

Acid rain and alkalization in southwestern China: chemical and strontium isotope evidence in rainwater from Guiyang

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Received: 25 July 2011 / Accepted: 18 January 2012 /

Published online: 4 February 2012

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Abstract A comprehensive study on the chemical compositions of rainwater was carried out from June 2007 to December 2008 in Guiyang, a city located on the acid rain control zone of southwest China. All samples were analyzed for pH, major anions (F^- , Cl^- , NO_3^- , SO_4^{2-}), major cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+), Sr^{2+} and Sr isotope. The pH increase is due to the result of neutralization caused by the alkaline dust which contain large amount of $CaCO_3$. It was observed that Ca^{2+} was the most abundant cation with a volume-weighted mean (VWM) value of 217.6 $\mu eq/L$ (52.7–1928 $\mu eq/L$), accounting for 66% (39%–88%) of the total cations. SO_4^{2-} was the most abundant anion with VWM value of 237.8 $\mu eq/L$ (49.6–1643 $\mu eq/L$). SO_4^{2-} and NO_3^- were dominant among the anions, accounting for 66%–97% of the total measured anions. The Sr concentrations vary from 0.01 to 0.92 $\mu mol/L$, and strontium isotopic ratios vary in the range of 0.707684–0.710094, with an average of 0.708092. The elements ratios and the $^{87}Sr/^{86}Sr$ ratios showed that the solutes of rainwater mainly come from weathering of carbonate and secondary dust input. Moreover, urbanization results in the calcium-rich dust increased and the high concentrations of alkaline ions (mainly Ca^{2+}) have played an important role to neutralize the acidity of rainwater, leading to the increase of arithmetic pH mean value by 0.5 units since 2002. It is worth noting that the emission of SO_2 and NO_x from the automobile exhaust is increasing and is becoming another important precursor of acid rain now.

Keywords Major ions · Rainwater · Strontium isotope · Base neutralization

1 Introduction

The chemistry of precipitation has been widely investigated in many areas in southwest China, which are significantly affected by acid rain since the last three decades (Zhao et al.

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1988, 1994; Zhao and Seip 1991; Seip et al. 1995, 1999; Wang and Wang 1995; Han and Liu 2006; Larssen et al. 2006; Aas et al. 2007; Han et al. 2010). But studies were focused on the distribution of precipitation pH and sulfur deposition. In China, the estimated emissions of SO₂ to the atmosphere were about 22 millions of tons in 2003, which lead to significant deposition of acid rain in the south of China (Larssen et al. 2006). However, the environmental impacts in Europe and North America associated with such high levels of strong acids in precipitation have not been widely detected in southwest China. This is partly due to the fact that acid deposition is heavily influenced and modified by natural soil dust from weathering of carbonate in southwest China. So it is very important to understand the sources of base cations. Larssen and Carmichael (2000) reported the high pH level problem in arid areas of China, but few results on the chemical composition of the rainwater and the impact of base cations on acid deposition in southwest China.

China has developed the concept of an acid rain control zone for setting priorities in the acid rain reduction policy (Hao et al. 2001). Guiyang city is located in the southwest of China and belongs to the defined acid control zone. In Guiyang city, the major air pollution source is coal combustion. Previous study (Han and Liu 2006) pointed out that the atmosphere of Guiyang was affected by various anthropogenic inputs. In order to improve air quality in Guiyang city, the Guiyang city government has taken some powerful measures (e.g. restrictions on the use of coal-fired household stoves, the relocation of heavily pollution industries in urban areas to the countryside) to control SO₂ emissions since 2004. These environmental protection and control measures have reduced greatly the frequency and intensity of acid rain. Lu et al. (2010) suggested that the acid rain problem in Chinese cities was alleviated in both frequency and average precipitation pH value after 2005. This study would present the results of chemical composition and Sr isotope ratios in rainwater collected from the 2007 to 2008 in the same site as Han and Liu (2006). The purpose is to present and to discuss the chemical and strontium isotopes characterization of rainwater, to identify possible sources of the rainwater and finally to evaluate the changes of quality of atmospheric environment in Guiyang city, which would possibly help the regulatory agencies develop strategies for acid rain control.

2 Sampling site and analytical methods

2.1 Sampling site description

Samples were collected in Guiyang city (N 26.34°, E 106.43°), southwest China. The city, which is one of the most polluted cities with the most population with the most population density in the urban and the city industry and traffic develop rapidly, lies in a wide karst valley basin with an elevation of around 1,000 m. The lithological characteristic of Guiyang city is dominated by carbonate (Fig. 1). The climate is sub-tropical and the average temperatures range from -1°C in the winter to 30°C in the summer. The dry season lasts from November to April and the wet season from May to October. Annual average precipitation of the city is 900–1,500 mm, 80% of which occurs from May to September. Since the 1980s, the city has undergone extensively urbanization and rapid industrial expansion. For example, the total city population increased by 137% from 1.5 million in 1989 to 3.5 million in 2005, and the industrial output increased by 824% from 7.7 billion yuan in 1989 to 71.4 billion yuan in 2005 (Guizhou Statistical Yearbook, 2005). On the contrary, the population growth or industrial expansions always associate with the decline of forests and lands for development.

