



## Tracing natural and anthropogenic sources of dissolved sulfate in a karst region by using major ion chemistry and stable sulfur isotopes

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### ABSTRACT

This paper presents hydrogeochemical and S isotopic characteristics of karstic surface and ground water in the karstic aquifers of Zunyi city of Guizhou Province, SW China. The average  $\delta^{34}\text{S}$  value of  $\text{SO}_4$  is +2.2‰ ( $n = 28$ ) in ground waters and +7.0‰ ( $n = 15$ ) in surface waters in the low flow season, while in the high flow season it is +1.0‰ in ground waters and +2.8‰ in surface waters. Natural and anthropogenic sources of the dissolved  $\text{SO}_4^{2-}$  can be discriminated by a combined approach using water chemistry and stable S isotope data. A pollutant source of  $\text{SO}_4$  is estimated to have very high TDS contents and a narrow range of  $\delta^{34}\text{S}$  values (0‰ to +5.0‰). The water with a distinctively high  $\delta^{34}\text{S}$  value of +30.5‰ originates from an evaporite (gypsum and anhydrite)-bearing aquifer, and the  $\delta^{34}\text{S}$  values lower than –10‰ suggest an origin by oxidation of sulfide minerals in coal seams with intermediate TDS contents.

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### 1. Introduction

Carbonate rocks, both outcropping and concealed, account for about 1/3 of the total territory of China, and natural karst water resources make up a 1/4 of the ground water resources in China. However, the karstic ground water systems are subject to the impact of human activities, and in most urban areas the water quality deteriorates, due to the high susceptibility and vulnerability of the karstic eco-environment (Veni, 1999; Mimi and Assi, 2009; Delgado et al., 2010).

The Zunyi area has typical karst landforms, and is the second biggest city and one of the important industrial centers of Guizhou Province, SW China. The ground water system has long served as the water resource for agriculture, industry and domestic usage in Zunyi city. However, the ground water system has been contaminated to some extent by agricultural, industrial and domestic inputs in recent years. In order to trace the sources of contaminants and their fate in the ground water system, a study was conducted on the geochemistry of major ions and multi isotopic tracers ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{34}\text{S}$  and  $\delta^{15}\text{N}$ ) in both surface and ground water of Zunyi city and its adjacent areas. The research on the stable isotope geochemistry of C and N has been published (Li et al., 2008, 2010). This paper presents the results of chemical analysis for major ions and S isotopic composition of  $\text{SO}_4^{2-}$ , and dis-

cusses the sources, both natural and anthropogenic, of  $\text{SO}_4^{2-}$  and its fate in the surface and ground water system.

### 2. Geological setting and sample measurement

Zunyi city is located in the north of Guizhou Province, with a great diversity of karstic landforms, a high elevation and low latitude, annual average temperature of 15.1 °C and annual precipitation of 1100 mm. The geological structures are characterized by the distribution of non-continuous strips of SW–NE orientation. The main aquifers in the study area are dominated by Jurassic, Permian and Triassic homogenous carbonate (limestone and dolomite) as well as carbonate units interbedded with clastic rocks. Sulfate evaporites (gypsum and anhydrite) and coal seams occur locally. The outcrops are mainly Jurassic clastic rocks and Triassic carbonate rocks in the center of the urban area. Soils are thin and discontinuous in study area.

Surface water (river and reservoir) and groundwater (spring, well, underground river, sinkhole) samples were collected from downtown Zunyi and its surroundings (Fig. 1) in July (high flow season) and December (low flow season) of 2002. At sampling sites G4 and G14, coal seams were found in drill core. A surface water sample (S38) was sampled from a tributary of Xiangjiang, in the south of the downtown, which was seriously polluted by salt, and had a black color. Temperature, pH, EC, total dissolved solids (TDS), dissolved  $\text{O}_2$  and alkalinity of the samples were measured at the sampling sites. The major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) were determined by AAS, and the major anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) were

