



# Source Quantification of Major Ions in Groundwater from Deep Limestone Aquifer System in Northern Anhui Province, China Based on Unmix Model

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Nat. Env. & Poll. Tech.

Website: [www.neptjournal.com](http://www.neptjournal.com)

Received: 03-02-2015

Accepted: 15-03-2015

## Key Words:

Groundwater

Source of major ions

Limestone aquifer

Hydrological implications

Unmix model

## ABSTRACT

Groundwater from the deep buried limestone aquifer system is important for coal mines in northern Anhui Province, China, not only because it can provide water supply in the area, but also threat for the safety of coal mining. In this study, major ion concentrations of 48 groundwater samples from the limestone aquifer system in Huaibei coalfield, northern Anhui Province, China have been measured and analysed by EPA Unmix model for tracing their sources. The results suggest that they can be classified as Na-Ca-Mg-Cl-SO<sub>4</sub> type according to their major ion concentrations, and the sources for the major ions are considered to be more than one according to the results of statistical analysis. Three sources have been identified by Unmix model, including carbonate-chloride, sulphate and silicate sources, and their contributions for the total dissolved solids are 43, 42 and 15%, respectively. The variations of contributions from the three sources of the samples probably related to, (1) the variations of mineral compositions in the aquifer system, and (2) the different locations (recharge or discharge) of the samples collected from.

## INTRODUCTION

Groundwater makes up nearly 70% of all the world's freshwater; only 0.2% is found in lakes, streams or rivers and 30% is bound up in snow and ice on mountains and in the polar regions. It plays a number of very important roles in our environment and in our economies. Nowadays, groundwater has become one of the most important natural resources in many countries of the world because of its advantages among other water suppliers (e.g. rivers and lakes) (Zektser & Everett 2004). It is often present in areas with surface water shortage, the quality of groundwater is usually very good, it also responds slowly to the changes in rainfall, and so it stays available during the summer and during droughts when rivers and streams have dried up.

Similar to other countries in the world, groundwater is important for the economic development, especially in the North China Plain (Foster et al. 2004, Chen et al. 2005), because near 56% of the water supply for more than 100 million people is provided by groundwater, and most of the areas in North China Plain use groundwater for irrigation (Zhang et al. 2000).

However, as to the coal mines, groundwater is a double-edged sword. It is important for the human activities in the coal mining areas, because most of the water used for drinking, irrigation and industrial purpose is obtained from underground (Sun & Gui 2013). However, it can also be a threat to the safety of coal mining area, because water is considered to be the most dangerous one among the five typical

disasters in coal mines (including water, fire, gas, dust and roof), as water inrush has brought to human with highest loss, not only the loss of property, but most importantly, the life of people (Gui & Chen 2007).

To be one of the most important tools, hydrochemistry has played an important role for water disaster controlling in coal mines, because it can be used for water source identification, which is essential for water disaster prevention and management. And therefore, a large number of studies related to groundwater hydrochemistry have been processed, and most of them are focused on statistics (Jiang & Liang 2006, Chen et al. 2009, Zhang et al. 2009, Zhou et al. 2010, Sun & Gui 2012). However, the mechanism about water-rock interaction in the groundwater system (such as the source of chemical constituents) has not been well understood, which limits the popularization and application of these methods.

Although different waters from different aquifers can be a threat to the safety of coal mining areas, the groundwater from the limestone aquifer system is considered to be the key threat, because the water in it is characterized by high pressure and large amounts. And therefore, the inrush water supplied by this aquifer can lead to serious damage to the coal mines. In 1988, the water inrush occurred in the Yangzhuang coalmine, northern Anhui Province, and had brought to a loss of 150 million Yuan, and in 1996, similar accident occurred in the Renlou coalmine had brought to a loss of 350 million Yuan. Both of them are water inrush related to the limestone aquifer (Gui & Chen 2007).

Therefore, in this study, a total of 48 groundwater samples from the limestone aquifer system in Huaibei coalfield, northern Anhui Province, China have been collected, and their major ion concentrations have been measured and analysed by EPA Unmix model. The goals of the study include: (1) understanding the chemical compositions of the groundwater from the aquifer system, (2) identifying and quantifying the sources of the major ions in the groundwater and (3) a preliminary understanding of the mineral compositions of the aquifer system, which cannot be simply obtained by drilling programs because of the spatial inhomogeneous.

