

# Chemical and sulfur isotopic composition of precipitation in Beijing, China

Guangxu Zhu<sup>1,2</sup> · Qingjun Guo<sup>1</sup> · Tongbin Chen<sup>1</sup> · Yunchao Lang<sup>2</sup> · Marc Peters<sup>1</sup> · Liyan Tian<sup>1</sup> · Hanzhi Zhang<sup>1</sup> · Chunyu Wang<sup>1</sup>

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**Abstract** China is experiencing serious acid rain contamination, with Beijing among the worst-hit areas. To understand the chemical feature and the origin of inorganic ions in precipitation of Beijing, 128 precipitation samples were collected and analyzed for major water-soluble ions and  $\delta^{34}\text{S}$ . The pH values ranged from 3.68 to 7.81 and showed a volume weighted average value (VWA) of 5.02, with a frequency of acid rain of 26.8 %. The VWA value of electrical conductivity (EC) was 68.6  $\mu\text{S}/\text{cm}$ , which was nearly 4 times higher than the background value of northern China.  $\text{Ca}^{2+}$  represented the main cation;  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were the dominant anion in precipitation. Our study showed that  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  originated from coal and fossil fuel combustion;  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  were from the continental sources. The  $\delta^{34}\text{S}$  value of  $\text{SO}_4^{2-}$  in precipitation ranged from +2.1 to +12.8‰ with an average value of +4.7‰. The  $\delta^{34}\text{S}$  value showed a winter maximum and a summer minimum tendency, which was mainly associated with temperature-dependent isotope equilibrium fractionation as well as combustion of coal with relatively positive  $\delta^{34}\text{S}$  values in winter. Moreover, the  $\delta^{34}\text{S}$  values revealed that atmospheric sulfur in Beijing are mainly correlated to coal

burning and traffic emission; coal combustion constituted a significant fraction of the  $\text{SO}_4^{2-}$  in winter precipitation.

**Keywords** Chemical composition · Sources · Sulfur isotope · Precipitation · Beijing

## Introduction

Acid rain is known to result in serious environmental damage in sensitive environments (Bytnerowicz et al. 2005). Hence, in recent years, more attention was paid to acid rain, which became a major issue in the field of environmental science of the 21st century (Likens et al. 1996; Evans et al. 2005). China is one of the three regions in the world with the highest occurrence of acid rain, next to Europe and North America (Zhang et al. 2010b). Widespread acid rain was observed in southern and southwestern China before the 1990s (Zhao et al. 1988; Wang and Wang 1995), and more recently, it has extended to eastern and central China (Huang et al. 2008; Xie et al. 2009; Tang et al. 2010). Beijing is located out of the traditional regions impacted by acid rain in China. However, Beijing has experienced rapid urbanization and motorization in the past three decades. Previous studies pointed out that Beijing has suffered from acid rain pollution in the recent past (Tang et al. 2005; Xu et al. 2012).

The chemical compositions of rainwater play an important role in scavenging soluble components from the atmosphere and helps to understand the actual status and level of acid rain (Hu et al. 2003). Moreover, investigations on the precipitation chemistry could provide a deeper insight into the changes and other characteristics of local or regional atmospheric pollution (Calvo et al. 2010). The origin of acid rain can be determined through the studies of chemical composition in rainwater, also combined with the meteorological information (Seto and Hara

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✉ Guangxu Zhu  
zhuguangxu@mail.gyig.ac.cn

✉ Qingjun Guo  
guoqj@igsnr.ac.cn

<sup>1</sup> Center for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

<sup>2</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

2006). Monitoring the amount, distribution and the chemical composition of precipitation are essential in environmental studies.

The atmosphere contains a variety of sulfur species derived from a number of potential sulfur sources. The latter can be separated into natural and anthropogenic sources. Natural sources include volcanic eruptions, the release of H<sub>2</sub>S by biological reduction in ocean anoxic environments and wetlands, marine salt, terrigenous biogenic volatile sulfide, and seaweed dimethylsulfide. Anthropogenic sources are represented by fossil fuel and coal combustion, smelting of metal sulfides, as well as sulfuric acid production (Canfield 2001; Mandeville et al. 2009). Sulfur from different sources shows distinct sulfur isotopic compositions depending on the isotope value of each source material (Lang et al. 2011). Therefore, the sulfur isotope ratio of SO<sub>2</sub> and sulfate in the atmosphere must be influenced by various isotopic source values. Sulfur isotopes have been widely used in the field of environmental geochemistry to trace the sources and fate of sulfur (e.g., Xiao and Liu 2002; Pruet et al. 2004; Ding et al. 2013; Yang et al. 2015). The sulfur isotopic signatures of rainwater sulfate may be used to delineate anthropogenic sulfur in the atmosphere, provided the isotopic composition of pollutant sulfur is distinct from that of sulfur from natural sources. Identification of atmospheric sulfur sources in rainwater has been conducted mainly in the acid rain regions through sulfur isotope analysis (Herut et al. 1995; Mast et al. 2001; Xiao et al. 2011a, b, 2014; Bai and Wang 2014). However, systematic observations on the chemical composition of precipitation combined with analysis of the  $\delta^{34}\text{S}$  values have not been carried out in Beijing.

