Hydrochemical Characteristics and Water Quality Assessment of Surface Water and Groundwater in Agriculture Demonstration Base, Jiagou District, Northern Anhui Province, China

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ABSTRACT

Jiagou district, located in Northern Anhui Province, China, has been taken as an agriculture demonstration base for several decades, but limited hydrochemical work has been conducted on the water resources. The objective of this research was to understand the controlling processes of hydrochemical evolution and the water quality for drinking and irrigation. Twenty-seven samples of surface water and groundwater have been collected and analysed for major ions. Although the values physicochemical parameters are subjected to spatial fluctuation in different water resources, calcium and bicarbonate is still the dominant ion in the cations and anions, respectively. The values of all the parameters are within the WHO maximum permissible limit for inhabitant drinking. The predominant water type is Ca-Mg-HCO$_3$ and Ca-HCO$_3$. The hydrochemical methods (Gibbs diagram, Mg/Na and HCO$_3$/Na versus Ca/Na diagram and ion ratios) suggest that rock-water interactions furnish the dominant major ion sources of the samples. Carbonate dissolution, silicate weathering and ion exchange have the predominant contribution to the origin of chemical solutes, as well as a slight function of halite dissolution. The USSL and Wilcox diagram reveal that all the samples have low salinity and low sodium water. It is of good quality suitable for irrigation, and it can be used for irrigation of most crops on most soils with less negative impacts.

INTRODUCTION

The global common and thorny issue of water shortage and pollution has restricted the development of social and regional economic development (Jaeger et al. 2013, Hanasaki et al. 2013). The concentration and form of chemical compositions have a significant influence on the water quantity and quality, and also play an important role to ensure ecological environment and regional economic development (Ayadi et al. 2018). As the increasing utilization of water resources for life, agriculture and ecosystems, etc., a series of geological environmental problems, such as water scarcity, land subsidence, sea encroachment and soil salinization have been induced and the geo-environment deterioration was irreparable (Melloul & Goldenberg 1998, Andaryani et al. 2019, Xie et al. 2019).

Acting as the carrier and link during the water-rock interaction, water with abundant solutes generally can be considered as a remarkable indicator to explain the change of environment. Hence, identifying hydrochemical characteristics is an effective tool to assess the mechanism of controlling water chemistry and discuss the origin of ions. Meanwhile, the content of solute compositions can be employed to evaluate the suitability for irrigation.

The study area named Jiagou district is one of the most important agriculture bases in Northern Anhui Province. Local water resources have been used for resident drinking, agriculture irrigation and small-scale industries for a long time. It is widely known for high-quality fruit and vegetable products and agriculture products. Especially, Jiagou aromatic rice is the most famous local product and ever paid as tribute to royalty during the period of the Qing Dynasty (A.D. 1796-1820). But long-term pumping and inconsiderate exploitation of water resources, coupled with the planting of agriculture products, inevitably have led to the degradation of soil and water quality. However, no systematic and profound

researches on the hydrochemical characteristics and water quality assessment have been performed in the study region (Zhang et al. 2010).

Therefore, to understand the controlling processes of hydrochemical evolution and the water quality for drinking and irrigation, the present study initiated to describe the hydrochemical characteristics and illustrate the source of water for proposing the valuable information of the water quality status of the various water source. It can also contribute to the sustainable development of irrigation as well as effective management of water resources in this region.

GEOLOGICAL AND HYDROLOGICAL CONTEXT

The study area, belonging to Huaibei plain, form a part of Suzhou city, Anhui Province and is located between latitudes 3391°' and 3396°' and longitudes 11700°' and 11707°' (Fig. 1). This region is characterized by a semi-humid monsoon climate, with annual average precipitation, evaporation and temperature as 866.1 mm, 988.0 mm and 14.5 , respectively. The overall terrain is mainly plain, topographic variation trend is that northwestern is higher than southeastern, and several mountains are scattered in the central section.

Geologically, the regional stratigraphic development includes Qingbaikou, Cambrian and Quaternary system, with the dominant distribution in NNE direction. The geological features are described as follows: (1) Qingbaikou system is chiefly characterized by limy dolomite and shaly sand. (2) Cambrian system is mostly constituted by limestone, marl, silty shale and arkosic quartz siltstone. (3) The quaternary system is mainly composed of unconsolidated silty clay, silty sand and fine sand.

