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RESEARCH ARTICLE

Contaminant sources and processes affecting spring water quality in a typical karst basin (Hongjiadu Basin, SW China): insights provided by hydrochemical and isotopic data

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Abstract

Springs are an important source of drinking water supply in mountainous karst areas of SW China. However, the quality of many spring waters has deteriorated greatly in recent years, which leads to a significant problem of drinking water scarcity. In this study, hydrochemistry and stable sulfur and oxygen isotopic compositions of SO_4^{2-} ($\delta^{34}S$ and $\delta^{18}O_{SO4}$) of 38 representative samples of waters (incl. spring water, surface water, rainwater, and sewage) from the Hongjiadu Basin, Guizhou province, SW China, were investigated in order to identify the sources of contaminates in spring waters and trace the processes affecting the karst groundwater quality. Approximately 28% of the total investigated springs has been suffered from serious contamination and the concentrations of NO_3^-, SO_4^{2-}, and total iron (TFe) in many spring waters have exceeded the standards for drinking water. The springs that have NO_3^- concentrations of > 30 mg/L are concentrated in residential and agricultural areas, suggesting that NO_3^- in spring water are mainly derived from chemical fertilizers, manure, and sewage. $\delta^{34}S$ and $\delta^{18}O_{SO4}$ data indicate that SO_4^{2-} in spring water mainly originates from sulfide oxidation, acid rain, and sewage. Furthermore, the high $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of SO_4^{2-} in some spring waters may be related to the occurrence of bacterial sulfate reduction. Some springs that are discharged from abandoned coal mines have SO_4^{2-} concentrations of > 250 mg/L, demonstrating that mining activities have accelerated the deterioration of spring water quality. Also, springs with TFe concentrations of > 0.3 mg/L are discharged from coal-bearing strata, revealing that iron in spring waters is mainly derived from the oxidation of pyrite. Our results show that the karst spring waters are highly vulnerable to anthropogenic contaminations and human activities, such as agricultural fertilizing and sewage and waste disposal as well as mining activities, which exert a great impact on the quality of groundwater in karst areas.

Keywords Spring · Water quality · Hydrochemistry · Sulfur and oxygen isotopes · Karst groundwater · Hongjiadu

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Highlights

- Conducted hydrochemical and isotopic analysis of waters, Hongjiadu Basin, China
- Focused on chemical compositions, $\delta^{34}S$ and $\delta^{18}O_{SO4}$
- Bulk of spring water exceeds limits for NO_3^-, SO_4^{2-}, and TFe in drinking water
- Method useful at revealing processes affecting spring water quality in karst basin
- Sewage, manure, chemical fertilizers, coal, acid rain, land use, etc. affected water quality

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Introduction

Karst groundwater is a vital water resource and more than 10 million people in southwest China rely on it for drinking water supply (Ford and Williams 2007). However, karst groundwater is highly vulnerable to pollution caused by human activities and the restoration of contaminated groundwater is difficult. With the development of society and economy, the contamination of karst groundwater draws more and more attention (Yang et al. 2019; Wu et al. 2018; Jakóbczyk-Karpierz et al. 2016; Li et al. 2016; Vesper and White 2004). Groundwater is a "hidden resource" and the prevention and monitoring of groundwater pollution and restoration of water quality are more difficult than that of surface waters due to its inaccessibility (Marques et al. 2013). Springs are the primary way for the discharge of groundwater from karst aquifers and contaminants entering into the aquifers ultimately appear in spring water (Vesper and White 2004). Therefore, the monitoring of springs can provide more insights into the hydrogeological and hydrogeochemical processes that occur in underground environments (Pu et al. 2013).

The hydrochemical and isotopic compositions of spring water can provide important information about the factors that determine groundwater quality, such as lithology, water–rock interaction, and land use (Merchán et al. 2014; Marques et al. 2013; Vesper and White 2004). Stable sulfur and oxygen isotopes of sulfate ($\delta^{34}S$ and $\delta^{18}O_{SO4}$) have been widely used to identify sulfur sources and trace the sulfur cycling processes (Dugin et al. 2009; Otero et al. 2007), especially in small watersheds (Merchán et al. 2014; Otero et al. 2008), and to investigate the redox state of an aquifer (Li et al. 2013).

Springs are the primary source of drinking water supply for approximately 95% of the population in the Hongjiadu Basin. The basin was originally dominated by agricultural land but has undergone substantial changes in terms of land use in recent years due to the rapid development of coal mining and thermal power generation industries which have resulted in the serious deterioration of local groundwater quality (Ren et al. 2017). Moreover, the population within the basin has increased from 10,000 to 30,000 during the recent years, causing a sharp increase in the demand for drinking water. In view of the deteriorating water quality and increased demand for

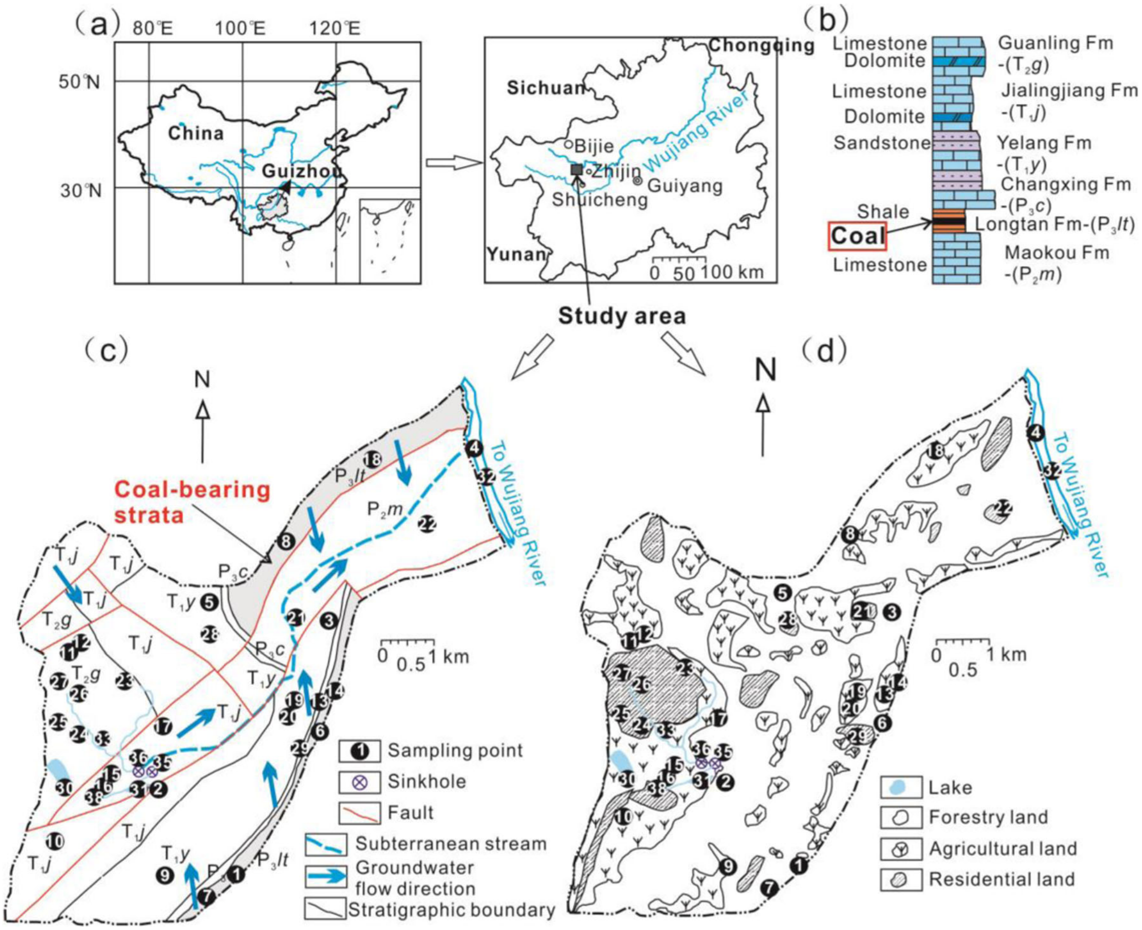

Fig. 1 **a** Maps of China and Guizhou Province showing the location of the study area; **b** the lithology of the study area; **c** a simplified geological map showing the sampling locations (sites 1–38); **d** the land use map of the Hongjiadu Basin

