Hydrogeochemical characteristics and water quality assessment of shallow groundwater: a case study from Linhuan coal-mining district in northern Anhui Province, China

Huili Qiu, Herong Gui, Lin Cui, Zhenggao Pan and Biao Lu

ABSTRACT

Major ion and trace element concentrations in shallow groundwater of Linhuan coal-mining district, Northern Anhui Province, China, were analyzed to determine its hydrogeochemical characteristics and to assess drinking and irrigation water quality. The relative abundance of cations and anions was $Na^{+} > Mg^{2+} > Ca^{2+} > K^{+}$, and $HCO_3^{-} > SO_4^{2-} > Cl^{-} > NO_3^{-}$, respectively. The concentrations of Na^{+}, HCO_3^{-}, NO_3^{-}, and total dissolved solids (TDS), and the electric conductivity (EC) values in some samples were higher than the permissible limits of the Water Health Organization (WHO). Gibbs diagrams showed that rock weathering mainly controlled the major ion chemistry of the groundwater, and the first aquifer of this study area had a weak hydraulic connection with atmospheric precipitation. The calculated sodium percentage (%Na) and sodium adsorption ratio (SAR) revealed that the slight sodium and high salinity hazards needed to be controlled before irrigation. According to the fuzzy comprehensive assessment, the groundwater samples were classified into four categories. The results showed that 92.86% of the groundwater samples were suitable for drinking use. For human health, the NO_3^{-} and Mn levels in the groundwater should be reduced before drinking, and treatment of the high salinity hazards is required before irrigation.

Key words | hydrogeochemistry, mining area, shallow groundwater, water quality assessment

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INTRODUCTION

Groundwater is an indispensable resource for human survival and development. It has been reported that about one-third of the world's population use groundwater as drinking water, and 38% of the global irrigated area uses groundwater as irrigation water (Siebert *et al.* 2010). With the development of modern industry and agriculture, groundwater contamination has become a world-wide environmental problem. Contaminated groundwater can not only endanger human health, but also cause a decrease in the quality of soil (Zhang *et al.* 2012). Therefore, it has become increasingly necessary to understand the hydrochemical characteristics of groundwater and evaluate its quality for drinking and irrigation (Al-Tabbal & Al-Zboon 2012).

Linhuan mining area is rich in coal resources, and is also one of the main bases for growing crops, such as wheat, corn, etc. The groundwater there is the essential water resource for irrigation and drinking use. Previous studies mainly focused on the concentration characteristics of heavy metals and the water quality of deep groundwater (Lin *et al.* 2016), and the pollution degree of trace elements and health risk assessment of shallow groundwater in the study area. In recent years, with the rapid development of the coal industry and agriculture in the region (Huang *et al.* 2018), one must ask: In what ways and to what extent is the groundwater contaminated by mining and surface environmental media (e.g. coal gangue and mining waste water, etc.)? How is the water quality for

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irrigation and drinking use impacted? Prior to this study, no authorized assessments of these questions have been presented in the literature.

In this study, 28 shallow groundwater samples were collected and analyzed to understand their hydrochemical characteristics. Moreover, the water quality for drinking and irrigation purposes was evaluated using fuzzy comprehensive assessment and the United States Department of Agriculture (USDA) salinity diagram, respectively. Principal component analysis (PCA) was used to find out the groundwater's hydrogeochemical information and trace the interactions between groundwater and rock-forming minerals. The results from this study are intended to provide a scientific foundation for protection of public health and groundwater resources.

MATERIALS AND METHODS

Study site

The Linhuan coal-mining district is situated in the north of Anhui Province, China. It covers a total area of over 892 km^2 , and is located between 116°15′ to 116°45′ E, and 33°20′ to 33°40′ N (Figure 1). The study area is a major district in the Huaibei coalfield and it comprises 12 mines (Figure 1(b)). It has a warm, temperate, monsoon climate. The annual average temperature is approximately 14.60 °C. The average annual precipitation is 867 mm, and most precipitation (60%) occurs during the summer. The annual evaporation is 832.40 mm (Qiu *et al.* 2018).

