

Seasonal variations in sulfur isotopic composition of dissolved SO_4^{2-} in the Aha Lake, Guiyang and their implications

SONG Liuting^{1,2,3}, LIU Congqiang^{3*}, WANG Zhongliang³, TENG Yanguo^{1,2}, WANG Jinsheng^{1,2}, LIANG Lili³, and BAI Li³

¹ College of Water Sciences, Beijing Normal University, Beijing 100875, China

² Engineering Research Center of Groundwater Pollution Control and Remediation, Ministry of Education, Beijing 100875, China

³ State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

* Corresponding author, E-mail: liucongqiang@vip.skleg.cn

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Abstract The Aha Lake is a seasonal anoxic water system in the southwest of Guiyang City, Guizhou Province, China. Seasonal variations in SO_4^{2-} concentrations and their isotopic compositions in lake water as well as in the tributaries were investigated in this study. The results showed that sulfate concentrations in river water range from 0.94 to 6.52 mmol/L and their $\delta^{34}\text{S}$ values range from -14.9‰ and 0.9‰, while lake water has sulfate concentrations ranging from 1.91 to 2.79 mmol/L, and $\delta^{34}\text{S}$ values from -9.8‰ to -5.9‰. It is suggested that coal mining drainage is the major source of SO_4^{2-} in the Aha Lake. Rainfall, sewage discharge, sulfide oxidation and gypsum dissolution have made only limited contributions. Different depth-dependent distributions of dissolved SO_4^{2-} and $\delta^{34}\text{S}$ were developed for both DB and LJK in summer and winter. Due to water overturn, $\delta^{34}\text{S}$ values display homogenous vertical distributions in winter and spring. While in summer and autumn, significant positive shifts of $\delta^{34}\text{S}$ were clearly observed in epilimnion and bottom strata as a result of water stratification. High $\delta^{34}\text{S}$ values in epilimnion may result from the retention of rainwater during water stratification. Dissimilatory sulfate reduction by bacteria was thought to be responsible for the increase of $\delta^{34}\text{S}$ value in hypolimnion.

Key words Aha Lake; sulfur isotope; source; geochemical cycling

1 Introduction

Sulfur isotope ratio measurements have been successfully used to identify and quantify sulfate sources and the behavior of sulfur in a given environmental system (Krouse and Grinenko, 1991). In the past decades, numerous studies have been carried out on acid mining lakes (Knöller and Strauch, 1999, 2002; Bozau and Strauch, 2002; Fauville et al., 2004; Pellicori et al., 2005; Trettin et al., 2007), marshes, rivers and lakes (Schiff et al., 2005; Jiang Yingkui et al., 2006, 2007; Wang Zhongliang et al., 2007), surface and ground waters (Chu Xuelei, 2000; Gu Weizu, 2000; Lang Yunchao et al., 2008), and acid rain (Hong Yetang et al., 1994; Yao Wenhui et al., 2003). The major origins of dissolved SO_4^{2-} are: (1) oxidation of pyrite; (2) mineralization of organically-bound sulfur in soil; (3) rain water; and (4) agricultural and industrial drainages and other natural sources (Robinson and Bottrell, 1997). Coal mining drainage usually has

low pH values and contains large amounts of toxic heavy metals and sulfates, which are considered as potential pollution for surrounding water systems, which is one of the crucial environmental problems in the world (Edraki et al., 2005; Johnson et al., 2004). Rivers and lakes may be the critical receptors for one or these multiple sulfur sources and the biogeochemical cycling of sulfur plays an important role in hydro-chemical development of lakes. Therefore, investigations on sulfur isotopic compositions of lake water and river water are of great importance in quantifying sulfate sources and related biogeochemical cycling within the water system.

The Aha Lake is one of the major water sources for 3.7 million people in Guiyang. More than 200 coal mines are widely distributed in the watershed, where a significant amount of acid mining drainage and dump filtrate were produced. The inflowing rivers were seriously contaminated by these coal mine drainages, dump leachates and sewage effluents as well, which

poses a great threat to the water quality of the Aha Lake. Numerous studies have been performed on heavy metals including Fe, Mn and Hg, sulfate-reducing bacteria and so on (Wan Guojiang et al., 1997; Liang Xiaobing et al., 2002; Wang Fushun et al., 2005; Bai Weiyang et al., 2006; Luo Shasha and Wan Guojiang, 1999; Wang Mingyi et al., 2007). However, little work has been done on sulfur isotope geochemistry (Wang Zhongliang et al., 2007). In this study, seasonal variations in the concentrations of dissolved SO_4^{2-} and their isotopic compositions coupled with hydro-chemical parameters in the lake water and its tributaries were investigated to get a better understanding of the sources and the biogeochemical cycling of sulfur in the Aha Lake.

