

Calculating groundwater mixing ratios in multi-aquifers based on statistical methods: a case study

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Abstract

Samples of river water and groundwater from Quaternary (QA), sandstone (SA), Taiyuan formation (TA), and Ordovician limestone (OA) aquifers in the Suxian coal-mining district, Anhui Province, China were collected. Their physicochemical properties, and major ion and isotopic compositions were determined. The samples were alkaline, with pH values exceeding 8, and the total dissolved solids concentrations depended on the water source. The δD and $\delta^{18}O$ contents were highest in the river water samples and lowest in the SA groundwater. The isotopic characteristics of the QA and OA groundwaters suggest recharge by rainfall and surface water. The isotopic characteristics of river water were controlled mainly by evaporation. Water–rock interactions, the flow rate, and the main water sources were the most important influences on groundwaters in QA, OA, and TA, but the properties of SA groundwater were controlled by static reserves. Two discriminant functions, explaining more than 98.2% of the total variances, indicated that QA, TA, and OA were hydraulically connected. Three groundwater sources were identified as end-members, and a conceptual model was established to calculate water mixing ratios.

Key words: coal mine district, groundwater, isotopic geochemistry, multi-aquifer

Highlights

- This paper systematically discusses the chemical characteristics of elements and isotopes of groundwater in multi aquifers in coal mine area, and establishes a mixed water source identification model by using statistical method. The research results have certain significance for the establishment of groundwater chemistry and water source identification model.

INTRODUCTION

Groundwater systems serving as major water resources are an important part of the earth's surface environment. Groundwater that flows through aquifers or remains in them for long periods contains abundant geological information. Geochemical indicators can therefore be effective tools for solving hydrological problems.

In mining areas, groundwater is exploited intensively for agricultural, urban, and industrial uses (Zouari *et al.* 2011; Ma *et al.* 2015), but also threatens the safety of coal mining activities. In the past few decades, incidents involving rapid groundwater inflows have occurred frequently as coal mining activities have gone progressively deeper below the surface in China. Thus, studies of the

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hydrochemistry and dynamics of groundwater are important, as they can improve understanding of regional hydrogeological conditions and water–rock interactions in coalfields.

Many studies have already examined runoff control, hydrologic processes, and the chemical and isotopic characteristics of groundwater (Gui *et al.* 2011; Sun *et al.* 2011; Chen & Gui 2015). However, few studies have examined the factors influencing the geochemical properties of groundwater in multiple aquifers. Since the concentrations of environmentally stable isotopes (D, ^{18}O) in groundwater change little with water–rock interactions at low temperatures, stable isotopes can be used to bridge this knowledge gap (Molla *et al.* 2007; Huang & Chen 2012). Groundwaters in diverse aquifers usually have hydraulic connections in coal mining districts, and both their hydrogeochemistry and stable isotope ratios can be used to characterize groundwater recharge processes and circulation mechanisms, and examine the mixing ratios of groundwaters in different aquifers (Chen *et al.* 2014).

Many previous studies have focused on the hydrogeochemical characteristics of groundwater from single aquifers, and overlooked the differences between the diverse aquifers in Huaibei coal mine (Gui 2014). Very few studies have used hydrogeochemical and stable isotope characteristics to examine interactive relationships between groundwaters from different aquifers and/or trace groundwater flow. For this study, surface- and groundwater samples were collected and analyzed in July 2015 in the Suxian coal-mining district in Anhui Province, China. The main objectives were (1) to define the geochemical characteristics of, and relationships between, groundwaters from different aquifers, (2) to understand the factors controlling the hydrochemical processes, and (3) to establish a model for calculating groundwater mixing ratios in coal mining districts.

GEOLOGICAL BACKGROUND

Huaibei Coalfield, in the north of Anhui Province, is the largest coal mining area in the North China Plain, and contains significant coal resources (Figure 1). The area has a marine-continental climate, with an annual average temperature of 14.9 °C. The average annual precipitation and evaporation are about 867.0 and 832.4 mm, respectively, and more than 50% of the total precipitation falls from June to September (Chen *et al.* 2014). There is little surface water in the study area, so groundwater is the main source of water for industrial and domestic uses.

