



Sulfur isotope and chemical composition of the rainwater at the Three Gorges Reservoir



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ABSTRACT

Rainwater samples were collected at the Three Gorges Reservoir (TGR) from June 2009 to July 2010 and the pH, major ion concentrations and $\delta^{34}\text{S}$ values of sulfate were measured. The results indicated that the rain in this region was seriously acidized, 60% of the rain events' pH were lower than 5.0. SO_4^{2-} and NO_3^- were the main anions, and their volume weighted mean (VWM) values were 161.9 $\mu\text{eq/L}$ and 65.2 $\mu\text{eq/L}$, respectively, which accounted for 71%–99% of the total measured anions. Ca^{2+} and NH_4^+ were the major cations with VWM values of 108.3 $\mu\text{eq/L}$ and 88.4 $\mu\text{eq/L}$. Sum of Ca^{2+} and NH_4^+ accounted for 25%–94% of the total cations. Analysis of the seasonal variations of the pH showed that the rainwater was more acidized in summer than in the other seasons. Investigations of neutralization factors (NFs) indicated that the acidity of rainwater in winter and spring was neutralized by NH_4^+ and Ca^{2+} . Studies of the origins of major ions showed that SO_4^{2-} and NO_3^- were from coal combustion and fossil fuels, and Na^+ and Cl^- were from sea sources, while Ca^{2+} , Mg^{2+} and K^+ were from the continental sources. The $\delta^{34}\text{S}$ values of SO_4^{2-} in rainwater ranged from -2.1‰ to 6.1‰ (mean value of 2.1‰). The $\delta^{34}\text{S}$ values of SO_4^{2-} in winter were much higher than those in other seasons. Analysis of the $\delta^{34}\text{S}$ values vs. SO_4^{2-} of rainwater combined with air mass trajectory showed that atmospheric sulfur at TGR was mainly associated with coal combustion and fossil fuels. The lower $\delta^{34}\text{S}$ values in summer at TGR could be explained by higher contribution of biogenic sulfur.

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1. Introduction

Severe acid precipitations were recognized and aroused widespread concern in China in the late 1970s and early 1980s (Zhao and Sun, 1986; Zhao et al., 1988; Wang and Wang, 1996). China has been recognized as one of the most important acidic gas emitting areas in the world followed by Northeast America and Central Europe (Wang and Wang, 1995). According to Tang et al. (2010), during 1992–2006, the area in the south of the Yangtze River is the largest continuous acid rain area, with the severe acid rain areas being mainly distributed in Zhejiang, Jiangxi, Fujian, Hunan, Guangdong, Guizhou, Chongqing, Hubei,

Sichuan and Guangxi. The precipitation acidity increased in a vast continuous area, including the North China Plain, Central China, and South China.

Investigation of the chemical composition and dynamics of atmospheric deposition is very important in environmental studies for it helps to distinguish the major source types that contribute to rainwater chemistry and to understand the dispersion (i.e. both local and regional scales) of elements, whether pollutants or not, and their potential impact on eco-hydro systems through deposition processes (Négrel et al., 2007). The precipitation chemistry has been widely investigated in many areas in China (Han and Liu, 2006; Huang et al., 2008b; Xu and Han, 2009; Zhao et al., 2008; Han et al., 2010, 2011; Wu et al., 2012; Niu et al., 2014), but most of the monitoring sites of air pollutants were mainly in urban areas.

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Aas et al. (2007) have emphasized that more integrated approach is required to address the acid rain problem in China.

Sulfur in the atmosphere occurs in a variety of gaseous, liquid and solid chemical forms. Major inputs include sea spray, biogenic emission (e.g. H₂S, OCS, DMS), volcanic gases, combustion of fossil fuel, biomass burning, and other human activities (Newman et al., 1991; McArdle and Liss, 1995). Sulfur isotopes have been traditionally used to identify and characterize the sources of sulfur in the atmosphere because sources such as anthropogenic SO₂, biogenic sulfur, and marine sulfur often possess different δ³⁴S values (Nielsen, 1974; Ohizumi et al., 1997; Herut et al., 1995; Kitayama et al., 2008; Toshiaki et al., 2012). Atmospheric isotopic signatures also can tell us about mixing processes, oxidation processes, transport pathways and deposition of sulfur in the environment (Ohizumi et al., 1997; Leung et al., 2001; Sinha et al., 2008). Sulfur isotope fractionation was affected by the fuels burning process and photochemical reaction in atmospheric processes (Nakai and Jensen, 1967; Zhang et al., 2010). But the sulfur isotopes in atmospheric aerosols over China have been observed to be similar to those in coal combusted in the region (Hong et al., 1992; Mukai et al., 2001). It was reported that high sulfur isotope ratios (both rainwater and atmospheric sulfur) were observed in northern China (Harbin, Changchun, and Dalian), and low isotope values were observed in southern China, especially in Guiyang (Hong et al., 1994; Zhang et al., 2010). Shanghai and Nanjing seemed to be within those ranges (about 3‰) on the average (Mukai et al., 2001). These differences were basically attributable to the differences in the characteristics of sulfur sources. In general, northern Chinese coals have been reported to have higher sulfur isotope ratios than southern Chinese coals (Hong et al., 1992). So the sulfur isotope ratio of sulfate in rainwater was considered as a useful method in tracking the source and distribution cycle of air pollutants.

As the largest hydroelectric project in the world, the Three Gorges Reservoir (TGR) on the Yangtze River extended a 660 km length of the Yangtze River from Yichang City to Chongqing Municipality and to cover an area of 1040 km². Such a huge reservoir has received increasing attention because of the effects of climatic fluctuations and the land use changes in the reservoir area. Previous studies (Miller et al., 2005; Wu et al., 2006) suggest that the TGR area will alter local scale (~10 km) meteorological conditions such as temperature and precipitation. However, the local climatic impacts have not been systematically quantified because of the change in surface area (Xiao et al., 2010).

This paper presents for the first time the characteristics of the sulfur isotope and chemical composition of rainwater collected at Three Gorges Reservoir. The purposes of this paper are to present and discuss the chemical composition and sulfur isotopic characteristics of rainwater, to identify possible sources of sulfur and the extent of seasonal of rainwater and this data will provide a potential solution to environmental problems of acid rain in the region.

2. Materials and methods

2.1. Study area description

The study site (Fig. 1) was located at the Zigui County, Hubei Province, Southern China (30°38′–31°11′N, 110°18′–111°0′E).

Altitude in Zigui ranges from 133 to 632 m above sea level. The relative humidity is 72%. This region has a typical subtropical monsoon climate with an annual mean air temperature of 18.0 °C and an annual frost-free period of 326 days. Annual precipitation averages 1164 mm, of which nearly 80% falls in hot humid season (April–September) and 20% in the cool-dry season (October–March).

Most of the Zigui area is hilly or mountainous with basic farming and green tea (*Camellia sinensis*) production. Arable cultivation on terraced fields is the dominant farming of the county. It is close to the TGR, and has geomorphologic landscape with many mountains after longtime geological evolution and exogenic force erosion of wind and rain. Though dominated by mountains, it is densely populated and has been intensively reclaimed and cultivated.