drinking water, it is crucial to investigate the current quality status of spring water and the relevant influencing factors within the basin. Therefore, a dual isotopes ($\delta^{34}S$ and $\delta^{18}O_{SO4}$) and hydrochemical analyses were used to investigate the effects of natural and anthropogenic factors on the quality of spring water in the basin. The specific objectives were to (1) identify the main sources of inorganic contaminants in spring water, (2) determine the effects of lithology and land use change on spring water quality, and (3) assess spring water quality and quantity with respect to the local demand for drinking water in the Hongjiadu Basin.

Study area

The Hongjiadu Basin is a small karst basin with a total area of 19.3 km^2. It is located approximately 130 km northwest of Guiyang, the capital of Guizhou Province, SW China (Fig. 1a). The region is characterized by a subtropical monsoon climate with 80% of the total annual precipitation (~ 1400 mm) occurring during the rainy season (May–October) and an mean annual air temperature of 14.4 °C. The land is mainly used for forest, agriculture, and residential purposes. Small lakes are distributed in this region.

The Hongjiadu Basin is located in the upper reaches of the Wujiang River. The underlying bedrock is mainly composed of Permian to Triassic sedimentary carbonate rocks with coal-bearing strata intercalated into the Permian Longtan Formation. No gypsum-containing evaporites are found in the basin (Fig. 1b). The carbonate rocks are the major aquifers and more than 85% of groundwater is hosted in limestone aquifers. In general, groundwaters in the basin are discharged from unconfined aquifers. The atmospheric precipitation is the main recharge source of groundwater. Sulfur-rich coals are primarily distributed in groundwater recharge areas in the northeast and southeast parts of the basin (Fig. 1c). Because coal is the major energy resource, the region has been characterized by high rates of acid deposition for several years. The study area contains two groups of faults that preferentially trend NE–SW. These faults cut through the bedrocks and are the main channels for groundwater infiltration and transport, affecting the development of subsurface karst. The groundwater flows from the southwest to the northeast and finally discharges into the Wujiang River. The spring at sampling site 4 is the main outlet of groundwater and has the highest flow rate. However, the utilization of this spring is difficult as it directly discharges into the Wujiang River at a low elevation.

Sampling and analytical methods

A total of 38 water samples, including 29 springs (Fig. 2c), four surface water, and four sewage as well as one rainwater were collected from the Hongjiadu Basin in December 2016. According to the land use, the groundwater samples were classified into three major groups: samples from forest, agricultural, and residential areas (Table 1). Some springs are also affected by abandoned coal mines, such as springs 6-8.

In the field, water temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) were measured using a multi-parameter portable meter (WTW3430, Germany) with analytical precisions of 0.01 °C, 0.01, 0.1 μS/cm, and 0.01 mg/L, respectively. The HCO_3^- concentration was measured by a titration kit with a precision of 0.1 mmol/L. Water samples was filtrated on site using disposable 0.45 μm filters and placed in 50 mL high-density polyethylene bottles for the laboratory analyses of anions (filtered and unacidified), cations, and major/tracer metals (filtered and acidified to pH < 2 with HNO_3). Samples for $\delta^{34}S$ and $\delta^{18}O_{SO4}$ analysis were collected in 10 L brown plastic bottles. The sulfate was extracted as $BaSO_4$ by the addition of $BaCl_2$ to the filtered water sample with the pH adjusted to < 2 (using HCl) to prevent the formation of $BaCO_3$. The $BaSO_4$ samples were freeze-dried in powder form and analyzed at the China University of Geosciences (Wuhan). Before sampling, all bottles were rinsed 3–4 times with filtered water. All water samples were stored at 4 °C in a dark environment before testing.

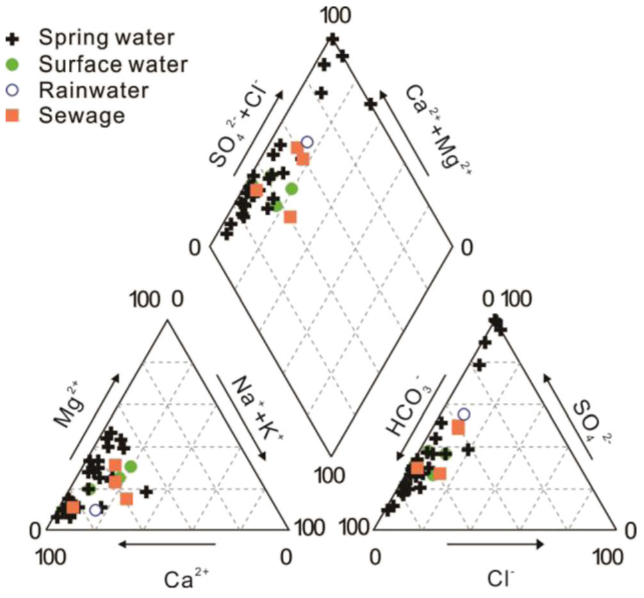

Fig. 2 Piper diagram of water samples collected from the Hongjiadu Basin

The concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, and TFe were measured by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, USA), and the concentrations of NO_3^-, SO_4^{2-}, and Cl^- were analyzed by an ion chromatography (Dionex ICS-1100, USA). The detection limits are 0.011, 0.013, 0.005, 0.02, 0.003, 0.05, 0.2, and 0.1 mg/L for Ca^{2+}, Mg^{2+}, Na^+, K^+, TFe, NO_3^-, SO_4^{2-}, and Cl^-, respectively. The samples for $\delta^{34}S$ and $\delta^{18}O_{SO4}$ analysis were measured using a combination

Table 1 Results of chemical and isotopic compositions of water samples collected from the Hongjiadu Basin ($n = 38$); see Fig. 1 for details of the lithology and land use types

