J Atmos Chem (2013) 70:269–281
DOI 10.1007/s10874-013-9268-3

Chemical composition and source apportionment of rainwater at Guiyang, SW China

Hong-Wei Xiao · Hua-Yun Xiao · Ai-Min Long · Yan-Li Wang · Cong-Qiang Liu

Received: 9 October 2012 / Accepted: 28 August 2013 /
Published online: 10 September 2013

Abstract This study systematically analyzed the concentrations of cations and anions and determined the pH in the rainwater at Guiyang from Oct. 2008 to Sep. 2009. The pH in the rainwater varied between 3.35 and 9.99 with a volume-weighted mean value of 4.23. The volume-weighted mean concentrations of anions followed the order SO_4^{2-}>Cl^->F^->NO_3^-, whereas the volume-weighted mean concentrations of cations followed the order Ca^{2+}>NH_4^+>Na^+>Mg^{2+}>K^+. This finding indicates that SO_4^{2-} was the main anion and that Ca^{2+} and NH_4^+ were the main cations. Significant correlations between each pair of ions (SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, and Mg^{2+}) were observed, suggesting that $CaSO_4$, $Ca(NO_3)_2$, $MgSO_4$, $Mg(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$, and/or NH_4HSO_4 exist in the atmosphere at Guiyang. The soil-derived species (such as Ca^{2+}) played an important role in the neutralization of the acidity in rainwater. The SO_4^{2-} and NO_3^- in the rainwater were mainly from anthropogenic sources, and their contributions accounted for 98.1 % and 94.7 %, respectively. NH_4^+ was also most likely derived from anthropogenic sources, such as domestic and commercial sewage, and played an important role in the neutralization of the rainwater at Guiyang.

Keywords Rainwater · Chemical composition · Anthropogenic source · Source contribution

1 Introduction

In the last three decades, China has been the third-largest acid rain area (after Europe and North America) due to the rapid development of the economy and the increasing demand for energy (Wang and Xu 2009). The chemical composition of rainwater has been widely

H.-W. Xiao (✉) · A.-M. Long
State Key Laboratory of Tropical Oceanography, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
e-mail: xiaohw@scsio.ac.cn

H.-Y. Xiao (✉) · C.-Q. Liu
State Key Laboratory of Environment Geochemistry, Institute of Geochemistry, Chinese Academy of Science, Guiyang 550002, China
e-mail: xiaohuayun@vip.skleg.cn

Y.-L. Wang
Chinese Research Academy of Environmental Sciences, Beijing 100012, China

investigated in many areas in China since the 1980s (Yu et al. 1998; Wang and Xu 2009). Acid rain is primarily caused by the precursors of strong acids, such as H_2SO_4 and HNO_3, which originate from fossil fuel combustion. According to statistical reports published by the State Environmental Protection Administration of China (2010), in 2009, acid rain was found in the highly developed regions in the eastern, southern, and central regions of China, which account for approximately 30 % of Chinese area (Fig. 1). In Guiyang City, Chengdu City, and Chongqing City (SW China), severe acid rainwater was observed prior to 2009 (Zhao et al. 1988; Wang 1994; Wang and Han 2011).

Rainwater plays an important role in the removal of atmospheric pollutants, including atmospheric particles and atmospheric gases, through two scavenging processes: rainout and washout. The rainwater matters originate from both the long-range transport of chemical species by clouds and the local scavenging of atmospheric aerosols or gases during the rain events (Gonçalves et al. 2002; Xiao et al. 2010a). The chemical compositions of rainwater can help us distinguish the major sources of anions and cations and understand the local and regional dispersion of pollutants and their potential impacts on ecosystems. For instance, the ammonium in rainwater has been reported primarily from the fertilizers used in agriculture, biomass burning, livestock breeding and stool, and natural activities (Migliavacca et al. 2005; Xiao et al. 2012a, b). Previous studies on the rainwater chemistry in some Chinese areas have revealed that the rainwater compositions are highly influenced by fossil fuel combustion, natural soil, and sewage (Lei et al. 1997; Wu et al. 2012; Xiao et al. 2012a). In Guiyang acid rain was found for a long time. Although the Guiyang government has taken some powerful measures to reduce the emissions of SO_2 from coal combustion and other pollutants, the pH value of rainwater was found low in some recent rainfall events (Fig. 2; Xiao et al. 2010a; Han et al. 2011). However, up to date, few systematic studies on the rainwater chemistry were carried out in Guiyang. And although the ammonium concentration has increased significantly because of human activities, some of these studies ignored the effect of ammonium on the acidity in rainwater (Xiao et al. 2012a, b).

In this study, we systematically analyzed the chemical compositions in rainwater in Guiyang City based on a large number of continuous rainwater samples (1,235 samples) collected from Oct. 1, 2008 to Sep. 30, 2009. This study provides useful information for the identification of potential sources of the pollutants in rainwater and for the evaluation of the air quality in Guiyang city.

2 Materials and methods

2.1 Description of the study area

Guiyang City, which is the capital of Guizhou Province, is located in Southwest China. It is surrounded by mountains (Fig. 1) and has a subtropical monsoon climate with an annual average temperature of 15.3 °C. The annual precipitation is 1,174 mm, and the annual average relative humidity (RH) is approximately 77 % (Xiao et al. 2012a). The mean concentrations of SO_2 and NO_2 in atmosphere were 0.064 mg/m^3 and 0.023 mg/m^3 in 2008 and 0.058 mg/m^3 and 0.026 mg/m^3 in 2009, respectively (Xiao et al. 2012b, c).

2.2 Sampling and chemical analysis

Two large aluminum sheets (7.14 m^2, each projected area was 2.1 m×1.7 m) were used to collect enough rain samples for chemical analysis even during light rain events (e.g. ~0.1 mm).