For the present study, we analyzed the chemical and sulfur isotopic composition of 128 precipitation samples collected continuously from September 2010 to October 2013 in the Beijing urban area. The objectives of this study are to (1) describe the pollution level and the chemical characteristics of precipitation in Beijing; (2) present and discuss the chemical composition and sulfur isotopic characteristics of rainwater; and (3) identify the sources of the chemical compounds in rainwater by analyzing the precipitation chemistry and  $\delta^{34}\text{S}$  values of dissolved sulfide. The data can be used for future strategies to reduce atmospheric pollution and to prevent further generation of acid rain in Beijing.

## Sampling and analytical methods

### Study area

Beijing is located in the north of China at 39.4° N–41.6° N and 115.7° E–117.4° E and comprises around 16411 km<sup>2</sup>. The city lies near the western slopes of the Yanshan Mountains, about

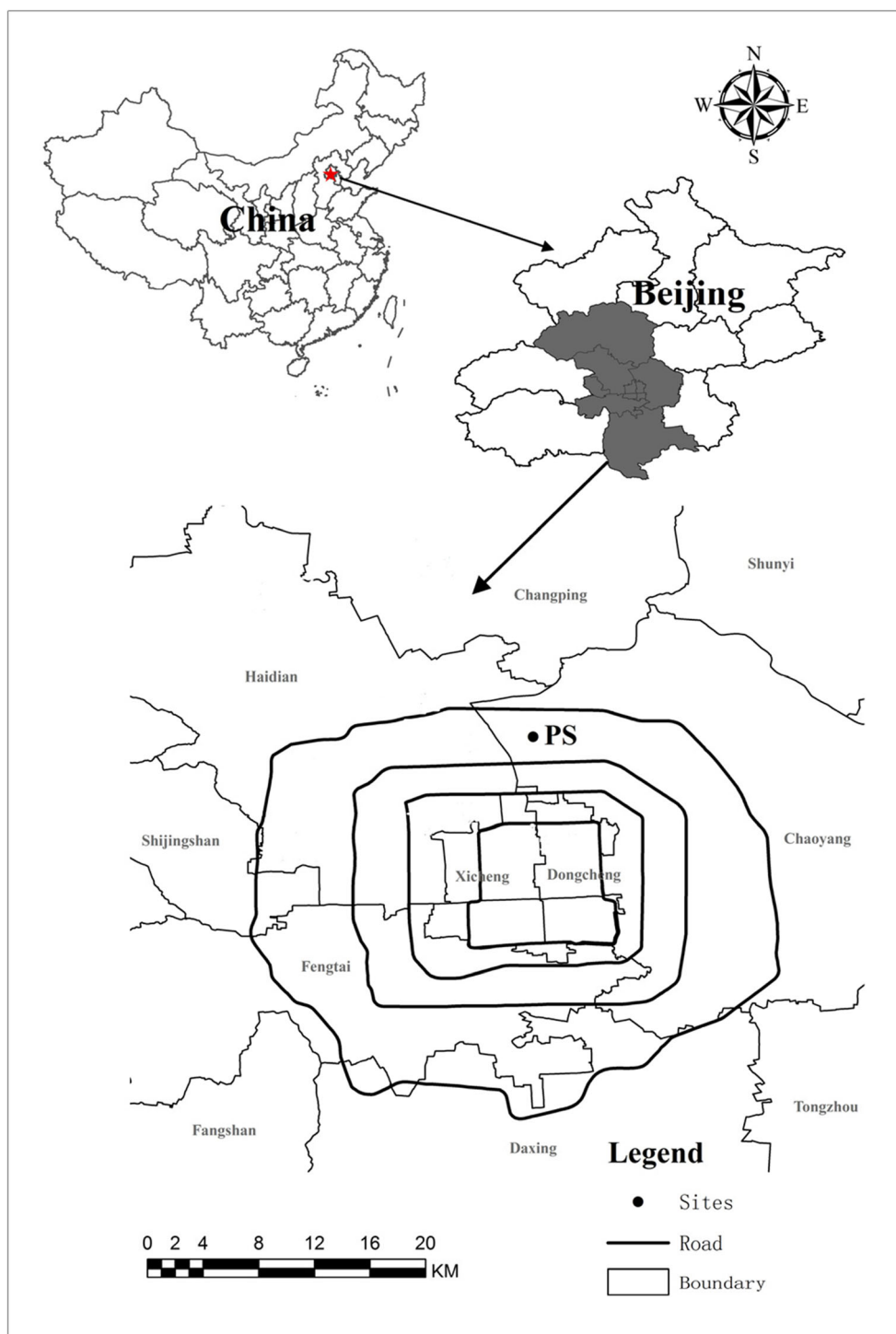
150 km to the west of the Bohai Sea at an altitude between 20 and 60 m above sea level. Beijing is in a zone with a semi-humid continental monsoon climate with hot and humid summers and cold and dry winters. The mean annual temperature is 12.8 °C. The average annual precipitation is 548 mm. About 80 % of the precipitation occurs between June and September (Statistical Yearbook of Beijing 2013).