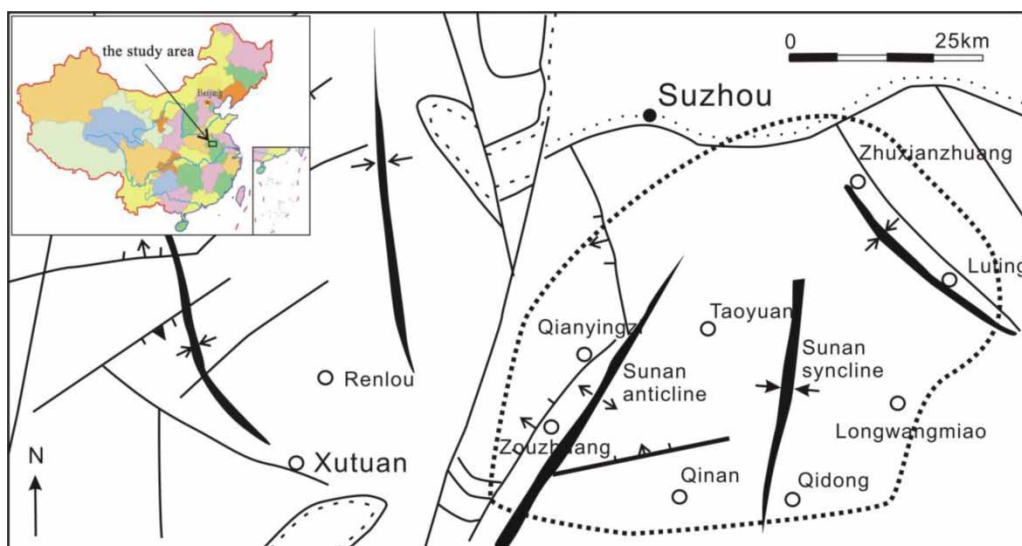


Figure 1 | Location and geological setting of the study area in northern Anhui Province, China.

The Huaibei Coalfield has three mining areas: Suixiao, Suxian, and Linhuan. In the Suxian area, the coal-bearing formations are distributed mainly through the Carboniferous and Permian, with a total thickness exceeding 1,300 m (Zheng *et al.* 2008). The formations in the study area comprise strata from the Cambrian, Ordovician, Carboniferous, Permian, and lower Triassic periods. The groundwater system in the Suxian coal-mining area includes four principal aquifers – a Quaternary aquifer (QA), a sandstone aquifer (SA), an aquifer from the Taiyuan formation (TA), and an Ordovician limestone aquifer (OA) – all of which pose threats to the mine (Figure 2).

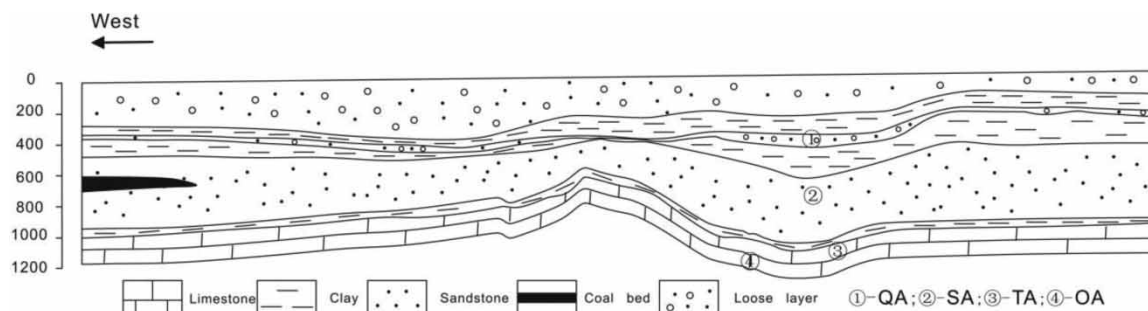


Figure 2 | Hydrogeological profile of the multilayer aquifer system studied.

The four aquifers differ in lithology, thickness, and water-bearing capacity:

The QA consists of conglomerate, sand, and clay, is between 11.7 and 132.9 m below sea level (bsl), and has a permeability (K) of 0.00043 to 0.0456 m/d.

The SA, characterized by sandstone, siltstone layers, and a coal seam, is between 459.4 and 864.6 m bsl, and its K is 0.0008 to 12.5 m/d. It is underlain by an aquitard that does not develop cracks or fractures, and is between 67 and 200 m thick.

The TA, a limestone, is evenly distributed throughout the district. It is between 8.36 m above sea level (asl) and 174.56 m bsl, and K is between 0.021 and 3.11 m/d.

The OA consists of gray or dark-gray thick-bedded limestone. The main aquitard between underlying TA and the OA is mudstone between 30 and 120 m thick.

Because of the aquifer's lithology, SA groundwater is mainly static reserves, with poor liquidity. The groundwaters in the TA and OA move laterally, and the flow directions are controlled by the Sunan anticline and syncline. In the TA and OA, groundwater runoff is from both the east and west into the middle. The exploitation of deep coal resources has led to recharge leakage throughout the aquifer system, especially in the QA, TA, and OA.