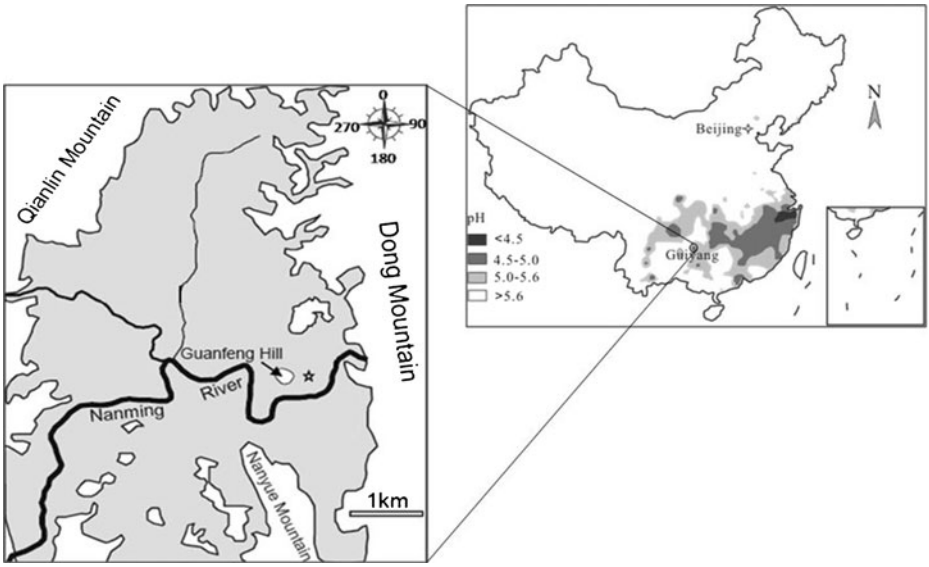

Fig. 1 Map showing sampling location in Guiyang and the distribution of rainwater acidity during 2009 in China (according to State Environmental Protection Administration of China)

The aluminum sheets were used as a sampler because these are easily washed and dried during two rain events. The aluminum sheets were fixed 1.5 m above the roof of a 5-m-high building through an aluminum-alloy bracket. Prior to use, the aluminum sheets were cleaned with Milli-Q water and dried. Between two rain events, the aluminum sheets were covered with a clean large polyethylene sheet to avoid being polluted by dry deposition. When it began to rain, the polyethylene sheet was removed, and the rainwater was collected from the aluminum sheet into 1.5-L pure plastic bottles, which were acid-cleaned prior to use. A total of 1,235 rainwater samples were collected from Oct. 1, 2008 to Sep. 30, 2009.

Immediately after sampling, the pH, electrical conductivity (EC), and temperature (T) of the samples were measured. These samples were passed through 0.45-μm acetate membrane

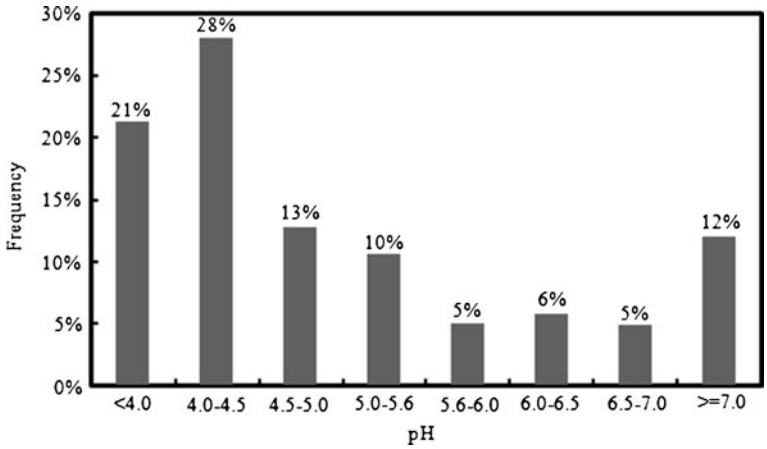

Fig. 2 The frequency distribution of pH value of rainwater in Guiyang

filters and maintained in a refrigerator at 4 °C. The major anions (Cl^-, F^-, SO_4^{2-}, and NO_3^-) were measured through ionic chromatography (DionexICS-90). The major cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were determined by ICP-OES. The NH_4^+ concentrations were determined by spectrophotometry after treatment with Nessler's reagent. The detection limits of all of these ions were found to be 0.1 mg/L, and the reproducibility was better than 2 % for the measurement of the major anions, 3 % for the measurement of the major cations, and 4 % for the NH_4^+ measurements.

2.3 Backward trajectories

Backward trajectories were estimated based on the movement path of air masses to analyze the sources and transmission path of air masses of the precipitation. In this study, the simulation was conducted using the TrajStat software (http://www.arl.noaa.gov/HYSPLIT.php) with GDAS data provided by the National Oceanic and Atmospheric Administration (NOAA ARL). For each precipitation event, a 3-day (72 h) air mass backward trajectory arriving at Guiyang at a height of 500 m above ground level was investigated with time ending at 0 a.m..

3 Results and discussion

3.1 Variation in the pH value

Table 1 shows the statistical results of the major ion concentrations, the pH, and the volume-weighted mean (VWM) of the pH and the concentrations of major ion in the rainwater at Guiyang. The pH of the rainwater samples ranged from 3.35 to 9.99, with a VWM value of 4.23. The frequency distribution of the pH of the 1,235 rainwater samples is shown in Fig. 2. Approximately 21 % of the rainwater samples exhibited pH values less than 4.00, and 72 % of the rainwater samples less than 5.60. The acidity of the rainwater samples are likely due to the presence of H_2SO_4, HNO_3, perhaps HCl from nature and anthropogenic emissions, and/or weak organic acids, which reflect the significant impact of anthropogenic activities (Dikaiaka et al. 1990; Wang and Han 2011). Due to the additional input of alkaline species (e.g., $CaCO_3$) mainly derived from the weathering of carbonate (Han et al. 2011), some rainwater samples showed higher pH values in rainwater (>6.0). In general, the higher pH values in rainwater were found in the initial stage of a rain event, and the pH values then decreased rapidly (Xiao et al. 2010a). This is because alkaline species, which are mainly derived from soils, were found in coarse particles (U.S. Environmental Protection Agency 1982) that are easily captured by rain droplets at the beginning of a rain event. Acid species, such as sulfate and nitrate ions, however, are mainly observed as fine particles (U.S. Environmental Protection Agency 1982), which are relatively difficult to be washed out by rain droplets. Because less alkaline species were captured by rainwater in the latter, the pH values decreased. These reasons may cause different pH between rain events.