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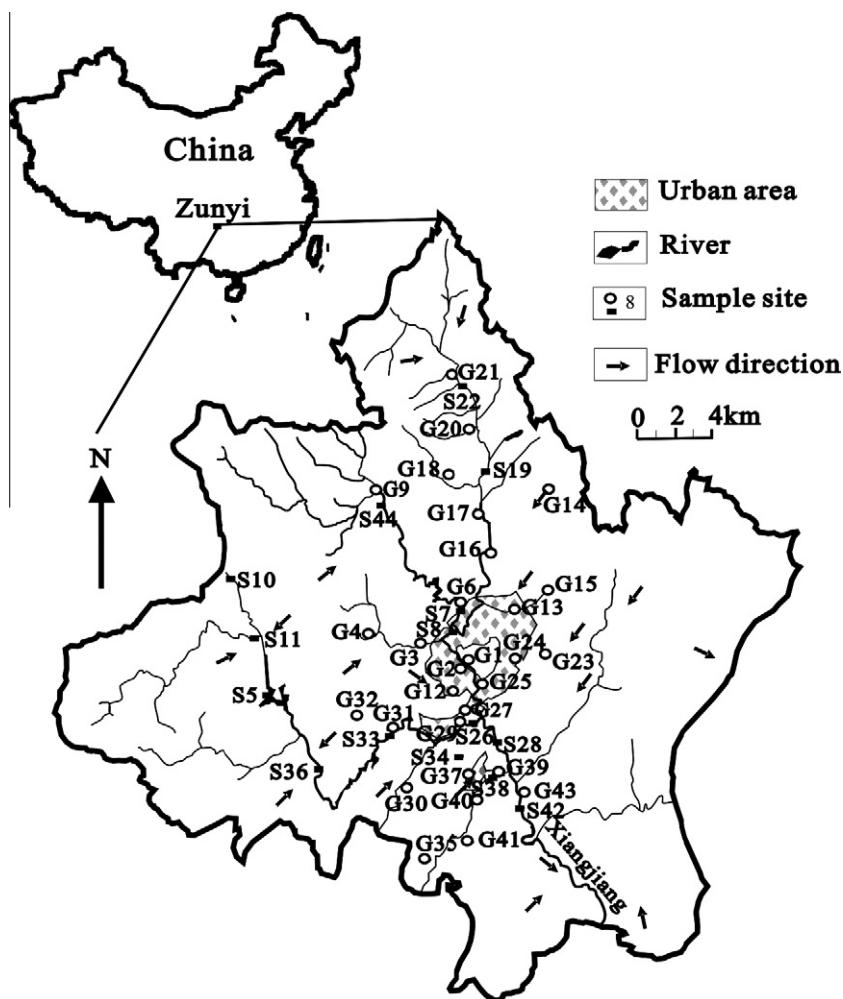


Fig. 1. Map showing the studied area and the sampling sites in Zunyi. The number of sampling sites with S indicates surface water sample, while G indicates ground water sampling site.

determined by HP1100. A detailed analytical procedure for stable S isotopic composition was given in Liu et al. (2008).

### 3. Results and discussions

#### 3.1. Hydrochemical characteristics and seasonal variation

Hydrochemical characteristics and their seasonal variations were listed in Table 1. The pH values of the sampled ground and surface waters varied from 6.8 to 9.0, showing that most of water samples are slightly alkaline. The ground water samples collected in the two seasons have pH values of from 6.8 to 8.4, while the surface water samples have pH values from 7.6 to 9.0. The surface water samples show higher pH values compared to the ground water samples. Ground water in the aquifers of different rock units has differing TDS values, with groundwater flowing through gypsum > groundwater flowing dolomite > groundwater flowing through limestone (or limestone with clastic rock) > river water.

Principal component analysis shows that most groundwaters are mainly Ca–HCO<sub>3</sub> and Ca–HCO<sub>3</sub>–SO<sub>4</sub> type. Most surface waters are Ca–Mg–HCO<sub>3</sub>–SO<sub>4</sub>, but a few samples show a trend to elevated Na<sup>+</sup>, Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> concentrations in some localities. In winter and summer, average Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of groundwater do not change significantly.

#### 3.2. Sources of dissolved sulfate and major contaminants

From the chemical composition of the contaminated samples (S38, Fig. 1), contaminants in the karstic ground water systems in the studied area are dominated by K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>. The Na<sup>+</sup> and Cl<sup>-</sup> concentrations of sample S38 are several times higher than those of the other samples. The ground water samples collected across the downtown area from north to south show high concentrations of both NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> and also high TDS values. Accordingly, the ground water system has been contaminated due to extensive use of fertilizer and recharge of agricultural and industrial wastewater into the ground water.