2.2. Analytical methods

Rainwater samples were collected on building roofs of Zigui County from June 2009 to July 2010. A polypropylene bottle fixed on a rack 150 cm above the roof, freed from any obstacles in sight, was used to collect the rain sample manually. All samples were of single precipitation events, collected from start to end. Prior to use, the polyethylene sheet was cleaned with 2 N HCl solutions and rinsed with Milli-Q water, and dried. Between rains, the polyethylene sheet was closed to avoid dry deposition and other contaminations. The pH and conductivity were instantaneously measured at the end of a rain event at the sampling site with a portable pH meter. After collection, the samples were immediately filtered to exclude material greater than 0.45 μm using acetate membrane filters. Some aliquots of these filtered samples were for chemical determination, while other aliquots were stored at 4 °C for isotopic analysis after poisoned by HgCl₂. Anions were measured by ion chromatography (Dionex ICS-90), the detection limits of F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ ions were found to be 0.03, 0.04, 0.06 and 0.10 mg/L. Cations were measured by a flame photometer (PE-5100, PE), the detection limits of K⁺, Na⁺, Ca²⁺, and Mg²⁺ ions were found to be 0.01, 0.03, 0.04 and 0.01 mg/L, respectively. NH₄⁺ concentration was determined by spectrophotometry using the Nessler method. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures; analytical precision was better than ± 5%. The criteria used for quality control of the precipitation samples, i.e. ionic balance, were satisfactory. The results of cation and anion balances of rainwater are depicted in Fig. 2. As shown, most of the samples present good ion balances, indicating the good quality of the species measurement.

The rainwaters used for sulfur isotope analysis were acidified at pH < 2 with ultra-purified hydrochloric acid, then sulfate was recovered from rainwater by precipitating BaSO₄ with enough 10% BaCl₂ solution. After precipitation for 48 h, the mixture was filtered through 0.22 μm acetate membrane filters. The precipitates (BaSO₄) on the filters collected from the rainwater were carefully rinsed with enough Milli-Q water to remove Cl⁻, and then transferred into crucibles with the filters and combusted at 800 °C for 40 min in the air. Thermal decomposition of BaSO₄ (Yanagisawa and Sakai, 1983) was conducted to prepare SO₂ for sulfur isotopic analysis in a Finnigan MAT-252 mass spectrometer. The standard deviation

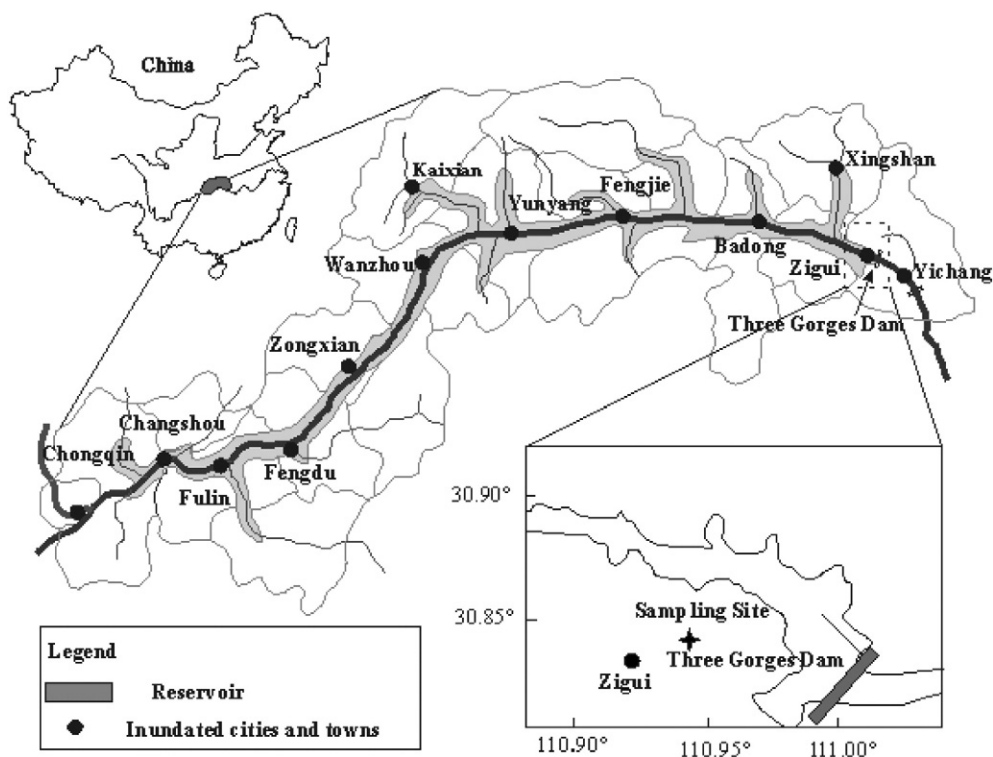


Fig. 1. Sketch map showing the sampling location and the Three Gorges Reservoir.

for the $\delta^{34}\text{S}$ analysis of NBS-127 (barium sulfate) was better than $\pm 0.2\%$ ($n = 10$).

2.3. Backward trajectories

To deduce the probable source regions of the air masses from which our water samples derived, the backward trajectories were modified based on the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<http://www.arl.noaa.gov/HYSPLIT.php>) (Draxler and Rolph, 2013; Rolph, 2013). Administration trajectories for time periods of 72 h were computed for 500 m, 1000 m and 3000 m above ground level (AGL). They correspond to 950 hPa, 850 hPa and 700 hPa, respectively,

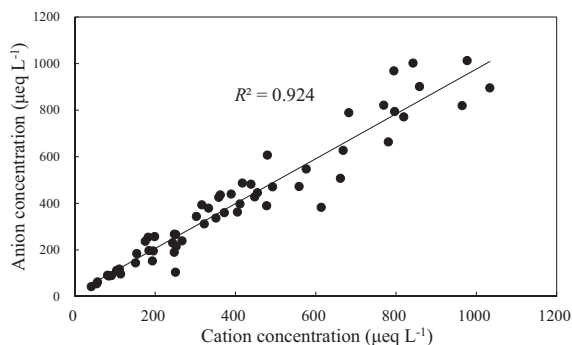


Fig. 2. Linear regression of sum of cations vs. sum of anions ($\mu\text{eq L}^{-1}$).

barometric levels at the end point of the trajectories. The trajectories were calculated for every rainwater-sampling day. This procedure helped to identify changes of sulfur isotopic and chemical data in the source regions for rainfall over our study site.

3. Results and discussion

3.1. Chemical composition of rain water at TGR

The pH, major ions and $\delta^{34}\text{S}$ of sulfate isotopic ratios are given in Table 1. The VWM values of the ionic compositions of rainwater samples and related statistical analyses are also shown in Table 2.

The pH values of rain samples range between 3.90 and 6.98. Most samples showed pH values from 3.90 to 5.50, while 4 rainwater samples exhibited pH values smaller than 4.00. The VWM value of pH was of 4.92 ± 0.76 , which lower than the natural acidity of rainwater (Charlson and Rodhe, 1982; Galloway et al., 1982; Pszenny et al., 1982). About 83% of the rainwater samples had a pH lower than 5.6, and 60% of the rainwater samples were lower than 5.0 during the study period, which demonstrates unambiguous damage to the ecological system of TGR.

