Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 13	No. 3	pp. 577-582	2014

Original Research Paper

Quality Evaluation and its Controlling Factors of Groundwater from Wolonghu Mining Area, Northern Anhui Province, China

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 26-12-2013
Accepted: 16-1-2014

Key Words:
Groundwater quality
Wolonghu mining area
Hydro-chemical processes
Piper diagram

ABSTRACT

Major ion concentrations were analysed for 29 groundwater samples collected from diverse aquifers in Wolonghu mining, northern Anhui province, China. The evaluation of groundwater quality and controlling factors analysis were obtained by the methods such as multivariate statistical approach and conventional graphical and calculation of a series of index. The results showed that the groundwater samples are alkaline in nature, with the high value of TDS ranging from 686 to 3927 mg/L, the concentrations of Cl^- are low for all groundwater samples, whereas the contents of SO_4^{2-} and HCO_3^- are high. The groundwater samples of QA and CA could be used for drinking and irrigation, whereas the groundwater of LA could not be used for irrigation for the high TDS concentration. The groundwater in the area is mainly controlled by silicate weathering, the evaporative dissolution and carbonate dissolution. Sulphate dissolution also played an important role in the groundwater quality.

INTRODUCTION

Groundwater has an important significance for the development of economy and society. In the North China Plains, with the water shortages problem becoming serious, exploitation of groundwater is the main water supply for domestic, agricultural and industrial use. The balance between groundwater and surface water was destroyed badly, what caused water table of groundwater in the area decreased seriously during the last twenty years. All these would cause water resource problems, such as groundwater pollution, and precipitation funnel. Thus, the studies on quality evaluation and influencing factors on groundwater are necessary.

In addition, groundwater always reserve some information what is inherited from the aquifer through the water-rock interaction over a long period of time. Previous studies, carried out on hydro-geochemical analysis, could contribute to the understanding of groundwater quality, varied aquifer groundwater differences and the anthropogenic influences on groundwater systems (Ramkumar et al. 2013, Kumar et al. 2009, Yin et al. 2011. However, the studies on hydro-geochemical processes in deep groundwaters are limited, for the difficulty of sample collection. Deep coal mining provide an opportunity for the research on deep groundwater, so many investigations on major ions, rare earth elements, etc. have been carried out in northern Anhui Province, China (Gui et al. 2011, Sun et al. 2011, Chen et al. 2013), where abundant coal resources are present. However, these studies always focused on the coal mining safety to discriminate the sources of inrush water; the studies about quality evaluation of groundwater are limited. Water quality analysis is one of the most important aspects in groundwater studies, what always is used as a basis to discuss utilizing groundwater (Nagarajan et al. 2010). The hydro-chemical study could reveal weather the groundwater is suitable or not for drinking, agriculture and industrial purposes.

The purpose of the study is to evaluate groundwater quality, revealing the controlling factors of the groundwater, using hydro-chemical and multivariate statistical analysis. Major ion concentration of groundwater samples, collected from Wolonghu mining area, northern Anhui Province, China, has been measured for the purpose. The results will be used as a basis for making sustainable groundwater development schemes, understanding the management and future development of groundwater resources in the area.

MATERIALS AND METHODS

The Wolonghu mining, belonging to Huaibei mining area, is located at northern Anhui Province, China, which is constituted of about 30 couples mines. Shallow groundwater is the main water sources for drinking, irrigation and industry. The climate in the area belongs to marine-continental climate, with an annual average temperature of 14.9°C.

Previous researches have shown that Wolonghu mining area includes three aquifers (Gui & Chen 2007), the quaternary aquifers (QA), coal bearing aquifer (CA) and