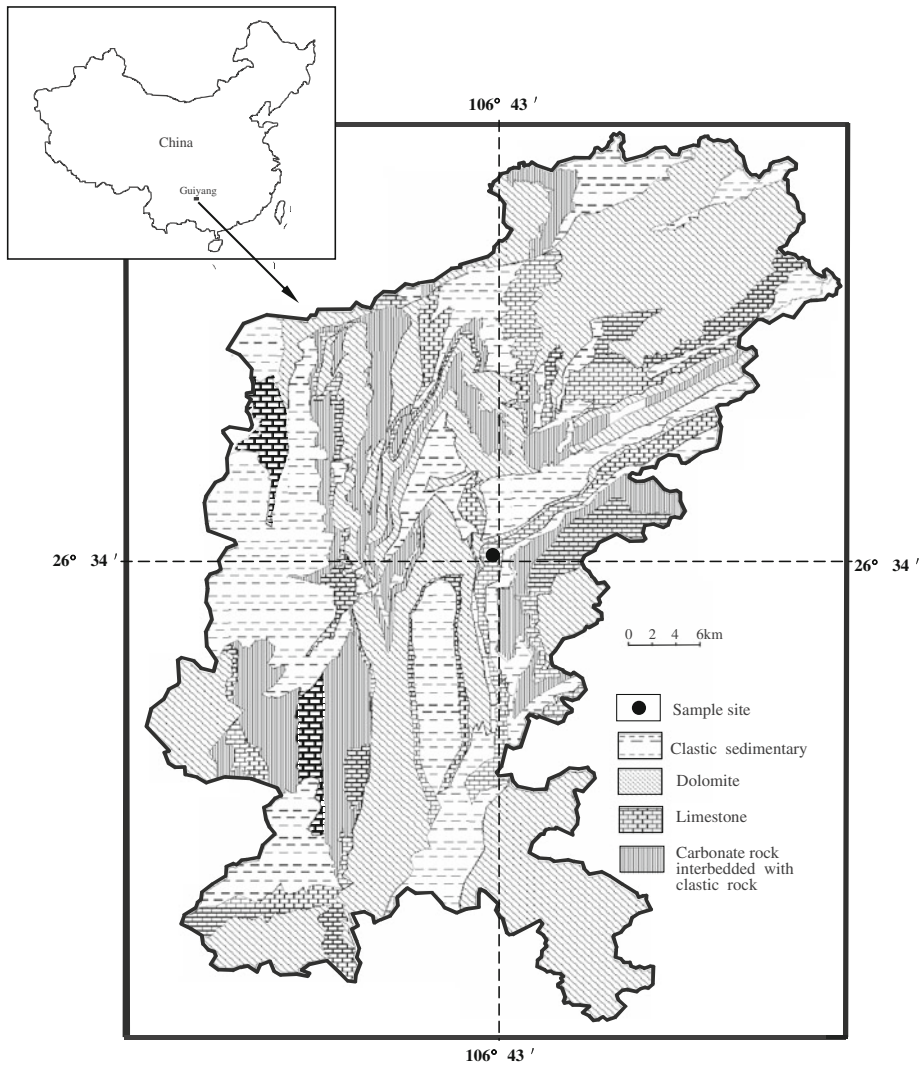


Fig. 1 A sketch map showing the lithology of Guiyang city, southwest China

2.2 Analytical methods

The sampler was located on the roof of a building about 15 m high from ground level in an office building in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (CAS). The rainwater samples were collected manually from the beginning of each rain event with a funnel sampler that was located approximately 120 cm above the roof. Prior to use, the sampler was cleaned with acid (2–3 N HCl) and soaked in with Milli-Q water (18.2M Ω ·cm), then finally rinsed with Milli-Q water and dried. In order to prevent contaminations from dry deposition, special attention was paid to open the sampler as quickly as possible after the onset of rainfall. Forty-one rainwater samples were collected from June in

2007 to December 2008. Most of our samples were collected in the rainy season, from July to August and there are few samples after September.