The ionic composition of precipitation TGR was dominated by SO_4^{2-} , Ca^{2+} , NH_4^+ and NO_3^- . The major anions are SO_4^{2-} and NO_3^- , with VWM values of 161.9 $\mu\text{eq/L}$ and 65.2 $\mu\text{eq/L}$, and sum of SO_4^{2-} and NO_3^- account for 71%–99% of the total anions. Assuming the equivalent ratio of $\text{SO}_4^{2-}/\text{Na}^+$ in seawater salts of 0.12 (Taylor, 1964), we determined that the sea-salt sulfate

Table 1
The chemical ($\mu\text{eq/L}$) and isotopic composition of the rain water at TGR.

Sampling date y/m/d	pH	H ⁺	NH ₄ ⁺	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	$\delta^{34}\text{S}$ (‰)
09/06/27	4.73	18.62	62.71	10.38	12.47	7.00	136.24	6.01	40.49	134.61	–
09/06/29	4.77	16.98	34.92	2.18	4.85	3.92	21.15	2.54	12.58	71.44	2.2
09/06/30	4.99	10.23	10.65	4.33	0.83	2.49	12.04	2.82	8.46	31.39	5.6
09/07/04	4.50	31.62	125.94	4.35	4.07	4.62	27.91	2.39	37.32	146.44	2.9
09/07/07	5.32	4.82	155.03	15.01	24.49	10.98	236.89	10.81	159.68	287.36	2.7
09/07/11	5.12	7.59	76.44	6.09	5.72	5.04	92.06	1.34	32.09	115.36	–
09/07/23	5.51	3.08	187.26	4.64	18.39	10.30	148.46	2.58	174.63	171.33	–
09/07/26	5.38	4.13	51.85	2.10	11.82	3.38	77.65	1.67	57.61	81.84	–
09/07/30	5.02	9.59	186.65	4.45	10.00	4.36	166.05	9.42	269.12	174.90	–
09/07/31	4.32	48.42	68.13	1.50	11.67	3.85	61.67	0.10	55.00	137.07	–
09/08/01	3.96	108.89	111.25	2.30	2.97	4.22	20.78	3.10	27.91	71.81	3.7
09/08/15	4.70	20.18	169.38	6.52	17.59	7.73	136.83	1.68	72.11	346.77	–
09/08/19	5.26	5.45	112.53	8.33	10.46	5.90	108.15	2.63	44.53	211.73	–
09/08/20	4.84	14.45	34.92	6.49	4.00	4.48	26.51	0.44	8.04	79.73	0.7
09/08/22	4.29	51.64	134.56	10.21	12.20	9.04	98.28	6.65	91.62	289.80	–
09/08/27	5.02	9.57	85.70	5.05	12.34	7.66	123.10	1.15	29.21	196.79	–
09/08/28	4.87	13.43	20.87	3.03	1.87	3.52	13.42	2.82	7.56	51.73	1.9
09/08/29	4.77	16.94	21.51	2.20	1.45	3.14	8.89	2.25	9.01	43.38	0.9
09/09/06	3.90	125.89	155.32	5.90	7.71	10.37	56.94	3.97	71.57	357.71	1.3
09/09/08	4.45	35.89	153.12	10.91	12.47	12.34	75.24	17.71	106.75	265.56	–
09/09/20	4.32	48.42	9.69	7.34	1.33	3.52	11.02	7.62	7.98	75.26	0.7
09/09/26	4.54	28.84	79.00	15.93	16.99	11.73	114.25	13.09	86.56	131.53	–
09/10/12	4.21	61.66	150.53	31.86	21.02	22.72	159.94	29.81	132.40	259.87	–
09/10/31	6.98	0.10	78.35	15.97	68.32	11.45	595.00	15.78	236.39	557.49	–
09/11/27	6.63	0.23	154.05	9.49	32.61	12.79	609.84	20.48	242.00	501.92	5.4
09/12/01	6.46	0.35	–	27.35	58.49	14.31	932.90	10.46	228.29	641.42	–
09/12/08	6.07	0.85	–	34.44	117.23	29.10	782.87	31.98	223.93	533.04	–
09/12/09	6.02	0.95	–	6.96	29.37	6.60	638.22	7.62	211.85	555.45	–
09/12/13	5.13	7.41	–	8.29	20.48	13.47	526.40	8.54	201.44	326.85	–
09/12/14	4.90	12.59	–	18.19	29.91	18.73	375.14	11.88	190.40	237.63	6.1
10/01/07	5.95	1.12	–	24.79	122.66	38.90	789.44	21.81	423.46	535.59	–
10/02/02	6.09	0.81	–	51.91	144.17	57.24	588.01	67.92	382.11	498.60	–
10/02/24	6.23	0.59	–	19.23	218.92	29.36	526.40	36.32	432.86	461.99	–
10/03/06	6.34	0.46	–	41.33	59.48	28.69	308.49	19.19	189.75	265.87	–
10/03/08	4.02	95.50	102.04	14.56	37.04	7.10	221.35	25.22	89.49	275.19	–
10/03/14	3.97	107.15	144.74	9.34	16.22	13.28	126.30	23.27	97.12	366.88	–
10/03/22	5.39	4.07	8.70	44.09	65.88	14.28	524.25	36.14	172.58	298.90	3.8
10/03/30	4.45	35.48	73.70	4.76	19.93	4.26	109.59	16.62	48.16	202.93	1.8
10/04/11	3.97	107.15	112.62	15.19	43.21	14.61	320.57	20.49	94.16	268.38	–
10/04/13	4.94	11.48	119.42	10.29	36.73	10.77	200.46	22.05	105.40	312.61	1.5
10/04/21	4.61	24.55	86.55	5.40	18.85	5.60	263.76	16.50	64.33	281.84	-0.4
10/04/25	4.63	23.44	135.67	72.51	102.73	14.28	447.64	82.37	175.93	536.16	–
10/05/04	5.10	7.94	116.78	9.66	22.86	5.10	159.72	19.32	35.45	256.91	–
10/05/07	4.16	69.18	203.31	38.72	63.72	12.61	393.05	41.22	128.19	494.53	–
10/05/13	4.20	63.10	130.00	15.66	17.92	8.10	98.10	31.13	61.83	286.62	2.0
10/05/17	4.36	43.65	187.44	98.89	64.80	39.49	423.98	110.49	122.99	668.14	-1.7
10/05/18	4.36	43.65	48.38	6.98	10.98	3.60	68.85	18.46	26.03	210.19	-2.1
10/05/28	4.07	85.11	135.29	12.34	3.12	31.31	35.43	39.54	49.16	255.32	2.5
10/05/31	3.99	102.33	142.09	6.66	19.62	10.27	198.37	29.76	109.79	467.87	3.2
10/06/06	4.17	67.61	75.59	1.29	2.96	2.76	24.98	15.48	30.24	191.58	2.6
10/06/21	5.31	4.90	96.75	15.82	41.21	19.45	489.92	24.17	210.58	392.67	–
10/07/03	5.74	1.82	103.17	5.24	12.06	3.43	126.30	12.31	43.20	159.72	2.1
10/07/04	5.44	3.63	43.47	7.61	3.27	1.59	54.23	13.96	21.66	61.42	2.0
10/07/08	5.09	8.13	71.81	0.97	8.52	0.93	13.49	13.10	15.49	83.62	1.6
10/07/10	4.39	40.74	50.27	0.50	1.42	1.09	16.63	13.21	27.33	77.37	2.9
10/07/13	4.37	42.66	78.23	0.34	2.66	0.93	29.16	13.14	30.74	140.70	2.9
10/07/15	4.28	52.48	99.39	3.34	1.58	2.59	24.98	14.62	27.91	155.06	-1.2
10/07/17	4.68	20.89	230.52	6.82	9.13	3.60	80.34	18.69	48.24	270.09	–

“–” means not determined, for there are not enough sample volume for sulfur isotope analysis.