Hydrogeologically, local water sources can be categorized into two types, including surface water (spring water and reservoir water) and groundwater. In terms of lithology and buried condition, the groundwater aquifer can be classified into two types, consisting of carbonate fractured aquifer and loose pored aquifer. Owing to a huge recharge area and the short distance supply-drainage condition, the water quantity of each aquifer is abundant with single well yield of 1000-5000 m^3/d, which is extensively utilized for agriculture product and resident use (Wang & Ma 2005). Meanwhile, the spring water and the reservoir water are employed for scenic landscape, irrigation and drinking water supply. Regardless of the water source, all of the water bodies have inherent features with nature pollution-free and 17 species minerals and trace elements. Consequently, Jiagou aromatic rice nourished by this excellent water resource is applauded for delicate fragrance, sweet and pure taste. On account of the superiority of the high content of protein and lysine, nowadays, it still has wide appeal and exports abroad in great demand.

SAMPLING AND METHODS

The sampling campaign was carried out from June to October 2017. Surface water and groundwater samples were collected from different water bodies at multi-sampling points in Jiagou district, northern Anhui province, China (Fig. 1). Four spring samples, eighteen reservoir samples and five groundwater samples, marked as SW, RW and GW, respectively, were obtained for hydrochemical analysis.

Electrical conductivity (EC), total dissolved solids (TDS) and pH were directly measured in situ using portable pH, TDS, and EC meters at each sampling site. Preservation and transportation of the samples followed the standard methods.
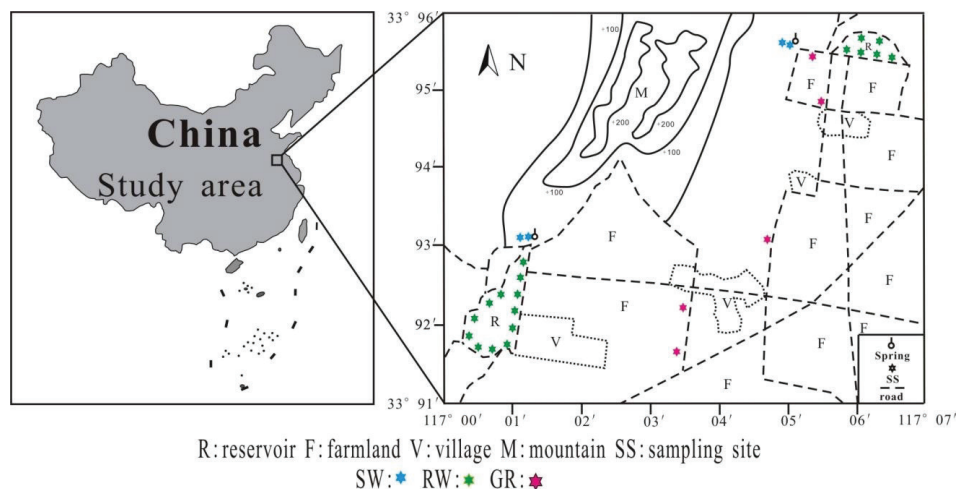

R : reservoir　F : farmland　V : village　M : mountain　SS : sampling site
SW : ✳　RW : ✳　GR : ✳

Fig. 1: Location of the study area and sampling sites.

The measurement of the parameters, which include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-) was conducted in the National Engineering Research Centre of Coal Mine Water Hazard Controlling, China. Major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were determined using the DIONEX-600 ion chromatography, and anions (Cl^- and SO_4^{2-}) were analysed by the DIONEX-900 ion chromatography while HCO_3^- was analysed by acid-base titration. All concentrations of the parameters are expressed in mg/L, except pH and EC.

Descriptive statistics were completed using Mystat 12.0 software. Piper, Gibbs and some traditional hydrochemical diagrams were conducted to elucidate the dominant factors and processes controlling the chemical characteristics. Drinking water quality was evaluated as per World Health Organization (WHO 1997). Irrigation suitability was evaluated using the USSL and Wilcox diagram.