The coalfields in this region are covered by the quaternary loose layer with a thickness of 100.50–771.70 m. The Cenozoic group in the study area contains four aquifers, namely (from top to bottom), the first aquifer, the second aquifer, the third aquifer, and the fourth aquifer. The shallow groundwater in this region originates from the first aquifer, where the main rock composition is mudstone and siltstone. The shallow aquifer is a phreatic aquifer or unconfined aquifer, and is featured by relatively stable distribution. The depth of the aquifer is about 3–5 m. The recharge sources of shallow groundwater are atmospheric precipitation or surface water. The groundwater is used for drinking, irrigation, and industrial purposes, and the water supply is in good condition (Qiu *et al.* 2018).

Sample collection and analysis

Twenty-eight shallow groundwater samples were taken from the study area during July 2017 (Figure 1). Samples were collected from 28 water wells (sampling depth <30 m). Water samples were filtered (0.45 μm Millipore membrane filter) and collected into 2.50 L polyethylene bottles with watertight caps that had been cleaned three times with deionized water

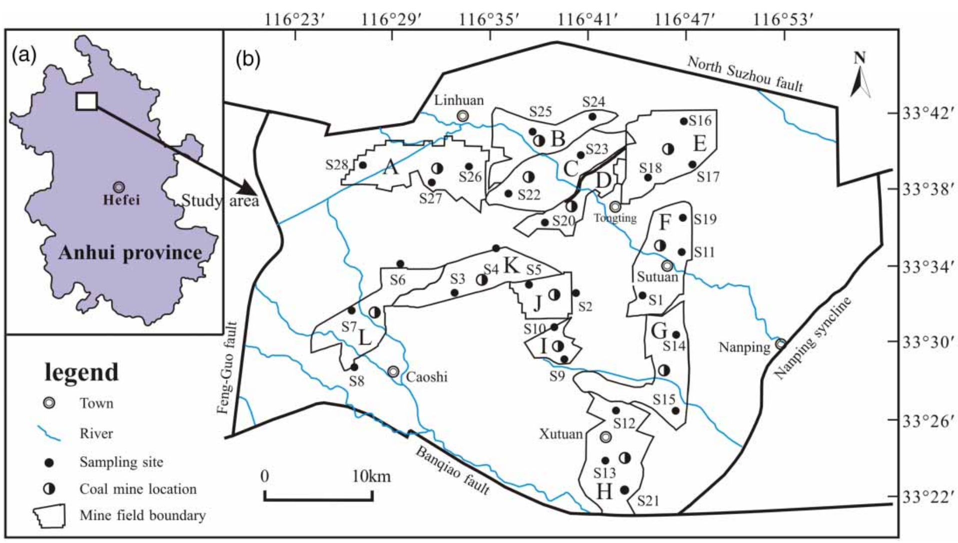

Figure 1 | Geographical location of the 28 sampling sites of the study area: (A) Qingdong; (B) Haizi; (C) Linhuan; (D) Tongting; (E) Yangliu; (F) Suntuan; (G) Renlou; (H) Xutuan; (I) Jiegou; (J) Wugou; (K) Yuanyi; (L) Yuaner.

in the laboratory. All of the samples were gathered, sent to the laboratory, and stored in an ice box for further analysis.

Electric conductivity (EC), pH, temperature and total dissolved solids (TDS) were measured *in situ* with a portable instrument. The major ions and trace elements were analyzed in the laboratory of the National Engineering Research Center of Coal Mine Water Hazard Controlling (Suzhou University). HCO_3^- was determined by the titration method. Major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) were measured by ion chromatography (IC). Trace elements were tested by ICP-MS. Ion balance errors were <5%.

Methods of water quality evaluation for irrigation use

To assess the water quality for irrigation purposes, the following parameters were calculated according to Equations (1) and (2):

$$\%Na = \frac{Na^+}{Na^+ + Ca^{2+} + Mg^{2+} + K^+} \times 100 \quad (1)$$

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \quad (2)$$

where %Na is the percentage sodium, SAR is the sodium adsorption ratio.

Methods of water quality evaluation for drinking use

To assess drinking water quality, we use the fuzzy comprehensive evaluation method. In general, semi-trapezoidal membership functions are introduced. The membership function of water quality at all levels is expressed as follows.