2 Study site

The Aha Lake is a seasonal anoxic lake located about 8 km southwest of Guiyang City (Fig. 1), with a surface area of 4.5 km^2 and a total volume of $5.4 \times 10^8 \text{ m}^3$. The average and maximum depths are 13 and 24 m, respectively. The retention time of lake water is about 0.44 year. The watershed area is 190 km^2 with the average annual precipitation of 1109 mm, the average annual evaporation of 932 mm, and the average annual temperature of 15.3°C . Sampling was performed at stations, Liang Jiang Kou (LJK) at the upstream site and Da Ba (DB) at the downstream site.

The bedrock of the Aha Lake watershed is mainly a mixture of Permian carbonate rock and coal-bearing strata covered by silica-alumina and silica-ferric yellow soil. There are also small amounts of exposed Triassic carbonate rock covered with black

and tan limestone soil. Previously, more than 200 coal mines were widely distributed in the watershed, where a significant amount of acid mining drainage and dump filtrate was produced. There are mainly six rivers flowing through the watershed area including five inflowing tributaries, the Youyu River (YR), Caichong River (CR), Lannigou River (LR), Baiyan River (BR) and Shahe River (SR), and only one discharging river, the Xiaoche River (XR) (Fig. 1). YR, CR and LR are the main tributaries for the LJK station while BR and SR are for the DB station. Within these rivers, YR, CR and BR are seriously contaminated by acid mine drainage. Lime added at upstream sites along these rivers moderates the solution pH but deteriorates the hardness of water.

3 Sampling and methods

River water and lake water samples were collected during different seasons. The sampling sites are shown in Fig.1. Polyethylene bottles and other vessels used for sampling were cleaned with acid and rinsed with Milli-Q water ($18.2 \text{ M}\Omega$) except those used for anion analysis. The bottles were pre-rinsed with the water samples for three times. A multi-parameter sensor was used to determine the pH value, water temperature (T), conductivity, and dissolved oxygen (DO). The alkalinities were also titrated with diluted HCl and bromocresol green-methyl red mixed indicator in field. Samples used for anion and cation analysis were filtered with $0.45 \mu\text{m}$ membrane filters in field and the filtered samples for cation and trace elements analysis were acidified to $\text{pH} < 2$ with distilled HNO_3 .

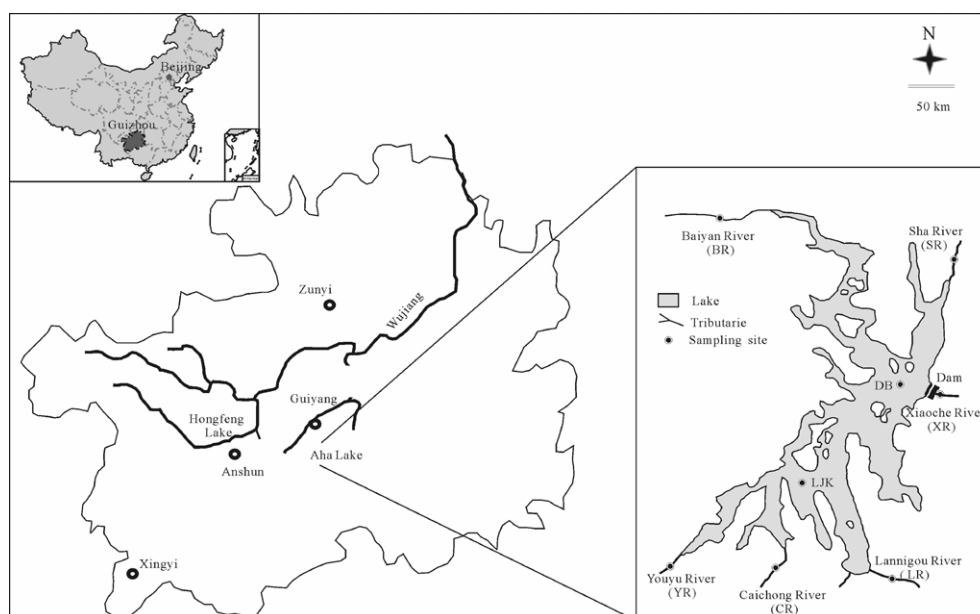


Fig. 1. Map showing the location of the Aha Lake location, its main tributaries and sampling sites.