The pH values were measured in situ at the end of the rain events. All the rainwater samples were filtered through 0.22 μm Millipore membrane filters using a pre-cleaned Nalgene filter apparatus. Filtrate was separated into two aliquots; one was stored in polyethylene bottles for measuring anions and the other was acidified with ultra-purified nitric acid to $\text{pH} < 2$ and stored in pre-cleaned polyethylene bottles for measuring cations, Sr concentrations and Sr isotopic ratios. Major anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) were measured by using a ionic chromatography (Dionex DX-120). The detection limits of F^- , Cl^- , NO_3^- and SO_4^{2-} ions were found to be 0.04, 0.07, 0.07 and 0.10 mg/l, respectively. Reproducibility of results was better than 5% for all major anions. NH_4^+ concentrations were determined by spectrophotometry using the Nessler method. The detection limit of NH_4^+ ion was found to be 0.01 mg/l. Reproducibility of results was better than 3%. Major cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) were determined by ICP-AES (Thermo's IRIS Intrepid II). The detection limits of K^+ , Na^+ , Ca^{2+} and Mg^{2+} 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. The concentrations of Sr^{2+} were measured by ICP-MS (VG POEMS III) in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. The detection limits of Sr^+ ions were found to be 0.02 $\mu\text{g/l}$. 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 better than $\pm 5\%$.

Separation of strontium from other major elements for isotopic analysis was carried out by a conventional ion-exchange technique using a Dowex 50 W \times 8 200–400 mesh resin in HCl media. The isotopic compositions of Sr were determined by TIMS (IsoProbe T) in the Institute of Geochemistry, Chinese Academy of Sciences. Mass 85 was measured to monitor the interfering ^{87}Rb . Prior to each measurement session, a gain calibration was carried out for all amplifiers. During the mass spectrometer runs, any fluctuation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio due to mass- and temperature-dependent isotope fractionation was normalized and corrected relative to the commonly accepted $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.375209. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of NBS987 strontium standard was 0.710235 ± 0.000018 (2σ , $n=50$) during the course of the study.

3 Results and discussion

3.1 pH value and ionic composition

The measured parameters, major ions, strontium concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are given in Table 1. The volume-weighted mean (VWM) value of the ionic compositions of rainwater samples and related statistical analyses are also shown in Table 2. According to previous studies, the natural CO_2 , NO_x and SO_2 can be dissolved into the clouds and droplets, resulting in pH values of the rain in the clean atmosphere to be between 5.0 and 5.6 (Charlson and Rodhe 1982; Galloway, et al. 1993). Rainwater showing pH value below 5.0 is due to the presence of natural H_2SO_4 , weak organic acids, or anthropogenic emission of H_2SO_4 and/or HNO_3 . The samples with pH values above 6.0 may suggest inputs of alkaline species into the precipitation in the study area. The frequency distribution of rainwater pH is shown in Fig. 2. The pH values of rain samples from Guiyang city range from 4.1 to 7.2 (with a mean pH value of 5.0). The highest acidity (value of 4.1) was observed on May 14th, 2008, and the lowest (value of 7.2) was on September 25th, 2008. Most samples show pH values from 4.1 to 5.0, while about one-fourth rainwater samples

Table 1 Concentrations ($\mu\text{eq/L}$) of major ions, Sr ($\mu\text{mol/L}$) and Sr isotope ratios in rainwater from Guiyang, southwestern China