The membership function of Class I is shown in Equation (3):

$$r_{ij} = \begin{cases} 1, & x_i \le s_{ij} \\ \dfrac{s_{ij+1} - x_i}{s_{ij+1} - s_{ij}}, & s_{ij} < x_i < s_{ij+1} \quad (j = 1) \\ 0, & x_i \ge s_{ij+1} \end{cases} \quad (3)$$

The membership function of Class II to Class IV is shown in Equation (4):

$$r_{ij} = \begin{cases} \dfrac{x_i - s_{ij-1}}{s_{ij} - s_{ij-1}}, & s_{ij-1} < x_i < s_{ij} \\ 0, & x_i \le s_{ij-1} \text{ or } x_i \ge s_{ij+1} \quad (j = 2, 3, 4) \\ \dfrac{s_{ij+1} - x_i}{s_{ij+1} - s_{ij}}, & s_{ij} < x_i < s_{ij+1} \end{cases} \quad (4)$$

The membership function of Class V is shown in Equation (5):

$$r_{ij} = \begin{cases} 1, & x_i \ge s_{ij-1} \\ \dfrac{x_i - s_{ij-1}}{s_{ij} - s_{ij-1}}, & s_{ij-1} < x_i < s_{ij} \quad (j = 5) \\ 0, & x_i \le s_{ij} \end{cases} \quad (5)$$

where x_i are the measured values of indicator i, s_{ij} are the standard values of indicator i to class j, r_{ij} are the fuzzy membership of indicator i to class j.

This paper determined the weight of indicators by the following Equation (6):

$$w_i = \frac{x_i}{s_i} \quad (6)$$

where w_i stands for the weight of indicator i, s_i indicates the average value of class I to class V. Normalization processing for the weight of each indicator must be carried out next, the formula for which is as follows in Equation (7):

$$W_i = \frac{x_i}{s_i} / \sum_{i=1}^{m} \frac{x_i}{s_i} = w_i / \sum_{i=1}^{n} w_i \quad (7)$$

where W_i stands for the normalized weight of indicator i. The membership matrix to each class (B) is as follows in Equation (8):

$$B = A \cdot R \quad (8)$$

R and A are the membership relation matrix and weight matrix, respectively. Each groundwater sample is assigned to its class by using the maximum membership.

Statistical analysis

IBM SPSS Statistics 20.0 was used to analyze the hydrochemical data. CorelDRAW 12 and OriginPro 8 were used for graphical processing and analysis.

RESULTS AND DISCUSSION

Conventional hydrochemical characteristics

Descriptive statistics of the groundwater's conventional hydrochemical characteristics are summarized in Table 1.

Table 1 | Descriptive statistics of the groundwater hydrochemistry

Item	Unit	Mean	Min	Max	SD	CV (%)	WHO (2008, 2011) Desirable	WHO (2008, 2011) Permissible
Na^+	mg L^{-1}	136.05	22.92	425.99	104.32	76.68	50	200
K^+	mg L^{-1}	0.03	0	0.25	0.07	244.03	100	200
Ca^{2+}	mg L^{-1}	46.32	19.16	150.19	29.10	62.82	75	200
Mg^{2+}	mg L^{-1}	58.75	29.09	175.13	30.56	52.01	75	200
Cl^-	mg L^{-1}	88.78	4.56	338.62	91.97	103.58	200	600
SO_4^{2-}	mg L^{-1}	97.52	0	363.42	92.44	94.79	200	400
HCO_3^-	mg L^{-1}	505.20	290.46	873.19	169.02	33.46	200	600
NO_3^-	mg L^{-1}	21.73	0	420.50	78.49	3.61	–	50
EC	μS cm^{-1}	1,089.25	451.00	2,730.00	563.87	51.77	750	1,500
pH		7.20	6.64	7.42	0.18	2.56	6.5–8.5	9.2
TDS	mg L^{-1}	701.82	272.19	1,717.44	365.28	52.05	500	1,500

SD indicates standard deviation, CV indicates coefficient variation.