RESULTS AND DISCUSSION

Major Ion Concentrations and Drinking Water Quality

Physicochemical characteristics of water sources are summarized in Table 1. As can be seen from Table 1, most of the coefficient of variations are less than 0.5, indicating that the majority of chemical constituents perform a low-medium spatial fluctuation. pH value of all the samples varies between 7.02 and 8.13, indicating a neutral to slightly alkaline conditions. TDS contents of spring water, reservoir water and groundwater range from 166.00 to 274.00, 94.00 to 167.00 and 149.00 to 262.00 mg/L, with an average concentration of 219.50, 129.61 and 216.00 mg/L, respectively. In-situ measured EC values (µS/cm) of spring samples, reservoir samples, and groundwater samples were in the range of 554.00 to 664.00, 296.00 to 515.00 and 512.00 to 699.00, with a mean value of 609.25, 365.11 and 571.20, respectively. It shows that the TDS, EC and pH values of samples are all within the maximum desirable limit according to WHO standard, indicating that the quality of all the water sources can meet the demand for inhabitant and suitable for drinking.

Among the cations of spring samples, the concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ range from 85.79 to 104.81, 13.80 to 16.20, 5.80 to 6.78, 0.60 to 1.62 mg/L, with an average value of 96.10, 14.98, 6.34 and 0.96 mg/L, respectively. Among the anions, the contents of HCO_3^-, SO_4^{2-} and Cl^- vary between 365.10 and 398.32, 23.19 and 26.82, 12.04 and 14.92 mg/L, with a mean of 388.46, 24.97 and 13.59 mg/L, respectively. As shown in the reservoir samples, the concentration of Ca^{2+}, Mg^{2+}, Na^+ and K^+ is ranging from 38.12 to 77.38, 11.70 to 15.31, 4.85 to 5.89, 0.81 to 2.18 mg/L, with an average concentration of 50.92, 13.63, 5.21 and 1.24 mg/L, respectively. While for the anions, the average concentration of HCO_3^-, SO_4^{2-} and Cl^- in the reservoir samples is 227.02, 24.66 and 9.61 mg/L, respectively. The concentrations of Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions in groundwater samples vary from 80.28 to 104.91, 9.35 to 15.78, 4.53 to 9.95 and 0.57 to 0.74 mg/L, with a mean value of 88.46, 13.10, 7.27 and 0.64, respectively. As to the anions, the values of HCO_3^-, SO_4^{2-} and Cl^- vary in the range from 296.12 to 395.62, 17.99 to 29.91 and 7.05 to 17.78, with an average concentration of 342.84, 22.91 and 12.63, respectively. Apart from some calcium contents of the samples are between the maximum desirable limit and the maximum permissible limit described by WHO standard, the concentrations of other major ions are within the maximum desirable limit, which indicates that all the water sources are properly suitable for drinking. In view of the lower content of potassium and inherent homology between sodium and potassium, Na^+ and K^+ are merged into Na^+ in the following discussion.

Table 1: Summary statistics for concentrations of physicochemical parameters.

Parameters		Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	TDS (mg/L)	EC (µS/cm)	pH
SW	Min	85.79	13.80	5.80	0.60	365.10	23.19	12.04	166.00	554.00	7.02
	Max	104.81	16.20	6.78	1.62	398.32	26.82	14.92	274.00	664.00	7.27
	Mean	96.10	14.98	6.34	0.96	388.46	24.97	13.59	219.50	609.25	7.15
	CV (%)	8.40	9.00	7.20	47.60	4.10	7.00	10.90	27.60	10.20	1.90
RW	Min	38.12	11.70	4.85	0.81	156.09	19.61	6.41	94.00	296.00	7.49
	Max	77.38	15.31	5.89	2.18	291.91	30.80	19.44	167.00	515.00	8.13
	Mean	50.92	13.63	5.21	1.24	227.02	24.66	9.61	129.61	365.11	7.88
	CV (%)	20.50	9.20	5.00	36.20	16.10	11.80	45.20	20.80	15.60	2.90
GW	Min	80.28	9.35	4.53	0.57	296.12	17.99	7.05	149.00	512.00	7.10
	Max	104.91	15.78	9.95	0.74	395.62	29.91	17.78	262.00	699.00	7.20
	Mean	88.46	13.10	7.27	0.64	342.84	22.91	12.63	216.00	571.20	7.15
	CV (%)	11.20	21.00	34.90	9.80	12.60	19.00	37.30	24.50	13.50	0.70
WHO 1997)	MDL	75	30	50	100	200	200	250	500	750	7.0-8.5
	MPL	200	150	200	200	600	600	600	1500	1500	6.5-9.2

SW, RW, GW, MDL and MPL represent spring samples, reservoir samples, groundwater samples, the maximum desirable limit and the maximum permissible limit, respectively.