Water samples for the measurement of sulfur isotopic compositions were filtered through a 0.45 μm Millipore HA membrane filter within 12 to 24 hours after sampling and were acidified to $\text{pH} < 2$. Dissolved sulfate was recovered as BaSO_4 after the addition of 10% BaCl_2 . The precipitation of BaSO_4 was rinsed with Milli-Q water (18.2 M Ω) until there was not Cl^- detected and the precipitation was then combusted at 900 $^\circ\text{C}$ in a muffle furnace. All sulfur isotopic compositions were determined with IsoPrime JB144 CF-IRMS (GV instruments). During the measurement, Sigma, GBW04414 and GBW04415 were used as standards and the results were reported as $\delta^{34}\text{S}$ in part per thousand deviations relative to the Vienna Cañon Diablo Troilite (V-CDT) standard with a reproducibility of $\pm 0.2\text{‰}$.

4 Results

4.1 Hydrochemical characteristics of lake water and river water

Cations in lake water are mainly Ca^{2+} and Mg^{2+} , while HCO_3^- and SO_4^{2-} are the main anions. The average concentrations of Ca^{2+} and SO_4^{2-} in the Aha Lake are 2.66 mmol/L and 2.30 mmol/L, respectively. Although there are slight decreases in Ca^{2+} and SO_4^{2-} concentrations, they are still higher than those of other lakes in the Wujiang River watershed. The average pH value of the Aha Lake is 8.13 and the pH values of all river water samples are higher than 7.

Environmental parameters for the DB and LJK stations are of depth dependence (Fig. 2). Thermal stratifications were clearly observed in summer and autumn with a temperature gradient of ca. 10 $^\circ\text{C}$. Being linked with water stratification, other parameters also show depth-dependence (Fig. 2). However, during winter and spring, water temperatures become low and nearly constant throughout the water column due to water overturn, resulting in a homogeneous water body. During summer and autumn stratification, the dissolved O_2 becomes almost depleted in hypolimnion, with the concentrations ranging from 1.6 to 2 mg/L and the hypoxic condition prevailed. There is also a marked decrease in pH (0.5–1.2 unit) with respect to the pH value measured in epilimnion (Fig. 2). The electrical conductivity is high with respect to other fresh lake water, which may be caused by the inflowing tributaries deteriorated by coal mine drainages and lime addition. In summer, electrical conductivity continuously increases with water depth until there is a sharp decrease of 102 $\mu\text{s}/\text{cm}$ in hypolimnion, especially, for the LJK station. The dissolved silica (H_4SiO_4) concentrations are only from 0.38 to 0.46 mg/L in epilimnion, being much lower than those of

inflowing tributaries (6.16–9.86 mg/L). But H_4SiO_4 concentrations increase continuously with the water depth in deep strata (Fig. 2). During summer, diatoms are the most abundant algae in the Aha Lake (Wang Baoli, 2005). It is considered that it is the diatom production that consumes the dissolved silica, and this is the case similar to that encountered in the near surface ocean water (John, 1986), which makes the epilimnetic concentrations of H_4SiO_4 become lower. Besides, the dilution of rainwater also has made some contributions to the low concentrations of silica in epilimnion. However, due to the depletion of dissolved oxygen, the regenerative processes and sediment-water fluxes seem to be high at the bottom, resulting in the continuous increase of H_4SiO_4 (D'Elia et al., 1983).