Sample ID	pH	DO mg/L	EC µS/cm	T °C	K^+ mg/L	Na^+	Ca^{2+}	Mg^{2+}	TFe	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	CBE %	$\delta^{34}S$ ‰	$\delta^{18}O_{SO4}$	Formation	Land use
Spring																		
1	5.63	5.55	197	9.50	4.14	3.41	24.8	13.8	0.58	4.70	123	0.00	4.32	− 5.31	− 4.1	8.1	P_3lt	Forestry
2	7.58	4.44	357	14.2	1.22	1.80	87.2	5.62	0.06	2.52	65.1	195	19.8	− 0.45	− 8.1	8.8	T_2j	Forestry
3	8.35	8.96	210	8.89	0.38	0.96	60.0	2.38	d.l.	1.09	47.3	117	16.1	1.45	− 6.1	6.9	T_1y	Forestry
4	8.19	7.40	307	17.5	1.92	5.94	57.9	9.23	d.l.	4.58	68.2	140	17.7	− 4.54	− 3.4	10.2	P_2m	Forestry
5	8.13	10.1	321	11.9	0.61	3.68	80.2	5.91	0.05	1.82	63.9	198	13.7	− 3.93	− 18.7	6.2	T_1y	Forestry
6	3.24	0.23	1761	10.4	1.94	8.26	330	99.6	76.7	0.92	1672	0.00	0.90	− 39.2	− 2.2	6.8	P_3lt	Forestry
7	7.61	0.36	484	10.5	2.72	4.29	104	25.4	1.38	2.92	335	47.1	1.27	− 4.14	0.30	6.9	P_3lt	Forestry
8	5.98	2.05	886	15.2	2.52	7.13	99.6	21.6	53.0	3.21	576	0.00	1.58	− 70.0	− 12.3	5.0	P_3lt	Forestry
9	7.73	8.43	375	2.73	4.24	5.99	102	5.50	d.l.	9.00	618	215	65.7	− 3.97	− 6.1	8.0	T_1y	Agriculture
10	7.46	3.52	540	14.2	5.15	5.79	97.1	31.2	d.l.	10.9	69.1	339	35.4	− 1.02	− 6.8	7.7	T_1j	Agriculture
11	7.54	3.66	397	10.2	4.00	2.09	70.9	35.2	0.16	5.60	35.7	347	5.34	− 0.71	–	–	T_2g	Agriculture
12	7.80	4.50	361	14.1	2.80	2.94	49.1	27.4	0.01	1.83	21.9	268	13.7	− 4.33	− 8.6	7.1	T_2g	Agriculture
13	7.66	4.31	373	14.2	0.72	2.90	88.8	5.80	0.20	3.44	58.6	204	25.0	− 0.11	− 10.9	6.4	P_3c	Agriculture
14	5.14	4.22	56.3	10.8	0.39	1.07	7.78	1.78	1.87	1.05	27.1	7.54	1.22	− 24.7	− 7.3	6.6	P_3lt	Agriculture
15	7.99	10.0	243	9.90	0.33	3.19	62.7	4.14	d.l.	4.52	66.6	102	26.5	0.13	− 5.3	7.1	T_1j	Agriculture
16	6.98	8.14	375	11.0	4.77	16.8	73.4	6.62	d.l.	28.6	75.8	104	73.5	− 4.31	− 8.1	8.5	T_1j	Agriculture
17	7.64	5.13	628	12.1	6.79	11.8	125	35.5	0.06	22.9	120	381	38.5	− 1.57	− 6.6	6.0	T_1j	Agriculture
18	8.12	7.84	1197	14.8	0.56	3.71	79.9	5.93	d.l.	1.78	64.4	187	13.6	− 0.40	− 13.8	7.2	P_3lt	Agriculture
19	7.55	4.88	405	11.3	0.32	2.25	107	7.16	d.l.	4.57	57.3	269	33.3	− 4.20	− 6.0	4.2	T_1y	Agriculture
20	7.75	5.30	360	13.8	0.70	1.74	86.3	9.42	d.l.	3.20	71.3	221	12.4	− 4.17	− 13.3	6.7	T_1y	Agriculture
21	7.43	5.16	497	12.6	8.55	7.90	111	8.80	d.l.	13.7	114	229	41.6	− 5.11	− 6.7	7.9	P_2m	Residence
22	8.38	8.55	602	17.1	3.23	6.08	106	28.3	0.19	6.33	191.4	222	29.7	− 4.33	–	–	P_2m	Residence
23	7.74	2.91	530	18.1	2.58	22.8	79.5	38.4	0.02	33.6	139	256	31.0	− 4.25	− 1.8	8.9	T_2g	Residence
24	7.48	2.58	593	16.9	7.69	22.6	98.0	22.4	0.00	21.6	111	298	28.6	− 4.41	− 4.5	10.3	T_2g	Residence
25	7.20	0.54	821	13.4	4.95	38.9	147	36.6	d.l.	19.7	154	463	16.9	4.49	− 4.9	6.8	T_2g	Residence
26	7.41	2.43	640	16.0	6.55	7.04	99.4	43.3	d.l.	12.6	74.6	445	9.57	− 4.02	− 0.8	6.7	T_2g	Residence
27	7.30	1.86	635	14.1	4.39	9.39	124	31.3	d.l.	28.4	85.1	379	56.1	− 4.39	− 6.3	10.3	T_2g	Residence
28	6.92	5.77	309	13.7	4.34	4.18	72.2	2.92	0.07	3.92	36.1	196	14.7	− 4.35	–	–	T_1y	Residence
29	7.16	6.73	383	15.2	1.00	3.94	84.5	8.21	d.l.	3.42	48.2	211	41.8	− 2.93	− 7.6	6.1	P_3c	Residence
Surface water																		
30	8.24	8.40	295	9.65	8.07	13.1	49.3	13.1	0.56	17.2	53.0	160	9.74	− 1.40	− 1.4	7.7		
31	8.28	8.35	277	9.19	1.81	1.74	80.8	5.31	0.15	2.43	65.5	185	10.2	− 0.75	− 8.1	7.9		
32	8.26	6.97	328	17.0	2.11	6.50	61.4	10.1	0.00	4.85	71.0	139	18.1	0.83	− 0.8	8.3		
33	8.46	11.47	389	8.55	23.17	16.54	67.6	24.6	0.21	26.2222	116	215	12.1	− 2.32	–	–		

Table 1 (continued)

Sample ID	pH	DO mg/L	EC µS/cm	T °C	K^+ mg/L	Na^+	Ca^{2+}	Mg^{2+}	TFe	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	CBE %	$\delta^{34}S$ ‰	$\delta^{18}O_{SO4}$	Formation	Land use
Rainwater																		
34	5.48	9.37	26.5	9.28	2.00	0.26	6.01	0.47	0.06	1.81	13.9	11.3	1.68	− 38.1	− 12.1	6.5		
Sewage																		
35	8.47	9.16	317	10.4	2.98	5.44	88.5	7.07	0.44	6.64	71.9	209	12.9	− 0.23	− 7.4	7.6		
36	8.51	8.36	737	13.0	4.95	28.7	119	39.9	0.42	34.2	220	227	57.4	3.68	− 8.2	8.3		
37	8.19	7.32	778	10.2	11.42	20.2	82.1	18.8	0.32	24.9	148	158	41.7	− 3.67	–	–		
38	8.34	8.64	457	8.80	24.46	27.0	82.2	12.6	0.18	34.2	89.4	254	9.08	− 3.03	–	–		
Threshold	6.5–8.5		≤ 2500			≤ 200			≤ 0.3	≤ 250	≤ 250		≤ 50					

d.l., detection limit; –, not measured; threshold, standards of drinking water in China; *T*, temperature

of an elemental analyzer (Carlo Erba 1108, USA) and a stable isotope ratio mass spectrometer (MAT 253, USA), with analytical precisions of ± 0.2‰ and ± 0.5‰, respectively. All measurements were performed at the Karst Geological Resources and Environment Supervision and Monitoring Center of the Ministry of Land and Resources.

Results

Chemical and isotopic compositions

The data of chemical and isotopic compositions of water samples are listed in Table 1. The pH values of spring water samples range from 3.24 to 8.38 with a mean value of 7.28 which is lower than the mean values of surface water (8.31) and sewage (8.38) but higher than that of rainwater (5.48). The sample that was collected from spring 6 located in an abandoned coal mine has the lowest pH value of 3.24. The total dissolved solids (TDS = Na + K + Ca + Mg + Cl + SO_4 + NO_3 + HCO_3) of both spring and surface water samples range between 47.9 and 2114 mg/L. The spring 6 sample also has the highest TDS, TFe, and SO_4^{2-} concentrations but the lowest DO value. Samples of both springs 7 and 8 were also collected from areas of abandoned coal mines and have relatively low pH values and high TFe and SO_4^{2-} concentrations. Except for samples of springs 6, 7, and 14 and rainwater, all samples have calculated charge balance errors (CBEs) within ± 5% (CBE = 100 × *($TZ^+ - TZ^-$)/($TZ^+ + TZ^-$), where $TZ^+ = Na^+ + K^+ + 2Ca^{2+} + 2Mg^{2+}$ and $TZ^- = Cl^- + 2SO_4^{2-} + NO_3^- + HCO_3^-$). The calculated CBEs for samples of springs 6, 7, and 14 and rainwater are far exceeded the permissible range (± 5%), suggesting there are unanalyzed ions in spring waters (Edmond et al. 1995; Li et al. 2011).