Sample number	Date (y-m-d)	pH	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	Sr^{2+}	$^{87}\text{Sr}/^{86}\text{Sr}$
GY-1	2007-6-12	4.7	20.94	3.17	3.21	84.00	6.58	4.04	0.63	6.97	101.50	0.11	0.708162
GY-2	2007-6-23	4.25	31.67	13.34	3.21	139.00	29.63	2.28	13.61	17.52	163.60	0.16	0.708328
GY-3	2007-6-26	4.13	12.78	2.94	0.41	162.50	15.64	3.36	2.30	7.79	162.45	0.08	0.708025
GY-4	2007-6-29	4.43	75.56	35.95	1.83	242.48	16.69	14.73	29.24	22.14	261.90	0.90	0.707874
GY-5	2007-7-1	4.95	10.00	79.35	3.43	231.50	15.64	28.74	66.00	18.11	292.80	0.63	0.707684
GY-6	2007-7-8	4.56	82.22	23.06	2.40	294.50	31.28	22.83	17.75	32.88	329.68	0.92	–
GY-7	2007-7-26	5.80	46.67	4.46	1.51	81.69	5.17	5.29	11.28	7.06	165.42	0.03	0.708320
GY-8	2007-8-14	4.52	533.89	29.03	6.37	620.04	81.76	114.12	36.39	190.00	808.54	0.40	0.708592
GY-9	2007-8-24	6.39	64.44	3.19	1.61	95.30	6.61	10.59	5.92	30.00	133.75	0.05	0.707823
GY-10	2007-9-3	4.47	53.89	3.80	0.98	281.11	40.33	20.00	5.36	38.24	361.46	0.06	0.708096
GY-11	2007-9-9	4.81	38.33	29.84	2.18	108.98	11.37	7.62	21.68	14.51	132.85	0.32	0.708066
GY-12	2007-9-13	4.54	43.33	39.79	10.19	384.15	19.07	26.43	18.70	18.68	420.99	0.45	0.707811
GY-13	2008-3-20	4.36	151.72	121.00	10.60	219.03	24.84	94.71	71.37	48.82	279.79	0.14	0.710094
GY-14	2008-4-21	4.86	75.00	5.66	0.99	171.18	15.00	8.82	10.16	117.65	138.33	0.04	0.708927
GY-15	2008-4-27	4.38	67.78	3.92	1.08	157.00	12.35	3.53	4.51	104.71	123.54	0.03	0.708588
GY-16	2008-5-3	4.68	80.56	4.74	2.79	187.25	18.19	24.12	14.10	38.24	250.21	0.10	0.707982
GY-17	2008-5-14	4.11	253.89	16.87	2.45	183.77	18.05	14.71	14.39	92.35	427.50	0.08	0.708384
GY-18	2008-5-18	4.24	419.44	32.38	2.69	381.39	21.84	11.18	19.18	205.88	654.17	0.14	0.708675
GY-19	2008-5-22	4.53	34.44	5.41	0.54	104.50	6.58	2.35	7.33	11.18	117.92	0.01	0.708973
GY-20	2008-5-26	5.35	76.11	5.90	1.30	149.00	15.64	11.76	11.00	31.18	189.79	0.09	0.707834
GY-21	2008-6-8	4.41	98.33	5.26	3.22	194.64	21.40	52.94	5.64	18.82	225.63	0.03	0.708092
GY-22	2008-6-12	4.53	148.33	5.82	1.28	147.03	15.40	22.94	13.26	17.06	261.67	0.09	0.707728
GY-23	2008-6-22	4.87	88.89	2.57	0.73	155.51	12.35	4.71	1.97	18.82	160.00	0.02	0.708295
GY-24	2008-6-27	5.39	31.11	4.72	0.79	106.50	9.05	13.53	10.16	8.24	106.67	0.05	0.708092
GY-25	2008-7-2	4.89	16.67	1.11	0.48	58.50	4.94	1.76	1.41	2.35	58.75	0.02	0.708037

Table 1 (continued)

Sample number	Date (y-m-d)	pH	NH ₄ ⁺	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Sr ²⁺	⁸⁷ Sr/ ⁸⁶ Sr
GY-26	2008-7-5	5.28	28.89	2.72	1.90	149.69	7.66	28.24	4.80	3.53	101.04	0.03	–
GY-27	2008-7-11	5.13	25.00	2.13	0.80	147.71	13.17	10.59	3.67	11.18	95.83	0.03	0.708016
GY-28	2008-7-16	5.37	76.11	4.65	1.89	173.14	19.50	22.35	6.77	25.88	260.63	0.08	–
GY-29	2008-7-22	4.93	20.00	1.44	0.28	155.50	11.18	9.41	1.13	4.71	105.21	0.03	0.708126
GY-30	2008-7-31	4.44	66.67	5.47	1.40	464.93	43.09	21.76	6.21	63.53	412.71	0.07	0.707694
GY-31	2008-8-2	5.5	62.78	5.17	1.10	169.74	13.77	17.65	5.36	28.24	271.04	0.10	–
GY-32	2008-8-6	6.75	123.89	15.27	2.06	313.84	44.12	13.53	9.87	27.65	334.79	0.21	0.708020
GY-33	2008-8-18	4.84	14.44	2.48	0.51	174.54	6.36	10.00	1.41	3.53	162.92	0.04	0.707723
GY-34	2008-8-25	4.85	38.89	4.50	0.88	197.55	10.61	3.53	4.80	20.00	131.04	0.05	0.707934
GY-35	2008-9-1	5.01	78.33	14.04	1.98	367.45	24.58	26.47	16.08	45.88	335.83	0.10	0.708068
GY-36	2008-9-25	7.22	27.22	3.12	0.75	52.72	3.48	2.94	5.08	7.65	49.58	0.04	0.707850
GY-37	2008-10-4	4.47	63.89	3.36	0.75	119.50	7.41	15.88	3.10	18.24	219.38	0.02	0.708160
GY-38	2008-10-25	4.88	103.68	9.08	1.85	383.01	44.21	8.09	11.84	133.56	313.01	0.09	–
GY-39	2008-10-31	5.57	14.24	0.88	0.28	173.17	10.35	2.01	1.36	13.21	56.05	0.04	0.708150
GY-40	2008-11-2	6.95	246.11	19.14	4.73	1928.17	176.13	27.06	25.11	291.76	1643.33	0.34	0.708182
GY-41	2008-11-6	5.16	73.89	5.17	2.18	57.81	10.33	6.47	10.16	16.47	184.17	0.04	0.708236