## MATERIALS AND METHODS

**Hydro and geological background:** The Huaibei coalfield is located in the east part of Yu-huai depression zone, the southeast margin of North China Craton. The coalfield is bounded by the Guzhen-Changdeng fault in the east, the Guangwu-Guzhen fault in the south, the Xiafu-Gushi fault in the west and the Fengpei fault in the north. The recharge, flow and discharge of the groundwater is controlled by the faults around the coalfield, and the field is a closed to semi-closed grid hydrogeological unit.

There are three-four aquifer systems related to the safety of the coal mines from shallow to deep: the loose layer (QA), coal bearing (CBA) and limestone aquifer systems (TA and OA, including Carboniferous and Ordovician limestone aquifer system). The distribution of the aquifer systems and the hydraulic connections between them can be found in Fig. 1.

All of these aquifer systems have different hydrological features, e.g. the loose layer aquifer system is mainly composed of conglomerate and loose sediments, and the hydrological condition is open as it can be recharged by precipitation or surface water. Whereas the coal bearing aquifer system is mainly composed of hard sandstones with cracks and coal seams, and the hydrological condition is relatively closed under the condition that there is no natural fault or cracks produced by coal mining activities. The limestone aquifer system is mainly composed of carbonate rocks, to a

lesser extent clastic rocks, and the hydrological condition is also open, as it can be recharged by surface water because the limestone stratas in the area have outcrops.

**Methods:** A total of 48 samples has been collected from eight coal mines in northern Anhui province, China. Concentrations of eight kinds of major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) and total dissolved solids (TDS) have been analysed, and because of the low concentrations of  $\text{Na}^+$  and  $\text{K}^+$  were merged to be one ( $\text{Na}^+\text{+K}^+$ ). The analytical methods are as follows:  $\text{Na}^+\text{+K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were analysed by ion chromatography, whereas  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  were analysed by acid-base titration in the Engineering and Technological Research Center of Coal Exploration, Anhui Province, China.

All of the analytical results were firstly processed by Mstat software (version 12) and the min, max, median, mean, coefficient of variation and p-value of Anderson-Darling test have been obtained. Then, the data were analysed by EPA Unmix model (version 6) following the processes: firstly,  $\text{CO}_3^{2-}$  concentrations have been removed because most of the samples have  $\text{CO}_3^{2-}$  concentrations equal to zero; secondly, factor analysis has been processed for obtaining the number potential sources of major ions; thirdly, all of the data were analysed by Unmix model for obtaining the number of sources, the compositions of the sources and their contributions for each sample. Lastly, the wall rock compositions and variations of the limestone aquifer system have been discussed according to the results obtained by Unmix model.

## RESULTS AND DISCUSSION

**Descriptive statistics:** All of the analytical results are shown in Table 1. As can be seen from the table, the groundwater samples have highest mean concentrations of  $\text{Na}^+\text{+K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  among other anions and cations, respectively. These groundwater samples are classified to be Na-Ca-Mg-Cl- $\text{SO}_4$  type according to their major ion concentrations. The mean concentrations of  $\text{Na}^+\text{+K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are 427, 275, 106, 729, 731, 270 and 7.43 mg/L, respectively.

Table 1: Major ion concentrations (mg/L) of groundwater from the limestone aquifer systems.

	$\text{Na}^+\text{+K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	TDS
N	48	48	48	48	48	48	48	48
Min	171	11.7	0.12	90.0	76.9	0	0	641
Max	800	439	245	1204	2288	572	238	3896
Median	452	293	96.2	912	552	297	0	2439
Mean	427	275	106	729	731	270	7.43	2410
CV	0.31	0.37	0.46	0.49	0.87	0.37	4.65	0.31
p-value	0.108	0.135	0.087	<0.01	<0.01	0.014	<0.01	0.137