The hydrochemical data of water samples from Hongjiadu Basin were plotted on a Piper diagram (Fig. 2). The dominant cations in the spring waters are Ca^{2+} and Mg^{2+} and the dominant anion is HCO_3^-. The studied spring waters are also rich in SO_4^{2-}. These hydrochemical characteristics are similar to those from the Shuicheng Basin near the study area (Fig. 1b; Li et al. 2010). The hydrochemistry of spring water is mainly of Ca–Mg–HCO_3 type (based on ions exceeding 20% of the total meq/L), followed by Ca–Mg–HCO_3–SO_4 type, and little of Ca–SO_4 type. The molar ratios of [SO_4]/[HCO_3] for the spring water samples are 0.1–9.02. This is consistent with the values of karst groundwater from Guiyang city that has high concentrations of SO_4^{2-} and complex sulfate sources (Lang et al. 2006).

The NO_3^- concentrations of spring waters range from 0.9 to 73.5 mg/L with a mean value of 23.8 mg/L. The mean value is higher than that of surface water (12.5 mg/L) and rainwater (1.68 mg/L) but lower than that of sewage samples (30.3 mg/L). In fact, springs 9, 16 from agricultural area and 27 from residential area have the highest NO_3^- concentrations (56.1–73.5 mg/L). The mean concentrations of Na^+, Cl^-, and K^+ are in the following order: sewage > surface water > spring water > rainwater, successively. The TFe concentrations of springs 1, 6–8, and 14 samples (0.58–76.5 mg/L, mean 26.7 mg/L) have exceeded the limit (< 0.3 mg/L) of drinking water established by the Chinese government.

The $\delta^{34}S$ values of sulfate in spring waters range from − 18.7 to + 0.3‰ (mean − 6.9‰) and the $\delta^{18}O_{SO4}$ values from + 4.2 to + 10.3‰ (mean + 7.4‰). The $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of surface water samples range from − 8.1 to − 0.8‰ and + 7.7 to + 8.3‰, respectively. The $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values are − 12.1‰ and + 6.5‰ respectively for rainwater and − 7.4‰ and + 7.6‰ respectively for sewage sample 35 and − 8.2‰ and + 8.3‰ respectively for sewage sample 36. The spring 7 sample collected from an abandoned coal mine has the highest $\delta^{34}S$ value of + 0.3‰.

Effects of anthropogenic activities on spring water quality

The excessive application of chemical fertilizers is a major cause of non-point source pollution in China (Hou et al. 2017). The chemical fertilizers used in the Hongjiadu Basin mainly include formula fertilizer (Cl-containing fertilizer with a moderate Cl^- concentration; N:P:K = 27:10:5), urea (total nitrogen ≥ 46.4%; Fig. 3a), and ammonium bicarbonate (total nitrogen ≥ 17.1%). If the fertilizer chemicals have not been totally taken up by crops, they will remain in the topsoil. In addition, manures including animal and human waste are applied to improve crop yields (Fig. 3b). The acids produced by the nitrification of chemical fertilizers and manure ($NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H_2O + 2H^+$) can take part in the weathering of carbonate rocks, which increasing the NO_3^- concentration of groundwater (Singh et al. 2014; Barnes and Raymond 2009; Jiang et al. 2009).

In addition, our survey found that in several small factories and residential area, untreated wastewater (e.g., sewage sample 36 that have a NO_3^- concentration of up to 57.4 mg/L; Fig. 3c) are discharged directly into sinkholes through which the wastewater eventually enters into the groundwater. NO_3^- has a high solubility and mobility in the environment, resulting in the widespread NO_3^- contamination of spring water in agricultural and residential areas (Négrel and Pauwels 2004). Correspondingly, spring water samples obtained from agricultural and residential areas, such as those from springs 9, 16, and 27 have high NO_3^- concentrations (65.7, 73.5, and 66.1 mg/L respectively). According to the land use surrounding the springs, the mean NO_3^- concentrations of the 29 spring water samples vary in the order as follows: residential land (30.0 mg/L) > agricultural land (28.8 mg/L) > forestry land (9.43 mg/L), successively. Figure 4a shows that the NO_3^- concentration in the spring water samples is not related to lithology but rather to land use. All the spring water samples with NO_3^- concentrations of > 30 mg/L were obtained from agricultural and residential areas (Table 1 and Fig. 4a), suggesting an anthropogenic sources of NO_3^- in spring water. The relatively low concentration of NO_3^- in rainwater (Table 1) indicates that the rainwater is not one of main source of NO_3^- in spring water. Our data thus reveal that the NO_3^- of spring water mainly originates from chemical fertilizers, manure, and sewage.

Table 2 gives the Pearson correlation coefficients of K^+, Na^+, Cl^-, SO_4^{2-}, NO_3^-, and TFe concentrations of spring water samples. There are significant positive correlations between NO_3^- and Cl^-, Cl^- and Na^+, and Na^+ and K^+, suggesting similar sources for these ions (Zhou et al. 2016; Jiang et al. 2009). In addition, the mean concentrations of K^+, Na^+, Cl^-, and NO_3^- could be classified in three groups in terms of the land use surrounding all 29 springs: residential area (K^+ = 4.81 mg/L; Na^+ = 13.7 mg/L; Cl^- = 16.0 mg/L) > agricultural area (K^+ = 2.56 mg/L; Na^+ = 5.03 mg/L; Cl^- = 8.14 mg/L) > forestry land area (K^+ = 1.93 mg/L; Na^+ = 4.44 mg/L; Cl^- = 2.72 mg/L). This further confirms that the K^+, Na^+, Cl^-, and NO_3^- in spring waters mainly originate from anthropogenic inputs, namely, chemical fertilizers, manure and sewage.

There is also a highly positive correlation between TFe and SO_4^{2-} concentrations (Table 2), which indicates the similarity in the sources of them. As the coal seams in the study area contain pyrite and other sulfur-bearing minerals, human activities, such as coal mining or water pumping, can alter the original redox conditions within the aquifer, leading to an increase of TFe and SO_4^{2-} in groundwater ($FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ and/or $FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$; Liu et al. 2008). Springs with TFe concentrations exceeding the drinking water limit of 0.3 mg/L are located in area of coal-bearing strata (Fig. 1 and

Fig. 3 NO_3^- sources in the Hongjiadu Basin: **a** chemical fertilizer, **b** manure, and **c** untreated sewage (sewage sample 36)