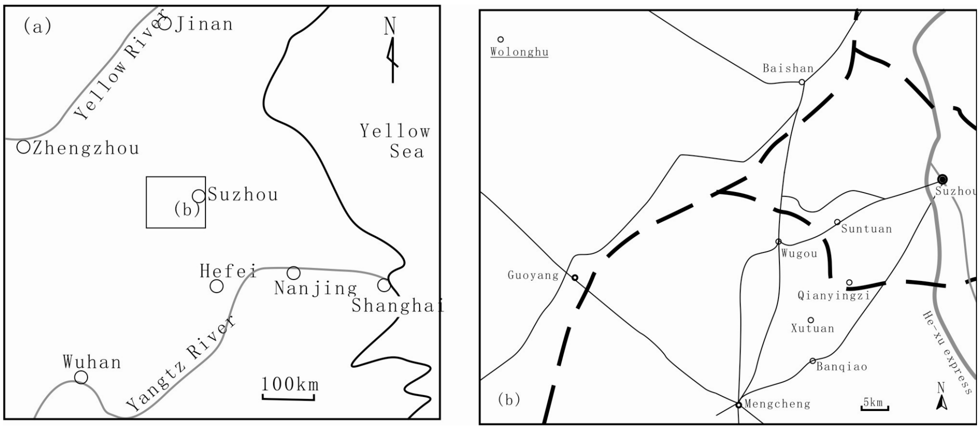

Fig. 1: Location of the study area.

limestone aquifer (LA). The Quaternary aquifer is constituted of yellow mudstone, sandstone and conglomerate, with a depth ranging from 280 to 300m. The coal bearing aquifer is characterized by mudstone, siltstone and sandstone, with a depth between 300 and 700m. Limestone aquifers are mainly composed of limestone with clastic rocks, which belong to Taiyuan formation and Ordovician.

This study focused on the groundwater quality from Wolonghu mining area, northern Anhui Province, China. Twenty nine groundwater samples were collected from three diverse groundwater aquifers, with ten samples from Quaternary aquifer, ten samples from coal bearing aquifer, five samples from limestone aquifer and four samples from mixed groundwater. Water samples were collected via drainage holes in alleys, and then filtered through 0.45 mm pore-size membrane and collected into polyethylene bottles that had been cleaned using trace element clean procedures. All the twenty five samples were analysed for major ions.

Water pH, total dissolved solids (TDS) and electrical conductivity were measured in the field with a portable pH and TDS meter. Major ions were analysed in the analysis testing centre of the Department of Coal Geology of Anhui province, China. The Piper diagram, which calculates the carbonate equilibrium, TDS, density, conductivity and hardness, was accomplished by software AqQa. The statistical analysis of data was completed by the SPSS (version 19), groundwater quality was assessed based on chemical comparison with drinking water standard from World Health Organization (WHO 1993) and a series of indices like residual sodium carbonate (RSC), sodium adsorption ratio (SAR) and percent sodium (Eaton 1950, USSL 1954).

RESULTS

Descriptive statistics: The analytical results of the groundwater from varied aquifers are given in Table 1. In general, the pH values of groundwater varied from 7.39 to 8.89, with an average value 8.06, which indicates that the groundwater is alkaline in nature. The amount of total dissolved solid (TDS) of groundwater ranges from 686 to 3927 mg/L, with an average value of 2127.7 mg/L. The concentrations of Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-} the groundwater ranged from 125 to 391, 2.5 to 2288, 131 to 1499 and 0 to 179 mg/L, with averaged 228.6, 827.2, 685.5 and 58.9 mg/L, respectively. The cations Na^+, Ca^{2+} and Mg^{2+} concentrations of the groundwater range from 156.7 to 988, 4.0 to 439.4, and 1.4 to 244.8 mg/L, with average values of 500.9, 136.5 and 85.6 mg/L, respectively.

The geochemical data of groundwater were plotted on a Piper diagram (Fig. 2) to obtain some information. The concentrations of Cl^- are low for all groundwater samples, whereas the contents of SO_4^{2-} and HCO_3^- are high with diversity degrees for groundwater collected from different aquifers. The cations also have the similar character with the anions. The most groundwater samples from coal bearing aquifer (CA) were characterized by the high concentrations of Na^+, and the anions are dominated by the SO_4^{2-} or HCO_3, thus, the groundwater could be described as the HCO_3-Na type. Two samples were different with the high concentrations of Ca^{2+} and Mg^{2+}, what could be revealed that the two diverse hydro-chemical processes are exiting in the coal bearing aquifers.

The groundwater samples from Quaternary aquifer (QA) have higher concentrations of Ca^{2+} and Mg^{2+}. The anions were consisted of SO_4^{2-} and HCO_3^-, which were similar with the coal bearing aquifer. The content of Ca^{2+} and Mg^{2+} were dominated in the groundwater from limestone aquifer (LA), with high concentration of SO_4^{2-}. In conclusion, the concentrations of Na^+ were decreasing as follows: LA < QA < CA, whereas the content of Ca^{2+} and Mg^{2+} were increasing

Table 1: Chemical summary of the groundwater samples form Wolonghu mining area (The values are in mg/L except pH).