- stands for no detection

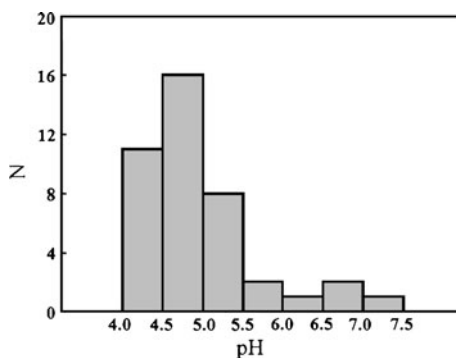
Table 2 Mean concentration (in $\mu\text{eq/L}$) of major ionic composition and pH (in unit) along with statistical results in rainwater

Component	VWM	Mean	Median	SD	Min	Max
pH	4.9	5.0	4.9	0.8	4.1	7.2
NH_4^+	77.0	88.3	64.4	105.0	10.0	533.9
K^+	11.1	14.2	5.2	22.7	0.9	121.0
Na^+	1.8	2.2	1.6	2.3	0.3	10.6
Ca^{2+}	217.6	243.1	171.2	294.8	52.7	1928.2
Mg^{2+}	18.6	22.5	15.4	28.7	3.5	176.1
F^-	14.3	18.4	11.8	22.4	1.8	114.1
Cl^-	9.8	12.9	9.9	15.1	0.6	71.4
NO_3^-	39.6	44.7	18.8	62.0	2.4	291.8
SO_4^{2-}	237.8	268.4	189.8	268.8	49.6	1643.3

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

have pH value below 4.5. This indicates that Guiyang city is impacted by acid rain. Compared to the previous data (Han and Liu 2006), the pH values increased and the frequency of $\text{pH} < 4.5$ decreased.

The equivalent ratio of the sum of anions to that of cations ($\Sigma_{\text{anions}}/\Sigma_{\text{cations}}$) is usually regarded as an indicator of the completeness of the measured major constituents (Al-Khashman 2005). The average equivalent sum of anions of that of cations ($\Sigma_{\text{anions}}/\Sigma_{\text{cations}}$) was 0.94. This suggests that all of the major ion were measured. From Table 1, it can be shown that the concentrations of major ions are in the order of $\text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{F}^- > \text{K}^+ > \text{Cl}^- > \text{Na}^+$ (VWM). Ca^{2+} is the most abundant ion among the cations, and its average concentration was 217.6 $\mu\text{eq/L}$ (VWM). Ca^{2+} accounts for 66% of the total cations. NH_4^+ is the second abundant cation and contributes 24% of the cations measured. SO_4^{2-} and NO_3^- are the dominant anions and account for 66%–97% of total anions measured. SO_4^{2-} was the most abundant anions, with average concentration 237.8 $\mu\text{eq/L}$ (VWM). SO_4^{2-} accounts for 50%–92% of the total anions, while the average NO_3^- concentration was 39.6 $\mu\text{eq/L}$ (VWM). The VWM values of rainwater samples are commonly less than the arithmetic means, indicating that the high concentrations of ions are usually associated with low precipitation. The data of the ion concentrations show a high relative standard deviation (from 2.3 to 294.8), indicating a large variability in the cation and anion concentrations in each rain events.

Fig. 2 The frequency distribution of rainwater pH in Guiyang

3.2 Correlation factors

Correlation analysis was performed to distinguish the possible common sources of ionic constituents. To determine the association among ionic constituents in rainfall, correlation coefficients (R) between ionic species in precipitation were calculated and listed in Table 3. There is no association between pH and SO_4^{2-} and NO_3^- . This indicated that most of the SO_4^{2-} and NO_3^- are present as salts (NH_4NO_3 , CaSO_4) rather than HNO_3 and H_2SO_4 , which are produced from neutralizing processes. K^+ is closely correlated with Cl^- ($R=0.95$), suggesting that the two species may originate from the same source. While there are no obvious correlations between Ca^{2+} and K^+ ($R=0.15$) and Ca^{2+} and Cl^- ($R=0.25$), indicating that K^+ and Cl^- originated from the same source without emission of Ca^{2+} . The K^+/Cl^- ratio (1.1) is much higher than that of sea water (0.061), suggesting that K^+ and Cl^- may not origin from the Ocean.