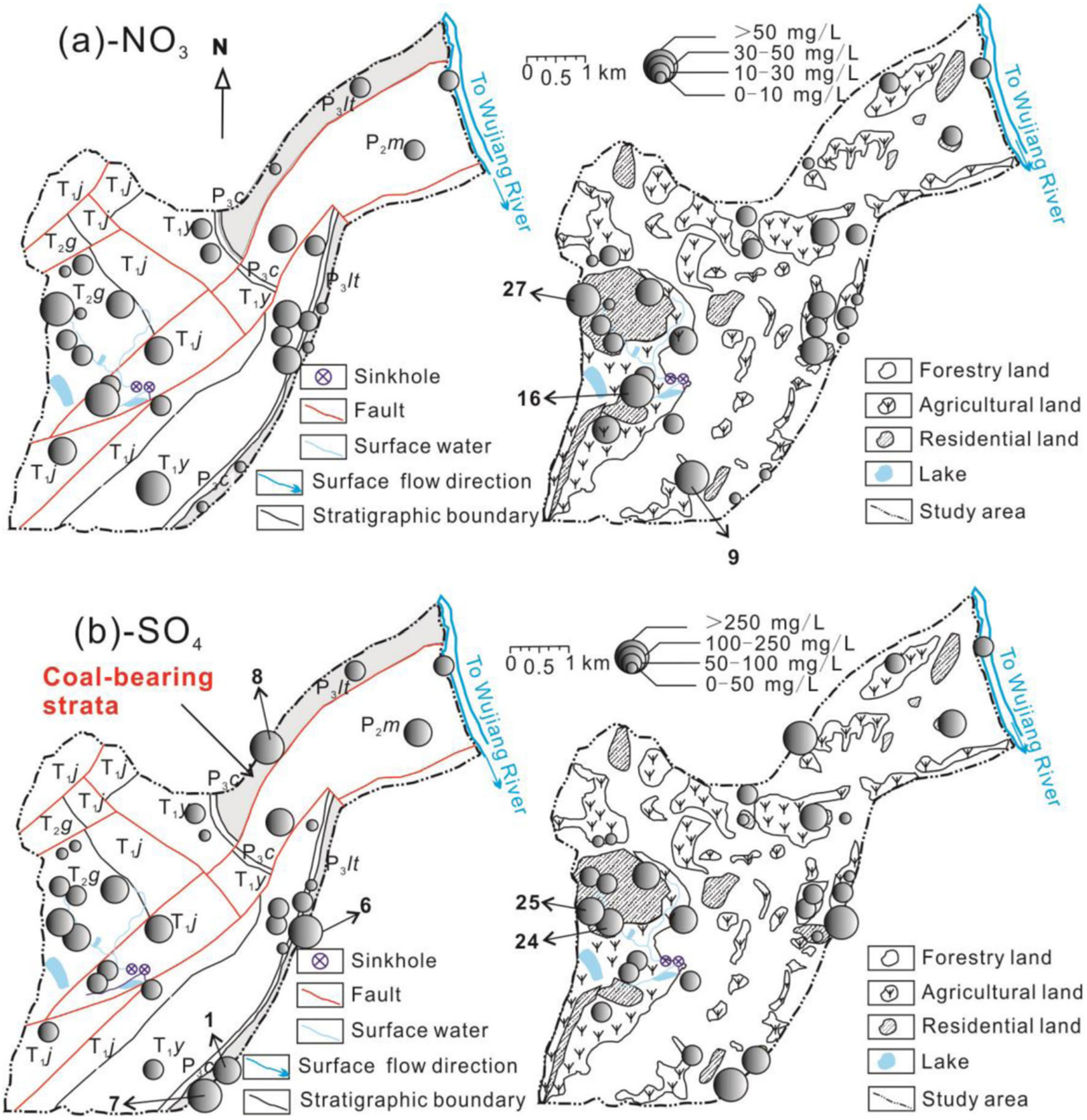

Fig. 4 Concentrations of **a** NO_3^- and **b** SO_4^{2-} plotted on the simplified geological and land use maps of the Hongjiadu Basin

Table 1), which shows that the lithology is an important factor affecting spring water quality in the study area.

There is no clear relationships between SO_4^{2-} and NO_3^-, SO_4^{2-} and K^+, SO_4^{2-} and Na^+, and SO_4^{2-} and Cl^- (Table 2). The samples with SO_4^{2-} concentrations of > 100 mg/L are taken from springs in both areas of coal-bearing strata (e.g., springs 1 and 6; Fig. 4b) and residential areas (e.g., springs 24 and 25; Fig. 4b). The springs with SO_4^{2-} concentrations exceeding the drinking water standard limit of 250 mg/L are only those that are discharged from abandoned coal mines (springs 6-8; Fig. 4b). This implies that human industrial activities have accelerated the deterioration of groundwater quality in the basin. This also reveals a more complex origin of SO_4^{2-} in spring waters, as discussed in the following section.

Table 2 Pearson correlation coefficients of chemical components of the spring water samples collected from the Hongjiadu Basin ($n = 29$)

Component	K^+	Na^+	Cl^-	SO_4^{2-}	NO_3^-	TFe[a]
K^+	1					
Na^+	0.476**	1				
Cl^-	0.595**	0.727**	1			
SO_4^{2-}	− 0.053	0.077	− 0.147	1		
NO_3^-	0.332	0.235	0.606**	− 0.302	1	
TFe	− 0.171	0.038	− 0.246	0.931**	− 0.443	1

**Significant at $P < 0.01$

[a] $n = 15$

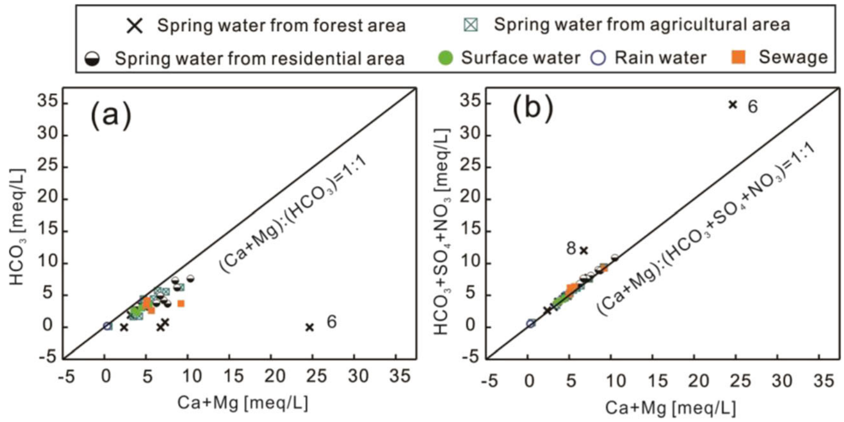

Fig. 5 Plots of **a** $(Ca^{2+} + Mg^{2+})$ vs. HCO_3^- and **b** $(Ca^{2+} + Mg^{2+})$ vs. $(HCO_3^- + SO_4^{2-} + NO_3^-)$ for water samples collected from the Hongjiadu Basin

Chemical weathering

The Ca^{2+}, Mg^{2+}, and HCO_3^- concentrations of groundwater in karst areas are mainly controlled by the weathering of carbonate rocks (Eqs. 1 and 2; Han and Liu 2004; Han et al. 2010). Waters affected by such carbonate rock weathering are enriched in 2 mol of HCO_3^- for each mol of $(Ca^{2+} + Mg^{2+})$.