SAMPLE COLLECTION AND ANALYSIS

Thirty two samples of river- and groundwater were collected from 6 coal mines in July 2015 – see Table 1 for information about the sampling and the sampling sites. Every fifth sample was collected in duplicate to check the accuracy of the analyses. River water samples were put into 2.5 L plastic barrels pre-rinsed 3 times with the water at the sampling site. Information about the site longitude and latitude, and water pH, conductivity, and total dissolved solids (TDS) content, was recorded *in situ*. Groundwater samples were collected from drainage holes in mine alleys and filtered through 0.45- μ m membranes into sterilized polyethylene bottles pre-washed in line with the cleaning procedures for standard trace element analysis. All samples were analyzed for major ion concentrations, and hydrogen and oxygen isotopic contents. Major ions were determined in the analytical laboratory of the Department of Coal Geology, Anhui Province, China. The $K^+ + Na^+$,

Table 1 | Sampling information – Suxian coal-mining district

Sample	Source	Mine	Water level elevation (m)	Location	Latitude (N)	Longitude (E)
1	River	Luling	9.8	Tuohe River	33.46025°	117.15302°
2	River	Taoyuan	10.0	Yunliang River	33.50755°	117.00642
3	River	Zhuxianzhuang	12.8	Xinbian River	33.62951°	117.1242°
4	River	Zhuxianzhuang	13.5	Tuohe River		
5	River	Qianyingzi	8.6	Huihe River	33.48469°	116.94886°
6	River	Qinan	9.6	Huihe River	33.43632°	117.01678°
7	QA	Zhuxianzhuang	-13.7	Hydrologic hole-84-22	33.63886°	117.09230°
8	QA	Zhuxianzhuang	-126.4	Hydrologic hole-84-14		
9	QA	Qianyingzi	-14.0	Hydrologic hole-2	33.47780°	116.93623°
10	QA	Qianyingzi	-11.8	Hydrologic hole-5	33.48311°	116.92879°
11	QA	Qidong	-466.0	Drain hole in South		
12	QA	Qinan	-12.7	Observation bh 02-4	33.46178°	116.98812°
13	QA	Zouzhuang	-21.0	Observation bh 10-2	33.40815°	116.86013°
14	SA	Qianyingzi	-520.0	E ₃ 211 coal face		
15	SA	Qianyingzi	-608.0	W ₃ 213 roadway		
16	SA	Qidong	-600.0	Hydrologic hole-7124		
17	SA	Qinan	-486.1	101 track lane		
18	SA	Zouzhuang	-440.0	3 ₂ transport roadways		
19	TA	Luling	24.0	Ventilating shaft	33.57288°	117.17794°
20	TA	Taoyuan	-400.0	1,035 coal face	33.50732°	116.99301°
21	TA	Taoyuan	-800.0	Drain hole II4 aea		
22	TA	Zhuxianzhuang	-130.0	Mine track riseII5		
23	TA	Qianyingzi	-5.1	Hydrologic hole-30B4	33.48235°	116.93677°
24	TA	Qidong	-17.0	Hydrologic hole-ST4	33.38862°	117.07508°
25	TA	Qinan	-538.5	3,682 coal face		
26	TA	Zouzhuang	0.6	Observation bh 11-1	33.43855°	116.85635°
27	OA	Luling	24.0	Luling middle school hole	33.51991°	117.18179°
28	OA	Taoyuan	-9.9	Observation bh 2014-2		
29	OA	Zhuxianzhuang	-2.7	Hydrologic hole 84-24	33.63434°	117.13338°
30	OA	Qianyingzi	-8.3	Hydrologic hole-T4	33.48391°	116.94859°
31	OA	Qidong	-10.0	Observation bh	33.40287°	117.12053°
32	OA	Qinan	-9.1	Observation bh 07-1	33.47383°	116.97445°

SO₄²⁻ and Cl⁻, Ca²⁺ and Mg²⁺, and alkaline concentrations were determined by atomic absorption spectrometry, ion chromatography, EDTA titration, and acid-based titration, respectively. The isotopic compositions were determined in the laboratory of the National Engineering Research Center for the Control of Coal Mine Water Hazards. The isotopic data are reported relative to Standard Mean Ocean Water (SMOW), and the precisions of δ¹⁸O and δD were ± 0.2‰ and 2‰, respectively.

RESULTS AND DISCUSSION

Hydrogeochemical characterization

Information about the major ion concentrations in the water samples is presented in Table 2 and Figure 3. The ionic balance was checked using AqQa software (RockWare Inc 2003). The pH of