Positive correlations are obtained between SO_4^{2-} and Ca^{2+} and Mg^{2+} ($R=0.95$ and 0.93 , respectively) and between NO_3^- and Ca^{2+} and Mg^{2+} ($R=0.79$ and 0.78 , respectively). These correlations indicate that acidic anions are neutralized by base cations. Especially the high correlations among Ca^{2+} and Mg^{2+} ($R=0.96$) indicated that these ions have a common source. Furthermore, correlation coefficient of NH_4^+ versus SO_4^{2-} ($R=0.67$) was lower than those of NH_4^+ versus NO_3^- ($R=0.77$), showing that NH_4NO_3 could be more predominant than $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 in the atmosphere. SO_4^{2-} and NO_3^- showed significant correlation among themselves ($R=0.84$) which may be attributable for the similarity of their chemical behaviors in precipitation and the co-emission of their precursor SO_2 and NO_x .

3.3 Origins of major ions in the rainwater

The most usual method of evaluating the contribution of sea salts to ion contents in precipitation is to compare the Cl^-/Na^+ ratio in rainwater to that of seawater. Sea is considered to be the major source of both ions, although they may also be emitted from other natural and industrial sources (Samara et al. 1992). Figure 3 provides elements-to- Na^+ ratios (X/Na^+) of rainwater from Guiyang city and the dashed lines in the figure show X/Na^+ values in seawater. All of rainwater samples significantly lie above the seawater line, reflecting the terrestrial influence on the elements content reported by previous studies (Berner and Berner 1987; Negrel and Roy 1998). Guiyang is located in inland and far from sea, so the major ions in rainwater from Guiyang are mainly of non-sea-salt origin (Han and Liu 2006). The arithmetic mean of the Cl^-/Na^+ molar ratio was found to be 6.2. This value is higher than the corresponding value for seawater, which is 1.17 (Berner and Berner 1987). This indicates that significant non-sea-salt Cl^- sources exist.

Table 3 Matrix of correlation coefficients (R) of ionic concentrations (in $\mu\text{eq/L}$) in rainwater samples from Guiyang city

ions	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
NH_4^+	1								
K^+	0.25	1							
Na^+	0.39	0.75	1						
Ca^{2+}	0.47	0.15	0.34	1					
Mg^{2+}	0.52	0.14	0.34	0.96	1				
F^-	0.60	0.59	0.70	0.28	0.37	1			
Cl^-	0.34	0.95	0.69	0.25	0.27	0.64	1		
NO_3^-	0.77	0.16	0.29	0.79	0.78	0.32	0.27	1	
SO_4^{2-}	0.67	0.23	0.42	0.95	0.93	0.40	0.34	0.84	1