4.2 Sulfate concentrations and sulfur isotopic compositions

4.2.1 River water

Sulfate concentrations of river water range from 0.94 to 6.52 mmol/L and their $\delta^{34}\text{S}$ values range from -14.9‰ to 0.9‰. Within the inflowing rivers, YR, CR and BR have higher sulfate concentrations and lower $\delta^{34}\text{S}$ values and no significant seasonal variation is observed. They have sulfate concentrations of 4.81, 2.78 and 4.66 mmol/L, and the $\delta^{34}\text{S}$ values of -14.2‰, -8.5‰ and -9.8‰, respectively (Table 1). In contrast, SR and LR have low sulfate concentrations of 1.27 and 1.00 mmol/L, and higher $\delta^{34}\text{S}$ values of -0.8‰ and -4.5‰, respectively. As the only outflow river, XR also displays a steady sulfate concentration and $\delta^{34}\text{S}$ value, 2.40 mmol/L and -8.5‰, respectively (Table 1).

4.2.2 Lake water

A smaller range of sulfate concentrations in lake water was observed from 1.91 to 2.79 mmol/L. Lake water samples are also depleted in ^{32}S with $\delta^{34}\text{S}$ values of -9.8‰ to -5.9‰. There is an average sulfate concentration of 2.38 mmol/L and an average $\delta^{34}\text{S}$ value of -8.3‰ at LJK, while those at the DB station are -8.0‰ and 2.25 mmol/L, respectively. Depth-related variations in $\delta^{34}\text{S}$ values and SO_4^{2-} concentrations are shown displayed in Fig. 3. Generally, there is no significant variation in ^{34}S values and SO_4^{2-} concentrations in winter and spring. While in summer and autumn, remarked increases in ^{34}S values and SO_4^{2-} concentrations were observed in both epilimnion and hypolimnion. The $\delta^{34}\text{S}$ value is -7.4‰ in the surface water, and -6.8‰ near the water-sediment at LJK (Table 1 and Fig. 3). The sulfate concentrations show an opposite variation trend (Fig. 3). At the DB station,

although lake water is well thermally stratified in summer and autumn, variations in sulfate concentrations and $\delta^{34}\text{S}$ values are not as significant as those at LJK (Fig. 3).

5 Discussion

5.1 Source controls on the sulfur isotopic compositions of river water and lake water in the Aha Lake watershed

In general, sulfur originates mainly from oxidation of pyrite, weathering of other sulfides, mineralization of organic sulfur in soils, dissolution of sulfate minerals, rainfalls, industrial and agricultural drainages and so on (Robinson and Bottrell, 1997). In the Aha Lake watershed, Permian limestone and coal-bearing strata are widely distributed with a small amount of outcrops of Triassic carbonate rocks. However, Permian and Triassic gypsum has high $\delta^{34}\text{S}$

values ranging from 10‰ to 28‰, while the studied water samples all have negative $\delta^{34}\text{S}$ values, indicating that dissolution of sulfate minerals has made little contribution to sulfate in river water. It is reported that yellow soil and limestone soil in the Wujiang River watershed had low contents of sulfate (Jiang Yingkui, 2007). Schiff et al. (2005) revealed that soil sulfur storage and release did not significantly change the sulfur isotopic composition of steam water at the Turkey Lakes Watershed in Canada. Most sulfides from ore deposits in the Wujiang River watershed have statistically positive sulfur isotopic compositions with an average $\delta^{34}\text{S}$ value of 8.4‰ (Wu Pan, 2002; Yang Yuangen et al., 2004; Zhang Guoping et al., 2004; Xia Xuehui, 1994). Therefore, oxidation of organic sulfur in soil and weathering of sulfides were not expected to be the main contributors for the depletion of ^{34}S in the Aha Lake watershed. Additionally, the concentrations of SO_4^{2-} and $\delta^{34}\text{S}$ values of rain water in Guiyang are low, being -4.0‰ in winter and -7.0‰ in summer