Table 2 | Major parameter values in the water samples

Sample	K ⁺ + Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	pH	TDS	Water type	δD	δ ¹⁸ O
1	166.6	105.	60.6	336.	162.2	283.1	0.0	8.15	1,300.	Na-Cl	-41.0	-4.80
2	470.4	72.1	46.6	490.8	432.4	211.2	37.5	8.91	2,680.0	Na-Cl	-52.41	-6.69
3	176.9	45.3	49.6	142.4	260.5	244.3	17.5	8.44	983.0	Na-SO ₄	-33.36	-3.01
4	314.7	80.2	97.2	223.1	638.0	394.4	0.0	8.12	1,910.0	Na-SO ₄	-36.06	-3.73
5	483.4	62.0	65.5	237.2	847.1	227.0	43.2	8.60	2,225.0	Na-SO ₄	-36.42	-4.01
6	420.2	65.6	59.4	269.4	560.6	363.9	35.0	8.53	2,010.0	Na-SO ₄	-43.17	-5.34
7	104.0	22.7	12.3	152.7	2.5	150.1	0.0	7.78	495.0	Na-Cl	-57.77	-7.64
8	143.1	4.0	4.9	158.7	4.1	0.0	72.0	10.70	539.0	Na-Cl	-57.57	-7.42
9	37.9	48.1	20.1	22.3	7.2	99.2	35.0	9.33	229.0	Ca-HCO ₃	-57.72	-7.98
10	199.7	1.6	4.9	135.6	5.8	62.6	126.1	10.02	707.0	Na-CO ₃	/	/
11	109.6	198.4	137.5	238.5	610.0	399.5	0.0	7.27	1,810.0	Mg-SO ₄	-63.42	-8.59
12	148.2	4.0	9.8	118.7	4.5	151.3	45.6	9.25	491.0	Na-HCO ₃	-61.58	-8.36
13	101.1	4.0	7.3	75.0	14.8	75.7	48.0	10.10	370.0	Na-CO ₃	-52.08	-7.02
14	519.1	10.5	4.9	120.4	55.2	1,157.0	0.0	7.81	1,680.0	Na-HCO ₃	-63.24	-8.43
15	865.4	10.5	4.9	144.8	96.7	1,981.9	0.0	7.80	2,870.0	Na-HCO ₃	-63.68	-8.38
16	593.0	4.1	9.3	229.9	40.3	1,185.8	0.0	8.04	2,100.0	Na-HCO ₃	-63.57	-8.48
17	449.3	12.1	3.9	155.2	182.3	749.3	0.0	8.20	1,550.0	Na-HCO ₃	-64.48	-8.28
18	1,104.7	105.3	109.2	254.0	2,357.6	369.0	0.0	7.44	4,740.0	Na-SO ₄	-66.27	-8.94
19	28.1	4.5	7.1	15.4	4.5	49.4	24.0	9.40	123.0	Na-HCO ₃	-71.83	-10.15
20	174.4	210.5	76.1	205.9	681.0	267.2	0.0	7.86	1,900.0	Ca-SO ₄	-62.10	-8.31
21	197.4	266.4	77.8	212.8	806.5	335.9	0.0	7.70	2,190.0	Ca-SO ₄	-62.16	-8.37
22	413.7	112.0	68.9	155.2	540.0	451.6	187.7	7.80	1,530.0	Na-SO ₄	-63.15	-8.44
23	95.4	5.3	9.1	34.3	2.5	221.4	20.0	8.62	333.0	Na-HCO ₃	-54.45	-7.46
24	50.5	4.9	6.4	20.6	7.4	104.3	17.5	9.26	172.0	Na-HCO ₃	-54.45	-7.49
25	194.6	204.8	109.0	248.8	676.7	399.5	0.0	7.82	1,950.0	Ca-SO ₄	-63.91	-8.33
26	43.1	4.8	6.4	14.0	15.6	73.2	21.6	10.10	150.0	Na-CO ₃	-49.09	-6.64
27	141.6	78.8	17.4	54.9	4.3	207.6	81.1	9.43	587.0	Na-HCO ₃	-42.76	-5.40
28	190.4	117.4	62.4	181.9	562.5	132.3	7.5	8.80	1,310.0	Na-SO ₄	-60.23	-8.07
29	77.1	4.1	3.0	56.6	2.5	100.8	23.5	9.13	279.0	Na-HCO ₃	-50.57	-6.73
30	130.1	9.3	4.7	49.8	181.7	3.6	39.0	10.45	691.0	Na-SO ₄	-47.98	-6.94
31	62.8	5.7	3.9	32.6	42.4	43.3	32.5	10.54	276.0	Na-HCO ₃	-47.69	-6.50
32	98.4	16.2	13.3	97.8	136.7	20.4	7.5	8.90	446.0	Na-SO ₄	-55.80	-7.51

river water was between 8.1 and 8.9, indicating that the water is alkaline. The river waters' TDS was between 983 and 2,680 mg/l. Cation concentrations in the river water decreased in the order: K⁺ + Na⁺ > Ca²⁺ > Mg²⁺, and anion concentrations: SO₄²⁻ > Cl⁻ > HCO₃⁻ > CO₃²⁻. The river water types were Cl-Na-K and SO₄-Na-K, and the principal ions Na⁺ + K⁺, Cl⁻, and SO₄²⁻.

The ionic compositions of the groundwaters from the different aquifers were variable and complex, and the water chemistry inconsistent.