	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-	pH	TDS
Max.	988.08	439.39	244.84	2288.08	391.57	1499.17	8.89	3927
Min.	156.68	3.96	1.41	2.47	125	131.33	7.39	686
Mean	500.85	136.52	85.55	827.24	228.59	685.48	8.06	2127.74
Std. Deviation	197.29	149.61	77.79	847.65	93.82	435.17	0.37	1030.46
LA_{mean}	504.81	400.01	200.28	2175.72	374.89	174.08	7.83	3763
QA_{mean}	377.34	51.98	56.56	318.58	147.95	803.29	7.83	1352.8
CA_{mean}	500.28	63.84	46.25	297.55	191.25	901.63	8.41	1634.4

Table 2: Correlation matrix of parameters for groundwater form Wolonghu mining in northern Anhui province, China (n=29).

	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Hardness	Alkalinity	pH	TDS
Na^+	1.00									
Ca^{2+}	-0.12	1.00								
Mg^{2+}	-0.26	0.95	1.00							
Cl^-	0.32	0.88	0.78	1.00						
SO_4^{2-}	0.09	0.95	0.90	0.95	1.00					
HCO_3^-	0.39	-0.80	-0.78	-0.65	-0.80	1.00				
Hardness	-0.19	0.99	0.99	0.84	0.94	-0.80	1.00			
Alkalinity	0.43	-0.79	-0.80	-0.62	-0.79	0.98	-0.80	1.00		
pH	0.43	-0.48	-0.57	-0.24	-0.46	0.54	-0.53	0.61	1.00	
TDS	0.37	0.87	0.79	0.98	0.95	-0.57	0.84	-0.55	-0.28	1.00

Table 3: Variance explained and component matrixes for groundwater from Wolonghu mining in northern Anhui province, China.

Parameter	PC1	PC2
SO_4^{2-}	1.00	-0.41
Ca^{2+}	0.96	-0.54
Cl^-	0.96	-0.16
Hardness	0.95	-0.60
TDS	0.95	-0.12
Mg^{2+}	0.91	-0.64
HCO_3^-	-0.78	0.77
Na^+	0.08	0.84
Alkalinity	-0.77	0.81
pH	-0.44	0.76
Initial Eigen value	7.14	1.92
Percentage of variance	71.40	19.19
Cumulative % of variance	71.40	90.59

from CA to LA oppositely. In addition, the four mixing groundwater samples were presented the characteristics among LA and CA, what could be revealed that the mixing action of LA and CA could be exited in the mixing groundwater.

Multivariate statistical analysis: Multivariate statistical analysis, such as Principal Component Analysis (PCA) and Correlation Analysis (CA) are usually used to reveal the relation between the parameter, which was an efficient way of displaying complex relationships among many variables and their roles (Chen et al. 2013). The multivariate methods of statistical analysis (PCA and CA) were applied in this study for indicating the character and relation between the hydro-geochemical data, the result are presented in Tables 2 and 3.

It could be concluded that strong positive correlation between cations was observed for Ca^{2+}- Mg^{2+}, with the correlation coefficient of 0.95, what could be indicated that dissolution of dolomite should occur in the hydro-geochemical process. The positive correlation exists between SO_4^{2-} and Mg^{2+}, Ca^{2+}, with the correlation coefficient of 0.95 and 0.90, what also showed that the sulphuric acid is causing the weathering reactions in the dissolution of dolomite. The chloride should be exited for the positive correlation between Cl^- and Ca^{2+}, Mg^{2+}, with the correlation coefficient of 0.88 and 0.78.