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \quad (1)$$

$$CaMg(CO_3)_2 + H_2O + CO_2 = Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (2)$$

Under normal conditions, the equivalent concentration of $(Ca^{2+} + Mg^{2+})$ in water is equal to that of HCO_3^-. In this study, we analyzed the correlation between the equivalent concentrations of $(Ca^{2+} + Mg^{2+})$ and HCO_3^- of different water samples. As shown in Fig. 5a, all the equivalent concentrations of $(Ca^{2+} + Mg^{2+})$ and HCO_3^- of spring water, surface water, and sewage deviate from the 1:1 line. This suggests that carbonic acid could not be the sole dissolution agent, i.e., other acids, possibly sulfuric and/or nitric acids, may have played a complementary role in the carbonate rock weathering. We also plotted $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{2-} + NO_3^-)$ and found that most samples fall on the 1:1 line (Fig. 5b). This evidence shows that the sulfuric and nitric acids have played a relatively important role in carbonate weathering (Eq. 3).

$$4Ca_xMg_{(1-x)}CO_3 + H_2CO_3 + H_2SO_4 + HNO_3 = 4\times Ca^{2+} + 4(1-x)Mg^{2+} + SO_4^{2-} + NO_3^- + 5HCO_3^- \quad (3)$$

Jiang (2012) reported that, together with carbonic acid, nitric acid from agricultural fertilizers, sewage, and soil and sulfuric acid from rainfall, fertilizers, sewage, and sulfide oxidation can participate in the carbonate weathering in the Nandong Underground River System which drains a lithological terrain similar to our study area. The weathering of carbonate rock by sulfuric and nitric acids leads to a noticeable increase of the NO_3^- and SO_4^{2-} in the local water. Thus, elevated NO_3^- concentrations are observed in the spring water samples collected from the agricultural and residential areas. The SO_4^{2-} concentrations of the samples collected from abandoned coal mines and residential areas are also elevated (Table 1). This suggests that human activities significantly impact spring water quality in the Hongjiadu Basin.

Discussion

Sources and influencing factors of SO_4^{2-} in groundwater

The potential SO_4^{2-} sources in groundwater mainly include (1) atmospheric precipitation, (2) sulfides, like the products of

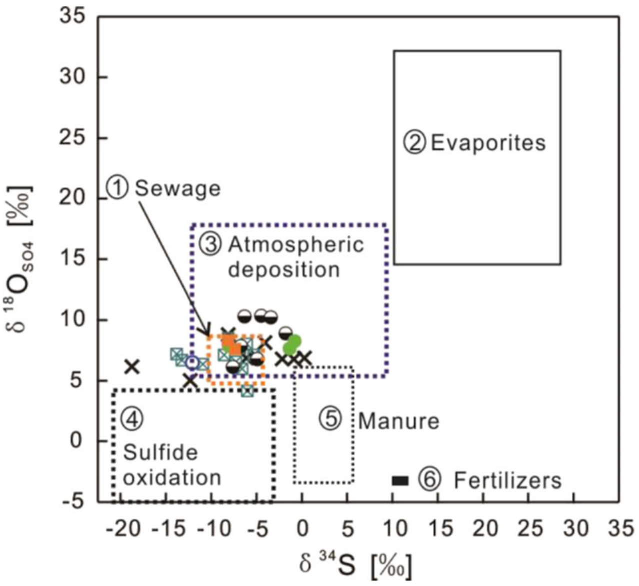

Fig. 6 Plots of $\delta^{34}S$ vs. $\delta^{18}O_{SO4}$ for water samples collected from the Hongjiadu Basin. Symbols are the same as those in Fig. 5

pyrite oxidation, (3) evaporites, like gypsum and anhydrite, (4) sulfate in soils, and (5) anthropogenic sources, such as sewage, chemical fertilizers, and manure. Under aerobic conditions, little sulfur isotopic fractionation occurs during the processes of mineral dissolution and/or precipitation, sulfide oxidation, soil adsorption, plant assimilation, and mineralization of organic sulfur. Hence, δ^{34}S has been widely used as a tracer for identifying the sources of SO_4^{2-} in groundwater (e.g., Li et al. 2013; Tuttle et al. 2009). Unlike δ^{34}S, δ^{18}O of SO_4^{2-} is often affected by the oxygen exchange between SO_4^{2-} and H_2O and/or O_2 during the process of sulfide oxidation, resulting in a change in the $\delta^{18}O_{SO4}$ value (Kroopnick and Craig 1972). Therefore, the $\delta^{18}O_{SO4}$ can be used to determine the oxidation or reduction state in karst aquifer environments (Samborska et al. 2013; Li et al. 2011). Under anaerobic, high-temperature conditions, bacterial sulfate reduction (BSR), and thermochemical sulfate reduction (TSR) result in a significantly increase of both δ^{34}S and $\delta^{18}O_{SO4}$ values and a decrease of SO_4^{2-} in groundwaters (Bottrell et al. 2008; Strebel et al. 1990). Thus, the combined use of δ^{34}S, $\delta^{18}O_{SO4}$, and SO_4^{2-} concentrations can not only enable the identification of SO_4^{2-} sources but also facilitate the investigation of biogeochemical processes, such as BSR and TSR.

The δ^{34}S and $\delta^{18}O_{SO4}$ values of water samples as well as the potential SO_4^{2-} end-members are plotted in Fig. 6. For spring waters, no correlation between δ^{34}S and $\delta^{18}O_{SO4}$ ($R^2 = 0.05$; $P > 0.05$; $n = 26$) is found, indicating that the SO_4^{2-} in spring waters originated from at least three different sources in the basin (Li et al. 2013; Samborska et al. 2013). As shown in Fig. 6, the δ^{34}S and $\delta^{18}O_{SO4}$ values of spring waters (− 18.7 to + 0.3‰ and + 4.2 to + 10.3‰, respectively) are out of the typical ranges of evaporite end-member (+ 10 to + 28‰ and + 14.5 to + 32.5‰, respectively; Krouse and Crinenko 1991). This suggests that evaporites are not the main source of SO_4^{2-} in spring waters, which is consistent with the lithology within the basin (Fig. 1b). Previous studies show that sulfur contents in soils in the upper reaches of the Wujiang River are relatively low (e.g., Jiang et al. 2006; Han and Liu 2004). The Hongjiadu Basin is located in the upper reaches of Wujiang River, so the soil sulfur source can be precluded (Fig. 1a). Alternatively, atmospheric deposition, sulfide oxidation, and anthropogenic inputs are likely to be the potential sources of SO_4^{2-} in spring waters.

Fig. 7 A large coal-fired power plant located in the Hongjiadu Basin

Atmospheric precipitation

Owing to the heavy use of sulfur-rich coal, the region of Guizhou Province has been greatly affected by acid rain that is characterized by low pH and high sulfate contents since the 1980s (Galloway et al. 1987). A large coal-fired power station that consumes approximately 2.54 MT coals per year is located in the basin (Fig. 7). The special topography of the basin prevents the timely dispersion of sulfur-containing gases and aerosols produced by coal combustion in this power plant. As a result, the deposition of combustion products ($SO_2 + 2OH \rightarrow H_2SO_4 \rightarrow SO_4^{2-} + 2H^+$) with rainwater occurs in the basin. In the Hongjiadu Basin, the rainwater has a low pH of 5.48 and a higher SO_4^{2-} concentration of 13.9 mg/L which is higher than that in the neighboring city of Guiyang (6.4 mg/L; $n = 3$; Liu et al. 2008) and the Nandong Underground River Basin (4.5 mg/L; $n = 3$; Jiang 2012). Figure 6 shows that the δ^{34}S and $\delta^{18}O_{SO4}$ values of most of spring water, surface water, and sewage samples fall within the typical ranges of rainwater (− 12 to + 9.4‰ and + 5 to + 17‰, respectively; Zhang et al. 2015; Xiao and Liu 2002). This further supports that acid rainwater is an important source of SO_4^{2-} in spring water from the Hongjiadu Basin.