The groundwater pH and TDS in QA ranged from 7.3 to 10.7, and from 229 to 1,810 mg/l, respectively, and the similarity of the QA and river water hydrochemical characteristics suggest that the QA is mainly recharged by surface water. SA groundwaters were of the Na-HCO₃ type, indicating long residence time in the aquifer and extensive water-rock interaction. TDS concentrations were highest in SA, ranging from 1,550 to 4,740 mg/l. TA groundwaters had high Ca concentrations, with TDS in the range 123 to 2,190 mg/l. The TDS concentration range was lowest in the OA groundwaters in OA

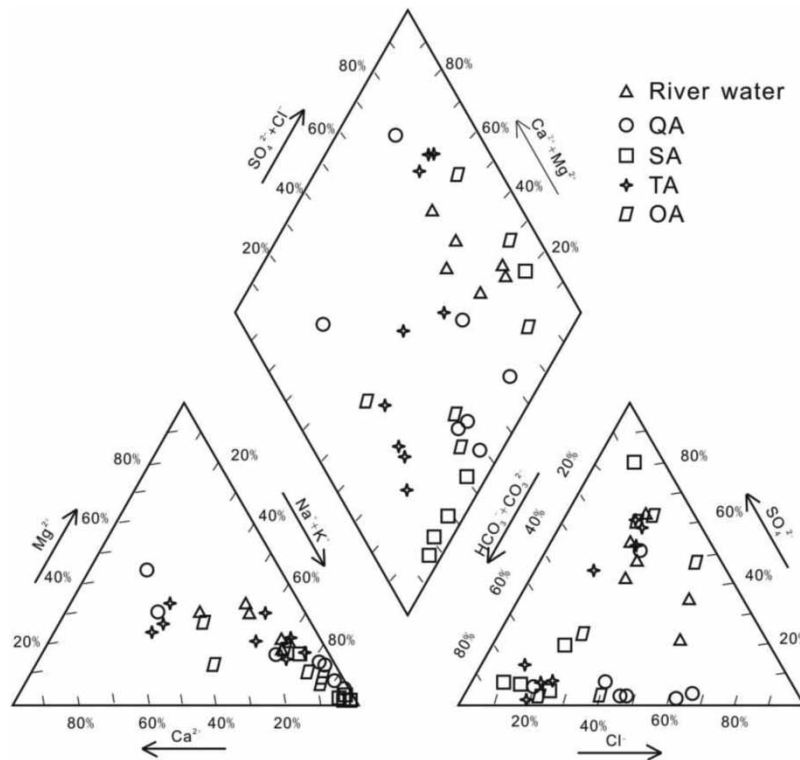


Figure 3 | Piper diagrams of waters from Suxian coal mining district.

(276 to 1,310 mg/l), suggesting quick runoff, good recharge and limited water-rock interaction. TDS concentrations were low in the QA and OA.

Isotopic characterization

Information about the δD and $\delta^{18}O$ concentrations is given in Table 2 and Figure 4, but these data must be seen in a wider context to provide some insight into the isotopic characteristics of the ground and surface waters. This is achieved by reference to the global meteoric water line (GMWL), local meteoric water line (LMWL), and local surface water line (LSWL) for δD and $\delta^{18}O$. The GMWL, as defined by Craig (1961), is described by $\delta D = 8 * \delta^{18}O + 10.56$; the LMWL was summarized by Zhang (1989) as $\delta D = 7.9 * \delta^{18}O + 8.2$, and the LSWL was summarized as $\delta D = 6.74 * \delta^{18}O - 3.33$ (Gui *et al.* 2005). These lines and the groundwaters' isotopic signatures are shown in Figure 4.

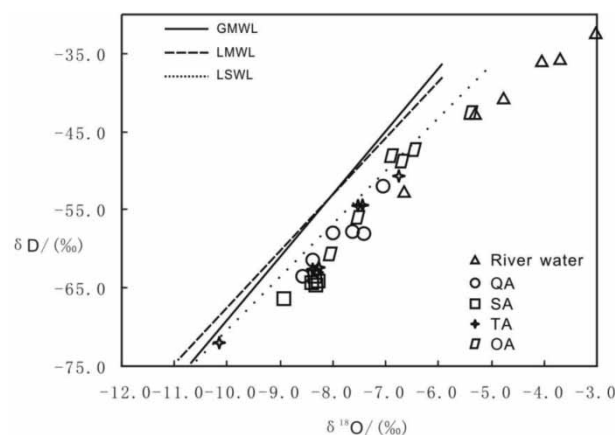


Figure 4 | δD and $\delta^{18}O$ of water samples from Suxian coal mining district.

The δD and $\delta^{18}O$ contents were highest in the river water, and ranged from -52.41 to -33.36‰ , and from -6.69 to -3.01‰ , respectively, and show clear heavy isotope enrichment. The samples were collected in July, when the climate was relatively dry, and the δD and $\delta^{18}O$ concentrations were probably controlled by evaporation.