Hydrochemical Facies

The hydrochemical facies were carried out using the Piper diagram (Fig. 2). According to the relative contents of each major ion, two main chemical types of the water sources have been identified: (1) Ca-HCO$_3$ (7 samples) and (2) Ca-Mg-HCO$_3$ (20 samples). The Ca-HCO$_3$ water types account for 75%, 5% and 60% of the spring samples, reservoir samples and groundwater samples, respectively. The Ca-Mg-HCO$_3$ types account for 25%, 95% and 40%, respectively.

Composition changes and hydrochemical characterization of the major ions can be described by the chemical ternary diagram (Palmer & Edmond 1992, Hou et al. 2009). On a ternary cation diagram, the plots falling towards Na$^+$ and Ca^{2+}-Mg^{2+} manifest the dissolution of evaporite and carbonate, respectively. Similarly, on a ternary anion diagram, the plots falling towards HCO$_3^-$ and Cl$^-$+SO$_4^{2-}$ indicate the dissolution of carbonate and evaporite, respectively. In Fig. 2a and 2b, most of cation and anion plots fall towards Ca^{2+} end-member and HCO$_3^-$ end-member, respectively, suggesting that carbonate dissolution are the dominant water-rock interactions with a relatively minor contribution from other reactions, such as silicate rocks, etc. It can properly prove that the flowing formation lithology of the watershed is mainly carbonate rocks.

Mechanism and Processes Regulating Hydrochemistry

To ascertain the sources of dissolved chemistry components, Gibbs proposed two semi-log diagrams known as Gibbs diagrams of TDS versus Na/(Na+Ca) and TDS versus Cl/(Cl+HCO$_3$) to elucidate three major natural mechanisms controlling water chemistry: atmospheric precipitation, rock dominance, and the evaporation (Gibbs 1970). The distribution of sample plots (Fig. 3) showed that the ratios plotted in the rock dominance zone, suggesting the dominant influence is related to water-rock interaction, such as mineral weathering and dissolution.

The plots of Mg/Na and HCO$_3$/Na versus Ca/Na can be further used to identify the source of solutes during water-rock interaction: carbonate dissolution, silicate weathering and evaporation dissolution (Nagaraju et al. 2018). As can be seen in Fig. 4, the ratios of Mg/Na, HCO$_3$/Na and Ca/Na range from 1.46 to 2.59, 8.29 to 25.96, 3.18 to 10.5, respectively, reflecting that carbonate dissolution and silicate weathering are the main functions in the hydrochemistry evolution.
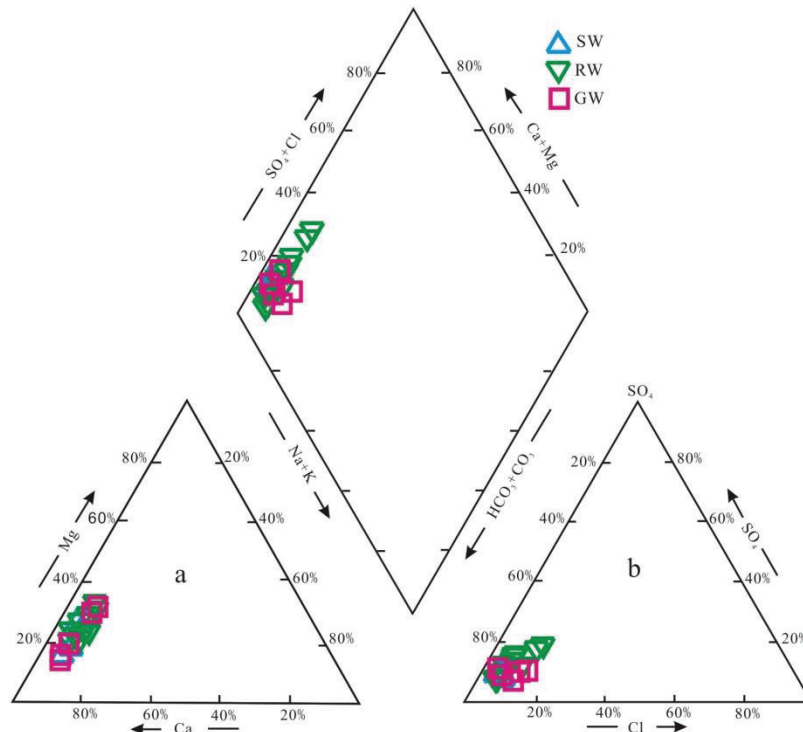