The VWM pH value at Guiyang was quite close to those in southern and other southwest Chinese cities such as Guangzhou, Changsha and Shenzhen (Table 2), but much lower than those in northern Chinese cities such as Beijing and Xi'an (Niu et al. 2008; Sun and Yuan 2008; Cao et al. 2009; Lu et al. 2011; Yang et al. 2012). The VWM pH value at Guiyang was similar to those in Tokyo, Seoul and Adirondack, but much lower than those in Tirupati and Montseny (Avila and Alarcón 1999; Lee et al. 2000; Ito et al. 2002; Mouli et al. 2005; Okuda et al. 2005).

Table 1 Volume-weighted mean (VWM) concentrations of major ion (μeq/L) and pH (unit) along with statistical results in 1235 rainwater samples in Guiyang

Component	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^+	NH_4^+
VWM	4.23	14.54	20.72	7.31	265.63	182.90	9.61	10.50	13.90	112.79
Mean	5.08	18.66	15.18	10.17	368.03	249.67	8.83	15.71	14.95	146.41
Median	4.52	9.45	8.26	6.47	161.74	129.36	2.80	L.D.	10.48	66.75
S.D.	1.40	28.01	15.58	9.47	682.92	292.72	11.81	28.55	10.35	163.03
Min	3.35	L.D.	L.D.	L.D.	14.72	L.D.	L.D.	L.D.	7.05	L.D.
Max	9.99	213.11	267.21	276.20	8636.48	1378.15	387.08	528.34	172.40	1986.69

VWM volume-weighted mean; *S.D.* standard deviation; *Min* minimum; *Max* maximum

L.D. lower than detection limits

3.2 Major ionic compositions in rainwater

As listed in Table 1, the total cation concentrations (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+) were larger than the total anion concentrations (F^-, Cl^-, NO_3^-, and SO_4^{2-}). The depletion of anion was possibly because we did not measure some inorganic anionic species, such as PO_4^{3-} and NO_2^- (Mello 2001), and some organic anionic species, such as formic, acetic, and oxalic acids (Mouli et al. 2005; Xu et al. 2010) which may be important anion species. Niu et al. (2010) reported that organic anionic species accounted for more than 15.0 % of the total anions. Xu et al. (2010) found that the total concentration of formic, acetic, and oxalic acids was 34.54 μeq/L at Guiyang, with a maximum value of 139.43 μeq/L for formic acid between Apr. 2006 and Apr. 2007. In the Amazon basin, 5.7 μeq/L of monocarboxylate (mainly $HCOO^-$) ions in the rainy season and ~29.7 μeq/L in the dry season were observed by Andreae et al. (1988, 1990).

As listed in Table 1, the concentrations of anions followed the order $SO_4^{2-}>Cl^->F^->NO_3^-$ (VWM), whereas the concentrations of cations followed the order $Ca^{2+}>NH_4^+>Na^+>Mg^{2+}>K^+$ (VWM). SO_4^{2-} was the most abundant anion and accounted for 86.2 % of the total anions with a VWM concentration of 265.63 μeq/L (ranging from 14.72 to 8,636.48 μeq/L). This result may be because high-sulfur coal is the major fuel consumption at Guiyang (Xiao et al. 2012b). The second-most-abundant anion was Cl^-, which exhibited a VWM concentration of 20.72 μeq/L. However, NO_3^- only accounted for 2.8 % of the major anions, with a VWM concentration of 7.31 μeq/L. Xiao et al. (2012c) suggested that NO_3^- in the atmosphere at Guiyang was mainly derived from coal combustion rather than gasoline combustion. The VWM concentration of NO_3^- in this study was much lower than that reported by Han et al. (2011), possibly related to the sample number and the sampling time between the two studies. Ca^{2+} and NH_4^+ were the two most important cations in the rainwater at Guiyang, and accounted for 55.5 % and 34.2 % of the total cations, respectively. The VWM concentrations of Ca^{2+} and NH_4^+ in rainwater were 182.90 and 112.79 μeq/L, with maximum values of 1,378.15 and 1,986.69 μeq/L, respectively. As showed above, SO_4^{2-}, Ca^{2+}, and NH_4^+ were the most important ions in rainwater at Guiyang, although previous studies showed that NO_3^- is important in some Chinese sites (Zhang et al. 2007; Lu et al. 2011; Wang and Han 2011; Wu et al. 2012).

Compared with the monitoring data from 1982 to 1984 at Guiyang (Zhao et al. 1988), the SO_4^{2-} and NO_3^- concentrations decreased by nearly half and by two thirds, respectively, whereas the Ca^{2+} concentration changed little. The reduction of atmospheric pollutants, was related to the movement of fire power plants from urban areas to suburban areas and the prohibition of the use of coal-fired household stoves by the Guiyang city government. We also compared our data with those in other Chinese cities, as listed in Table 2 (Zhao et al. 1988; Niu

Table 2 Comparison of pH (unit) and major ions (μeq/L) at Guiyang with other sites in China and worldwide