### Sampling and chemical analysis

The sampling site was located on a building roof of the Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (Fig. 1), which is adjacent to the Beijing Olympic Forest Park, between the 4th and 5th ring road in the northwest of Beijing (40°07.3" N, 116°22'45.1" E). Rain from precipitation events were sampled with 50 L polyethylene buckets (30 cm diameter and 50 cm height) that were fixed at approximately 1.5 m above the roof. In most cases, samples were collected from the beginning to the end of the precipitation events. Before sampling, the buckets were cleaned with 2 N hydrochloric acid solution and rinsed with Milli-Q water. To minimize the influence of dry deposition, the buckets were deployed for sampling immediately prior to precipitation events and recovered soon after each event. The amount of precipitation and the duration of the event were recorded. In total 128, samples were collected in the time from September 2010 to October 2013 (no precipitation after October 22th 2013). These samples represent about 85 % of the total precipitation events that occurred in the Beijing area during the study period. Nineteen samples did not provide enough material for sulfur isotope analyses.

Immediately after arrival at the laboratory, pH and electrical conductivity (EC) of the water samples were measured using a multi parameter pH meter (SX731, Sanxin). The water samples were subsequently filtrated through 0.45  $\mu\text{m}$  pore size membrane acetate filters. A subsample of each water sample (15 mL) was cooled at 4 °C for the determination of major anions and cations. Major anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>) were quantitatively determined by ion chromatography (ICS-900, Dionex). The detection limits of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> ions were found to be 0.01, 0.01, 0.01, and 0.02 mg/L, respectively. Reproducibility of results was better than 5 % for all major anions. Inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, PerkinElmer) was used to measure major cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>). The detection limits of K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> ions were found to be 0.004, 0.002, 0.010, and 0.003 mg/L, respectively. Reproducibility of results was better than 5 % for all major cations. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures, and the blanks were all below the detection limit of the measure species. The analytical precision of the data are

**Fig. 1** Map showing the sampling sites in Beijing. *PS* precipitation sample site



better than  $\pm 5\%$ . Analyses of major ions were conducted within 2 weeks after sampling.

The remaining subsamples were acidified by ultra-pure hydrochloric acid ( $\text{pH} < 2$ ) and treated with 10% barium chloride ( $\text{BaCl}_2$ ) solution in order to precipitate the dissolved sulfate as  $\text{BaSO}_4$ . After precipitation, the samples were heated up to 70–80 °C for 2 h and filtered through 0.45  $\mu\text{m}$  membrane acetate

filters. The precipitates ( $\text{BaSO}_4$ ) on the filters were rinsed with Milli-Q water and oven-dried at 40 to 50 °C.

Approximately 250  $\mu\text{g}$  of  $\text{BaSO}_4$  precipitate was used for the determination of  $\delta^{34}\text{S}$ , using elemental analyzer-continuous flow-isotope ratio mass spectrometry (EA-CF-IRMS) at the Institute of Geology and Paleontology, University of Münster, Germany. The analytical results are

expressed in the usual  $\delta$  notation in per mil, relative to the Canyon Diablo Troilite (CDT) standard. The standard deviation of the isotopic measurements was  $\pm 0.3\text{‰}$ .

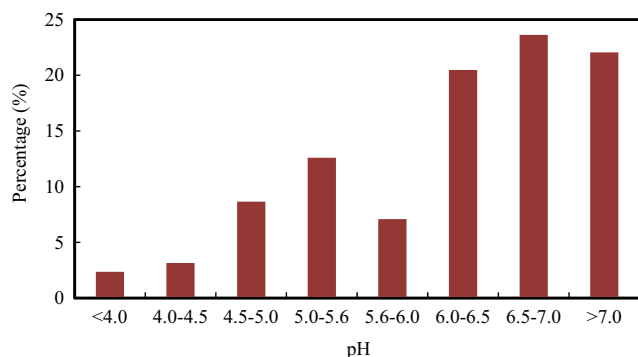
Statistical analyses were performed with SPSS 22.0 (Statistical Package for the Social Science) and EXCEL software.