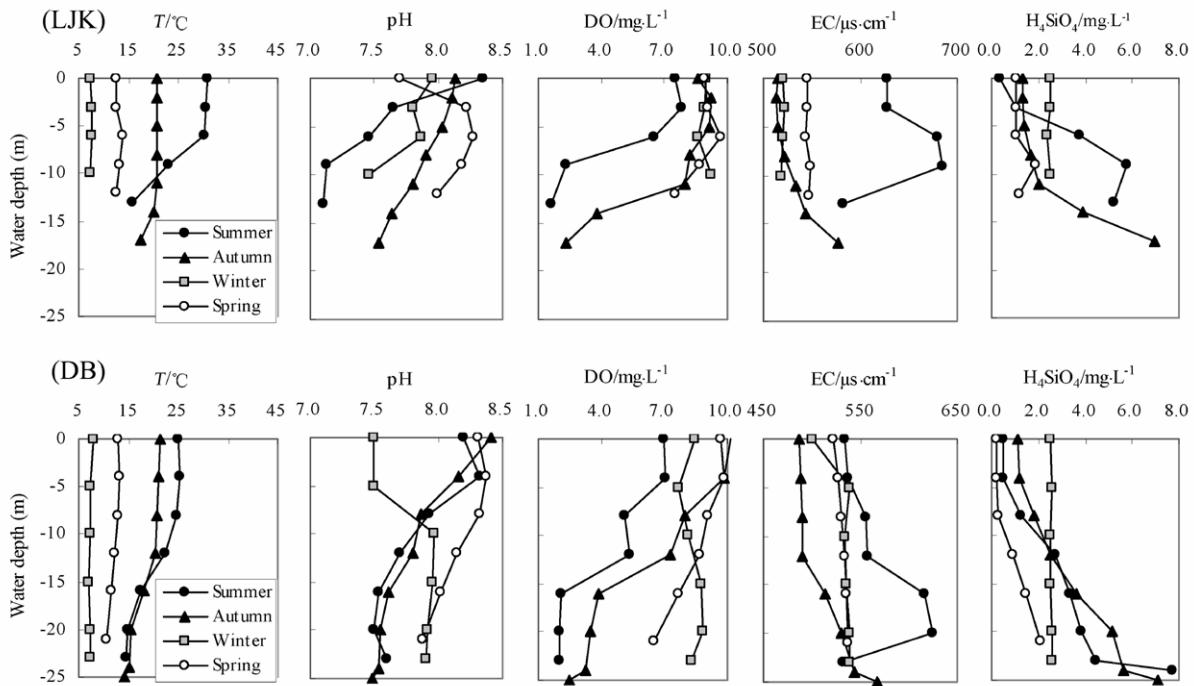


Fig. 2. Plots of environmental parameters in the water columns of the DB and LJK stations in the Aha Lake.

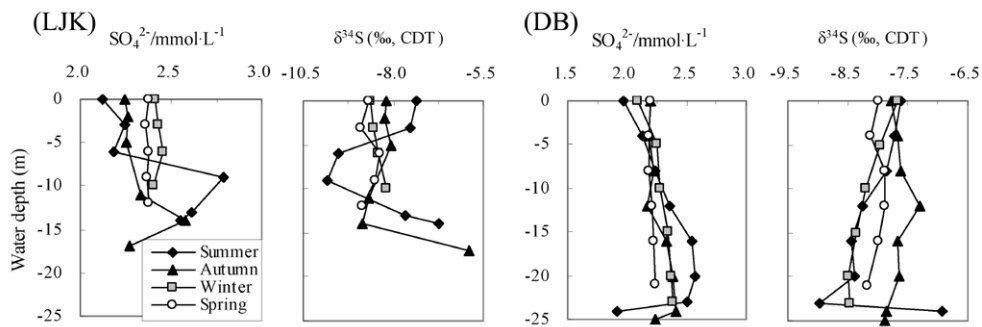


Fig. 3. Plots of sulfate concentrations and $\delta^{34}\text{S}$ values in the water columns of the DB and LJK stations in the Aha Lake.

Table 1 Sulfate concentrations and $\delta^{34}\text{S}$ values of lake water and river water samples in the Aha Lake watershed