The SO<sub>4</sub><sup>2-</sup> in inland regions has multiple origins, mainly from precipitation (acid rain), dissolution of sulfate evaporites, oxidation of sulfide minerals and organic S in the strata, and anthropogenic inputs. The highest SO<sub>4</sub><sup>2-</sup> concentrations were measured in sample G16 in winter. The value of Cl/SO<sub>4</sub><sup>2-</sup> (molar ratio) should be high if the water is polluted by salt and gasoline. Most of Cl/SO<sub>4</sub><sup>2-</sup> values are lower than 1, but two samples, S38 and G18 (polluted by salt and gasoline, respectively), show significantly high Cl/SO<sub>4</sub><sup>2-</sup> values. High SO<sub>4</sub><sup>2-</sup> contents and Cl/SO<sub>4</sub><sup>2-</sup> values were found for the water samples collected in the city center and ambient areas.

The SW of China is impacted by acid rain. Many studies on carbonate dissolution by H<sub>2</sub>SO<sub>4</sub> have been reported (e.g. Hanshaw and Back, 1979; Macpherson, 1996; Massmann et al., 2003; Han and

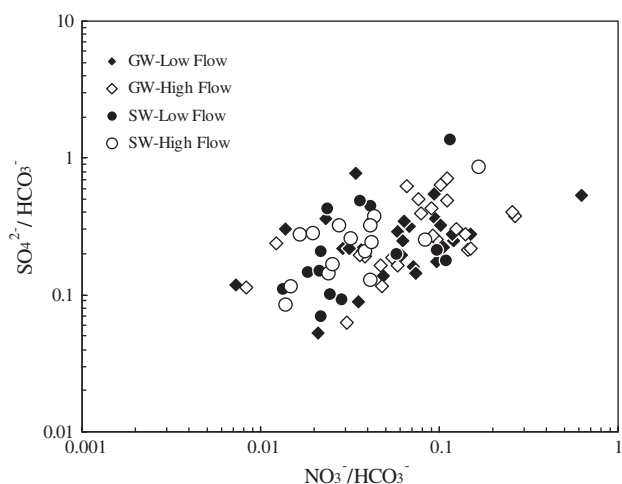
**Table 1**  
Sample statistics of water chemistry characteristics of surface and ground water in Zunyi.

Contents	T (°C)	pH	K <sup>+</sup> (mmol/L)	Na <sup>+</sup> (mmol/L)	Ca <sup>2+</sup> (mmol/L)	Mg <sup>2+</sup> (mmol/L)	NO <sub>3</sub> <sup>-</sup> (mmol/L)	Cl <sup>-</sup> (mmol/L)	SO <sub>4</sub> <sup>2-</sup> (mmol/L)	HCO <sub>3</sub> <sup>-</sup> (mmol/L)
<i>GW low flow, n = 28</i>										
Min	5.8	6.94	0.02	0.03	0.73	0.17	0.01	0.01	0.02	1.62
Max	17.7	7.85	0.43	3.17	4.29	2.78	1.74	4.51	3.24	6.58
Mean	15.5	7.26	0.10	0.52	2.49	0.76	0.32	0.74	1.09	4.22
<i>GW high flow, n = 29</i>										
Min	16.7	6.83	0.02	0.02	0.96	0.13	0.01	0.06	0.13	1.63
Max	26.5	8.37	0.57	4.41	4.10	1.55	1.46	4.77	2.86	5.96
Mean	19.8	7.37	0.15	0.72	2.38	0.63	0.32	0.75	1.21	4.06
<i>SW low flow n = 15</i>										
Min	5.0	7.56	0.02	0.05	0.86	0.50	0.05	0.05	0.21	2.07
Max <sup>a</sup>	15.5	8.73	0.44	16.77 (2.08)	6.79	1.55	0.53	31.49 (4.23)	3.05	4.90
Mean <sup>b</sup>	8.4	8.13	0.13	1.60 (0.51)	2.16	1.13	0.17	2.73 (0.68)	1.06	3.96
<i>SW high flow n = 15</i>										
Min	23.4	7.65	0.04	0.07	0.69	0.34	0.04	0.07	0.24	1.80
Max	28.5	9.04	0.34	3.15	3.02	1.15	0.30	7.34	1.54	4.70
Mean	27.3	8.12	0.11	0.49	1.47	0.76	0.11	0.73	0.76	3.11

n = sample size.

<sup>a</sup> Indicates the next to the highest value.

<sup>b</sup> Indicates the highest value is not included in statistics.