Site	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^+	NH_4^+	References
Guiyang	4.23	14.5	20.7	7.3	265.6	182.9	9.6	10.5	13.9	112.8	This study
Guiyang	4.07	N.D.	8.2	21.0	411.0	231.2	26.4	56.5	10.1	78.9	Zhao et al. (1988)
Beijing	6.00	15.4	34.9	106	314	209	13.8	48.4	22.5	236.0	Yang et al. (2012)
Shenzhen	4.48	18.7	24.5	23.6	66.1	59.4	5.9	10.7	14.4	30.7	Niu et al. (2008)
Changsha	4.07	6.2	13.2	24.0	167.8	111.2	4.8	10.8	4.3	71.9	Sun and Yuan (2008)
Guangzhou	4.49	12.7	86.8	53.4	163.3	103.6	32.9	17.0	55.0	70.6	Cao et al. (2009)
Xi'an	6.64	28.7	38.7	128.8	489.7	425.6	13.8	36.6	31.1	229.8	Lu et al. (2011)
Tokyo, Japan	4.52	N.D.	55.2	30.5	50.2	24.9	2.9	11.5	37.0	40.4	Okuda et al. (2005)
Seoul, Korean	4.70	N.D.	18.2	29.9	70.9	34.9	3.5	6.9	10.5	66.4	Lee et al. (2000)
Tirupati, India	6.78	4.7	33.9	40.8	128.0	151.0	33.9	50.5	33.1	20.4	Mouli et al. (2005)
Adirondack, America	4.45	N.D.	2.14	22.6	36.9	3.6	0.3	1.0	1.6	10.5	Ito et al. (2002)
Montseny, Spain	6.40	N.D.	28.4	20.7	46.1	57.5	4.0	9.8	22.3	22.9	Avila and Alarcón (1999)

N.D.: no data

et al. 2008; Sun and Yuan 2008; Cao et al. 2009; Lu et al. 2011; Yang et al. 2012), and found that the ionic concentrations of rainwater in Guiyang were higher than those observed in Shenzhen and Changsha but lower than those in Beijing and Xi'an. The SO_4^{2-} concentration in Guiyang was in the highest except for that in Beijing, whereas the NH_4^+ concentration was similar to that in other cities but lower than that in Beijing. In contrast, the NO_3^- concentration at Guiyang was the lowest among these Chinese cities. The concentrations of SO_4^{2-} and NH_4^+ in the rainwater in Guiyang, as well as that of the soil-derived ion Ca^{2+}, were higher than those in Tokyo, Seoul, Tirupati of Asia, Adirondack of North America, and Montseny of Europe, whereas the concentration of NO_3^- in Guiyang was also the lowerest among these foreign cities (Avila and Alarcón 1999; Lee et al. 2000; Ito et al. 2002; Mouli et al. 2005; Okuda et al. 2005). The higher level of SO_4^{2-} in the rainwater in Guiyang compared with the other cities is likely attributable to the excessive use of high-sulfur coals (Xiao et al. 2012b). The higher level of NH_4^+, may be due to a higher number of emissions from industrial processes, transportation, biomass combustion in the northwest, and domestic commercial sewage in the Nanming River located in the south of the city (Fig. 1; Xiao et al. 2012a). Although the number of owned cars increased from 6.4×10^4 in 2001 to 48.9×10^4 in 2009, the atmospheric concentration of NO_2 reported changed little (Guizhou Statistical Yearbook 2002 2010). This maybe indicates that this decrease in the emission of NO_x from coal combustion is similar to the increase in NO_x emissions from car exhaust (Guiyang Environmental Protection Bureau 2009).

3.3 Seasonal variations of inorganic ions

As shown in Fig. 3, the inorganic ionic concentrations were generally higher in the winter and lower in the summer. This was related to the precipitation volume. When the precipitation volume reached the lowest level between Dec. 2008 and Jan. 2009, the highest ionic concentrations were observed (2,708.5 μeq/L in Dec. 2008 and 2,672.6 μeq/L in Jan. 2009),

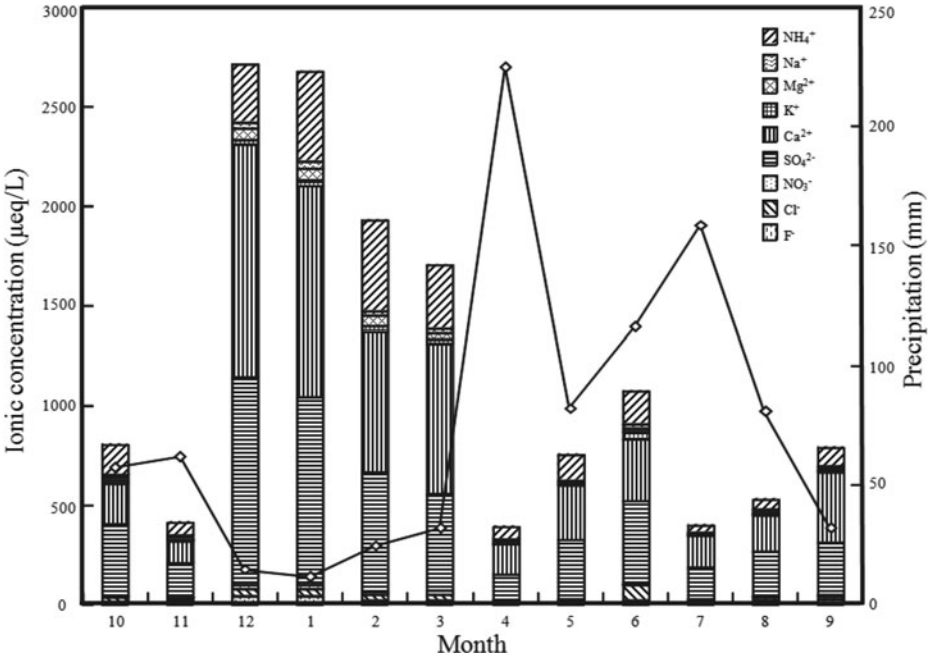

Fig. 3 Seasonal variations of ionic concentration in Guiyang

suggesting that, in the absence of precipitation, contaminants readily accumulate in the atmosphere. The maximum of ionic concentration in rainwater may be caused by an increase in the contaminants in the local region during the winter and/or an increase in the transport of contaminants from the cold air masses from Siberia toward the south.