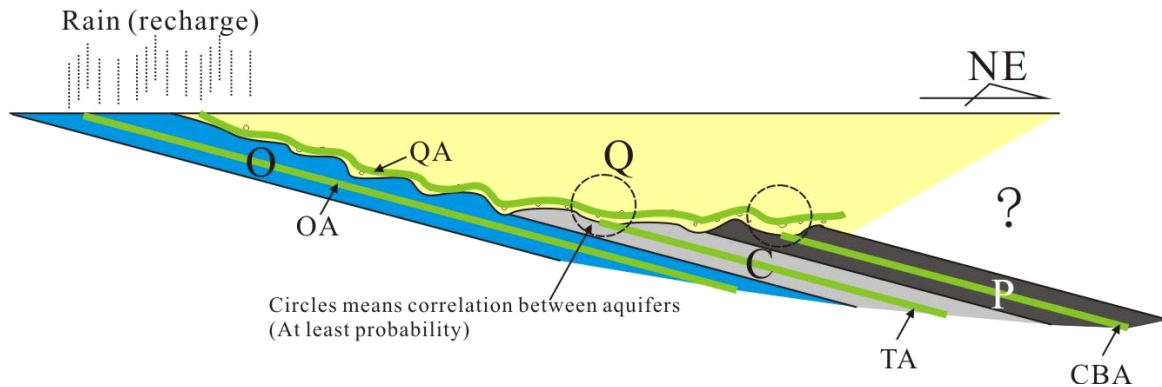


Fig. 1: Cartoon illustration showing the distribution of aquifer systems and hydraulic connections between aquifer systems. (QA, CBA, TA and OA mean loose layer, coal bearing sandstone, Carboniferous and Ordovician limestone aquifer systems, respectively)

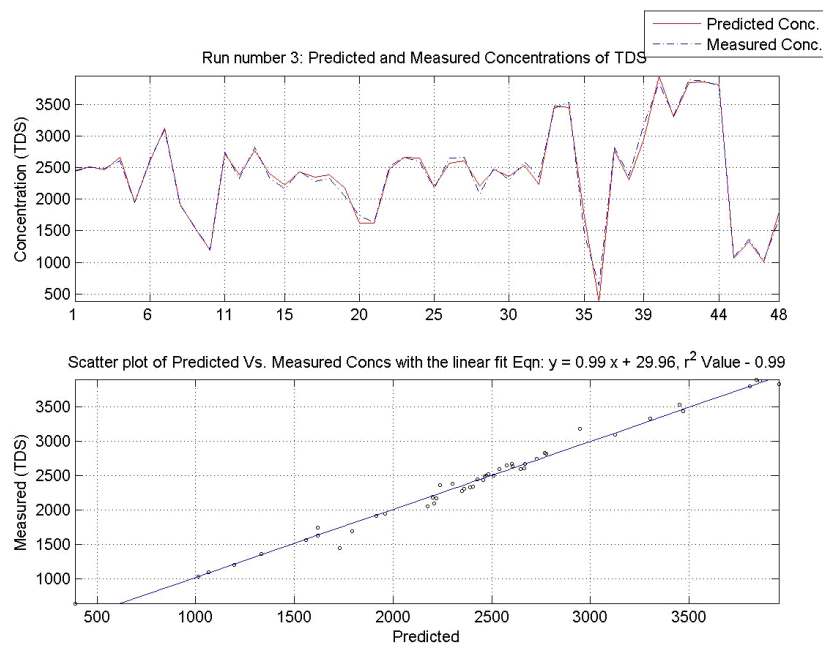


Fig. 2: Predicted versus measured concentrations of TDS.

The groundwater can be classified into 3 kinds based on the total dissolved solids (TDS): <500 mg/L means desirable for drinking, 500-1000 mg/L means permissible for drinking, and >3000 mg/L can only be used for agricultural purposes (Davis & De Wiest 1966). Based on this criterion, the groundwater samples in this study can be used for agricultural purposes, whereas they must be treated before drinking.

Previous environmental studies revealed that a low coefficient of variation (< 10%) indicates the low degree of anthropogenic contribution, whereas a high coefficient of variation (> 90%) indicates high degrees of anthropogenic

contribution (Zhang & McGrath 2004). In this study, major ion concentrations of the groundwater samples have coefficient of variations ranging from 0.31 to 4.65, which indicates that all of them are statistically inhomogeneous and cannot be contributed by a single source. Moreover, the p-values of Anderson-Darling test for  $\text{Na}^+\text{+K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are higher than 0.05, which indicates that their concentrations are in normal distribution. However, none of the anions could pass the normality test (Table 1).

**Source identification:** Factor analysis is considered to be one of the most popular tools for identifying the source of

Table 2: Results of factor analysis (after varimax rotation).