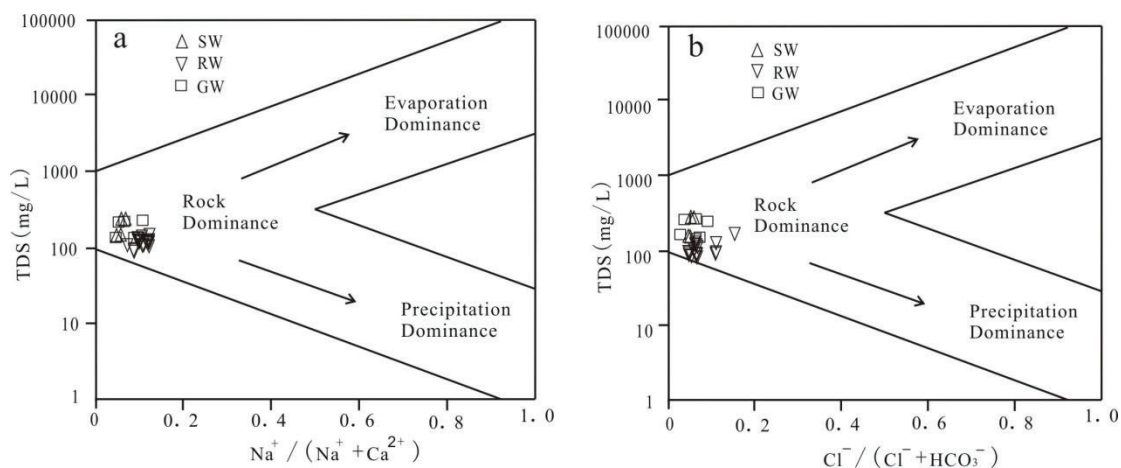Fig. 2: Piper diagram for hydrochemical facies classification.

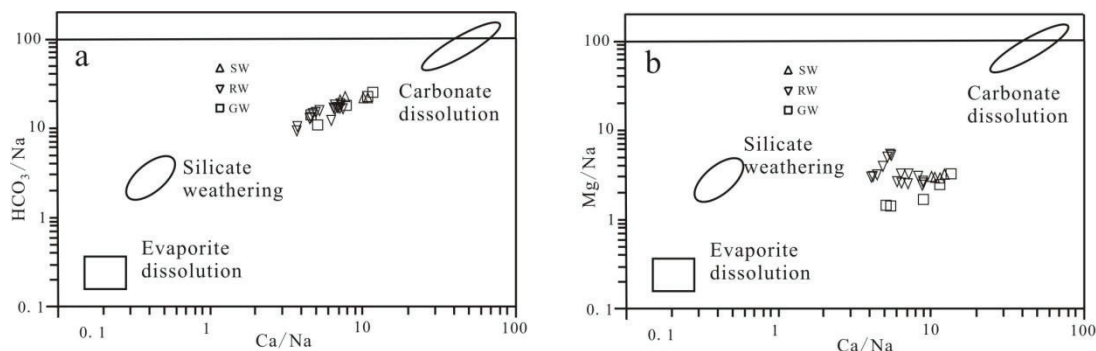Fig. 3: Gibbs plots of TDS values versus $Na^+/(Na^++Ca^{2+})$ (a), TDS values versus $Cl^-/(Cl^-+HCO_3)$ (b).

Fig. 4: Na^+ normalized $Ca^{2+}-HCO_3^-$ (a) and $Ca^{2+}-Mg^{2+}$ (b) plots.