3.4 Acid neutralization

The pH in rainwater is strongly controlled by the concentrations of acid-forming ions, such as SO_4^{2-} and NO_3^- (Overrein et al. 1972), and the concentrations of alkaline species that can neutralize the acidity in rainwater. The typical alkaline species that neutralize the acidity are NH_3 and/or carbonate materials (Zhang et al. 2007). The alkaline species in rainwater mainly originate from particulates derived from soil, road-dust, and construction (Xiao and Liu 2004). The pH in rainwater at Guiyang was found to be 4.23 in this study, lower than that in Northern China. This may be because that the contents of Ca^{2+} and Mg^{2+} in the soils at Guiyang (4.83 mg/g and 0.44 mg/g, unpublished data) are markedly lower than those in Northern Chinese soils (Wang and Wang 1996).

In general, SO_4^{2-} and NO_3^- are considered the main acidifying components in rainwater. According to Balasubramanian et al. (2001), the fractional acidity (FA) is calculated as $FA=[H^+]/([SO_4^{2-}]+[NO_3^-])$. The FA value at Guiyang was found to be 0.22 in this study, which implies that approximately 78.0 % of the acidity in the rainwater was neutralized by alkaline constituents. The FA value at Guiyang was close to that in most southern Chinese cities (Zhang et al. 2007; Cao et al. 2009) but much higher than that in most northern Chinese cities (Lu et al. 2011), indicating that there

is a large difference in the neutralization ability of alkaline constituents between Northern and Southern China. For instance, the total rainwater concentration of alkaline ions in Xi'an City (Northern China) reached 736.9 μeq/L (Lu et al. 2011), whereas a total concentration of 279.1 μeq/L was found in Guangzhou (Southern China; Cao et al. 2009). The relative contribution of NO_3^- to the acidification is calculated by $[NO_3^-]/([SO_4^{2-}]+[NO_3^-])$ (Cao et al. 2009). At Guiyang, the annual mean ratio was found to be 0.027, suggesting that approximately 97.3 % of the acidity in rainwater was due to SO_4^{2-}.

It is well known that Ca^{2+}, NH_4^+, and Mg^{2+} can neutralize the acidity in rainwater. A regression analysis between SO_4^{2-} +NO_3^- and Ca^{2+} +Mg^{2+} +NH_4^+ is presented in Fig. 4, and this analysis yielded a satisfactory regression coefficient of 0.92. Neutralization factors (NF) are also used to evaluate the acid neutralization of alkaline species in rainwater and is calculated as $NF_{Xi}=[Xi]/([SO_4^{2-}]+[NO_3^-])$, where *Xi* is the chemical component of interest and all of the ion concentrations are expressed in μeq/L. In this study, the NF values for Ca^{2+}, NH_4^+, K^+, Mg^{2+}, and Na^+ in the rainwater at Guiyang were found to be 0.67, 0.41, 0.04, 0.04, and 0.05, respectively, which indicates that Ca^{2+} and NH_4^+ are the dominant neutralization constituents while K^+ and Mg^{2+} are less significant.

3.5 Origins of the major ions in the rainwater

3.5.1 Ion correlation analysis

In this study, a correlation analysis was used to characterize the relationships among the ions in rainwater and to distinguish the potential sources of the ionic constituents. Table 3 shows the correlation coefficients among the ions in the rainwater at Guiyang. Good correlations were found between each pair of ions (SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, and Mg^{2+}) in the rainwater at Guiyang, indicating that these ions may exist in the following forms: $CaSO_4$, $Ca(NO_3)_2$, $MgSO_4$, $Mg(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$, and/or NH_4HSO_4. These same forms are also found in the total atmospheric suspended particles at Guiyang, as reported by Xiao and Liu (2004). The strong correlation between Ca^{2+} and Mg^{2+} suggested that these ions were mainly originated from crust components. K^+ shows a good correlation with Cl^-, which indicates that the weathering of sylvite (KCl) partly controlled the K^+ chemistry and/or that

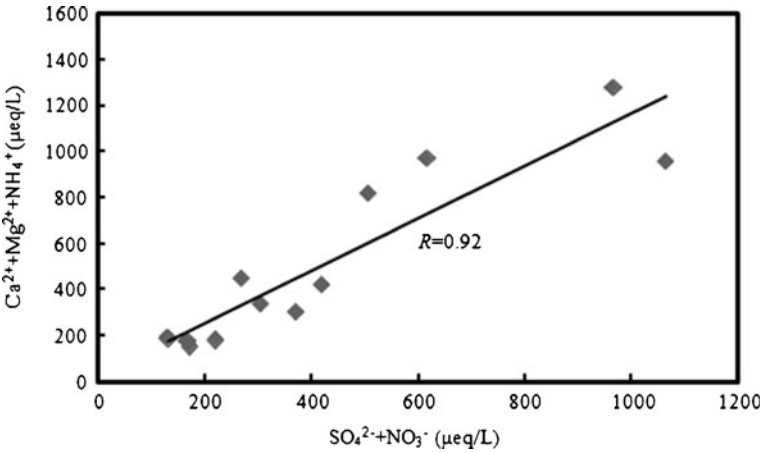

Fig. 4 Relation between (SO_4^{2-}+NO_3^-) and (Ca^{2+}+Mg^{2+}+NH_4^+) of monthly rainwater in Guiyang

Table 3 Coefficients among the major ions in precipitation

	F^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	K^+	Mg^{2+}	Na^+	NH_4^+
F^-	1								
Cl^-	0.07*	1							
NO_3^-	0.58**	0.05	1						
SO_4^{2-}	0.66**	0.05	0.84**	1					
Ca^{2+}	0.68**	0.12**	0.71**	0.85**	1				
K^+	0.12**	0.99**	0.12**	0.13**	0.19**	1			
Mg^{2+}	0.63**	0.07*	0.79**	0.90**	0.77**	0.15**	1		
Na^+	0.51**	0.07*	0.60**	0.70**	0.66**	0.14**	0.61**	1	
NH_4^+	0.47**	0.01	0.82**	0.80**	0.65**	0.08**	0.76**	0.48**	1