Because of the rapid conversion of rainwater and surface water into groundwater in karst areas, they should have similar

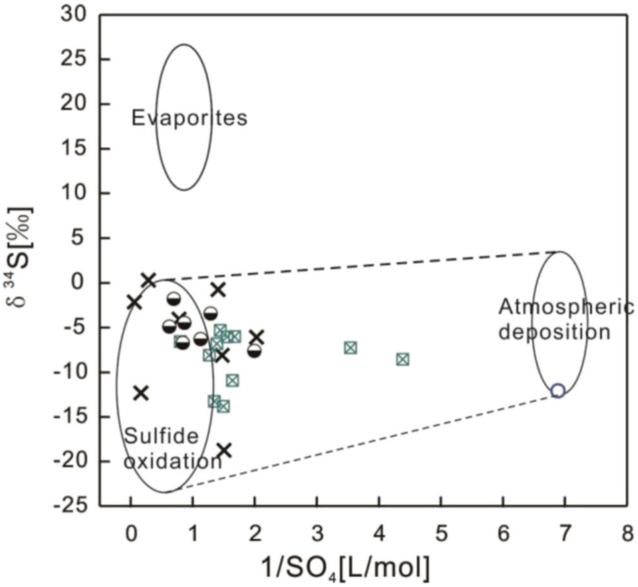

Fig. 8 Plot of δ^{34}S vs. $1/SO_4$ for spring water and rainwater samples collected from the Hongjiadu Basin. Symbols are the same as those in Fig. 5

chemical and isotopic characteristics (Liu et al. 2008). As mentioned above, springs in the Hongjiadu Basin are mainly recharged by atmospheric precipitation. However, great differences of both SO_4^{2-} contents and $\delta^{34}S$ values between the spring waters and rainwater are observed (Fig. 8), suggesting there are other sulfate sources and processes that control the chemical and isotopic properties of spring waters (LeDoux et al. 2016).

Sulfide oxidation and bacterial sulfate reduction

Due to the special geological and hydrogeological features in karst areas, karst aquifers are vulnerable to contamination. Groundwaters in karst areas of southwest China are often reported to contain excess amounts of TFe and SO_4^{2-}, which are mainly associated with the coal mining upstream (Liu et al. 2008).

The main sulfide mineral in coal-bearing strata from Guizhou Province is pyrite that has $\delta^{34}S$ values of − 20.4 to − 2.51‰ (Ren et al. 2017; Liu et al. 2008). Although the typical range of $\delta^{18}O_{SO4}$ values of sulfides reported in the literature is − 5 to +4‰ (Krouse and Mayer 2000), the varying proportions of O_2 and H_2O involved in sulfide oxidation often lead to a lower $\delta^{18}O_{SO4}$ value during the rainy season but a higher value during the dry season (Li et al. 2011).

The springs 1, 14, and 18 discharged from coal-bearing strata (Fig. 1c) have $\delta^{34}S$ values ranging between − 13.8 and − 4.1‰ which are within the range of pyrite in the region of Guizhou (− 20.4 to − 2.51‰). This suggests that the products of the oxidation of pyrite from the coal seams are probably the main source of SO_4^{2-} in these three spring waters. In addition, the $\delta^{34}S$ values of springs that are discharged from non-coal-bearing strata, for an example, springs 13 (− 10.9‰) and 20 (− 13.3‰), also fall within the range of pyrite from the Guizhou Province (− 20.4 to − 2.51‰). The coal seams in the study area are mainly distributed in the recharge areas of groundwater. This, together with the presence of numerous faults that provide channels for groundwater flowing through the basin (Fig. 1c), suggests that when groundwater discharged from non-coal-bearing strata are recharged by surface and groundwaters from coal-bearing strata, the sulfide in spring waters can have $\delta^{34}S$ characteristics of the products of pyrite oxidation. Therefore, sulfide oxidation is another important processes affecting the SO_4^{2-} in spring waters in downstream areas without the distribution of coal-bearing strata .

Samples 6–8 that collected from springs in abandoned coal mines have $\delta^{34}S$ values of − 2.2‰, + 0.3‰, and − 12.3‰, respectively. Only the spring 8 has a $\delta^{34}S$ value that is close to the mean value of groundwater from abandoned coal mines in Guizhou Province (− 13‰, $n = 5$; Jiang et al. 2006). Compared with − 13‰, the $\delta^{34}S$ values for the springs 6 and 7 samples are much heavier. Six samples, including springs 1, 6–8, 14, and 18 that are discharged from coal-bearing strata have $\delta^{18}O_{SO4}$ values of > + 4‰, suggesting that other processes may affect the isotopic ratios of SO_4^{2-}, such as (1) the reduce of groundwater table in winter, resulting in greater participation of atmospheric O_2 in the sulfide oxidation, (2) the occurrence of BSR and/or TSR, and (3) anthropogenic input of contaminants with higher $\delta^{18}O_{SO4}$ values.

The participation of more O_2 in the process of sulfide oxidation can result in an increase of $\delta^{18}O_{SO4}$ values, but little change in $\delta^{34}S$ (Zhang et al. 2015; Li et al. 2010). Tuttle et al. (2009) also reported that the lower groundwater level in winter can result in more O_2 involving in sulfide oxidation, resulting in higher $\delta^{18}O_{SO4}$ values in water samples collected from the Canadian River (+ 6.5 to + 17‰; mean + 10‰; $n = 10$). Such values are higher than those in this study (+ 4.2 to + 10.3‰; mean + 7.4‰; $n = 26$). The participation of O_2 may partly explain the elevated values of $\delta^{18}O_{SO4}$ but cannot fully explain the elevated values of $\delta^{34}S$, especially that of spring 6 and 7 samples. This suggests that there are other processes that determine the $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of spring water in the basin.

Previous studies have demonstrated that both BSR and TSR can increase the $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of residual sulfates (e.g., Watanabe et al. 2009; Tostevin et al. 2016). The temperature of all spring waters is 2.73–18.1 °C, and thus the effects of TSR should be insignificant (Tostevin et al. 2016; Worden and Smalley 1996). The occurrence of BSR in coal-bearing strata often results in high $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values, and high TFe and low DO in groundwater (McMahon et al. 2010; Samborska et al. 2013; Puig et al. 2013). Compared with −13‰ and + 4‰, the spring 6 has higher $\delta^{34}S$ and $\delta^{18}O_{SO4}$ (− 2.2‰ and + 6.8‰, respectively). The TFe concentration of this spring water is as high as 76.7 mg/L, but the DO concentration as low as 0.23 mg/L. Also, the spring 7 has heavy $\delta^{34}S$ and $\delta^{18}O_{SO4}$ (+ 0.3‰ and + 6.9‰, respectively), and TFe concentration as high as 1.38 mg/L and the DO value as low as 0.36 mg/L. These hydrochemical and isotopic data support the occurrence of BSR in the waters of springs 6 and 7. In contrast, the higher concentration of SO_4^{2-} in the springs 6 and 7 could be attributed to the rapid dissolution of secondary SO_4-bearing minerals, such as jarosite ($KFe^{3+}(SO_4)_2(OH)_6$), coquimbite ($Fe^{3+}{}_2(SO_4)_3{\cdot}9H_2O$), pickeringite ($MgAl_2(SO_4)_4{\cdot}22H_2O$), and roemerite ($Fe^{2+}Fe^{3+}{}_2(SO_4)_4{\cdot}14H_2O$; Cravotta 1994; Sharma et al. 2013; Sun et al. 2013). Sharma et al. (2013) also reported that both the BSR and the dissolution of secondary SO_4-bearing minerals occurred in an abandoned coal mine in Pennsylvania, USA. Hence, we suspect that the high $\delta^{34}S$, $\delta^{18}O_{SO4}$ and SO_4^{2-} contents of groundwater from the Hongjiadu Basin are associated with the occurrence of BSR and the dissolution of sulfate minerals.