	Factor 1	Factor 2	Factor 3
Na <sup>+</sup> +K <sup>+</sup>	0.54	0.66	0.20
Ca <sup>2+</sup>	0.61	0.43	-0.41
Mg <sup>2+</sup>	0.91	-0.08	-0.01
Cl <sup>-</sup>	-0.24	0.94	-0.14
SO <sub>4</sub> <sup>2-</sup>	0.95	-0.24	-0.11
HCO <sub>3</sub> <sup>-</sup>	-0.08	-0.02	0.94
TDS	0.90	0.39	-0.13
Eigenvalue	3.48	1.62	1.04
Explained covariance (%)	49.70	23.10	14.90

pollutants in environmental studies (Garcia et al. 1996, Lin et al. 2002, Liu et al. 2003). In this study, three factors have been obtained with eigen value higher than one after varimax rotation (Table 2), and the total variance explanation is 87.7%. The first factor, which accounts for 49.7% information, is dominated by Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and TDS, to a lesser extent, Na<sup>+</sup>+K<sup>+</sup>; factor 2 accounts for 23.1% information and is dominated by Na<sup>+</sup>+K<sup>+</sup> and Cl<sup>-</sup>, whereas factor 3 accounts for 14.9% information and is dominated by HCO<sub>3</sub><sup>-</sup>. These results suggest that at least three sources are responsible for the major ion concentrations in this study, and they might be carbonate and sulphate (factor 1), chloride (factor 2) and silicate (factor 3) minerals. However, factor analysis can give only the number of potential sources, and other method is needed for calculating the contributions of the sources.

Based on the calculation of Unmix model, three sources have been identified and the results are listed in Table 3.

These three sources have Min Rsq = 0.97, representing that more than 97% of the variance information can be explained by the modelling and it is higher than the minimum requirement of the model (Min Rsq > 0.8). Moreover, the Min Sig/Noise is 2.30, also higher than the minimum requirement (Min Sig/Noise > 2). It can also be obtained from Fig. 2 that the relationship between predicted and observed values of TDS is significant ( $r^2 = 0.99$ ), suggesting that the modelling is efficient (Ai et al. 2014). The detailed explanations about these three sources are as follows:

Source 1 has the highest loadings of Na<sup>+</sup>+K<sup>+</sup>, Ca<sup>2+</sup> and Cl<sup>-</sup>, and moderate loadings of HCO<sub>3</sub><sup>-</sup> among the three sources. This source has 47, 54, 83 and 24% contribution for Na<sup>+</sup>+K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>, respectively (Table 3). This source can be explained to be the carbonate and chloride source, such as calcite, dolomite and halite in the strata. The contribution of the source for the TDS is 43%.

Source 2 has the highest loadings of Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, and moderate loadings of Na<sup>+</sup>+K<sup>+</sup> and Ca<sup>2+</sup> among the three sources. The contributions of this source for Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>+K<sup>+</sup> and Ca<sup>2+</sup> are 50, 81, 32 and 38%, respectively. This source can be explained to be sulphate source, such as gypsum, mirabilite. The contribution of the source for the TDS is similar to source 1 (42%).

Most of the major ions have lowest loadings in source 3 except for HCO<sub>3</sub><sup>-</sup>, whose 55% is contributed by this source. This source can be explained to be silicate source, because the weathering of silicate minerals can release Na<sup>+</sup> and

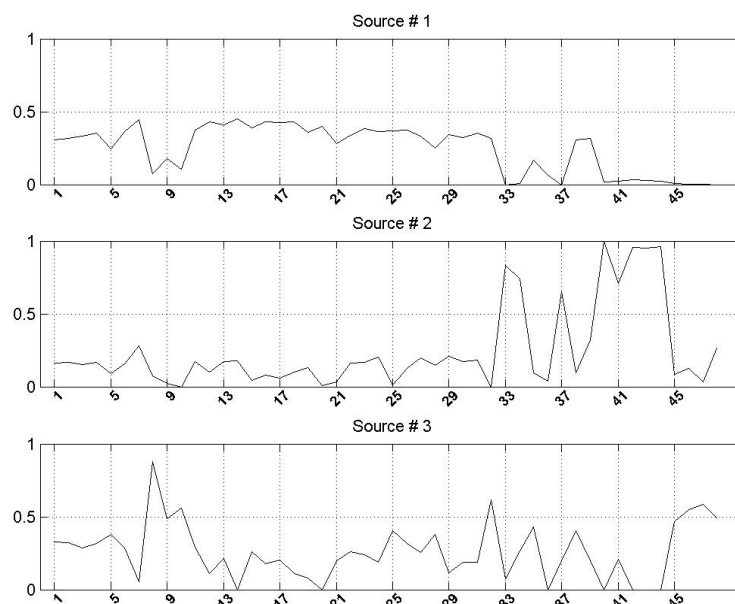


Fig. 3: Variations of source contributions.