**correlation is significant at 0.01 level (2-tailed); * correlation is significant at 0.05 level (2-tailed)

biomass combustion may be an important source (Jalali and Kolahchi 2008; Sequeira and Lai 1998). Other possible sources of K^+ in rainwater are the weathering of K-feldspars and K-bearing minerals. Aas et al. (2007) suggested that coal combustion accounted for approximately 70.0 % of the commercial energy production in China and led to large amount of SO_2 emissions. The SO_4^{2-} in the rainwater at Guiyang may also be derived from SO_2 emissions in the processing of coal combustion due to their similar sulfur isotope values (Xiao et al. 2010b). Additionally, we also found a good correlation between SO_4^{2-} and NO_3^- in the rainwater at Guiyang, which may be attributed to the similarity of their chemical behaviors in rainwater and atmospheric particles and to a common source (coal combustion) of their precursors SO_2 and NO_x (Xiao et al. 2010b, c). In a previous study, we showed that the nitrogen isotope value of nitrate in the rainwater at Guiyang was approximately +2.3‰, reflecting that they mainly originates from coal combustion (Xiao et al. 2012c).

3.5.2 Source contribution

If the contributions from volcanic and other natural sources are negligible, the ionic compositions in rainwater would be mainly from anthropogenic sources, sea spray, and terrestrial dust from weathering (Zhang et al. 2007; Cao et al. 2009). To determine the source contributions to the ionic compositions in rainwater, the sea salt fraction (SSF) and the none sea salt fraction (NSSF), including the crust fraction (CF) and the anthropogenic fraction (AF), are calculated using the following equations:

$$SSF(\%) = 100(X/Na^+)_{sea}/(X/Na+)_{rainwater}$$
$$CF(\%) = 100\left(X/Ca^{2+}\right)_{soil}/\left(X/Ca^{2+}\right)_{rainwater}$$
$$AF(\%) = 100-SSF-CF$$

where X represents the ionic composition.

The approximate contributions of different sources to the ionic composition in rainwater are listed in Table 4. Cl^-, as a sea salt-derived ion, mainly originated from sea spray (77.8 %), although a small fraction is of an anthropogenic origin (19.4 %). The data in Table 4 show that almost all of NO_3^-, SO_4^{2-}, Ca^{2+}, K^+, and Mg^{2+} in rainwater in Guiyang appear to be of none sea salt origin. Most of Ca^{2+} and K^+ in the rainwater were from the weathering of crust, whereas most of SO_4^{2-} and NO_3^- were from anthropogenic sources. The same results were also reported in other southern cities in China (Zhang et al. 2007; Cao et al. 2009). As presented in Table 4,

Table 4 Contributions to a variety of sources from different ion composition in rainwater

ion	SSF(%)	NSSF(%)	
		CF(%)	AF(%)
Cl^-	77.8	2.8	19.4
NO_3^-	0.004	5.3	94.7
SO_4^{2-}	0.6	1.3	98.1
Ca^{2+}	0.3	99.7	
K^+	2.9	97.1	
Mg^{2+}	15.2	84.8	

SSF sea salt fraction, *NSSF* none sea salt fraction, CF crust fraction, *AF* anthropogenic fraction NH_4^+ is mainly from anthropogenic source

most of the NH_4^+ in the rainwater was likely originated from anthropogenic sources, such as human and animal excretions (Xiao et al. 2012a, c).

3.5.3 Backward trajectories

A backward air mass trajectory analysis was applied to evaluate the sources of rainwater ions. As shown in Fig. 5, the seasonal characteristics of air masses were much different in Guiyang city. In the spring, the air masses in the city were predominantly from two directions: northern

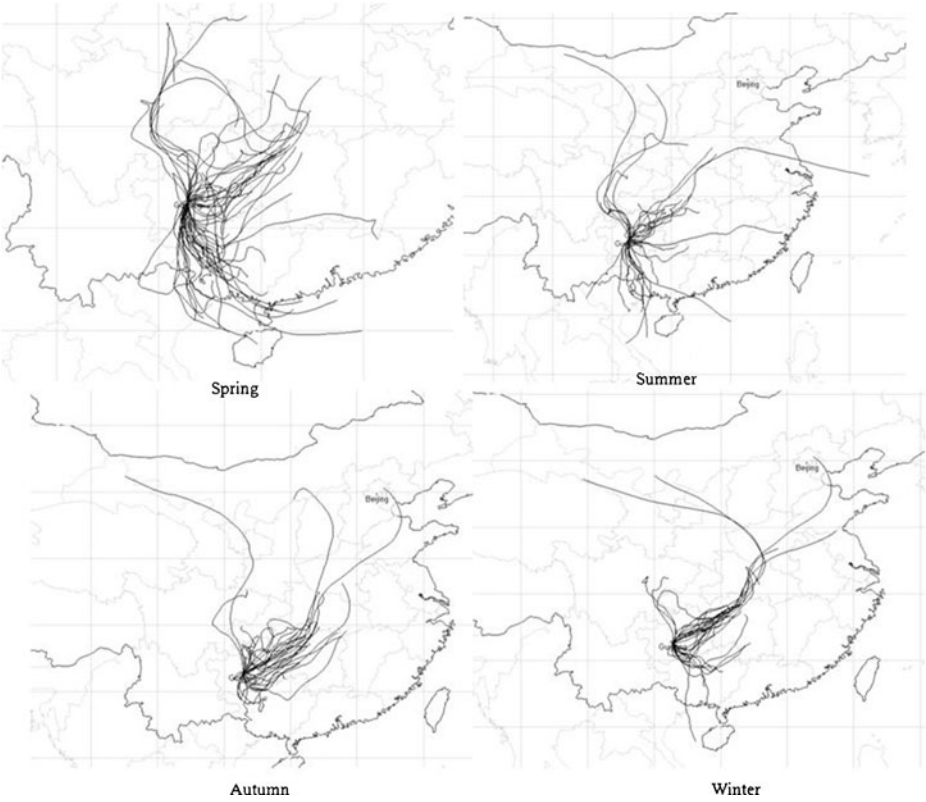

Fig. 5 Backward trajectory of air mass in different seasons

cold air masses and southern warm air masses. In the summer, the air masses were dominated by those from the South China Sea and the East China Sea. In the autumn, the local air masses exhibited a higher contribution. In the winter, the air masses were mainly from Northern China. Because the air masses from Northern China bring higher amounts of Ca^{2+} and other pollutions (e.g., SO_4^{2-}) through long-distance transmission (Zhang et al. 2007), the ratio of Ca^{2+}/Na^{+} (in μeq/L) in the winter was approximately three fold higher than that in the summer.