The contents of δD and $\delta^{18}O$ in groundwater from QA ranged from -63.42 to -52.08‰ and from -8.59‰ to -7.02‰ . The $\delta^{18}O$ and δD contents in groundwater from OA varied from -8.07‰ to -5.40‰ , and from -60.23‰ to -42.76‰ , respectively. The plots for the QA and OA groundwaters are distributed along the LSWL, with similar line slopes to that of the GMWL, indicating that rainfall and surface water recharge may have occurred, and this view is supported by previous work (Chen *et al.* 2008). The δD and $\delta^{18}O$ concentrations in the SA, however, were lower, ranging from -66.27 to -63.24‰ , and -8.94 to -8.28‰ , respectively, and plotted away from the LSWL. The δD and $\delta^{18}O$ concentrations in LA groundwater ranged from -71.83 to -49.09‰ , and -10.15 to -6.64‰ , respectively.

Influences on the isotopic contents of water samples

Usually, the sources of solutes in water bodies are complex, and can be influenced by both natural conditions and human activities. If not influenced by other factors, the TDS concentrations in river water derived directly from precipitation are low (Gibbs 1970). The TDS concentrations in river water in this study were high, however, which could indicate strong evaporative effects, although other factors can also have the same effects. The river waters also have the highest δD and $\delta^{18}O$ concentrations, which is a strong indication of evaporation.

Figure 5 shows that the river water concentrations of δD and $\delta^{18}O$ generally fell with increasing TDS – that is, the δD , $\delta^{18}O$, and TDS were negatively correlated, and the δD and $\delta^{18}O$ concentrations in river water are influenced by evaporation and other factors. The negative TDS – δD , $\delta^{18}O$, correlations suggest that water-rock interactions may also influence the δD and $\delta^{18}O$ contents of water bodies (Chen *et al.* 2008).

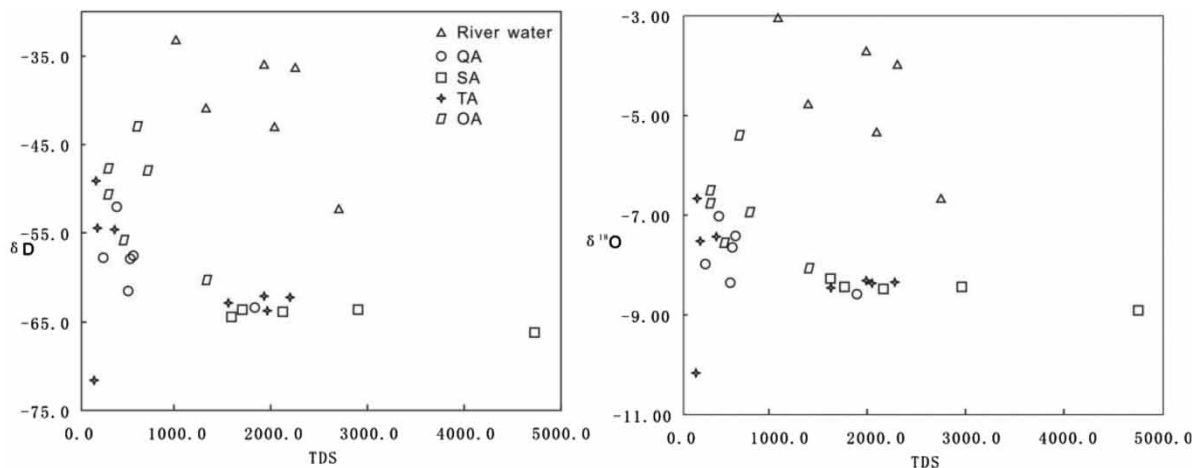


Figure 5 | Plots of TDS- δD , $\delta^{18}O$ in waters from Suxian coal mining district.

The TDS concentrations in QA and OA groundwater were lower than those in the SA and TA, suggesting that the QA and OA are recharged by precipitation and the groundwaters are not subject to evaporation. This is also suggested by the δD and $\delta^{18}O$ properties (Figure 4). The isotopic properties of QA and OA groundwater show evidence of water-rock exchange reactions, leading to slight isotopic enrichment of the groundwater. Further, δD , $\delta^{18}O$, and TDS in QA and OA groundwater were

negatively correlated (Figure 5). The TA groundwater TDS concentrations were higher than those of QA and OA, indicating water-rock interaction occurrence in the TA – that is, carbonate dissolution has more influence on groundwater in TA than in QA and OA.

The δD - $\delta^{18}O$ concentrations in waters from the river, QA, TA, and OA were all similar (Figure 5), with negative TDS- δD , - $\delta^{18}O$ correlations. The general decrease in stable isotope concentrations as TDS increased, suggests that the isotope concentrations in all four sources are controlled mainly by water-rock interactions. The SA groundwater differed from the other waters, however. Its TDS concentrations were higher than in the other aquifers, and the δD and $\delta^{18}O$ concentrations were the lowest in any groundwater sampled. Further, the δD and $\delta^{18}O$ concentrations in SA groundwater were stable, and did not vary as the TDS concentration changed. These properties indicate that SA groundwater is dominated by static reserves, with either slow or zero flow.