## Results and discussion

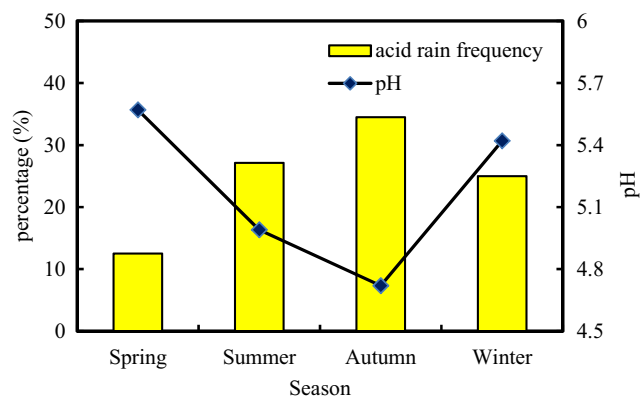
### pH and EC distribution

Seventy of the 128 precipitation samples were collected in summer (June to August), which exhibits 54.7 % of the annual precipitation, whereas autumn, spring, and winter occupied 28, 16, and 14 rainwater samples, respectively. The pH value of the 128 precipitation samples varied from 3.68 to 7.81 with an arithmetic average of 6.21 and a volume weighted average (VWA) value of 5.02. 26.8 % of the total rainwater samples can be classified as acid rain ( $\text{pH} < 5.6$ ). Specifically, the annual fraction of acid rain was 29 %, 11 %, and 38 % in the year 2011, 2012 and 2013, respectively, indicating an apparent yearly variation of acid rain pollution. Approximately 80 % of the acid rain was only slightly acidic ( $4.5 \leq \text{pH} < 5.6$ ). Moreover, more than 44 % of the sampled precipitation showed intermediate pH values between 6.0 and 7.0 (Fig. 2).

A seasonal variation in the volume weighted average pH values and in the acid rain fraction could be observed. The pH values during autumn and summer were lower than in spring and winter (Fig. 3); hence, the fraction of acidic precipitation was also higher in autumn and summer compared to winter and spring. This is comparable to the results from other regions in North China (Shen et al. 2012; Zhang et al. 2012) but reverse to data from Hangzhou (Xu et al. 2011) and Anhui (Huang et al. 2012) in the south of China. The acidity of the precipitation depends on the concentrations of acid-forming ions and of alkaline species neutralizing the acidity (Zhang et al. 2007). In northern China, storm events occur with high frequency from December to April, which transport crustal



**Fig. 2** Frequency distribution of pH in precipitations from Beijing

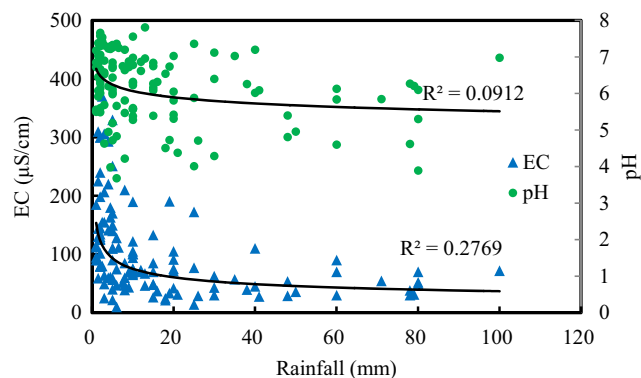


**Fig. 3** Seasonal variations of average pH values and acidification frequency of precipitations

dust particles into the atmosphere. These particles persist in the air for a long time and can accumulate to a relatively large amount (Han et al. 2005). During the rainfall events, the large amount of alkaline particles could neutralize the acid-forming ions. In the rainy season, alkaline species were scavenged by frequent precipitation, resulting in poor neutralization and more acid rain in summer and autumn.

Electric conductivity of precipitation is a good indicator for the amount of total soluble ionic components in the atmosphere and the anthropogenic impact (Arsene et al. 2007). The electric conductivity (EC) of the precipitation samples varied from 10.1 to 370.2  $\mu\text{S}/\text{cm}$  with a VWA value of 68.6  $\mu\text{S}/\text{cm}$ , which is significantly higher than the average EC value of 14.8  $\mu\text{S}/\text{cm}$  for rainwater samples from the Waliguan Mountain located at the eastern tip of Qinghai-Tibetan plateau, World Meteorological Organization (WMO). This location represents the background monitoring site for the chemical composition of precipitation in northern China (Tang et al. 2000). The relatively high EC values of the sampled precipitation reflect a rather high degree of atmospheric pollution in Beijing.

An inverse relationship between the amount of precipitation and EC values could be observed (Fig. 4); higher EC values correlate with little amounts of precipitation ( $< 10$  mm). During the initial stages of the rainfall event,



**Fig. 4** The relationship of pH and electrical conductivity with rainfall

rainwater absorbed the atmospheric pollutants rapidly, resulting in high EC. After that the ion concentrations of the precipitation decreased due to dilution and the EC consequently, showed an obvious descending trend. However, no correlation between pH and the amount of rain could be seen.