Table 3: Results of source estimation (mg/L).

	Source 1	Contribution 1	Source 2	Contribution 2	Source 3	Contribution 3
Na <sup>+</sup> +K <sup>+</sup>	203	47%	139	32%	85.8	20%
Ca <sup>2+</sup>	147	54%	105	38%	21.9	8%
Mg <sup>2+</sup>	28.2	26%	53.6	50%	24.6	23%
Cl <sup>-</sup>	606	83%	84.7	12%	39.1	5%
SO <sub>4</sub> <sup>2-</sup>	22.3	3%	593	81%	117	16%
HCO <sub>3</sub> <sup>-</sup>	65.5	24%	55.2	21%	149	55%
TDS	1040	43%	1000	42%	361	15%

HCO<sub>3</sub><sup>-</sup> into the groundwater simultaneously. The contribution of the source for the TDS is only 15%.

**Hydrological implications:** The compositions of underground rocks are still mysterious to all of us. Although we can get the information based on drilling cores, which can be obtained from drilling programs, there are still some unknown areas, because drilling gets only the information from one point. However, the underground water, which has followed through large areas, should have more information about their wall rocks, because the chemical compositions of the groundwater are controlled water-rock interactions. And therefore, the chemical compositions of groundwater can provide reliable information for understanding the wall rock compositions of the aquifer (Sun et al. 2011).

As can be seen from Fig. 3, the contributions of each source for the groundwater samples in this study vary significantly, which might be an indication that the mineral compositions of the limestone aquifer system are spatially inhomogeneous because the samples in this study are collected from different coalmines.

Most of the samples (31) have relative constant contributions (near 40%) from source 1. However, 17 samples have lower contributions from this source (< 20%) and 12 of them have almost no contributions from this source. This result indicates that the concentrations of carbonate and chloride minerals in most of the areas of the limestone aquifer system are stable. However, different from source 1, 39 samples have contributions lower than 30% from source 2, with only 9 samples have contributions more than 60% from source 2, suggesting that the contributions from the dissolution of sulphate minerals are low except for some of the areas. Moreover, the contributions of source 3 for all of the samples changed significantly, range from 0 to > 80%, implying that the contents of silicate minerals in the aquifer system vary significantly.

Another interesting information can be obtained from Fig. 3 is that most of the samples with low contributions from the source 2 have high contributions from the source 1, whereas the samples with high contributions from the source

2 have low contributions from the source 1. In consideration with the different means of these two sources, along with the different abilities of weathering resistance of the minerals (silicate > carbonate > sulphate > chloride), this phenomenon can be explained to be the result of: (1) the mineral compositions in the limestone aquifer system are inhomogeneous and (2) the samples with high contributions from the source 2 are located in the discharge zone, whereas the samples with high contributions from the source 1 are located in the flowing zone.

## CONCLUSIONS

Based on the analysis of the major ion concentrations of the deep limestone aquifer system in northern Anhui province, China by Unmix model, the following conclusions have been obtained:

1. The groundwater samples are classified to be Na-Ca-Mg-Cl-SO<sub>4</sub> type according to their major ion concentrations, and they can be used for agricultural purposes, but must be treated before drinking according to their high TDS contents.
2. Coefficients of variations, as well as the p-values of Anderson-Darling test of the major ion concentrations, suggest that three sources are responsible for the major ion concentrations.
3. Three sources have been identified by Unmix model, and the major ion concentrations of the groundwater samples are mainly contributed by the carbonate-chloride and sulphate sources, and to a lesser extent the silicate sources.
4. The contributions of the three sources of the samples vary significantly, which can be explained by the inhomogeneous of mineral compositions in the aquifer system and, the different locations (recharge or discharge) of the samples collected from.

## ACKNOWLEDGEMENTS

This work was financially supported by National Natural Science Foundation of China (41302274), the Foundation

of Scholarship Leaders in Suzhou University (2014XJXS05) and the Foundation of Scientific Platform in Suzhou University (2014YKF05).

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