Fisher discriminant analysis

The results presented above show that ground and surface waters have variable features inherited either from their immediate environment through water-rock interactions or from evaporation. The property variations can be used to identify the water types and origins. Previous studies have shown that discriminant analysis is an efficient way to identify water sources and types (Chen *et al.* 2013). The data from this study were analyzed using Fisher discriminant analysis (SPSS version 19) (IBM Corp. 2010), and the results are presented in Tables 3 and 4, and Figure 6. Two discriminant functions were obtained, and the related parameters are listed in Table 3. The Fisher discriminant functions can be expressed as:

$$F_1 = 0.002X_1 - 4.76X_2 - 0.03X_3 + 0.01X_4 + 0.006X_5 - 15.8$$

$$F_2 = -0.002X_1 - 13.16X_2 + 0.05X_3 - 0.08X_4 + 0.004X_5 - 48.93$$

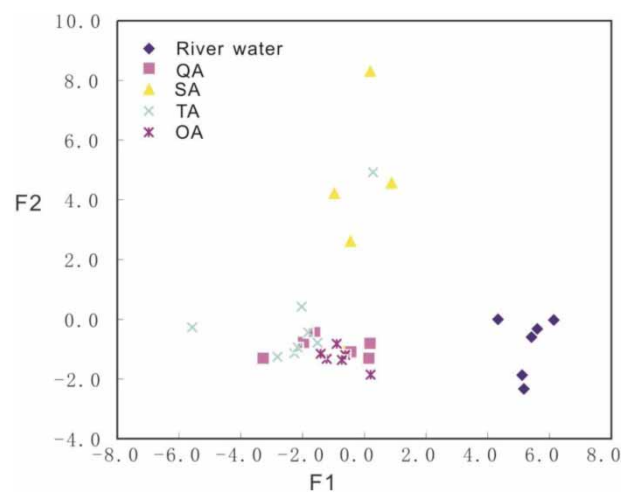
Table 3 | Fisher discriminant function parameter values for waters in Suxian coal mining district

Parameter	F1	F2
TDS	0.002	-0.002
$\delta^{18}O$	-4.76	-13.16
Ca^{2+}	-0.03	0.05
Cl^-	0.01	-0.08
HCO_3^-	0.006	0.004
Constant	-15.80	-48.93
Variance (%)	60.0	38.2
Eigenvalue	8.79	5.59
RA (central value)	5.29	-0.86
QA (central value)	-1.30	-1.01
SA (central value)	-0.01	4.92
TA (central value)	-2.42	-0.72
OA (central value)	-0.75	-1.27

Functions F_1 and F_2 are the first and second discriminant functions, and X_1 , X_2 , X_3 , X_4 , and X_5 represent the concentrations of TDS, ^{18}O , Ca^{2+} , Cl^- , and HCO_3^- , respectively. In total, 98.2% of the variance was explained by the first and second functions, with eigenvalues of 8.79 and 5.59, respectively – that is, most of the ground and surface water information can be interpreted from these two functions, including identifying confined groundwaters.

Table 4 | Discriminant results of water and actual source in the study area

Sample	Actual source	Discriminated source	Sample	Actual source	Discriminated source
1	River	River	17	SA	SA
2	River	River	18	SA	SA
3	River	River	19	TA	TA
4	River	River	20	TA	TA
5	River	River	21	TA	TA
6	River	River	22	TA	TA
7	QA	QA	23	TA	<u>QA</u>
8	QA	QA	24	TA	<u>QA</u>
9	QA	<u>TA</u>	25	TA	TA
10	QA	<u>OA</u>	26	TA	<u>OA</u>
11	QA	<u>TA</u>	27	OA	OA
12	QA	QA	28	OA	<u>QA</u>
13	QA	<u>OA</u>	29	OA	OA
14	SA	SA	30	OA	OA
15	SA	SA	31	OA	OA
16	SA	SA	32	OA	<u>QA</u>

**Figure 6** | Fisher discriminant diagram for waters in the study area.

The discriminant analysis results – [Table 4](#) – show that nine samples were inconsistent with their actual sources. For example, the samples from the river and SA were all recognized correctly, but there were 4, 3, and 2 discriminated erroneous samples from QA, TA, and OA, respectively. The similarity of the hydrochemical and isotopic characteristics of some groundwaters in QA, TA, and QA, suggests that that the three aquifers OA are hydraulically connected. The waters fell into three clear groups between the first and second functions on function score scatter diagrams ([Figure 6](#)), comprising the river water, and sandstone and limestone aquifer components. [Figure 6](#) also shows the mixing processes between QA, TA, and OA waters suggested in earlier discussion of hydrochemical characteristics.