**Ion concentrations in precipitation**

The concentrations of major ions in the precipitation samples are given in Table 1. The average concentration of ionic species in precipitation decreased in the following order:  $SO_4^{2-} > Ca^{2+} > NO_3^- > Cl^- > F^- > Mg^{2+} > Na^+ > K^+ > H^+$  (VWA). The average concentrations of  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ , and  $F^-$  were 279, 147.6, 121.9, and 63.1  $\mu eq/L$  with maximum of 4299.4, 1951.3, 1018.3, and 271.5  $\mu eq/L$ , respectively.  $SO_4^{2-}$  represents the predominant anion accounting for 45.6 % of the total anion load, due to the fact that coal represents the major energy source in China and the contribution of coal burning to atmospheric sulfur oxide is significant (Aas et al. 2007; Li and Leung 2012). The second most abundant anion was  $NO_3^-$ , and sum of  $SO_4^{2-}$  and  $NO_3^-$  account for 44.2–98.3 % of the total anions. The average  $SO_4^{2-}/NO_3^-$  ratio was 1.89, suggesting that acid rain pollution in Beijing is still sulfur type with a trend to sulfuric-nitrous mixed type, which can be ascribed to reduced  $SO_2$  emissions and the expansion of industrial activities as well as the rapid increase of the number of motor vehicles in the past years. The average  $SO_4^{2-}/NO_3^-$  ratio between the seasons followed the order: winter (5.22) > spring (2.53) > autumn (1.84) > summer (1.72). These can be ascribed to a significantly increased degree of coal combustion in the cold season compared to the warm season.

$Ca^{2+}$  is the most abundant cation with a VWA concentration of 182.3  $\mu eq/L$  and a maximum value of 3997.5  $\mu eq/L$ , followed in decreasing order by  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ , and  $H^+$ . Most of the VWA values are lower than the arithmetic average (AA) values indicating that higher concentrations of ions are usually associated with low precipitation. It was mainly due to the removal of particles through washout in the initial phases of precipitation (Hontoria et al. 2003). The concentration data

showed relatively high standard deviations, indicating a large variability in the cation and anion concentrations in the precipitation events.

**Source identification of major ions in precipitation**

In order to identify the association among ions and get a quick overview of the possible source identification of major ions in precipitation, correlation coefficients (*R*) between ions in the rainwater were calculated. Data for concentrations of ions were not normally distributed and therefore analyzed after logarithmic transformation. As shown from the inspection of these values (Table 2), significant correlations existed between  $Ca^{2+}$  and  $Mg^{2+}$  ( $R=0.933$ ),  $Ca^{2+}$  and  $K^+$  ( $R=0.825$ ), as well as  $Mg^{2+}$  and  $K^+$  ( $R=0.801$ ), suggesting their origin from similar sources, because of their common occurrence of these ions from a crustal origin. The good correlation between  $SO_4^{2-}$  and  $NO_3^-$  ( $R=0.640$ ) might be attributable to their similar chemical behavior in precipitation and the co-emission of their precursor compounds ( $SO_2$  and  $NO_x$ ) from the combustion of fossil fuel and industrial activities.  $H^+$  showed no correlation with any other anions and had significant negative correlation with base cations. These correlations indicate that acidic anions are neutralized by base cations. The correlation of  $SO_4^{2-}$  with  $Ca^{2+}$ ,  $K^+$ , and  $Mg^{2+}$  ( $R=0.829$ , 0.816, and 0.832, respectively), as well as of  $NO_3^-$  with  $Ca^{2+}$  and  $K^+$  and  $Mg^{2+}$  ( $R=0.592$ , 0.591, and 0.598, respectively) supported this suggestion. Moreover, this indicates that acid pollutants might be absorbed on the surface of particulate matter and react with cations. Positive correlations are obtained between  $Cl^-$  and other ions;  $F^-$  correlated only poorly with other ions, except with  $NO_3^-$ .

Except for anthropogenic emissions, the chemical composition of rainwater is mainly affected by sea salts, crustal dust from wind erosion, provided that contributions from volcanic and other natural sources are negligible (Négrelet et al. 2007). To further derive these fractions, Na and Ca were taken as reference element for seawater and continental crust, respectively (Cao et al. 2009). The sea salt fraction (SSF), crust

**Table 1** Concentrations ( $\mu eq/L$ ) of major ions in precipitation from Beijing

Ions	Samples	Maximum	Minimum	VWA	AA	Standard deviation
$SO_4^{2-}$	128	4299.4	46.4	279	546.3	619.2
$NO_3^-$	128	1951.3	21.4	147.6	218.4	262.9
$Cl^-$	119	1018.3	8.9	121.9	155.2	206.5
$F^-$	115	271.5	26.5	63.1	95.8	55.6
$Ca^{2+}$	128	3997.5	14.1	182.2	489.5	655.3
$Mg^{2+}$	128	539	4.3	34.3	75.0	87
$K^+$	128	239.6	0.66	13.2	28.8	36.1
$Na^+$	128	935.6	0.97	26.3	74.9	151.1
$H^+$	128	208.9	0.02	10.8	8.0	26.4