(SS-SO₄²⁻) contributed only 0.66% of the total SO₄²⁻ in rain water of TGR. Most of SO₄²⁻ was no-sea-salt (NSS) contribution.

Ca²⁺ and NH₄⁺ are the major cations with VWM of 108.3 $\mu\text{eq/L}$ and 88.4 $\mu\text{eq/L}$. Sum of Ca²⁺ and NH₄⁺ account for 25%–94% of the total cations. Most of the VWM values are

lower than the mean values indicated that higher concentrations are associated with lower rainfalls. It was mainly due to the removal of particles through washout in the initial phases of precipitation (Hontoria et al., 2003). The VWM of major inorganic ions in rainwater at TGR together with those reported

Table 2

The concentrations of chemical species ($\mu\text{eq/L}$) of samples at TGR during 2009–2010.

Species	Number of samples	Range	Median	Mean	VWM
pH	58	3.90–6.98	4.8	4.9	4.8
H^+	58	0.10–30.84	17.0	30.8	27.3
NH_4^+	49	8.70–230.52	102.0	102.6	88.0
Na^+	58	0.34–98.89	8.0	14.4	8.9
K^+	58	0.93–57.24	7.69	11.28	6.64
Mg^{2+}	58	0.83–218.92	16.61	30.25	13.6
Ca^{2+}	58	8.89 to –932.90	126.3	225.13	108.34
Cl^-	58	0.10–110.49	13.59	18.2	11.12
NO_3^-	58	7.56–432.86	71.84	109.32	65.24
SO_4^{2-}	58	31.39–668.14	258.39	268.34	161.9
$\delta^{34}\text{S}$ (‰)	28	–2.1 to 6.1	2.1	2.1	–

in other selected areas around China are presented in Table 3. The data compared with those of other areas reveal that concentrations of both NO_3^- and SO_4^{2-} are higher than Maolan and Eastern Tien Shan (sites far away from cities, Han et al., 2010; Zhao et al., 2008), but lower than the big cities such as Shanghai and Beijing (Huang et al., 2008a; Xu and Han, 2009).

3.2. Temporal variation

The seasonal variation of pH of rainwater is depicted in Fig. 3. The pH showed no significant seasonal variations at spring, summer and autumn. The previous studies have found the pH value of rain water in winter and spring usually lower than in the other seasons due to the intensification of coal burning processes for heating purposes (Liu et al., 2006; Arsene et al., 2007), but the pH observed at TGR in winter was higher than the other seasons, which could possibly be explained by the more Ca^{2+} input in winter.

Fig. 4 clearly illustrated that the highest concentrations of all the ions occurred in winter, which is mainly because of the dry climate and scarce rainfall during this time. It can be seen from Fig. 4a that the temporal behavior of Ca^{2+} was similar to that of pH which is due to the fact that incorporation of dust particles into rain drops is accompanied by a strong increase in the dissolved Ca^{2+} content. Smaller amount of rainwater often result in higher concentration of chemical composition in rainwater (Fig. 4b). Because the removal of suspended particles by wet deposition is maximum and the possibility for photochemical formation of aerosol particles from their gaseous precursors is at a minimal (Whitby, 1978; Guo et al., 2012). Furthermore, high concentrations of Ca^{2+} were also associated with high concentrations of SO_4^{2-} and NO_3^- . These

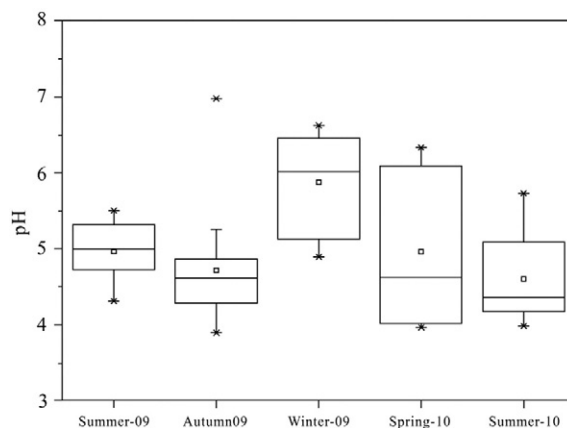


Fig. 3. Seasonal variability of the pH during June 2009 to July 2010: The lower boundary of the box indicates the 25th percentile, a line within the box marks the average value, and the upper boundary of the box indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles.

observations suggest that the terrestrial sources mainly influenced the ion composition and the acidity of precipitation is probably neutralized by Ca^{2+} , Mg^{2+} and NH_4^+ .

3.3. Origins of major ions in rainwater

In order to find possible association between ions in precipitation, and consequently, the likely sources of pollutants, correlation between ions in precipitation was calculated and presented in Table 4. A significant correlation was found between SO_4^{2-} and NO_3^- ($r = 0.71$) indicating their origin from similar sources. This was due to the similarity in their behavior in precipitation and result of the emissions of their precursors SO_2 and NO_x (Kaya and Tuncel, 1997; Mphepya et al., 2004). The alkaline ions Ca^{2+} and Mg^{2+} correlated well ($r = 0.74$) suggesting their origin from similar sources, because of their common occurrence of these ions form crustal origin. Analogously, a good correlation is seen between Na^+ and Cl^- ($r = 0.89$), due to the common sea salts source. Other relatively good correlations were observed between Ca^{2+} and NO_3^- , Ca^{2+} and SO_4^{2-} , Mg^{2+} and SO_4^{2-} , Mg^{2+} and NO_3^- (Table 4). Most of these well-correlated pairs have common sources or occur in precipitation as a result of atmospheric chemical reactions, such as reaction of the acids H_2SO_4 and HNO_3 with alkaline compounds rich in Ca^{2+} and Mg^{2+} carried into the atmosphere by wind-blown dust. This shows that wind carried dust and soil

Table 3

Comparison of the major ions concentration and pH at TGR with other sites in China ($\mu\text{eq}\cdot\text{L}^{-1}$).