Sewage, chemical fertilizers, and manure

The $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of the sewage samples from Hongjiadu Basin (mean − 7.8‰ and + 8.0‰, respectively) are similar to previously reported values of sewage in China (− 8 to − 4.3‰, and + 4.7 to + 7.5‰, respectively; Liu et al. 2008; Zhang et al. 2015). The SO_4^{2-} concentrations in the sewage samples (e.g., sewage sample 36 that is directly discharged into the Hongjiadu karst aquifer; Fig. 3c) are as high as 220 mg/L, suggesting that sewage is another source of SO_4^{2-} in spring water. The $\delta^{34}S$ values (− 7.6 to − 4.5‰; Table 1) of most water samples of springs located in residential areas (e.g., springs 21, 24, 25, 27, and 29) are within the range of the published values of sewage (Fig. 6). This further confirms that the SO_4^{2-} input of sewage into spring water in the study area is significant. The mean value of $\delta^{18}O_{SO4}$ of sewage samples is + 8.0‰ (n = 2) which is heavier than that of spring waters (+ 7.4‰; $n = 26$). The mean values of $\delta^{18}O_{SO4}$ of spring waters vary in the following order: residential area (+ 8.6‰) > agricultural area (+ 6.9‰) and forestry area (+ 6.9‰). This also shows that anthropogenic contaminants, likes sewage, result in an increase of $\delta^{18}O_{SO4}$ values in spring waters from the Hongjiadu Basin. Studies of other regions, such as Manila, Philippines (Hosono et al. 2010), and Birmingham, UK (Bottrell et al. 2008), have also revealed that sewage input resulted in heavier $\delta^{18}O_{SO4}$ values of groundwater.

Different raw materials and methods are used to produce chemical fertilizers in different countries, which results in significant differences in $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of chemical fertilizers that vary between − 6.5 and + 21.4‰ and + 7.7 and + 16.5‰, respectively (Vitòria et al. 2004). Previously published values of $\delta^{34}S$ for chemical fertilizers in southwestern China are thus used as reference values in this study. Li et al. (2010) obtained $\delta^{34}S$ values of + 10.9‰ and + 11.1‰ for two types of sulfur-containing chemical fertilizers used in the Shuicheng Basin which is near the Hongjiadu Basin (Fig. 1a). The $\delta^{34}S$ values of all the samples from the Hongjiadu Basin, even those springs in agricultural areas (< −5‰) are much lower than these

Table 3 Details of spring water quality in the Hongjiadu Basin

Spring	Utilization status	Discharge rate(L/s)	Drinkable	Undrinkable	Indicator of contamination
1	Drinking water	0.01		Yes	TFe
2	Drinking water	7.56	Yes		
3	Drinking water	0.01	Yes		
4	Non-drinking water	36.25	Yes		
5	Drinking water	0.02	Yes		
6	Non-drinking water	1.25		Yes	TFe, SO_4^{2-}
7	Non-drinking water	0.86		Yes	TFe, SO_4^{2-}
8	Non-drinking water	3.12		Yes	TFe, SO_4^{2-}
9	Drinking water	0.001		Yes	NO_3^-
10	Drinking water	0.25	Yes		
11	Drinking water	0.37	Yes		
12	Drinking water	0.56	Yes		
13	Drinking water	0.05	Yes		
14	Drinking water	0.01		Yes	TFe
15	Drinking water	0.06	Yes		
16	Drinking water	0.07		Yes	NO_3^-
17	Drinking water	0.15	Yes		
18	Drinking water	0.01	Yes		
19	Drinking water	0.01	Yes		
20	Drinking water	0.01	Yes		
21	Drinking water	0.12	Yes		
22	Drinking water	0.38	Yes		
23	Non-drinking water	2.36	Yes		
24	Drinking water	0.21	Yes		
25	Non-drinking water	0.08	Yes		
26	Drinking water	0.04	Yes		
27	Drinking water	0.13		Yes	NO_3^-
28	Drinking water	0.02	Yes		
29	Drinking water	0.04	Yes		

two reported values, which indicates that chemical fertilizers did not significantly contribute to the SO_4^{2-} in the spring waters.

In contrast to chemical fertilizers, manure often has a relatively small difference in the $\delta^{34}S$ values. The values reported in previous studies are − 0.9 to + 5.8‰ in the USA (Cravotta 1994), + 4‰ in the UK (Bartlett et al. 2010), and 0 to + 5‰ in Spain (Otero et al. 2007). Unfortunately, there are no reported $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of manure in the Honjiadu Basin and its neighboring areas. The $\delta^{34}S$ and $\delta^{18}O_{SO4}$ data of manure from other regions are thus used as references in this study, that is, − 0.9 to + 5.8‰ and − 3.8 to +6‰, respectively (Cravotta 1994; Bartlett et al. 2010; Otero et al. 2007). As shown in Fig. 6, none of the samples from the study area have $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values within the range of reported values. Nevertheless, the input of manure cannot be totally excluded as a possible explanation for the increased $\delta^{34}S$ values at individual sampling sites.

Assessment of spring water quality and quantity

Human activities have significantly impacted spring water quality in the Hongjiadu Basin. Thus, an assessment of spring water quality and quantity is important to determine whether they meet the local demand for drinking water. Table 3 presents the utilization status, discharge rates, indicators of water contamination and other information of the studied 29 springs. The main components that exceed the drinking water standards in spring water are TFe, SO_4^{2-}, and NO_3^- and groundwaters from springs 1, 6–9, 14, 16, and 27 are not potable anymore (Table 3).

The daily water consumption per capita in Chinese villages is about 70 L. For a population of 28,500 in the Hongjiadu Basin, the daily water consumption is approximately 2 million liters. The daily discharge volume of potable spring water within the basin is approximately 4.2 million liters which is twice the required volume and should theoretically meet the local need for drinking water. However, as noted in "Study area", the utilization of spring 4 which has the highest discharge rate in the basin is currently unfeasible. Excluding spring 4, the daily discharge volume of the basin springs is approximately 1.07 million liters which is just about half of the local need of drinking water.

A new industrial park is currently being planned in the study area, which would progressively increase the water demand and intensify human interference on the groundwater. In the absence of timely intervention by authorities in the effective management groundwater resource, the current shortage of drinking water in the Hongjiadu Basin is likely to be exacerbated.

Conclusions

The contaminants in spring waters from the Hongjiadu Basin are mainly NO_3^-, SO_4^{2-}, and TFe, the concentrations of which have exceeded the standard limits for drinking water. The NO_3^-, Cl^-, K^+, and Na^+ in spring waters mainly derived from chemical fertilizers, manure, and sewage. The results of $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values show that the SO_4^{2-} in spring waters mainly originates from acid rain, sulfide oxidation, and sewage. The springs suffered from NO_3^- contamination are located in agricultural and residential areas, revealing that the anthropogenic input significantly impacted the NO_3^- contamination of groundwater in the study area. The springs in residential areas and coal-bearing strata have high concentrations of SO_4^{2-}, particularly those discharged from abandoned coal mines. This shows that the interference of human activities on natural processes have accelerated the deterioration of spring water quality. The BSR in several studied springs has increased the $\delta^{34}S$ and $\delta^{18}O_{SO4}$ values of the residual sulfates. Approximately 28% of the investigated 29 springs are unsuitable for drinking as some of the components in waters have exceeded the standard limits of drinking water. Except for the main spring that flows into the Wujiang River and is thus difficult to utilize, the daily total water discharge volume of springs in the Hongjiadu Basin is approximately 1.07 million liters, which can only satisfy half of the drinking water demand of the population in the basin. Considering that there is no abatement in agricultural activities in the study area and industrial activities are continually increasing, the shortage of drinking water in the Hongjiadu Basin is expected to be continued.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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