4 Conclusions

The chemical compositions of the rainwater at Guiyang, which is located in the southwestern China, were investigated during the period of Oct. 2008 to Sep. 2009. The pH ranged from 3.35 to 9.99, and the volume-weighted mean value of the pH in rainwater was 4.23. 72 % of the rainwater samples had pH values less than 5.60 due to poor acid neutralization. In Guiyang city, SO_4^{2-} in the rainwater was the dominant anion and accounted for 86.2 % of the total major anions, whereas Ca^{2+} and NH_4^{+} were the dominant cations and accounted for 55.5 % and 34.2 % of the total major cations, respectively. NO_3^{-} only accounted for 2.8 % of the total major anions, and the relative contribution of NO_3^{-} to rainwater acidification was approximately 2.7 %. Good correlations were found between each pair of ions (SO_4^{2-}, NO_3^{-}, NH_4^{+}, Ca^{2+}, and Mg^{2+}) in the rainwater at Guiyang, indicating that they maybe exist in the following forms: $CaSO_4$, $Ca(NO_3)_2$, $MgSO_4$, $Mg(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$, and/or NH_4HSO_4. Ca^{2+} and Mg^{2+} mainly originated from crust components, and Ca^{2+} played an important role in the neutralization of the acidic compounds in rainwater. The crust contributions of Ca^{2+} and Mg^{2+} accounted for 99.7 % and 84.8 %, respectively. K^{+} mainly came from the weathering of sylvite (KCl), K-feldspars, K-bearing minerals, and/or biomass combustion. Cl^{-} was mainly from sea spray (77.8 %), although a small amount was of an anthropogenic origin (19.4 %). The anthropogenic contributions of SO_4^{2-} and NO_3^{-} accounted for 98.1 % and 94.7 %, respectively. A good correlation was found between SO_4^{2-} and NO_3^{-}, suggesting that these ions share a common source, i.e., the combustion of coal. The NH_4^{+} in rainwater was most likely originated from anthropogenic sources and played an important role in acid neutralization at Guiyang.

Acknowledgments This study work was kindly supported by the National Natural Science Foundation of China through Grants 41203015(H.-W. Xiao), 41273027, 41173027 (H.-Y. Xiao) and 40721002 (C.-Q. Liu).

References

Aas, W., Shao, M., Jin, L., Larssen, T., Zhao, D., Xinag, R., Zhang, J., Xiao, J., Duan, L.: Air concentrations and wet deposition of major inorganic ions at five non-urban sites in China, 2001–2003. Atmos. Environ. **41**, 1706–1716 (2007)

Andreae, M.O., Talbot, R.W., Andreae, T.W., Harriss, R.C.: Formic and acetic acid over the central Amazon Region, 1, dry season. J. Geophys. Res. **93**(D2), 1616–1624 (1988)

Andreae, M.O., Talbot, R.W., Berrsheim, H., Beecher, K.M.: Precipitation chemistry in central Amazonia. J. Geophys. Res. **95**(D10), 16987–16999 (1990)

Avila, A., Alarcón, M.: Relationship between precipitation chemistry and meteorological situations at a rural site in NE Spain. Atmos. Environ. **33**(11), 1663–1677 (1999)

Balasubramanian, R., Victor, T., Chun, N.: Chemical and statistical analysis of precipitation in Singapore. Water Air Soil Pollut. **130**(1), 451–456 (2001)

Cao, Y.Z., Wang, S., Zhang, G., Luo, J., Lu, S.: Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. Atmos. Res. **94**(3), 462–469 (2009)