Date	Sample station	Water Depth (m)	SO_4^{2-} (mmol/L)	$\delta^{34}\text{S}$ (‰)	Date	Sample station	Water depth (m)	SO_4^{2-} (mmol/L)	$\delta^{34}\text{S}$ (‰)	
Summer (2006-08)	LJK	0	2.12	-7.4	Winter (2007-01)	LJK	0	2.41	-8.6	
		-3	2.24	-7.5			-3	2.43	-8.6	
		-6	2.19	-9.6			-6	2.46	-8.4	
		-9	2.79	-9.8			-10	2.40	-8.2	
		-13	2.61	-7.7			DB	0	2.09	-7.7
	-14	2.55	-6.8	-5		2.24		-8.0		
	0	1.97	-7.6	-10		2.27		-8.2		
	-4	2.13	-7.7	-15		2.35		-8.4		
	-8	2.24	-7.9	-20		2.37		-8.5		
	DB	-12	2.35	-8.2		-23	2.39	-8.5		
		-16	2.55	-8.4		YR	4.20	-13.8		
		-20	2.57	-8.4		CR	2.27	-8.4		
		-23	2.51	-9.0		LR	0.94	-3.3		
		-24	1.91	-6.9		BR	5.96	-9.6		
		YR	5.44	-14.0		SR	1.31	-2.3		
		CR	2.40	-8.7		XR	2.36	-8.5		
		LR		-4.6		Spring (2007-04)	0	2.38	-8.7	
		BR	4.06	-10.2			LJK	-3	2.36	-8.9
		SR	1.20	0.9				-6	2.37	-8.4
	XR	2.64	-8.7	-9				2.36	-8.5	
			-12	2.38	-8.9					
			0	2.19	-8.0					
Autumn (2006-10)	LJK	0	2.25	-8.2	DB	-4	2.18	-8.1		
		-2	2.27	-8.2		-8	2.19	-7.9		
		-5	2.25	-8.1		-12	2.21	-7.9		
		-11	2.33	-8.7		-16	2.22	-8.0		
		-14	2.58	-8.9		-21	2.23	-8.2		
	DB	-17	2.27	-5.9	YR	4.80	-14.9			
		0	2.19	-7.8	CR	3.67	-8.3			
		-4	2.19	-7.7	LR	1.05	-5.7			
		-8	2.23	-7.6	BR	3.95	-9.5			
		-12	2.17	-7.3	SR	1.30	-1.1			
		-16	2.32	-7.7	XR	2.20	-8.4			
		-20	2.39	-7.7						
		-24	2.41	-7.9						
		-25	2.23	-7.9						

(Hong Yetang et al., 1994). There are intensive and frequent rainfalls especially in peakflow periods, but the concentrations of SO_4^{2-} in rain water are low with an average value of 0.1 mmol/L (Xiao Huayun et al., 2003; Han Guilin and Liu Congqiang, 2006), which suggests that meteoric water is not the major sulfate source, either.

YR, CR and BR are characterized by high concentrations of SO_4^{2-} and lower and steady $\delta^{34}\text{S}$ values (Table1), suggesting that SO_4^{2-} is mainly derived from pyrite oxidation in coal mine drainages collected in the Wujiang River watershed, which tends to have high sulfate concentrations (12.96 mmol/L) and be seriously depleted in ^{34}S ($\delta^{34}\text{S} = -13\text{‰} \pm 2\text{‰}$) (Jiang Yingkui et al., 2006). Considerable domestic sewage is discharged into the LR and it has an average $\delta^{34}\text{S}$ value of -4.5‰, which is in agreement with the data (-4.5‰) obtained by Jiang Yingkui et al. (2005) in their research on urban sewage in the Wujiang River watershed, which implies that dissolved SO_4^{2-} in LR is mainly from domestic sewage effluent. Within all tributaries of the Aha Lake, SR has the highest $\delta^{34}\text{S}$ values, ranging from -2.3‰ to 0.9‰, which may probably result from contamination of both domestic sewage and industrial drainage as SR flows through Yeya Town, Guizhou Tyre Factory and Guizhou University of Technology.

Numerous studies have been performed on the sulfur isotopic composition of lake water and a fairly variable range of $\delta^{34}\text{S}$ values of sulfate were found due to different sources of sulfate in lake water. Studies on Lake Ontario, Lake Erie in North America, Lake Tanganyika in Africa, Lake Baykal in Russia and Biwa Lake in Japan and so on revealed that the $\delta^{34}\text{S}$ values of lake water vary widely between -32‰ and 87‰, and most of them fall between 5‰ and 15‰ (Krouse and Grinenko, 1991; Trettin et al., 2007; Schiff et al., 2005; Ingri et al., 1997; Varekamp and Kreulen, 2000; Knöller et al., 2004; Torfstein et al., 2005; Hosono et al., 2007). Generally, the Aha Lake has low $\delta^{34}\text{S}$ values, ranging between -9.8‰ and -5.9‰, with an average value of -8.1‰. In order to get a better understanding of the sources of sulfates in the Aha Lake, the $\delta^{34}\text{S}$ values of dissolved sulfates were plotted with $1/\text{SO}_4^{2-}$ (Fig. 4), where coal, sulfides and rainfall were considered as the main end-members. As is shown in Fig. 4, the sulfur isotopic compositions of most water samples at both LJK and DB stations are fairly concentrated and they are significantly influenced by the end-member "coal" while rainfall and sulfide oxidation have made less important contributions. The results are consistent with those described in Wang Zhongliang et al. (2007). There were also a few samples scattered in summer and autumn (Fig. 4a,