Sites	Sampling time	pH	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	References
TGR	2009–2010	4.85	11.82	63.2	177.2	90.6	7.5	11.7	142.6	18.3	This study
Maolan	2007–2008	5.1	9.5	2.9	39.2	56.8	6.9	6.0	14.8	2.6	Han et al. (2010)
Eastern Tien Shan	2003–2004	–	16.0	31.7	107	23.2	8.2	16.3	432.2	56.1	Zhao et al. (2008)
Yichang	2001	4.99	38.6	52.1	201.3	188.33	–	–	154.3	–	Du et al.(2003)
Chengdu	2008	5.1	8.9	156.2	212.8	150.5	6.6	1.4	196.6	16.2	Wang and Han (2011)
Beijing	2008	5.1	104.0	109.0	315.8	185.6	17.7	25.0	607.2	40.4	Xu and Han (2009)
Shanghai	2005	5.1	89.6	77.9	274.7	136.4	29.8	68.4	243.7	41.5	Huang et al. (2008a)
Shenzhen	2004–2005	4.48	62.6	63.6	83.7	48.2	9.1	35.7	112.5	11.3	Huang et al. (2008b)

All of the data were volume-weighted mean (VWM) values.

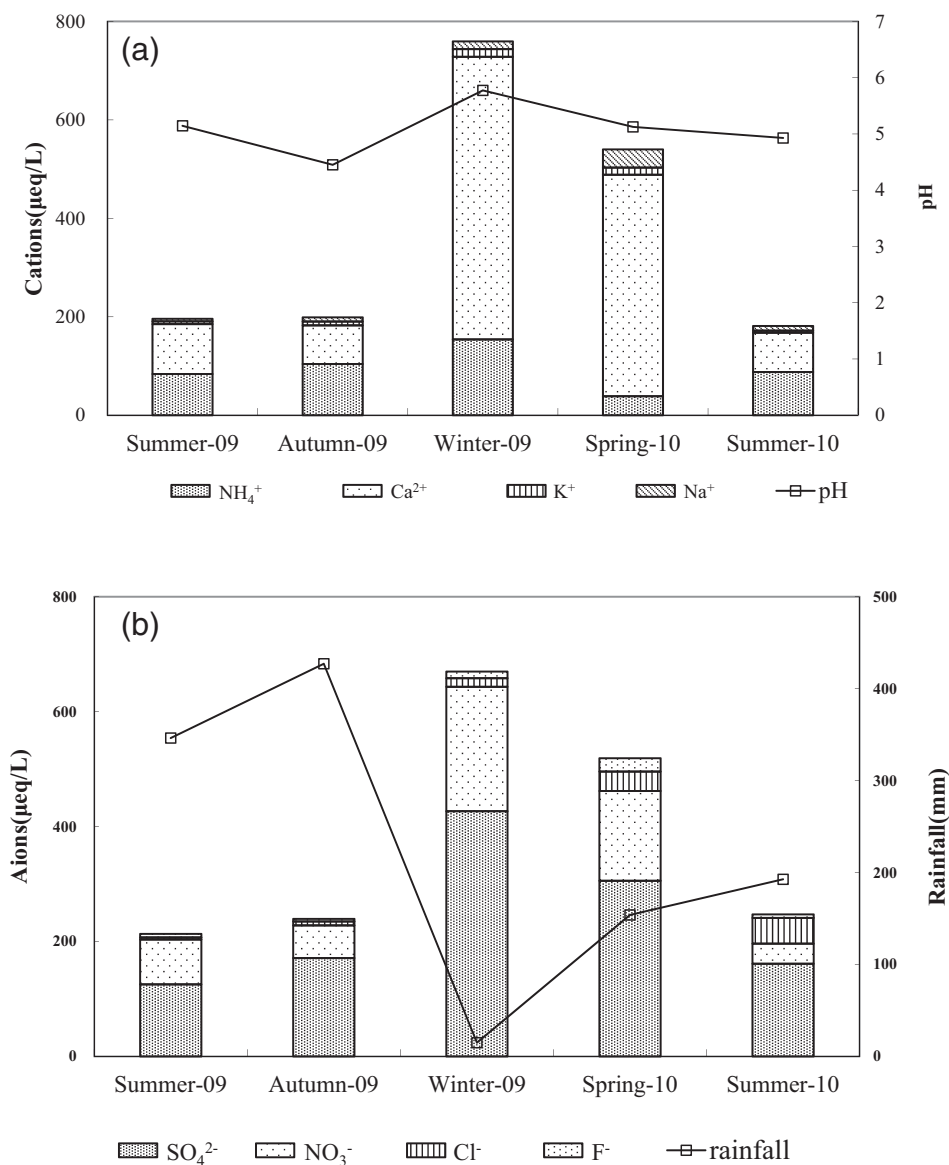


Fig. 4. Seasonal variations of ionic concentration at TGR.

Table 4
Correlation coefficients (*r*) of ionic concentrations in rainwater samples from TGR.

	NH ₄ ⁺	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
NH ₄ ⁺	1							
Na ⁺	0.30*	1						
Mg ²⁺	0.27	0.60**	1					
K ⁺	0.44**	0.70**	0.74**	1				
Ca ²⁺	0.2	0.53**	0.74**	0.62**	1			
Cl ⁻	0.36*	0.89**	0.57**	0.67**	0.40**	1		
NO ₃ ⁻	0.50**	0.44**	0.83**	0.72**	0.83**	0.38**	1	
SO ₄ ²⁻	0.61**	0.64**	0.67**	0.63**	0.84**	0.62**	0.71**	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 5
Proportions (in %) of the NSS contribution in the rainwater samples at TGR. Seawater X/Na data come from Berner and Berner (1987) and crust X/Ca data from Taylor (1964).

Ion	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	K ⁺	Ca ²⁺	Mg ²⁺
Rainwater (µeq·L ⁻¹)	11.12	65.24	161.9	6.64	106.8	13.6
SS (%)	92.9%	0.0%	0.7%	2.9%	0.4%	14.9%
NSS	CF (%)	3.0%	0.3%	1.2%	97.1%	99.6%
(%)	AF (%)	4.1%	99.7%	98.1%	0.0218	0.0439
Seawater X/Na		1.16	0.0002	0.121		
Crust X/Ca		0.0031	0.0021	0.0188	-	-