PCA is usually conducted for obtaining the detailed statistical information, the rotated PCA loadings are presented in Table 3. Two Principal Components were emerged, with more than 90.59% of cumulative variance. The parameter of SO_4^{2-}, Ca^{2+}, Cl^-, hardness, TDS and Mg^{2+} are all have high value in PC1, with the value 1.0, 0.96, 0.96, 0.95, 0.95 and 0.91, revealing that the factor has the influence on weathering of limestone, dolomite and calcareous concretions. In detail, the aquifer rock, such as limestone, dolomite and calcareous concretions could provide the Mg^{2+} and Ca^{2+}, with the weathering action by sulphuric acid and acid chloride. All the parameters have high value, what combined with more than 71.40% variance could be explained by the Factor 1, revealing that the

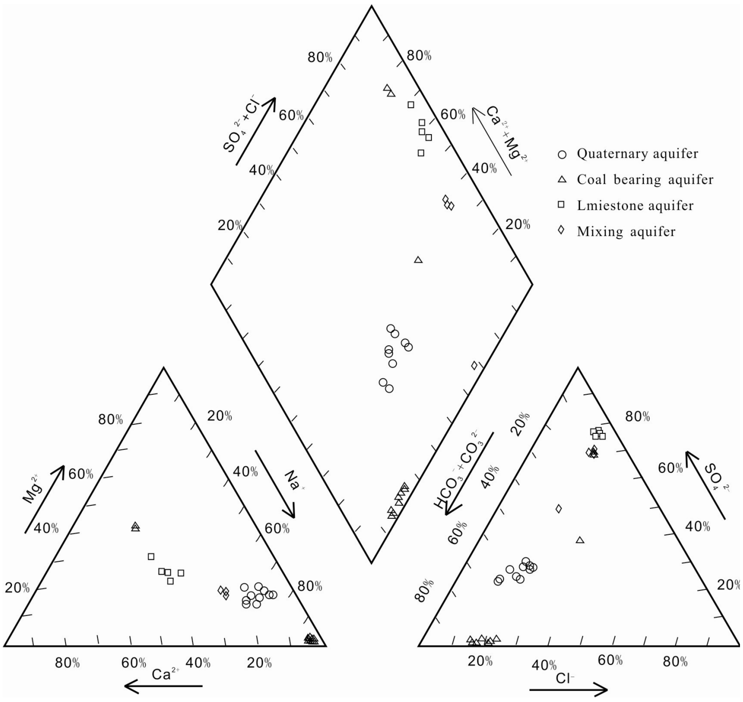

Fig. 2: Piper diagram.

Factor 1 is the major factor for the ions form of groundwater samples. The Factor 2 accounts for 19.19% of total variance, with the high loading for HCO^{3-}, Na^+, alkalinity and pH, attributed form the feldspar weathering.

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 accorded with the frontal information obtained by the conventional graphical method.

DISCUSSION

Quality evaluation: The analytical results have been evaluated to ascertain the suitability of groundwater in the study area for domestic purpose based on the WHO standard (WHO 1993). The results showed that the mean concentration of magnesium (85.55mg/L), calcium (136.52mg/L) and pH values of all the samples can meet the demand of WHO (150 mg/L, 200mg/L and 6.5-8.5), otherwise, the other parameters are all exceed the boundary value. Especially, almost all the TDS values of groundwater samples are higher than 1000 mg/L, with the mean value of 2127.7 mg/L, what revealed that the groundwater could only be used for irrigation rather than drinking. The concentration of SO_4^{2-} is higher than the demand of WHO, with the mean value of 827.2 mg/L, however, the value of Cl^- is low with the mean value of 228.6 mg/L.

In detail, the groundwater samples of QA could basically meet the demand of drinking water, for the mean values of the parameters are almost lower than the WHO standard, especially the concentrations of Ca^{2+}, Mg^{2+} and Cl^-. The groundwater of CA could be used for irrigation, rather than drinking, and the groundwater of LA could not be used for irrigation for the high TDS concentration (> 3000mg/L).

A series of index values are usually used to evaluate the irrigation usability of groundwater, such as the concentration of percent sodium (%Na) and residual sodium carbonate (RSC), what could be calculated by the formula $\% Na = 100 \times Na^+/(Na^++Ca^{2+}+Mg^{2+})$ and $RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} - Mg^{2+})$, respectively. Previous studies showed that five categories could be made basing the value of %Na: excellent (<20), good (20-40), permissible (40-60), doubtful (60-80) and unsuitable (>80) (Eaton 1950). The calculated results showed that the groundwater in the area has %Na ranging form 19.75 to 98.62, with an average value of 67.05, revealing that the groundwater could be used cautiously for irrigation. The high RSC could injure the plant development and is not suitable for irrigation; waters are of excellent irrigation quality with RSC lower than 1.25, and not acceptable for irrigation when the values are high than 2.5 (USSL 1954). Calculated results showed that the groundwater is good for irrigation, with the average value of 1.18.