b), which might be induced by other sulfur sources or biogeochemical cycling processes within the lake. In general, dissolved sulfates in the studied water samples in the Aha Lake watershed originated mainly from pyrite oxidation in coal mine drainages, which is consistent with the fact that there are large numbers of medium- and small-sized coal mines distributed in the studied area.

5.2 Seasonal variations in sulfur isotopic compositions in the Aha Lake watershed and biogeochemical cycling

Seasonal variations in SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values in the Aha Lake were clearly observed (Fig. 4), being similar to those of the Hongfeng Lake (Song Liuting et al., 2008), which is probably related to water stratifications in summer and autumn while overturn mixing in winter and spring. Significant variations in SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values in epilimnion and hypolimnion suggest that the sulfur isotopic composition of lake water is controlled not only by fluvial inputs, but also by the biogeochemical processes within the lake.

In summer, peak water flow occurs with plentiful and frequent rainfall. The rainwater tends to have higher $\delta^{34}\text{S}$ values (about -7‰) and lower SO_4^{2-} concentrations (about 0.1 mmol/L) (Hong Yetang et al., 1994; Xiao Huayun et al., 2003; Han Guilin and Liu Congqiang, 2006). Meanwhile, the Aha Lake is well thermally stratified with a temperature gradient of ca. 10 °C, which can make the rainwater retained in epilimnion for a period of time. It is considered that the retention of rainwater is responsible for the drop of SO_4^{2-} concentrations and the increase of $\delta^{34}\text{S}$ values in epilimnion, which agrees well with the results of Song Liuting et al. (2008). YR, CR and LR are the main inflowing tributaries for the LJK station, with sulfate concentrations being 4.20, 2.27, and 0.94 mmol/L, and the $\delta^{34}\text{S}$ values being -13.8‰, -8.4‰ and -3.3‰ in winter, respectively, and in summer, their sulfate concentrations are even higher, being 5.44, 2.40 and 1.00

mmol/L respectively, whereas the $\delta^{34}\text{S}$ values are even lower, being -14.0‰, -8.7‰ and -4.6‰, respectively. However, SO_4^{2-} concentrations in epilimnion of LJK are lower in summer (2.18 mmol/L) than those in winter (2.42 mmol/L), while the corresponding $\delta^{34}\text{S}$ value is higher in summer (-7.4‰) than that in winter (-8.6‰). Moreover, the SO_4^{2-} concentrations in epilimnion are also lower than those in hypolimnion (Fig. 3), which further indicates that the low SO_4^{2-} concentrations are attributed to the retention of rainwater in epilimnion during water stratification. In contrast, there is no significant seasonal variation in SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values in epilimnion at the DB station (Fig. 3). Compared to the inflowing tributaries of the LJK station, there is a stronger increase in SO_4^{2-} concentrations and also a decrease in $\delta^{34}\text{S}$ values of BR in summer. Therefore, there is no significant difference in sulfate concentrations and $\delta^{34}\text{S}$ values between in summer and in winter, although SR and rainfalls lead to a decrease in epilimnetic SO_4^{2-} concentrations and an increase in $\delta^{34}\text{S}$ values in summer at the DB station.