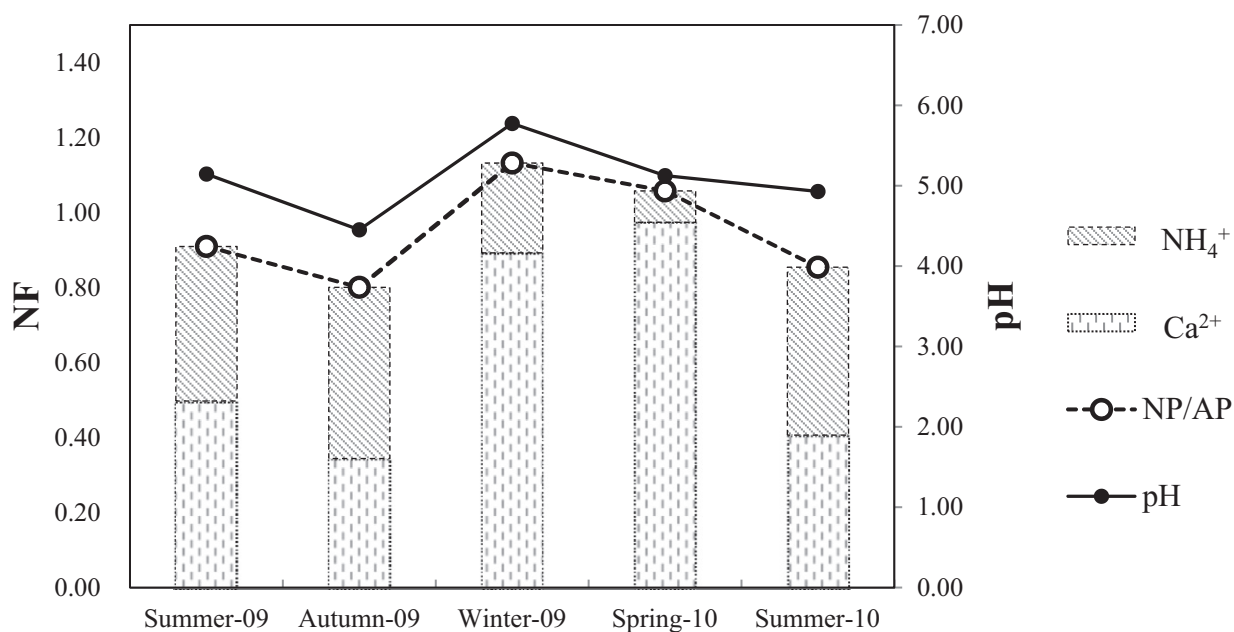


Fig. 5. Seasonal variations of neutralization factors (NFs) at TGR.

plays an important role in neutralizing acidic gas (Khemani et al., 1985). There are good correlations between SO_4^{2-} and NH_4^+ ($r = 0.61$), NO_3^- and NH_4^+ ($r = 0.50$), suggesting that NH_4^+ also play an important role in neutralizing acidic sulfur gas. The significant correlation of K^+ and Cl^- , K^+ and NO_3^- , and K^+ and SO_4^{2-} indicates that biomass combustion may be an important source (Jalali and Kolahchi, 2008).

Except for anthropogenic sources, the ions in precipitation are mainly derived from sea spray and terrestrial dust by wind erosion (Zhang et al., 2007). To further estimate marine, crust and anthropogenic contributions to different ionic species in rainwater, the sources of ionic components in rainwater were calculated by means of

$$\text{SSF} (\%) = 100 \left(\frac{X/\text{Na}^+}{\text{seawater}} \right) / \left(\frac{X/\text{Na}^+}{\text{rainwater}} \right) \quad (1)$$

$$\text{CF} (\%) = 100 \left(\frac{X/\text{Na}^+}{\text{crust}} \right) / \left(\frac{X/\text{Na}^+}{\text{rainwater}} \right) \quad (2)$$

$$\text{AF} (\%) = 100 - \text{SSF} - \text{CF} \quad (3)$$

where SSF, CF and AF refer to sea salt fraction, crust fraction and anthropogenic fraction, respectively. And X is the ion of interest. The elemental ratios (X/Na) were determined according to the composition of seawater given by Berner and Berner

(1987) and X/Ca^{2+} of crust is the ratio from crustal composition (Taylor, 1964). For it is difficult to distinguish which parts of K^+ , Mg^{2+} and Ca^{2+} stemmed from crust sources or anthropogenic sources (i.e. sources such as agriculture, biomass burning, atmospheric dust), we merged these two sources into non-sea-salt. The results, expressed in percentage, are given in Table 5. It can be seen that most of Cl^- (92.9%) come from sea salt, and Ca^{2+} , Mg^{2+} and K^+ mainly are from non-sea-salt. More than 98% of SO_4^{2-} and 99% of NO_3^- come from non-sea-salt input, which could derive from various pollution sources including coal combustion, automobile exhaust fumes.

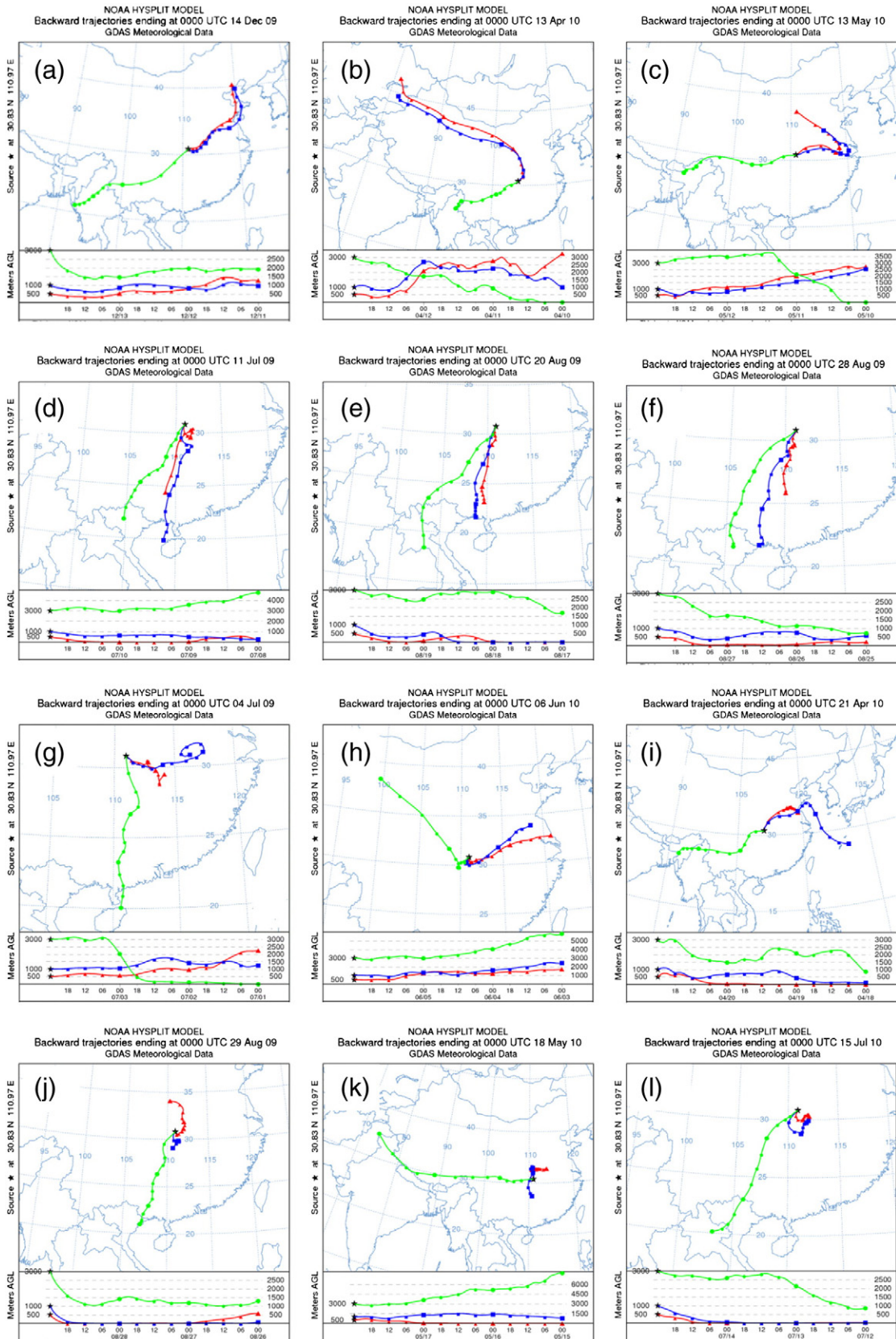
3.4. Acid neutralization

The protons from sulfuric and nitric acids are taken up by bases such as NH_3 and various anions (oxides, carbonates or bicarbonates, etc.) of base cations like Ca^{2+} , Mg^{2+} , K^+ , etc. Neutralization of the acids by these base cations was validated by calculating the neutralization factors (NFs) using the following equation (Zhang et al., 2007; Wang and Han, 2011):