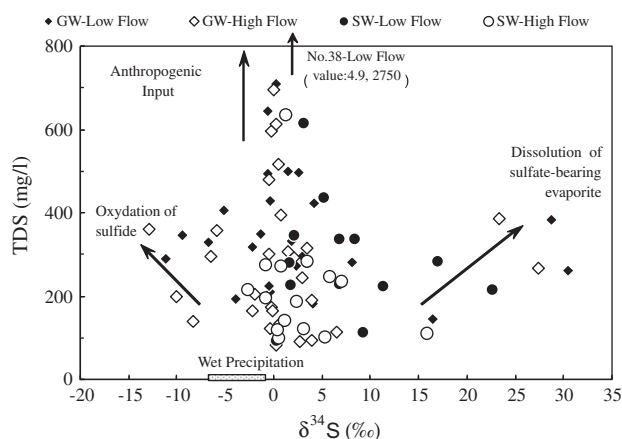


**Fig. 2.** Co-variations of HCO<sub>3</sub><sup>-</sup>-normalized SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> values (molar ratio) of surface and ground water in Zunyi.

Liu, 2004). Fig. 2 shows the relationship between HCO<sub>3</sub><sup>-</sup>-normalized SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> values in surface and ground water samples. There is a general positive relationship between these two values in both the surface and ground water. The maximum SO<sub>4</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup> and high NO<sub>3</sub><sup>-</sup>/HCO<sub>3</sub><sup>-</sup> values in the water sampled at the sampling site S38 indicate an industrial source of these two contaminants.

### 3.3. Distinguishing the natural and anthropogenic sources by stable sulfur isotope

Sulfur from different sources has differing S isotopic composition, and hence the S isotopes have been widely used to trace the sources of S. The ground water samples from Zunyi city have δ<sup>34</sup>S values of SO<sub>4</sub><sup>2-</sup> from -12.9‰ to +27.4‰ in summer and from -11.1‰ to +30.5‰ in winter. The surface water samples show δ<sup>34</sup>S values of from -2.7‰ to +15.9‰ in summer and from +0.3‰ to +22.6‰ in winter. Sulfur isotopic composition of the SO<sub>4</sub><sup>2-</sup> in both ground and surface water is shown in Fig. 3, together with the TDS values. The correlation between TDS and δ<sup>34</sup>S of SO<sub>4</sub><sup>2-</sup> in surface and ground waters suggests that a mixing of four major sources is needed to interpret the distribution of the data. The four major sources likely are: (1) precipitation (acid rain) with the low-



**Fig. 3.** Variations of δ<sup>34</sup>S values with TDS contents of the surface and ground water in Zunyi.

est TDS and intermediate δ<sup>34</sup>S values (around ~0.5‰), (2) dissolution of sulfate evaporates (gypsum or anhydrite) with an intermediate or high TDS and the highest δ<sup>34</sup>S value, (3) oxidation of sulfide minerals, characterized by intermediate or high TDS and low δ<sup>34</sup>S value, and (4) anthropogenic inputs with the highest TDS and a δ<sup>34</sup>S value similar to that of the precipitation.

The identification of the SO<sub>4</sub><sup>2-</sup> sources is supported by several lines of evidence. According to the unpublished δ<sup>34</sup>S data of Dr. X.D. Li, the annual average δ<sup>34</sup>S values of rain water in Zunyi is about +0.4‰. Previously published δ<sup>34</sup>S values for the marine evaporate minerals are +23.7‰ to +29.6‰ (Han and Jin, 1996), which are similar to those of the ground water sampled in winter. The lowest δ<sup>34</sup>S values found here are similar to those found in the karstic ground water system of Guiyang, the capital city of Guizhou Province, which was ascribed to the oxidation of sulfide minerals in coal-containing strata. The average δ<sup>34</sup>S values of anthropogenic inputs is similar to that of rain water in Zunyi, different from that of sewage in Guiyang (-8.0‰ to -4.3‰).

### 4. Conclusions

The relationships between the chemical and S isotopic compositions of the surface and ground waters in Zunyi city and the adja-

cent area offer the possibility of distinguishing the natural and anthropogenic sources of the solutes. Four major sources of  $\text{SO}_4^{2-}$  in waters, which are acid rain, evaporite dissolution, oxidation of sulfide minerals, and anthropogenic inputs, are recognized. This research suggests that the karstic ground water system is subject to contamination and the contaminants are usually complex.

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