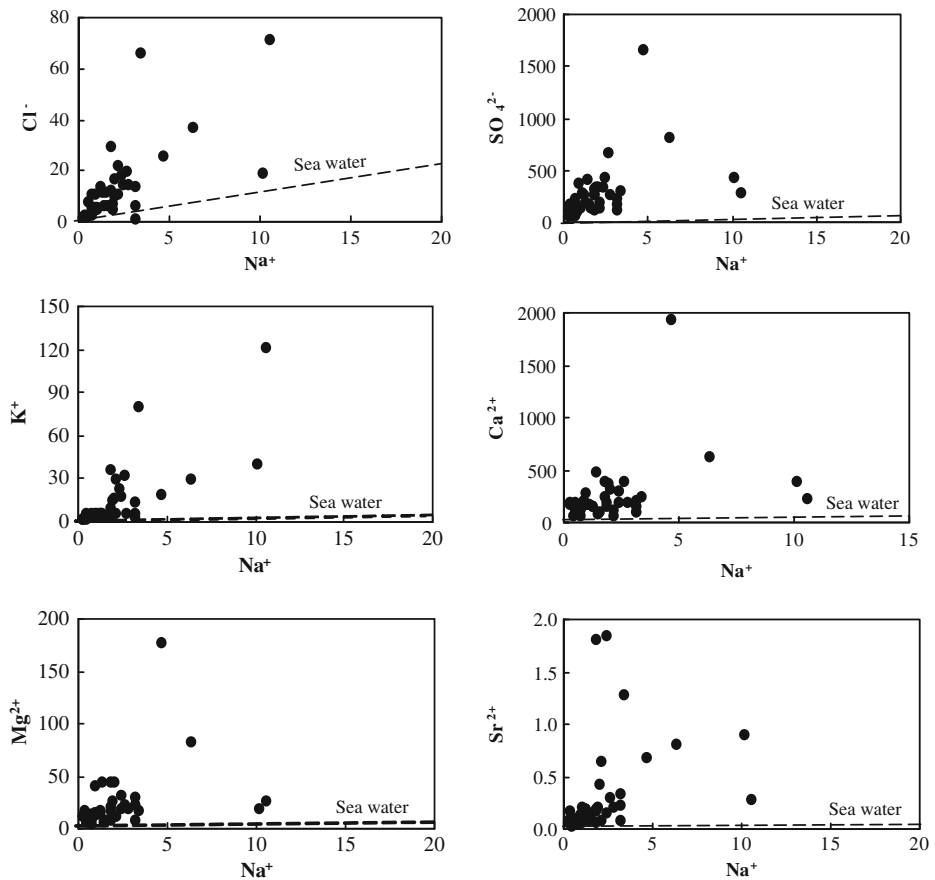


Fig. 3 The relationship between solutes and sodium in the rainwater samples. The line in each diagram shows the corresponding ratios of sea water (sea water data come from Berner and Berner 1987)

The non-sea-salt Cl^- may be derived from natural sources, for example, the dissolution of evaporate minerals (halite, sylvite) from soil dust. However, the $\text{Cl}^-/(\text{Na}^+ + \text{K}^+)$ ratios of most samples is still higher than 1, suggesting the presence of anthropogenic sources of Cl^- . Only one rain events are of lower Cl^-/Na^+ ratios, which can be explained by the presence of terrigenous Na^+ , or in terms of replacement of Cl^- by SO_4^{2-} or NO_3^- (Clegg and Brimblecombe 1985, 1986; Keene et al. 1990).

Ca^{2+} is very important to neutralizing acidity of rain (Nakano and Tanaka 1997; Larssen and Carmichael 2000). One of the non-sea-salt Ca components of rainwater may be related to calcic particles from vicinal soil dust. Guiyang is surrounded by carbonate terrain (Fig. 1), the source of soil dust in atmosphere is weathering of carbonate. There are many possible sources of Ca in Guiyang city aerosols besides soil particles: road dust, suspended in the lower troposphere due to daytime convection and vehicle/wind-driven roadside dust (Ali et al. 2004); road deposits, mixed soil components from various local soils transported by automobiles with some anthropogenic materials, such as, concrete and fly ash. The Ca component of these sources consists of soluble carbonate species, mainly soluble CaCO_3 . The large turbulences generated by construction can also enhance the spread of aerosols in

the atmosphere (Sanusi et al. 1996). In recent years, Guiyang government developed the municipal administration construction which results in the concentration of Ca^{2+} in rainwater increased.

According to Flues et al. (2002), high concentration of NH_4^+ found in rainwater could be related to gaseous ammonia (NH_3) introduced into the atmosphere, mainly by cattle breeding (80%), fertilizer use (17%) and industrial processes. Guiyang city is the capital in Guizhou Province and therefore gaseous ammonia is the potential NH_4^+ source. The high level of NH_4^+ in rainwater coincides with the fact that the emission of ammonia to the atmosphere from agriculture activities is enormous in the Asian regions. It is several times higher than that in North America and Europe (Galloway 1995).

SO_4^{2-} in rainwater may also originate from anthropogenic emissions of SO_2 . Aas et al. (2007) suggested that coal combustion accounts for about 70% of the commercial energy production in China; leading to large amount of SO_2 emissions, which has been the most important precursor of acid rain in China. Guiyang city government has taken a lot of measurements (e.g. restrictions on the use of coal-fired household stoves, the relocation of heavily pollution industries in urban areas to the countryside) to control the emissions of coal combustion since 2004, resulting in decrease of SO_2 and NO_x emissions of coal-fired. But, in Guiyang, the urban road network is developed and the car has exceeded 380 thousands by the end of 2008, which will result in increase of SO_2 and NO_x emissions of fossil fuel combustion. A highly positive correlation between SO_4^{2-} and NO_3^- ($R=0.84$), SO_4^{2-} and Ca^{2+} ($R=0.95$) indicates that they are from similar sources, and reflects the input of pollutants from fossil fuel combustion in Guiyang city.

From the data set in Table 4, it can be seen that the concentration of F^- in rainwater from Guiyang city is higher than that from other sites worldwide except Qinghai (Zhang et al. 2003a). Fluorine is one of the most toxic and volatilized elements present in coal. During combustion, it is emitted as HF, SiF_4 , and CF_4 (Liu et al. 2006). Therefore, coal combustion has been identified as an important source of F emissions. The higher correlation between F^- and Cl^- ($R=0.64$) indicate the common sources of these elements as fly ash and flue gases of coal burning in power plants and domestic heating (Brueggemann and Rolle 1998).