$$\text{NF}_X = [X] / [\text{NO}_3^- + \text{SO}_4^{2-}] \quad (4)$$

where X is the component of interest (NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , etc.), with all the ions expressed in $\mu\text{eq/L}$. The NF values of NH_4^+ ,

Fig. 6. Air-mass back trajectories observed during 2009 and 2010 for the selected four sectors: Cluster 1: Air mass from North China (a, b, c); Cluster 2: Air mass from South China (d, e, f); Cluster 3: Air mass from East China (g, h, i); and Cluster 4: Air mass from local regions/Central China (j, k, l). Red triangles = trajectories arriving at an altitude of 500 m; blue squares = of 1000 m, green circles = of 3000 m.



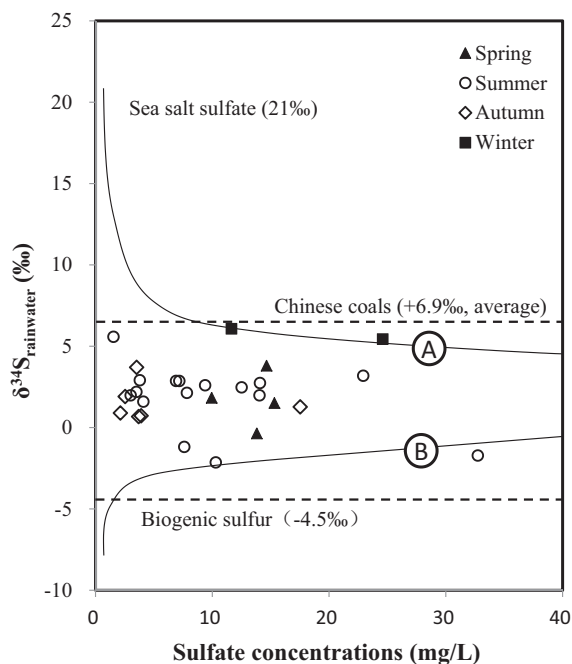


Fig. 7. The $\delta^{34}\text{S}$ values vs. sulfate concentrations in rainwater at the Three Gorges Reservoir: Curve A: Mixing between anthropogenic sulfate with a $\delta^{34}\text{S}$ value of about 3‰ and sea salt sulfate with a $\delta^{34}\text{S}$ value of about 21‰ (Ohizumi et al., 1997; Lim et al., 2014); Curve B: Mixing between pollutant sulfate with a $\delta^{34}\text{S}$ value of about 0‰ and biogenic sulfur with a $\delta^{34}\text{S}$ value of about -4.5% (Panettiere et al., 2000).

Ca^{2+} , Mg^{2+} , K^{+} in the rainwater at TGR are 0.39, 0.48, 0.06, 0.03, respectively. The results indicate that NH_4^{+} and Ca^{2+} are the dominant neutralization substances in the rainwater, whereas the neutralization by Mg^{2+} and K^{+} is negligible. The seasonal variation of NF (Ca^{2+} and NH_4^{+}) was presented at Fig. 5. The higher NF was observed at the dry season (winter and spring), which indicated that the rainwater was more neutralized at this season. From Fig. 5, it can be seen that NF of Ca^{2+} accounts for a larger percentage at cold seasons (winter and spring) than NF of NH_4^{+} . While, the NF of Ca^{2+} and NH_4^{+} were equally important for neutralization at warmer season (summer and autumn). The enrichment of Ca^{2+} in the rainwater samples in winter and spring is mainly due to the less precipitation during these dry seasons, while the enrichment of NH_4^{+} in summer and autumn is consistent with increased agriculture activity in these seasons and more efficient ammonia emissions at higher temperature. To assess the balance between acidity and alkalinity, the ratio of neutralizing potential (NP) to acidifying potential (AP) was calculated (Cao et al., 2009) as below:

$$\text{NP/AP} = \left([\text{Ca}^{2+}] + [\text{NH}_4^{+}] \right) / \left([\text{NO}_3^{-}] + [2\text{SO}_4^{2-}] \right). \quad (5)$$

It can be seen that the $(\text{NF}_{\text{Ca}^{2+}} + \text{NF}_{\text{NH}_4^{+}})$ was equivalent to NP/AP (Fig. 5). The values of NP/AP which were greater than 1 (winter and spring) indicated that alkaline constituents neutralize the acidity, which explained the higher pH in winter at TGR.

3.5. Sulfur isotopes

The $\delta^{34}\text{S}$ values of the rainwater samples at TGR range between -2.1% and 6.1% ($n = 28$), and the mean value is 2.1% . The isotopic composition is different from most of sulfur isotope values observed at the other place in China (Mukai et al., 2001). Precipitation at TGR displayed significantly lower $\delta^{34}\text{S}$ values than precipitation from northern cities such as Xi'an ($+8.71\%$ to $+19.05\%$, $n = 30$; Bai and Wang, 2014), Beijing ($+6.78\%$), Haerbin ($+5.39\%$), Urumchi ($+7.68\%$; Hong et al., 1994), and southern megalopolis such as regions of the Pear River Delta (1.9% to $+10.3\%$; Zhang et al., 2002). It showed a comparable range of variation with several southern cities such as Liuzhou (-4.8% to $+3.1\%$) and Hengyang (-4.7% to 3.9% ; Zhang et al., 2002), contributions to whom were mainly from anthropogenic sources and biogenic emission. The $\delta^{34}\text{S}$ values of different sulfur sources generally show completely different range depending on the nature of the sources. For example, the $\delta^{34}\text{S}$ average of sea spray sources is around 21% (McArdle and Liss, 1995) while most of the biogenic emissions are lighter (-10% to -2%) (Liu et al., 1996; Panettiere et al., 2000; Xiao et al., 2011; Zhang et al., 2010), -21.9% to 12.1% from H_2S of land and seawater, 4.7% from volcano gas (Newman et al., 1991). The $\delta^{34}\text{S}$ values of anthropogenic SO_4^{2-} showed a wide range of variation depend on the sources (Harris et al., 2012; Hong et al., 1992; Lim et al., 2014; Nielsen, 1974; Xiao et al., 2014). The $\delta^{34}\text{S}$ values of the rainwater samples at TGR display no significant seasonal variations at spring, summer and autumn, and peak in winter. It may be mainly due to the higher sulfur dioxide emissions from anthropogenic sources and less contribution of biogenic sulfur (Xiao and Liu, 2002; Han et al., 2010; Xiao et al., 2014).