The Origin of Solutes

The ratio of Na/Cl has been proposed to identify the origin of Na^+ and Cl. If Na^+ and Cl^- are mainly from the dissolution of halite, the expected ratio will be 1:1. Values exceeding 1 indicate the dissolution of silicate minerals and wastewater, whereas values much lower than 1 show the dissolution of carbonate minerals and ion exchange (Jalali 2005, Sun & Gui 2014). Local government has implemented strict laws and enforcement to protect the farmland under the pollution-free environment. So based on this actual condition, sodium and chlorine cannot be originated from the anthropogenic activities. As can be seen in Table 1, compared to the content of Ca^{2+} and HCO_3^-, Na^+ and Cl^- show a low to medium concentration, indicating the watershed undergone play a slight reaction of the dissolution of halite. Meanwhile, all the spring samples in Fig. 5a shows the excess of Cl^- relative to Na^+, this feature suggest that apart from the dissolution of halite, the carbonate dissolution and/or ion exchange also

occurred during the water-rock interaction. The plots of RW and GW deviated from the 1:1 relation can be explained by the interactions of water-rock, such as the weathering of silicate and the dissolution of carbonate and/or ion exchange.

As can be seen in Fig. 5b, the scatter plots of calcium and sulphate shows that all the samples deviate from the 1:1 line, indicating another source of calcium, which may be accounted for the process of cation exchange.

The plots of $(Ca^{2+}+Mg^{2+})$ versus $(HCO_3^-+SO_4^{2-})$ were used to illustrate the solute origin of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^-, which are acquired from the simple dissolution of calcite, dolomite and gypsum with the expected ratio of 1:1. Points fall below the equiline, indicating the effect of silicate minerals weathering. Points fall above the equiline, implying the effect of carbonate minerals dissolution. In Fig. 5c, except for one groundwater sample, other points all fall around and below the equiline, reflecting the dominant water-rock interactions are the weathering of silicate minerals and the dissolution of calcite, dolomite and gypsum.

Dissolution of undesirable constituents in aquifer system cannot be controlled, but it is essential to understand the changes undergone by water during the runoff and infiltration. According to Schoeller (1977), ion exchange can be inferred by analysing the chloro-alkaline indices.

$$CA\text{-}I = [Cl^- - (Na^+ + K^+)]/\ Cl^-$$

$$CA\text{-}II = [Cl^- - (Na^+ + K^+)]/(SO_4^{2-} + CO_3^{2-} + HCO_3^-)$$

Positive values of CA indices indicate that Na^+ and K^+ in the water are exchanged with Mg and/or Ca in the host rocks, whereas negative values indicate there is a reverse cation exchange. As can be seen in Fig. 6, all the spring samples show positive chloro-alkaline values, 33% of the reservoir samples are positive and 67% negative, 20% of the groundwater samples are positive and 80% negative, respectively, which confirm that ion exchanges have an important
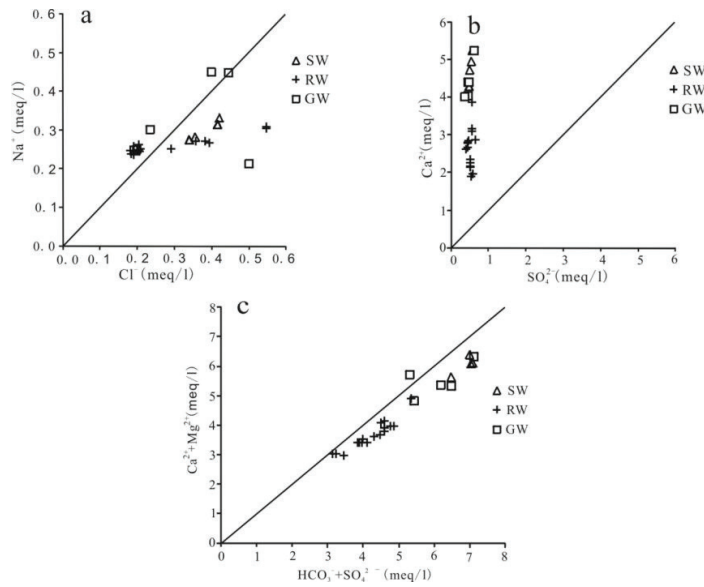