During summer stratification, anoxic conditions prevailed gradually with the degradation of organic matter in deep strata of the Aha Lake. According to Wang Mingyi et al. (2007), there existed sulfate reducing bacteria in hypolimnion of the Aha Lake in June and the amount of bacteria increased with increasing water depth. Experimental studies indicated that ^{32}S is preferentially consumed by sulfate reduction bacteria during dissimilatory reduction processes to increase the $\delta^{34}\text{S}$ value of the remaining sulfate, and the produced S(II) has very low $\delta^{34}\text{S}$ values. The $\Delta\delta^{34}\text{S}_{\text{sulfate-S(II)}}$ varies between 2‰ and 47‰, depending on the growth rate and reduction rate of bacteria and the surrounding environments (Rees, 1973; Canfield, 2001; Detmers et al., 2001; Brunner and Bernasconi, 2005; Mayer et al., 2007). The $\Delta\delta^{34}\text{S}_{\text{sulfate-S(II)}}$ can be as high as 60‰–70‰ when the reduction rate is fairly slow (Goldhaber and Kaplan, 1980; Ryu et al., 2006). In this study, the increase of $\delta^{34}\text{S}$ values in deep strata of the Aha Lake is also considered as being related

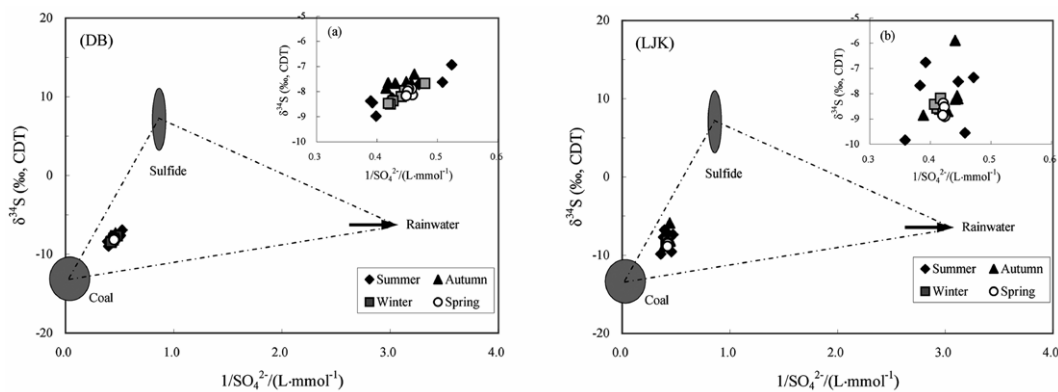


Fig. 4. Correlations between $\delta^{34}\text{S}$ values of lake water samples and the corresponding sulfate concentrations.

with similar bacterial sulfate reduction processes in summer and autumn. Furthermore, the drop of concentrations of sulfates was clearly observed in hypolimnion at both LJK and DB stations in summer and autumn (Fig. 3), which further confirms that sulfate reduction occurs in hypolimnion of the Aha Lake.

In autumn, lake water is still well stratified with good reduction environments in hypolimnion, which can be seen from the *in-situ* analysis of water temperature and dissolved oxygen (Fig. 2). The SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values in autumn vary in a similar trend with those in summer at the LJK station. In contrast, there is no remarkable variation at the DB station in autumn. The DB station is located at the downstream site of the Aha Lake watershed and water at the LJK station can be considered as one more tributary when there is a large amount of discharge near the dam. Lake water at the LJK station has lower $\delta^{34}\text{S}$ values and higher sulfate concentrations. The differences between these stations can be explained with the influence of the LJK station on the DB station. To confirm this hypothesis, detailed work is necessary in future studies.

6 Conclusions

(1) At the watershed area of Aha Lake, tributaries contaminated by coal mine drainage tend to have low and steady $\delta^{34}\text{S}$ values, while tributaries contaminated by industrial sewage effluents have higher $\delta^{34}\text{S}$ values with slight seasonal variations.

(2) The sulfur isotopic compositions of dissolved sulfates in the Aha Lake are controlled mainly by SO_4^{2-} formed from pyrite oxidation within coal mine drainage, while rainfall, sewage discharge, gypsum dissolution and other sulfides oxidation have made limited contributions.

(3) Due to water stratification, depth-dependent distribution of $\delta^{34}\text{S}$ values is observed in summer and autumn, while overturn mixing results in a homogeneous water column in winter and spring. The positive shift of $\delta^{34}\text{S}$ values in epilimnion may result from the retention of rainwater during water stratification and dissimilatory sulfate reduction by bacteria, and is thought to be responsible for the increase of $\delta^{34}\text{S}$ in hypolimnion.

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