3.6. Source identification by backward trajectories

All samples are evaluated using backward trajectories to better understand sources of rainwater at TGR. When higher than 2000 m AGL in the free troposphere, SO_2 concentration is very low (Wang et al., 2008). According to the 500 m and 1000 m AGL backward trajectories, the air mass in the rainy days at TGR can be divided into 4 clusters (Fig. 6). Air masses in Cluster 1 were from North China (Fig. 6a–c), with an average value of $+3.3\%$ (range from 1.5% to 6.1% , $n = 11$). Precipitation in this cluster display the highest $\delta^{34}\text{S}$ values, which were consist with the previous that north Chinese coal characterized with $+6.9\%$ as the median of sulfur isotope ratio (Ohizumi et al., 1997; Mukai et al., 2001), indicating a considerable contribution of coal combustion in North China to the sulfur compounds in the atmosphere at TGR. These samples depleted in ^{34}S , which could be mainly due to the homogeneous oxidation during the transmission of SO_2 from North China to Central China. Because most of these samples was collected in summer when homogeneous oxidation was dominant rather than heterogeneous oxidation (Mukai et al., 2001; Zhang et al., 2010). Air masses in Cluster 2 were from South China (Fig. 6d–f), with an average of $+2.2\%$ (range from 0.7% to 3.7% , $n = 5$). The cluster of air mass was mainly from Guangxi, Guangdong, and Hunan province, which has a lower sulfur isotope value, at about -4.8% to 10.3% (Zhang et al.,

2002). Air masses in Cluster 3 were from East China (Fig. 6g–i), with the average of +1.7‰ (range from –0.4‰ to 2.9‰, $n = 5$). This cluster of air mass was mainly from Zhejiang, Shanghai, and Jiangsu and displayed $\delta^{34}\text{S}$ of SO_2 varying from 1.0‰ to 7.5‰ (Zhang et al., 2010). Air mass in Cluster 4 was mainly from local regions/Central China (Fig. 6j–l), for the backward trajectories of these samples were confined to 200 km around the sampling site. All sulfur isotopic compositions in precipitation samples from local sources depleted in ^{34}S , ranging from –2.1‰ to 0.9‰, with an average of –1.0‰ ($n = 4$). Scarcely any previous researches studied on sulfur isotopic ratios in Hubei coal, but the reports show that the coal of Hubei Province is mainly from northern Provinces such as Shanxi, Henan, etc. (Jia, 2006), where the coal enriches in ^{34}S . So it is not possible emission for combusting coal with low sulfur isotope such as Guiyang (Mukai et al., 2001). The negative values of sulfur isotope in precipitation usually reflect a contribution from biogenic sulfur that contain lighter isotope (Nakai and Jensen, 1967; Nielsen, 1974; Nriagu et al., 1987). The atmosphere at TGR probably contains a high proportion of gaseous S from biological source, due to extensively distribution of water and rich in paddy field, e.g. Three Gorges Reservoir, Honghu Lake, Longganhu Lake and Liangzihu Lake.

These observations indicated a major anthropogenic origin of SO_4^{2-} in the precipitation at TGR. The minor source is from biological activity. Plots of $\delta^{34}\text{S}$ vs SO_4^{2-} for precipitation could usually yield further insight into atmospheric sulfur sources (Panettiere et al., 2000; Xiao et al., 2011). The plots in TGR produce patterns such as those shown in Fig. 7, where minor sources are only evident at lower concentrations (Newman et al., 1991). More negative $\delta^{34}\text{S}$ values were observed in precipitation during summer than the other seasons, which is likely caused by higher contribution of biogenic sulfur (Zhang et al., 2002; Xiao et al., 2011). Large area of water, wetland and paddy field around the sampling site, could be the possible sources of biogenic sulfur. The $\delta^{34}\text{S}$ values in rainwater and sea spray are sufficiently distinct to be able to conclude that seawater contributions are negligible. The dominant anthropogenic source of rainwater sulfate appears to have a nearly constant $\delta^{34}\text{S}$ value between 0‰ and +4‰ which is within the range of –5.2‰ to +19.0‰ (average, +6.9‰) observed in Chinese coals (Hong et al., 1992; Ohizumi et al., 1997). Biogenic sulfur was mainly produced by microbial sulfate reduction in waters (sea and oceans, lakes, rivers, and swamps). During dissimilatory SO_4^{2-} reduction by strict anaerobes, copious dissolved sulfide species are produced in either anoxic waters or sediments, releasing in forms of H_2S , DMS, COS, CS_2 , etc., and they have lower sulfur isotopes compare with the original matters (Newman et al., 1991). Previous studies indicate that because of the special ecological system of water and land alternation in wetland, its sulfur release quantity is one or several orders of magnitude larger than that of terrestrial soil (Li et al., 2005). Fig. 7 illuminated most of the lower and negative samples occurred in summer. After the impoundment of the TGR, water area increased and much soil of both sides was flooded, forming 1084 km^2 of artificial lakes. The highest water level was 175 m in winter, while the lowest water level was 145 m in the summer. During this period it formed a maximum height difference of 30 m of the water-level-fluctuating zone wetland, with an area of 300 km^2 . The increase of water area and the water-level-fluctuating zone wetland

area owing to the impoundment may be a reason for significant light sulfur isotopes in summer precipitation.

4. Conclusions

One year study on rainwater chemistry and sulfur isotope was performed at the Three Gorges Reservoir. The pH values varied from 3.90 to 6.98 for all the rainwater samples, with a VWM value of 4.9. SO_4^{2-} was the most abundant ionic species, followed by Ca^{2+} , NH_4^+ , NO_3^- , Mg^{2+} , Na^+ , Cl^- and K^+ in sequence.

Seasonal variation analysis showed that the pH value in winter was higher than in the other seasons. And the cause is the frequent rains between spring and summer washed off the airborne particulate, which is important to acidity of precipitation. Analysis of the ions sources suggested that Na^+ and Cl^- come from sea salt, while Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , SO_4^{2-} are mainly non-sea-salt origin.

The sulfur isotopic values during the survey period ranged from –2.1‰ to 6.1‰. The backward trajectory analysis showed that the air masses originated from northern China usually showed high $\delta^{34}\text{S}$ values, and those from local could be affected more by the biomass emissions. Most sulfur isotopic values at TGR showed the evidence of anthropogenic input, however, the lower $\delta^{34}\text{S}$ values of rainwater in summer likely due to influence of biogenic sulfur owing to the impoundment of Three Gorges Reservoir, or the lakes and paddy field around the sampling site. There are scarcely available researches about sulfur sources in central China (especially around TGR) and the isotopic composition of biogenic emissions is difficult to establish. Thus, more researches are needed to better understand the acidification of rainwater in these area.

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