VWA volume weighted average; AA arithmetic average



**Table 2** Matrix of correlation coefficients among major ions and conductivity in precipitation

Ions	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	F <sup>-</sup>
SO <sub>4</sub> <sup>2-</sup>	1								
NO <sub>3</sub> <sup>-</sup>	0.640 <sup>a</sup>	1							
H <sup>+</sup>	-0.218 <sup>b</sup>	-0.209 <sup>b</sup>	1						
Ca <sup>2+</sup>	0.829 <sup>a</sup>	0.592 <sup>a</sup>	-0.324 <sup>a</sup>	1					
K <sup>+</sup>	0.816 <sup>a</sup>	0.591 <sup>a</sup>	-0.350 <sup>a</sup>	0.825 <sup>a</sup>	1				
Mg <sup>2+</sup>	0.832 <sup>a</sup>	0.598 <sup>a</sup>	-0.379 <sup>a</sup>	0.933 <sup>a</sup>	0.801 <sup>a</sup>	1			
Na <sup>+</sup>	0.809 <sup>a</sup>	0.473 <sup>a</sup>	-0.219 <sup>a</sup>	0.778 <sup>a</sup>	0.817 <sup>a</sup>	0.766 <sup>a</sup>	1		
Cl <sup>-</sup>	0.431 <sup>a</sup>	0.290 <sup>a</sup>	0.070	0.294 <sup>a</sup>	0.348 <sup>a</sup>	0.322 <sup>a</sup>	0.349 <sup>a</sup>	1	
F <sup>-</sup>	0.108	0.535 <sup>a</sup>	-0.248	0.138	0.094	0.082	0.194	0.211 <sup>b</sup>	1

<sup>a</sup> Correlation is significant at the 0.01 level (2-tailed)

<sup>b</sup> Correlation is significant at the 0.05 level (2-tailed)

fraction (CF), and anthropogenic fraction (AF) were calculated using the following equations:

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

$$\%CF = 100(X/Ca^{2+})_{\text{crust}} / (X/Ca^{2+})_{\text{rainwater}} \quad (2)$$

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

where  $X$  is the ion of interest. The elemental ratios ( $X/Na^+$ ) were determined according to the composition of seawater given by Berner and Berner (1987),  $X/Ca^{2+}$  of the crust is the ratio from crustal composition (Taylor 1964). Since it is difficult to distinguish which parts of  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  stem from crustal or anthropogenic sources (Wu and Han 2015), we merged these two sources into a non-sea-salt source.

The contributions from different sources to the chemical composition of rainwater are shown in Table 3. It is revealed that nearly half of  $Cl^-$  and small amounts of  $Mg^{2+}$  (20.7 %) were of marine origin. In addition, the proportion of  $Cl^-$  coming from anthropogenic sources is about 48.4 %. The

**Table 3** Source contributions for different ionic constituents in rainwater

Ions	Sea salt fraction (%)	Terrestrial fraction	
		Crust fraction (%)	Anthropogenic fraction (%)
SO <sub>4</sub> <sup>2-</sup>	2.3	1.2	96.5
NO <sub>3</sub> <sup>-</sup>	–	0.6	99.4
Cl <sup>-</sup>	50.2	1.4	48.4
Ca <sup>2+</sup>	0.8	99.2	
Mg <sup>2+</sup>	20.7	79.3	
K <sup>+</sup>	6.5	93.5	

anthropogenic input of  $Cl^-$  could come from various pollution sources including automobile exhaust, coal combustion, and fertilizers (Négre and Roy 1998). The majority of  $SO_4^{2-}$ ,  $Ca^{2+}$ , and  $K^+$  appears to be of non-marine origin. Previous study revealed that  $Ca^{2+}$  in Beijing rainwater is mainly derived from the dissolution of  $CaCO_3$  from soil dust transported either from local areas or from desert and loess areas in northern China (Xu and Han 2009). Our data exhibit that the primary source of  $K^+$  is terrestrial;  $K^+$  can be also emitted by biomass burning (Khare et al. 2004).

Considering no nitrate from a marine source, the contributions from anthropogenic sources were obtained by subtracting the soil contribution from that of total nitrate in rainwater. About 99.4 % of  $NO_3^-$  in Beijing Precipitation was attributed to an anthropogenic source, which is mainly represented by the combustion of fossil fuel. Rainwater  $SO_4^{2-}$  was characterized by only a small contribution from a crustal source, about 96.5 % of total  $SO_4^{2-}$  was derived by the anthropogenic sources. Aas et al. (2007) suggested that coal combustion accounts for about 70 % of the commercial energy production in China, leading to a large amount of  $SO_2$  emissions, which to date represent the most important reason for acid rain in China. Besides, with the rapid increase of vehicles,  $SO_2$  from traffic is playing a more important role. To further identify the source of atmospheric sulfur, the sulfur isotopic composition of dissolved sulfate from Beijing precipitation was analyzed.