Controlling factors: Hydrochemistry of groundwater always

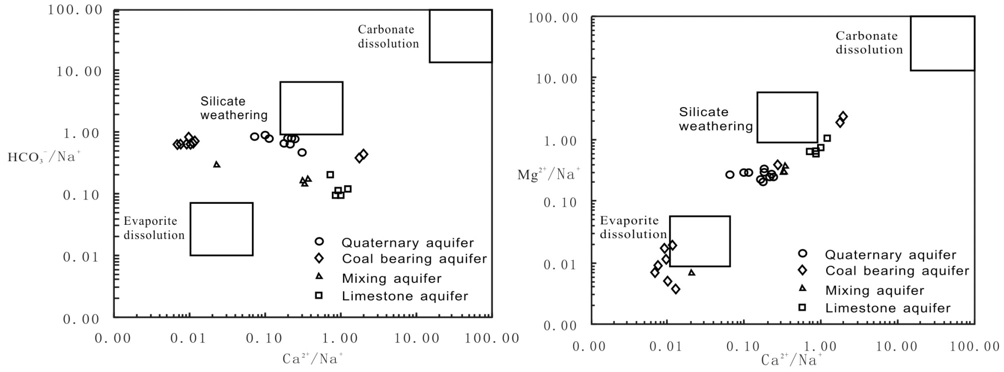

Fig. 3: Na^+ normalized Ca^{2+}-HCO_3^- and Ca^{2+}-Mg^{2+} plots.

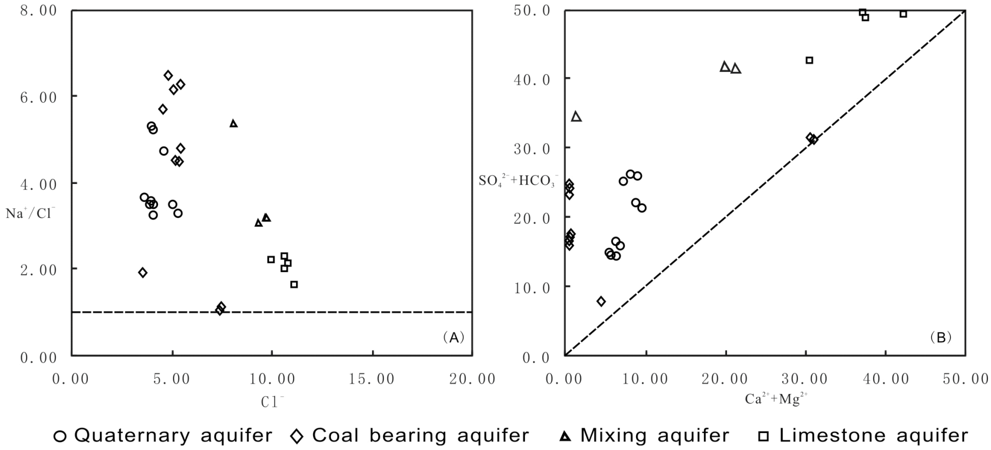

Fig. 4: Scatter diagrams of Cl^--Na^+/Cl^- and $(Ca^{2+}+Mg^{2+})$-$(HCO_3^-+SO_4^{2-})$.