Calculating water mixing ratios

Previous studies have shown that mixing processes are common in multi-aquifer systems ([Hamed et al. 2011](#)). This is particularly true in coal-mining areas, where the mining activity may strengthen

the hydraulic connectivity between aquifers, resulting in groundwater mixing (Carreo'n-Diazconti *et al.* 2003). Major ion geochemistry and environmental isotopes have also been used successfully to identify the origins and mixing ratios in multi-layer aquifer systems (Hamed *et al.* 2011). Multivariate statistical analysis, like principal component and discriminant analysis, have also been used to establish models for calculating groundwater mixing ratios in multi-aquifer systems (Chen *et al.* 2014).

As shown, the groundwater in the study area is recharged mainly by precipitation or river water, and is subject to the influence of water-rock interactions. The geological conditions and hydrochemical properties indicate that the carbonate and silicate contents in TA and SA are the two principal controls on the hydrochemical features, so the waters in the rivers, TA, and SA can be considered the three end-members of the multi-aquifer system in the Suxian area. The discriminant functions scores of the 32 water samples are plotted in Figure 7, where they are surrounded by a triangle whose vertices – A, B, and C – reflect the water recharge end-members in the area.

- A represents river water, recharged by precipitation. It has higher $\delta^{18}\text{O}$ and δD values because of evaporation.
- B represents SA groundwater, which had the highest TDS, and lowest $\delta^{18}\text{O}$ and δD concentrations because of the long aquifer residence time.
- C represents groundwater influenced by carbonate-rock interactions. While the QA, OA, and TA groundwaters are all influenced by carbonate-rock interactions, their extent varies according to the flow rate in the aquifer – higher flow rates reduce the interaction opportunities.

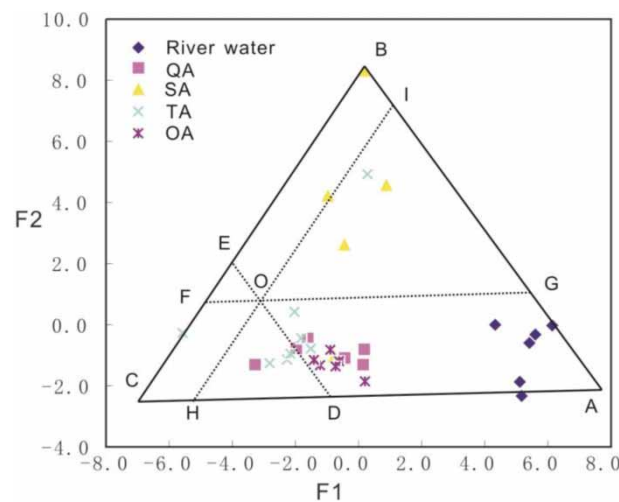


Figure 7 | Calculating water mixing ratio calculation model for Suxian coal mining district.

A conceptual model was developed to calculate the groundwater mixing ratio, based on the three end-members and groundwater sampling points. The calculation method is based on Laaksoharju *et al.*'s mass balance model (1999). In this, if dot (O) – the sample investigated – is within ABC, the mixing degree is assessed mainly by calculating the end-member groundwater mixing ratios of A, B, and C (Figure 7). End-member A's mixing ratios can be represented by Equation (1):

$$\text{MixA} = \frac{R_A}{\sum_{i=A}^C R_i}, R_A = \frac{CD}{AC} \quad (1)$$

B and C's mixing ratios can be calculated similarly.

CONCLUSIONS

The major ion contents, and hydrogen and oxygen isotopic properties of 32 ground and river water samples collected in the Suxian coal-mining area, Anhui Province, China, were determined. Discussion of the hydrochemical characteristics, main influences, and mixing processes is based on traditional graphs and discriminant analysis. The conclusions are as follows:

- (1) All waters sampled were alkaline, while TDS concentrations differed according to the source. The TDS concentrations were highest in SA and lowest in OA groundwaters, with its concentrations in river water, and TA and QA groundwaters in between and in that order. δD and $\delta^{18}O$ concentrations were highest in river waters and lowest in SA groundwater. Distribution of the QA and OA groundwater isotope values along the LSWL, and the distribution line's slope being close to that of the GMWL, indicate that the QA and OA are recharged by rainfall and from surface water.
- (2) The relatively higher TDS concentrations, and the δD and $\delta^{18}O$ enrichment in river water reflect evaporation in the relatively dry climate. The QA, OA, and TA groundwaters were influenced mainly by water–rock interactions. The carbonate rocks in the TA may have offered the maximum water-rock interaction capacity. Such interactions were weak in the QA and OA, where groundwater flow rates were relatively high. SA groundwater has different characteristics, and the δD and $\delta^{18}O$ concentrations determined were stable, indicating that SA groundwater is dominated by static reserves.
- (3) Two Fisher discriminant functions were determined and explained 98.2% of the variance. The discriminant diagrams were divided into three groups, which can be considered the three water source end-members. The 32 points on the diagram were surrounded by a triangle, with vertices A, B and C, and a conceptual model was established to calculate groundwater mixing ratios between the end-members and the groundwater sampling points.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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