### Sulfur isotope composition of sulfate in precipitations

The  $\delta^{34}S$  values of dissolved sulfate in the analyzed precipitation samples ranged from +2.1 to +12.8‰ with an average value for the study period of  $+4.7 \pm 1.8$ ‰. The maximum value was shown by a rainwater sample from a precipitation event on October 18<sup>th</sup> 2010. The minimum value was revealed by a sample taken on May 8<sup>th</sup> 2011. Compared with the

previous report on  $\delta^{34}\text{S}$  values of  $\text{SO}_4^{2-}$  in the precipitation from other cities, the average  $\delta^{34}\text{S}$  value of Beijing precipitation was higher than that of precipitation from Guiyang ( $-2.8\text{‰}$ ; Xiao et al. 2011a), Zigui ( $+2.1\text{‰}$ ; Wu and Han 2015), Nanchang ( $+2.1\text{‰}$ ; Xiao et al. 2011b), and Seoul ( $+3.7\text{‰}$ ; Lim et al. 2014). The  $\delta^{34}\text{S}$  value of sulfate in precipitation in Xi'an was reported in the range of  $+8.71$  to  $+19.05\text{‰}$  with a mean value of  $+13.41 \pm 2.35\text{‰}$  (Bai and Wang 2014), which was significantly higher than the sulfur isotope value in this study.

Figure 5 shows the  $\delta^{34}\text{S}$  variation with time for the precipitation in the study area. A prominent “U”-shaped variation pattern for the  $\delta^{34}\text{S}$  signatures with time can be observed. The maximum average  $\delta^{34}\text{S}$  value of  $+7.9\text{‰}$  was derived from precipitation in January; the minimum value of  $+3.4\text{‰}$  originated from precipitation in August. The  $\delta^{34}\text{S}$  values range from  $+3.4$  to  $+4.1\text{‰}$  from April to September and were relatively stable with a range from  $+7.6$  to  $+7.9\text{‰}$  in winter. In March, October, and November, the  $\delta^{34}\text{S}$  values were  $+6.7$ ,  $+5.8$ , and  $+6.2\text{‰}$ , respectively. This indicates that the relative contribution of different sulfur sources to the atmosphere in this area varies with season.

There is no large scale of reducing environment in Beijing and its surroundings. Furthermore, the geographical feature in the study area is obviously different from that in South China with a rather humid climate, which is appropriate for intense rice farming. The contribution of biogenetic to atmosphere sulfate in the Beijing area should be insignificant. On the other hand, there is no active volcanism releasing volcanic sulfur into the atmosphere of the study area. Consequently, atmospheric sulfur in Beijing is mainly associated with anthropogenic source.

In China, coal is used as the main energy source and its combustion produces a large amount of  $\text{SO}_2$  released into the atmosphere (Li and Leung 2012). Previous studies (e.g., Mukai et al. 2001; Xiao and Liu 2002; Zhang et al. 2010a) have suggested that coal burning gives a significant contribution to rainwater sulfate in most Chinese cities. The  $\delta^{34}\text{S}$  values of Chinese coals exhibit a very wide range ( $-15$  to  $+50\text{‰}$ ).

In contrast to coals from southern China, the sulfur isotopic composition of the coals from northern China is rather positive (Xiao and Liu 2011). The central heating period in Beijing is from November 15th to March 15th characterized by intense coal combustion. In this study, the  $\delta^{34}\text{S}$  values around winter are close to that of the coal from northern China ( $+7.9\text{‰}$  in average, Maruyama et al. 2000). These observations support coal as the major source of  $\text{SO}_4^{2-}$  in the precipitation of Beijing in this season.

Since the year 2000 the Beijing government has carried out numerous measures in order to control the emissions of coal combustion with the result that  $\text{SO}_2$  emissions of coal-fired power plants decreased rapidly. However, in the meantime urban traffic increased significantly up to 5.32 million registered cars in Beijing by the end of 2014. Therefore, the emissions of  $\text{SO}_2$  and sulfate particles emitted from vehicles represent another important source of  $\text{SO}_4^{2-}$  in rainwater next to coal combustion (Liu et al. 2008). Norman et al. (2006) reported that sulfate from vehicle exhaust shows the  $\delta^{34}\text{S}$  values of around  $+5\text{‰}$ . Therefore, it can be deduced that dissolved sulfate in Beijing precipitation is contributed by a mixture of sulfate from coal burning and vehicle exhaust.

We assume that the rates of sulfur supply from local anthropogenic sources are constant throughout a year, thus, the  $\delta^{34}\text{S}$  values in rainwater do not vary significantly. However, in the present study, the  $\delta^{34}\text{S}$  values in October were higher than that in summer by  $+1.7$  to  $+2.4\text{‰}$ . Caron et al. (1986) and Alewell et al. (2000) pointed out that sulfur isotope fractionation may be expected in the processes of heterogeneous and homogeneous oxidation of  $\text{SO}_2$  caused by temperature change, which results in a seasonal variation of  $2\text{--}3\text{‰}$ . With decreasing temperature, heterogeneous oxidation is accompanied by a large equilibrium fractionation, resulting in the accumulation of isotopically heavier sulfur. Thus, the sulfur isotope values of sulfate from precipitation in winter are higher than in summer. Accordingly, the isotopic variations with time are interpreted to result from isotopic fractionation during equilibrium reactions. This was shown in a previous study for aerosol in Beijing air (Guo et al. 2014).