The pH was slightly acidic, as values were between 6.64 (S12) and 7.42 (S1) with a mean value of 7.20. These values were within the range (6.5–8.5) set by WHO (2011). TDS values varied from 272.19 to 1,717.44 mg L^{-1}, with an average of 701.82 mg L^{-1}. These values were much lower than the coal-bearing aquifer of the Linhuan coal-mining district (which varied from 804 to 3,640 mg L^{-1}, with a mean value of 2,074 mg L^{-1}) (Lin *et al.* 2016). The EC values were between 451 and 2,730 μS cm^{-1} (with a mean of 1,089.25 μS cm^{-1}). About 21.43% of the samples were above the permissible value of 1,500 μS cm^{-1} set by WHO (2008). According to previous studies (Islam *et al.* 2017), higher EC values in groundwater were mainly attributed to the ion exchange and increased concentration of dissolved solids.

The orders of relative abundance for cations and anions were $Na^+ > Mg^{2+} > Ca^{2+} > K^+$, and $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$, respectively. According to the WHO's guideline values (Table 1), apart from the ion concentration of K^+, the concentrations of all the ions exceeded the desirable values. However, only the concentrations of HCO_3^-, Na^+, NO_3^-, TDS, and EC exceeded the permissible limits. The Na^+ concentrations found in the groundwater originated from rock–water interaction, including the dissolution of sodium plagioclase. The higher concentration of Na^+ in the groundwater has usually been considered to be an important feature of the coal-bearing aquifer in the Linhuan coal-mining district (Lin *et al.* 2016). The variation of HCO_3^- derives from the weathering of minerals. In general, the high concentration of NO_3^- might have been influenced by anthropogenic activities to some extent (El Tahlawi *et al.* 2016).

Hydrogeochemical processes

To better understand the relation of the chemical composition of groundwater, Gibbs diagrams were created (Murkute 2014). Figure 2 indicates that the major ion chemistry of the groundwater in the study area was determined by rock weathering.

In addition, no sample fell in the precipitation area, demonstrating that there was no direct hydraulic connection between the groundwater and atmospheric precipitation. According to previous studies, isotope (T, D, ^{18}O, $^{87}Sr/^{86}Sr$, $^{13}C_{dic}$ and $^{18}O_{dic}$) analysis of 23 groundwater samples of the Linhuan coal-mining district suggested that rock weathering was the major controller of ion chemistry. Moreover, the site's aquifer was determined to be a relatively closed system (Gui & Chen 2016), which was consistent with the Gibbs plots (Figure 2) in this study.

Principal component analysis was used for multivariate data analysis. Factor loading of principal components (eigenvector >1) and their cumulative variance were obtained (Figure 3). We extracted two components, which had a cumulative variance explanation of 78.52%. Figure 3

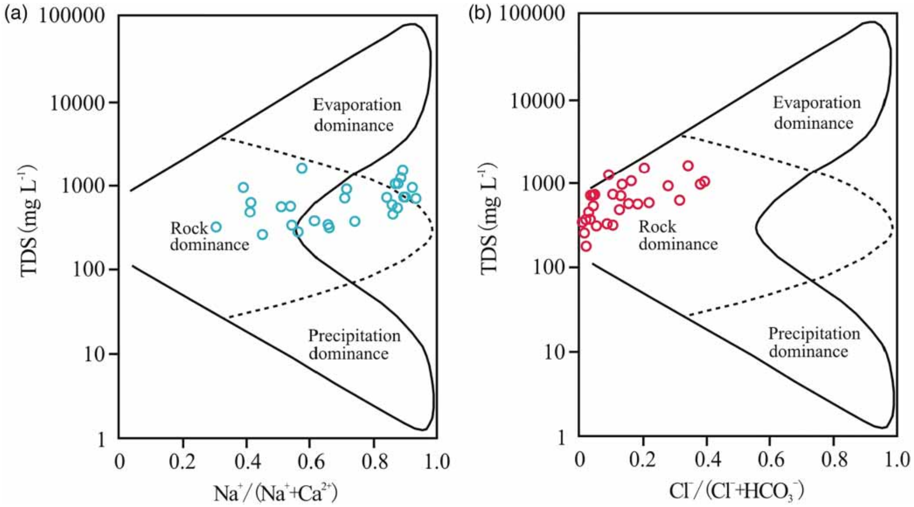

Figure 2 | The Gibbs diagrams of the groundwater from the study area.

