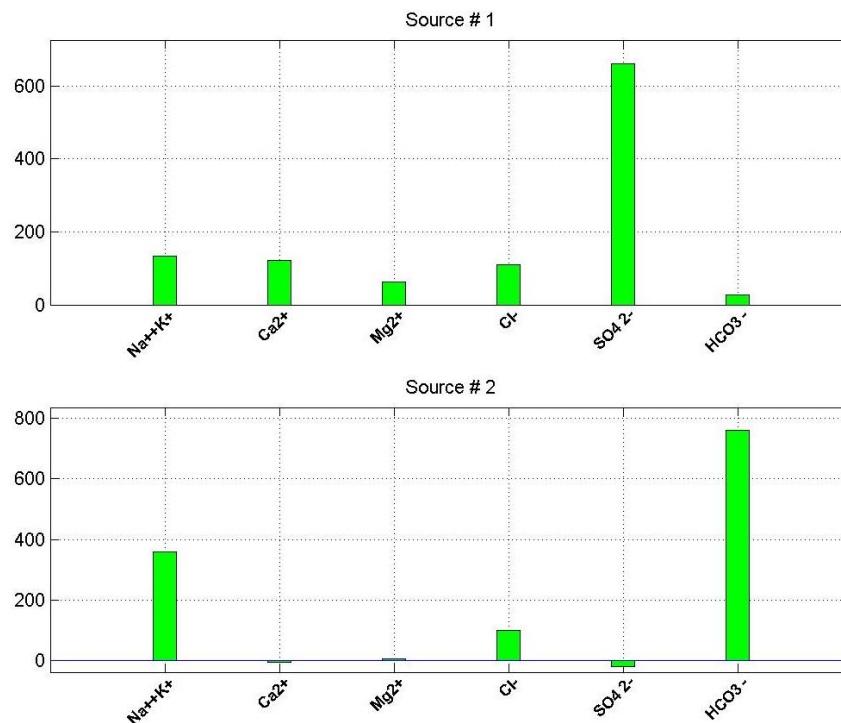


Fig. 5—Source compositions revealed by EPA Unmix model.

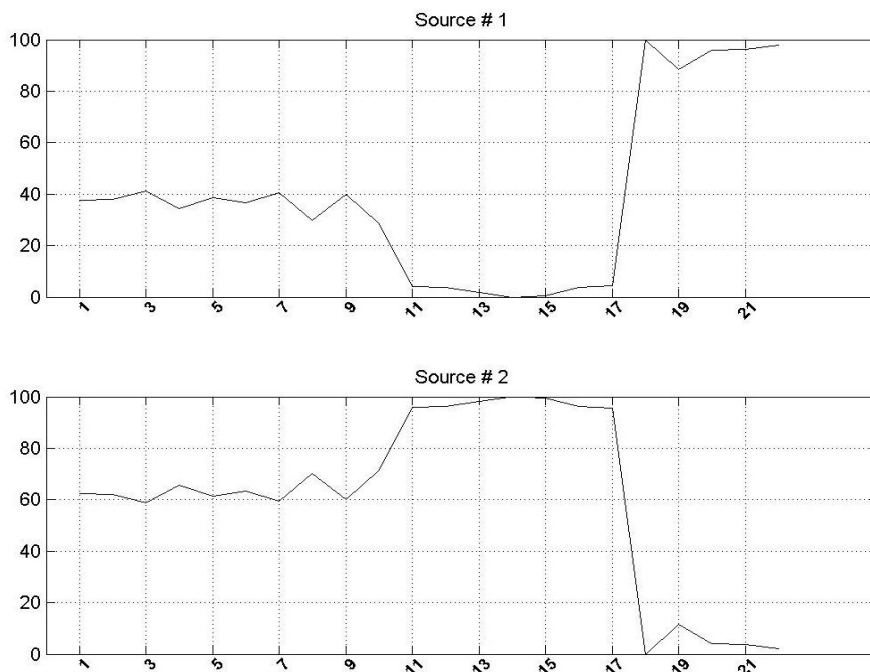


Fig. 6—Source contributions calculated by EPA Unmix model (samples 1-10, 11-17 and 18-22 are collated from LA, CA and TA, respectively).

Table 3—Results of factor analysis.

	Factor 1	Factor 2
Na ⁺ +K ⁺	0.010	0.997
Ca ²⁺	0.994	-0.073
Mg ²⁺	0.956	-0.172
Cl ⁻	0.967	0.205
SO ₄ ²⁻	0.994	-0.067
HCO ₃ ⁻	-0.809	0.543
Eigenvalue	3.827	1.372
% variance	63.8	22.9

Further discussions:

Because of the variations of geo- and hydrological, climate and anthropogenic conditions, the hydrochemical evolution of groundwater is considered to be complicated with hydrochemical processes, especially the water rock interaction. And therefore, a large number of studies have been carried out with different methods and / or models, such as the traditional methods applied in this study and Feflow, GMS, Modflow, Netpath and PHREEQC et al²³⁻²⁵. However, to be one of the most important aspect of water rock interaction, the source of chemical constituents in the groundwater is always qualitative rather than quantitative.

In this study, the EPA Unmix model has been applied for the hydrochemical data and quantified the source of major ions in the groundwater, which has

successfully provided the quantitative information about the water rock interaction. Moreover, this work provided the possibility for tracing the wall rock compositions of the aquifer system, although the result is rough because of the lack of partition coefficients of chemical constituents between water and rock, which should be considered in the future.

Conclusion

Based on the analysis of hydrochemistry of deep groundwater from the Wolonghu coal mine in northern Anhui province, China, by using traditional and statistical methods, the following conclusions have been obtained:

(1) Groundwater samples from three aquifer systems have different concentrations of major ions, implying that they have undergone different kinds and degrees of water rock interactions;

(2) Relationships between major ions or their ratios, as well as statistical analyses suggested that water rock interactions are the main mechanism controlling the groundwater chemistry. However, these analyses give only qualitative results without quantitative information;

(3) EPA Unmix model has identified two sources responsible for the hydrochemistry of the groundwater, sulfate-carbonate (source 1) and silicate-chloride (source 2) sources. Groundwater

from the TA and CA are mainly contributed by source 1 and 2, respectively. As to the groundwater from the LA, the contributions of the source 1 and 2 are 4: 6.

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