Fig. 5: Relationship between cations and anions of the samples in the study area.
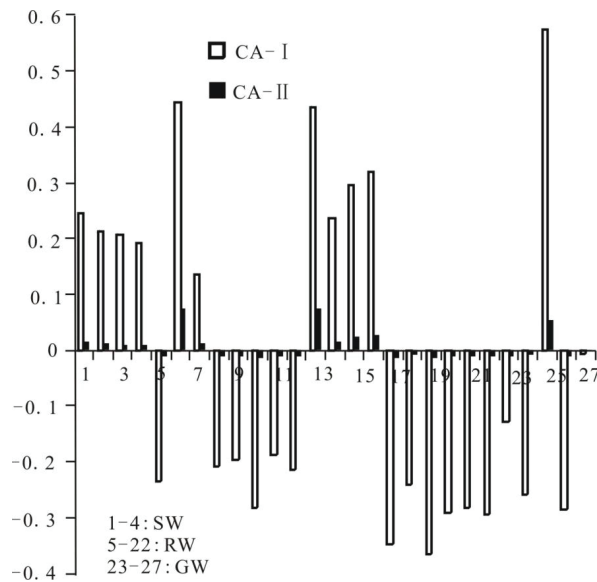

Fig. 6: Chloro-alkaline indices of the samples in the study area.

contribution to hydrochemical components.

Irrigation Water Quality

As to evaluate the irrigation suitability, it is necessary to determine the parameters in terms of salinity and sodium hazard. Sodium adsorption ratio (SAR), sodium percentage (%Na) and electrical conductivity (EC) are the important parameters to assess the water quality for irrigation. The notable problem with a high sodium concentration is leading to degradation of soil structure and decreases on soil perme-

ability. Regardless of the sodium content, samples with the EC less than 200 µS cm^{-1} promotes soil crusting and reduces water penetration (Zaman et al. 2018).

In the study area, variation in EC was observed with the minimum value of 296.00 µS cm^{-1} and the maximum value of 699.00 µS cm^{-1}. According to Wilcox classification (Kaur et al. 2017), all the water samples belonged to the good class for irrigation. The values of SAR were in the range from 0.14 to 0.28, according to Richards classification, 100% of the samples can be classified to excellent for irrigation. The

Table 2: Classification of samples for irrigation purposes.