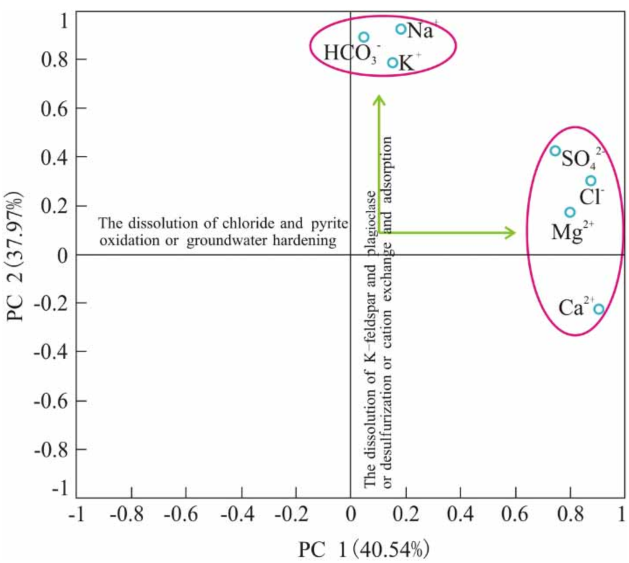

Figure 3 | Load distribution for the analysis variables in the Linhuan coal-mining district.

shows that the first component (PC1) explained 40.54% of the cumulative variance with positive loading on Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}. These ions had higher loads in the PC1, indicating that pyrite oxidation or groundwater hardening played the main roles in water–rock interaction (Chen *et al.* 2014). A positive correlation is observed between Na^+, K^+, and HCO_3^-, and they were associated in a second principal component (PC2) that explained 37.97% of the total variance. These ions had higher loads in the PC2, indicating that the dissolution of K-feldspar and plagioclase or desulfurization or cation exchange and adsorption played the main roles in water–rock interaction in the groundwater.

Groundwater for irrigation use

The groundwater is mainly used for drinking and irrigation. To assess the suitability of the groundwater for irrigation use, classification diagrams (Figure 4) were created.

The calculated %Na values were between 15.16% and 75.65% (mean value 41.10%). Generally, the %Na values <60, indicating the groundwater's suitability for increasing crop yields (Xiao *et al.* 2014). In this study, approximately 35.71% of %Na values exceeded 60. The Wilcox diagram (Wilcox 1955) (Figure 4(a)) shows that the groundwater samples had been divided into four categories. Eleven groundwater samples were classified as excellent-to-good, seven samples were placed in good-to-permissible, eight samples were in permissible-to-doubtful, and only two groundwater samples (S12 and S15) were categorized as doubtful-to-unsuitable.

Another index to assess the water quality for irrigation use was SAR. The SAR values range from 0.60 to 8.10 (mean value 3.30). The USSL diagram (Figure 4(b)) shows that 35.71% of samples were categorized as C2S1, and were considered safe for direct irrigation (Xiao *et al.* 2014). About 39.29% and 17.86% of samples were categorized as C3S1 and C3S2 with a high salinity hazard. Both categories could be used to irrigate for soils with good permeability