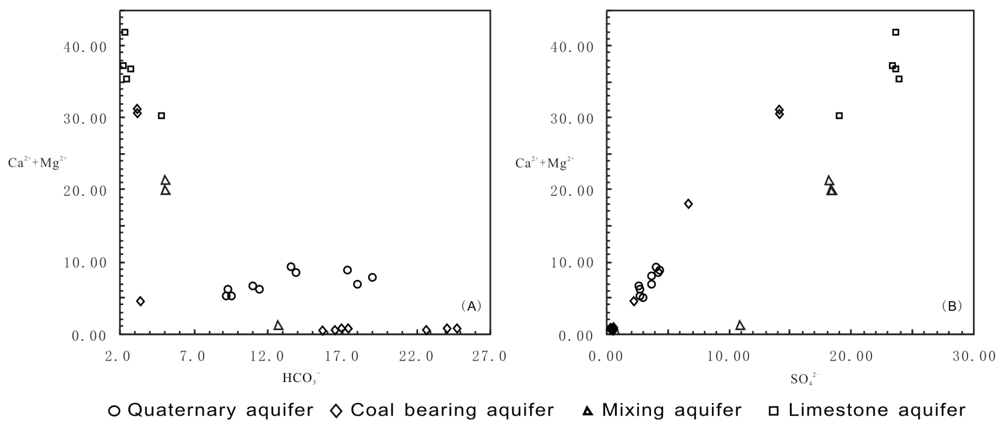

Fig. 5: Scatter diagrams of $(Ca^{2+}+Mg^{2+})$-HCO_3^- and $(Ca^{2+}+Mg^{2+})$-SO_4^{2-}.

influenced by such factors like recharging and water-rock interaction, and the degree of water-rock interaction controlled by residence time within the aquifer. Three general processes contributing to the generation of solutes in groundwater are evaporate dissolution, carbonate dissolution and silicate weathering. As can be seen from Fig. 3, the groundwater in the area is mainly controlled by silicate weathering, the evaporate dissolution and carbonate dissolution also played important role in the groundwater from CA and LA, respectively (Gaillarde et al. 1999).

Mechanism of acquiring salinity in groundwater systems could be identified using the Na-Cl relationship, for the dissolution of halite in water releases equal concentration of Na^+ and Cl^- into the solution (Sami 1992). Thus, the value Na^+/Cl^- could be present a line, if Na^+ and Cl^- came from halite dissolution only. The Fig. 4A presents different vision with Na^+/Cl^- ratios of most samples above one, only two samples close to one. What could be implied that additional Na^+ comes probably from other source. Generally, the additional Na^+ in groundwater could be originated from weathering of silicate minerals, the views could be supported by some silicate mineral found in the aquifer rocks. And the weathering process often along with increased HCO_3^- concentrations, what is presented from Fig. 4B.

The source of Ca^{2+} and Mg^{2+} in groundwater could be determined from the ratio of $(Ca^{2+}+Mg^{2+})/HCO_3^-$. The ratio would be about 0.5, if Ca^{2+} and Mg^{2+} in groundwater come only from dissolution of carbonates in the aquifer, or from the weathering of pyroxene and amphibole (Meybeck 1987). The ratio of the groundwater samples in the area ranges from 0.02 to 18.23, with an average value of 3.8 (Fig. 5A), revealing that the balance between concentration of $Ca^{2+}+Mg^{2+}$ and HCO_3^- is changed by some reason. The strong positive correlation between $Ca^{2+}+Mg^{2+}$ and SO_4^{2-} is presented by Fig. 5B. Table 2 suggests that sulphate dissolution could be important for the extra $Ca^{2+}+Mg^{2+}$. In addition, the low $(Ca^{2+}+Mg^{2+})/HCO_3^-$ ratio of few groundwater samples could be the result of $Ca^{2+}+Mg^{2+}$ depletion by cation exchange.

CONCLUSIONS

The concentrations of major ions in groundwater samples collected from diverse aquifers in Wolong mining, northern Anhui Province, China has been analysed, combined with the evaluation of groundwater quality and controlling factors analysis, and the following conclusions can be made.

1. The groundwater samples are alkaline in nature, with the high value of TDS ranging from 686 to 3927 mg/L. The concentrations of Cl^- are low for all groundwater samples, whereas the contents of SO_4^{2-} and HCO_3^- are high. The concentrations of Na^+ were decreasing as follows: LA < QA < CA, whereas the content of Ca^{2+} and Mg^{2+} were increasing from CA to LA oppositely.
2. The groundwater samples of QA could meet the demand of drinking water, otherwise, the groundwater of CA only could be used for irrigation. However, the groundwater of LA could not be used for irrigation for the high TDS concentration.
3. The groundwater in the area is mainly controlled by silicate weathering, the evaporate dissolution and carbonate dissolution also played important role in the groundwater from CA and LA, respectively. Sulphate dissolution could be important for the extra $Ca^{2+}+Mg^{2+}$.

ACKNOWLEDGEMENTS

The study was supported by the National Nature Science Foundation of China ((41373095, 41173106), the Anhui Province Department of Education Natural Science Foundation (KJ2013A249), the Program for Innovative Research Team in Suzhou University (2013kjtd01) and the opening scientific research platform in Suzhou University (2013YKF01, 2013YKF02).

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