Dikaiaka, J.G., Tsitouris, C.G., Siskos, P.A., Melissos, D.A., Nastos, P.: Rainwater composition in Athens, Greece. Atmos. Environ. **24B**(1), 171–176 (1990)
Gonçalves, F., Ramos, A.M., Freitas, S., Silva Dias, M.A., Massambani, O.: In-cloud and below-cloud numerical simulation of scavenging processes at Serra do Mar region, SE Brazil. Atmos. Environ. **36**(33), 5245–5255 (2002)
Guiyang Environmental Protection Bureau. Guiyang Environmental Bulletin (in Chinese) (2009)
Guizhou Statistical Yearbook: 2002. (2010).
Han, G., Tang, Y., Wu, Q., Tan, Q.: Acid rain and alkalization in southwestern China: chemical and strontium isotope evidence in rainwater from Guiyang. J. Atmos. Chem. **68**, 139–155 (2011)
Ito, M., Mitchell, M.J., Driscoll, C.T.: Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. Atmos. Environ. **36**(6), 1051–1062 (2002)
Jalali, Kolahchi: Groundwater quality in an irrigated, agricultural area of northern Malayer, western Iran. Nutr. Cycl. Agroecosyst. **80**, 95–105 (2008)
Lee, B.K., Hong, S.H., Lee, D.S.: Chemical composition of precipitation and wet deposition of major ions on the Korean peninsula. Atmos. Environ. **34**(4), 563–575 (2000)
Lei, H.C., TannerMei-Yuan, P.A., Shen, Z.L., Wu, Y.X.: The acidification process under the cloud in southwest China: observation results and simulation. Atmos. Environ. **31**(6), 851–861 (1997)
Lu, X., Li, L.Y., Li, N., Yang, G., Luo, D., Chen, J.: Chemical characteristics of spring rainwater of Xi'an city, NW China. Atmos. Environ. **45**, 5058–5063 (2011)
Mello, W.Z.D.: Precipitation chemistry in the coast of the Metropolitan Region of Rio de Janeiro, Brazil. Environ. Pollut. **114**, 235–242 (2001)
Migliavacca, D., Teixeira, E.C., Wiegand, F., Machado, A., Sanchez, J.: Atmospheric precipitation and chemical composition of an urban site, Guaíba hydrographic basin, Brazil. Atmos. Environ. **39**(10), 1829–1844 (2005)
Mouli, P.C., Mohan, S.V., Reddy, S.J.: Rainwater chemistry at a regional representative urban site: influence of terrestrial sources on ionic composition. Atmos. Environ. **39**(6), 999–1008 (2005)
Niu, Y.W., He, L.Y., Hu, M.: Chemical characteristics of atmospheric precipitation in Shenzhen. Environ. Sci. **29**(4), 1014–1019 (2008) (in Chinese with English abstract)
Niu, Y.W., Gu, J.Q., Yu, X.M., Jiang, H.R.: Impact of organic acids on rainwater acidification in the background air of the Yangtze River Delta. China Environ. Sci. **30**(2), 150–154 (2010) (in Chinese with English abstract)
Okuda, T., Iwase, T., Ueda, H., Suda, Y., Tanaka, S., Dokiya, Y., Fushimi, K., Hosoe, M.: Long-term trend of chemical constituents in precipitation in Tokyo metropolitan area, Japan, from 1990 to 2002. Sci. Total Environ. **339**(1), 127–141 (2005)
Overrein, L.N., Seip, H.M., Tollan, A.: Acid precipitation-effects on forest and fish. Final report of the SNSF-project 1972–1980. (1980).
Sequeira, Lai: Small-scale spatial variability in the representative ionic composition of rainwater within urban Hong Kong. Atmos. Environ. **32**, 133–144 (1998)
State Environmental Protection Administration of China. 2010 report on the state of Environment China, Beijing, China (2010).
Sun, X.H., Yuan, S.P.: The chemical compositions and variation trend of rainwater in three cities of central and western China. Ecol. Environ. **17**(8), 572–575 (2008) (in Chinese with English abstract)
U.S. Environmental Protection Agency. Air Quality Criteria for Particulate Matter and Sulfur. EPA-600/882-029b, December 1982 (1982).
Wang, W.X.: Study on the origin of acid rain formation in China. China Environ. Sci. **14**(5), 323–329 (1994) (in Chinese with English abstract)
Wang, H., Han, G.: Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China. Atmos. Res. **99**(2), 190–196 (2011)
Wang, W., Wang, T.: On acid rain formation in China. Atmos. Environ. **30**(23), 4091–4093 (1996)
Wang, W.X., Xu, P.J.: Research progress in precipitation chemistry in China. Prog. Chem. **21**(2), 266–281 (2009) (in Chinese with English abstract)
Wu, Q., Han, G., Tao, F., Tang, Y.: Chemical composition of rainwater in a karstic agricultural area, Southwest China: the impact of urbanization. Atmos. Res. **111**, 71–78 (2012)
Xiao, H.Y., Liu, C.Q.: Chemical characteristics of water-soluble components in TSP over Guiyang, SW China, 2003. Atmos. Environ. **38**(37), 6297–6306 (2004)
Xiao, H.W., Xiao, H.Y., Wang, Y.L., Tang, C.G., Liu, X.Y.: Chemical characteristics of 9 d continuous precipitation in a typical polluted city: a case study of Guiyang, China. Environ. Sci. **31**(4), 865–870 (2010a) (in Chinese with English abstract)
Xiao, H.W., Xiao, H.Y., Tang, C.G., Liu, X.Y., Liu, C.Q., Ling, B.N.: Estimation of ammonia emission in Guiyang City. Earth Environ. **1**, 21–25 (2010b) (in Chinese with English abstract)

Xiao, H.W., Xiao, H.Y., Long, A., Wang, Y.L.: Who controls the monthly variations of NH_4^+ nitrogen isotope composition in precipitation? Atmos. Environ. **54**, 201–206 (2012a)

Xiao, H.W., Xiao, H.Y., Long, A.M., Wang, Y.L.: Sulfur isotopic geochemical characteristics in precipitation at Guiyang. Geochimica **40**(6), 559–565 (2012b) (in Chinese with English abstract)

Xiao, H.W., Xiao, H.Y., Long, A.M., Wang, Y.L.: Nitrogen isotopic composition and source of nitrate in precipitation at Guiyang. Acta Sci. Circumstantiae **32**(4), 940–945 (2012c) (in Chinese with English abstract)

Xu, G., Li, X.Q., Lv, Y.C., Chen, Y.J., Huang, D.K.: Seasonal variations of carboxylic acids and their contributions to the rainwater acidity: a case study of Guiyang and Shangzhong, China. Chin. Sci. Bull. **55**(16), 1667–1673 (2010)

Yang, F., Tan, J., Shi, Z.B., Cai, Y., He, K., Ma, Y., Duan, F., Okuda, T., Tanaka, S., Chen, G.: Five-year record of atmospheric precipitation chemistry in urban Beijing, China. Atmos. Chem. Phys. **12**, 2025–2035 (2012)

Yu, S., Gao, C., Cheng, Z., Cheng, X., Cheng, S., Xiao, J., Ye, W.: An analysis of chemical composition of different rain types in Minnan Golden Triangle'region in the southeastern coast of China. Atmos. Res. **47**, 245–269 (1998)

Zhang, M., Wang, S., Wu, F., Yuan, X., Zhang, Y.: Chemical compositions of wet precipitation and anthropogenic influences at a developing urban site in southeastern China. Atmos. Res. **84**(4), 311–322 (2007)

Zhao, D.W., Xiong, J.L., Xu, Y., Chan, W.H.: Acid rain in southwestern China. Atmos. Environ. (1967) **22**(2), 349–358 (1988)