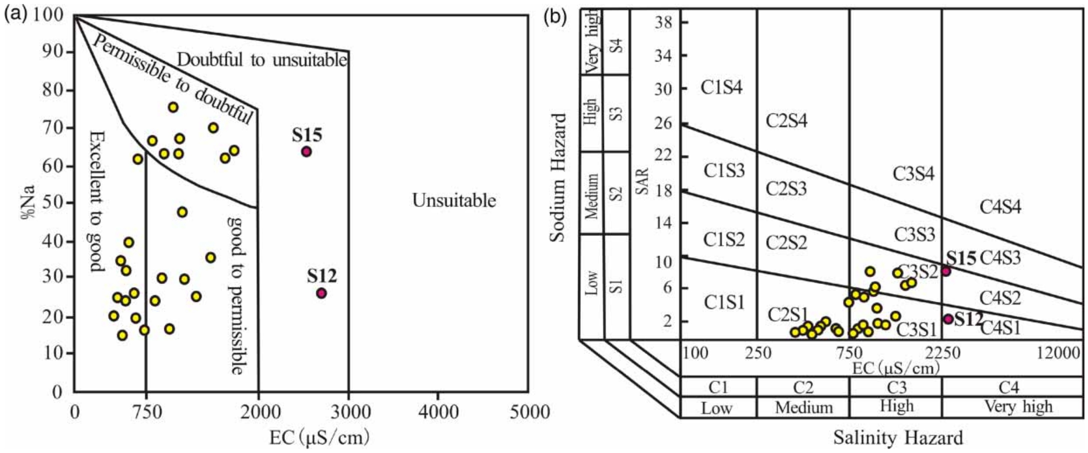

Figure 4 | (a) Wilcox diagram (percentage of sodium vs EC) and (b) USSL diagram (SAR vs EC).

(Rao *et al.* 2012). About 7.14% of samples were categorized as C4S1 and C4S2 with a very high salinity hazard, indicating that the groundwater was not suitable for irrigating soils with restricted drainage. The results showed that the irrigation water quality of shallow groundwater was better than the coal-bearing aquifer of this region (almost all the groundwater samples have very high salinity and alkalinity hazard values) (Lin *et al.* 2016).

Groundwater for drinking use

The groundwater is used not only for irrigation, but also for drinking. Fuzzy comprehensive assessment was used to evaluate the suitability of the groundwater for drinking use according to quality standards (General Administration 1993, 2006; MoH *et al.* 2006) (Table 2). In this study, five evaluation parameters (Cl^-, SO_4^{2-}, NO_3^-, Mn, and TDS) were chosen and Equations (3)–(8) were used. The calculated results showed that the water quality could be categorized into class I, II, III, and V, which accounted for 25%, 39.29%, 28.57%, and 7.14% of the total, respectively. Generally speaking, the groundwater quality was good. The results of this study showed that the water quality was better than the shallow groundwater of the urban area in Suzhou (about one-third of the samples are classified as heavily polluted) (Sun & Peng 2014). Sample S12 fell into class V, as its concentrations of Cl^-, NO_3^-, and TDS exceeded the permissible values; NO_3^- concentration was 4.75 times the allowable value of class III. Sample S15 also fell into class V, because the concentration of SO_4^{2-} and TDS exceeded the allowable values of class III. Sample S21 fell into class II, but its Mn concentration was 2.90 times the allowable value of class III. Therefore, the water quality indicators that exceeded the limits were mainly Cl^-, NO_3^-, SO_4^{2-}, Mn and TDS.

Table 2 | Groundwater quality standards for drinking and irrigation

Class	Cl^-	SO_4^{2-}	NO_3^-	Mn	TDS	Suitability
I	50	50	8.86	0.05	300	Drinking, Irrigation
II	150	150	22.14	0.05	500	Drinking, Irrigation
III	250	250	88.57	0.10	1,000	Drinking, Irrigation
IV	350	350	132.86	1	2,000	Irrigation
V	>350	>350	>132.86	>1	>2,000	Not suitable

Ion concentration (mg/L), TDS (mg/L).

CONCLUSIONS

Twenty-eight shallow groundwater samples were collected from the study area. The purpose was to determine the hydrogeochemical characteristics and also to assess the quality for both drinking and irrigation use. SAR and %Na suggested that most shallow groundwater can be used directly for irrigation water without treatment, but some shallow groundwater requires treatment to reduce the salinity hazard before it can be used for irrigation. The results of fuzzy comprehensive assessment showed that the water quality could be categorized into class I, II, III, and V, which accounted for 25%, 39.29%, 28.57%, and

7.14% of the total, respectively. Based on the findings of this study, it can be concluded that the groundwater in the study area is suitable for drinking use except samples S12 and S15. Therefore, after treatment for the heightened levels of NO_3^- and Mn, the groundwater would be suitable for drinking. Moreover, it could be used for irrigation after treatment for the salinity hazard. This study provides a reference point for future in-depth studies of the hydrochemical characteristics and groundwater quality in other similar areas.

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