| Parameters	Range	Classification	Number of samples		
			SW	RW	GW
Salinity hazard (EC)	<250	Excellent	0	0	0
	250-750	Good	4	18	5
	750-2250	Permissible	0	0	0
	2250-3000	Doubtful	0	0	0
	>3000	Unsuitable	0	0	0
Sodium hazard (SAR) (Richard 1954)	<10	Excellent	4	18	5
	10-18	Good	0	0	0
	18-26	Doubtful	0	0	0
	>26	Unsuitable	0	0	0
Percent sodium (%Na) (Wilcox 1955)	<20	Excellent	4	18	5
	20-40	Good	0	0	0
	40-60	Permissible	0	0	0
	60-80	Doubtful	0	0	0
	>80	Unsuitable	0	0	0
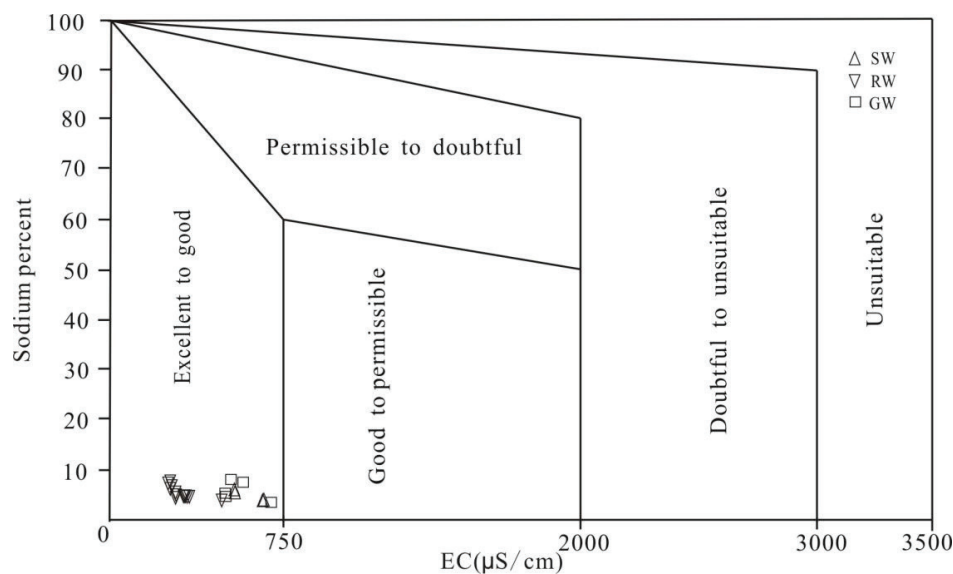
Fig. 7: Water classification based on per cent sodium and electrical conductivity (after Wilcox 1955).
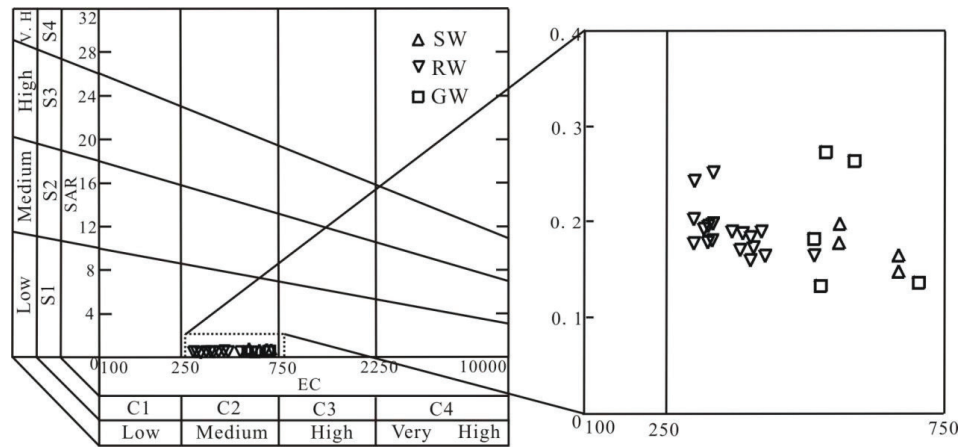
Fig. 8: Water classification based on the USSL diagram.

values of %Na varied from 3.8% to 9.2%, indicating all the samples had excellent suitability for irrigation (Table 2).

The general suitability categorization of waters for irrigation was evaluated using USSL and Wilcox diagram (Etteieb et al. 2017, Zouahri et al. 2015, Bhardwaj & Singh 2011). Wilcox proposed %Na and EC to assess the water quality using Wilcox diagram (Fig. 7). The scatter plots on Wilcox diagram illustrates that all the samples fall in excellent to good categories and can be properly used for irrigation. The USSL Staff presented SAR and EC to evaluate irrigation using USSL diagram (Fig. 8). The plots of data on the US salinity diagram show that all of the water samples fall in the category C2S1, indicating low sodium and medium salinity water. It can be used for irrigation of most crops on most soils with less negative impacts.

CONCLUSIONS

The hydrochemical analysis of surface water and groundwater from Jiagou district, Northern Anhui Province, China reveals that the processes of water-rock interaction and suitability for irrigation. All the parameters concentration can meet the demand for inhabitant and suitable for drinking. Two main chemical types of the water sources have been identified: (1) Ca-HCO$_3$ (7 samples) and (2) Ca-Mg-HCO$_3$ (20 samples). Gibbs diagram suggests that the dominant influence is related to water-rock interaction. The plots of Mg/Na and HCO$_3$/Na versus Ca/Na, and the ion ratio of Na/Cl, Ca^{2+}/ SO$_4^{2-}$, (Ca^{2+}+Mg^{2+}) /(HCO$_3^-$+SO$_4^{2-}$) reflect that carbonate dissolution, silicate weathering have the predominant contribution to the origin of chemical solutes, with a slight function of halite dissolution. Meanwhile, ion exchange has an important contribution to hydrochemical components. Wilcox diagram illustrates that all the samples fall in excellent to good categories and the US salinity diagram

show that all of the water samples fall in the category C2S1, indicating low sodium and medium salinity water. It is concluded that all the samples are suitable for drinking and irrigation purpose.

ACKNOWLEDGEMENTS

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