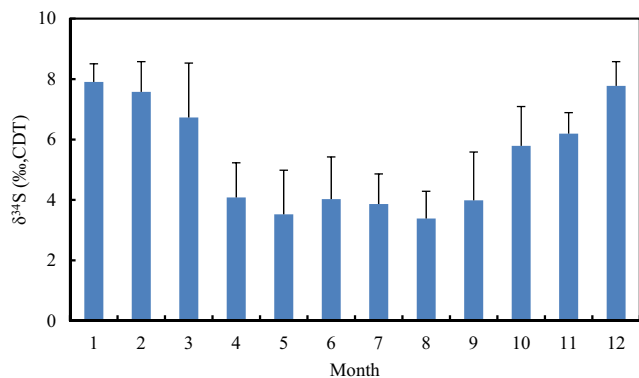


Fig. 5 Monthly variations of  $\delta^{34}\text{S}$  in precipitations from Beijing

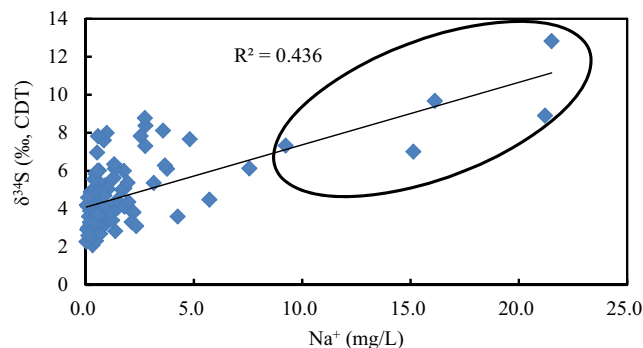


Fig. 6  $\delta^{34}\text{S}$ – $\text{Na}^+$  plot of the precipitation samples

Seawater releases sulfate into the atmosphere by sea spray detached from the ocean surface. The isotopic composition of S in modern marine sulfate is relatively constant within narrow limits and with a  $\delta^{34}\text{S}$  value of about +20.1‰ (Wadleigh et al. 1996; Pichlmayer et al. 1998). Generally, sea spray contributes only to a negligible amount of sulfate to the total sulfate pool in inland rainwater (Herut et al. 1995), while in coastal areas, sea spray is the main source of sulfate in precipitation (Wadleigh et al. 1994). Xiao and Liu (2002) observed in Guiyang, a city in southwest China, that negative  $\delta^{34}\text{S}$  values in rainwater from light rainfalls were associated with local sulfur sources while sulfur in rainwater from heavy rainfalls showed positive  $\delta^{34}\text{S}$  values, which indicated a rather maritime origin. Beijing is located about 150 km west of the Bohai Sea. Hence, sea spray may represent one of the sources of sulfate in the precipitation of Beijing.

Na has been used as a reference element for sea salt, the  $\delta^{34}\text{S}\text{--Na}^+$  plot can be used to identify whether rainwater is affected by sea salt (Samara et al. 1992). Figure 6 shows the relationship between the  $\text{Na}^+$  concentrations and the  $\delta^{34}\text{S}$  values of dissolved sulfate in Beijing precipitation. The plot shows a positive relationship between the  $\text{Na}^+$  concentration and the  $\delta^{34}\text{S}$  values, especially for the samples with relatively high  $\text{Na}^+$  concentrations, suggesting an impact of sea spray on Beijing precipitation.

## Conclusions

- (1) The volume weighted average pH value of precipitation from Beijing was 5.02; 26.8 % of the total precipitation can be classified as acid rain (pH <5.6); precipitation in autumn and summer displayed lower pH values and a higher fraction of acidic precipitation compared to those in winter and spring.
- (2) The volume weighted average value of EC in precipitation was 68.6  $\mu\text{S}/\text{cm}$ , which was  $\sim 4$  times higher than the background value in northern China.  $\text{Ca}^{2+}$  was the predominant cation, and  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were the most abundant anions. The average  $[\text{SO}_4^{2-}]/[\text{NO}_3^-]$  ratio is 1.89, with the maximum value in winter.  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  originated from anthropogenic sources, such as fossil fuel and coal combustion,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  were derived from crustal sources.
- (3) The average  $\delta^{34}\text{S}$  values of  $\text{SO}_4^{2-}$  dissolved in Beijing precipitation was +4.7‰ (+2.1 to +12.8‰). There is an obvious seasonal variation apparent in the  $\delta^{34}\text{S}$  signatures with higher values in winter and lower values in summer, which are mainly ascribed to isotopic fractionation of equilibrium reaction and intensive coal combustion in winter. Analysis of the  $\delta^{34}\text{S}$  values confirm that sulfur in Beijing precipitation is strongly influenced by coal and fossil fuel burning; sea spray also contributed considerably to Beijing rainwater during several precipitation events.

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