3.4 Strontium: concentration and isotopic composition

Compare to the previous study (Table 4), the concentrations of SO_4^{2-} show increase while the pH values don't show any decrease in the rainwater from Guiyang. This is attributed to the increase of base cations (mainly Ca^{2+}). Identifying the provenance of Ca^{2+} in precipitation is very important because this element is a dominant cation which neutralizes acidity of rainwater and indispensable for plant growth (Hedin and Likens 1996; Schmitt and Stille 2005). Strontium acts as proxy for Ca because both are alkaline earth elements with similar ionic radii and the same valences and similar geochemical behaviors (Capo et al. 1998; Nakano et al. 2006). For these reasons, Sr isotope system can be used to investigate the mixing of different Sr sources (or by the inference of Ca) when coupled with Sr concentrations in rainwater (Herut et al. 1993; Negrel and Roy 1998; Negrel et al. 2001, 2007; Chabaux et al. 2005; Han and Liu 2006; Xu and Han 2009; Han et al. 2010).

The Sr concentrations of rainwater in Guiyang show a range from 0.01 to 0.92 $\mu\text{mol/L}$, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios span a range from 0.707684 to 0.710094, with an average value of 0.708092. Most of the rainwater samples collected in Guiyang have $^{87}\text{Sr}/^{86}\text{Sr}$ ratio lower than that of seawater (0.70917; Dia et al. 1992), except sample GY-13 ($^{87}\text{Sr}/^{86}\text{Sr}=0.710094$), which reflects a contribution from at least one low-radiogenic Sr source. The most suitable candidate would be

Table 4 Comparison of the major ion concentrations ($\mu\text{eq/l}$) and pH values in Guiyang city with other sites in China and worldwide

site	pH	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NH ₄ ⁺	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Date	references
Guiyang (VWM)	4.9	14.3	9.8	39.6	237.8	77	11.1	1.8	217.6	18.6	2007–2008	This study
Guiyang (Mean)	5.0	18.4	12.9	44.7	268.4	88.3	14.2	2.2	243.1	22.5	2007–2008	This study
Guiyang (Mean)	4.5		21.2	48.2	188		11	4	113.2	25.2	1999–2001	Han and Liu 2006
Beijing (VWM)	5.12	15.7	104	109	316	186	17.7	25	607	40.4	2006	Xu and Han 2009
Shanghai (VWM)	4.49	11	58.3	49.8	199.6	80.9	14.9	50.1	204	29.6	2005	Huang et al. 2008
Nanjing (VWM)	5.51		143	39.6	242	193	12.1	23	295	31.7	1992–2003	Tu et al. 2005
Chengdu (VWM)	5.1	6.2	8.9	156.2	212.8	150.5	6.6	1.4	196.6	16.2	2008	Wang and Han 2011
Chengdu (VWM)	4.4		42.3	30.4	431.5	250.7	20.8	22.6	192	33.2	1989	Lei et al. 1997
Chongqing (VWM)	4.6		40.3	43.2	421.8	386.6	15.2	39.8	207.2	13.2	1989	Lei et al. 1997
South of China (mean)	4.41		16.3	28.2	166.3	61.7	10.8	11.3	82.1	21.5	2001–2003	As et al. 2007
Lhasa (VWM)	7.5	0.4	9.7	6.9	5.2	14.3	5.14	11.2	197	10.9	1997–1999	Zhang et al. 2003b
Qinghai (VWM)	7.1	46.6	48.8	48.1	84	161	69.2	96.6	314	37.9	1999	Zhang et al. 2003a
Lanzhou (VWM)	7.7	13.6	27.9	74.4	208	57.2	7.26	12.3	886	46.5	2007	Xu et al. 2009
Ankara (Turkey)	6.3		20.4	29.2	48	86.4	9.8	15.6	71.4	9.3	1994–1996	Topcu et al. 2002
Tokyo (VWM)	4.52		55.2	30.5	50.2	40.4	2.9	37	24.9	11.5	1990–2002	Okuda et al. 2005
Massif Central (Mean)	5.22		19.6	36.2	22.3		5.7	14.4	14.6	3.4	1994–1995	Negrel and Roy 1998
Istanbul (VWM)	4.81		124.8	33.4	115.2	12.8	57.4	75.2	285	99.6	2001–2002	Basak and Alagha 2004
Itatiaia massif (VWM)	4.94		5.2	11.8	15.5	13.5	1.3	3.9	4.3	2.2	1999–2000	Mello and Almeida 2004
Mexico (VWM)	5.08		9.6	42.6	61.9	92.4	2.2	7	26.4	2.5	2001–2002	Baez et al. 2007

the input of soil dust from local and human activities, which are obviously more non-radiogenic. From Fig. 4, it can be seen that the variation of the pH, Ca and Mg content had the same trend. But the Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio have no obvious variation. The temporal variation of the pH, Ca, Mg and Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio reflects a significant impact of the input of soil dust in the atmosphere at the different season in Guiyang city.

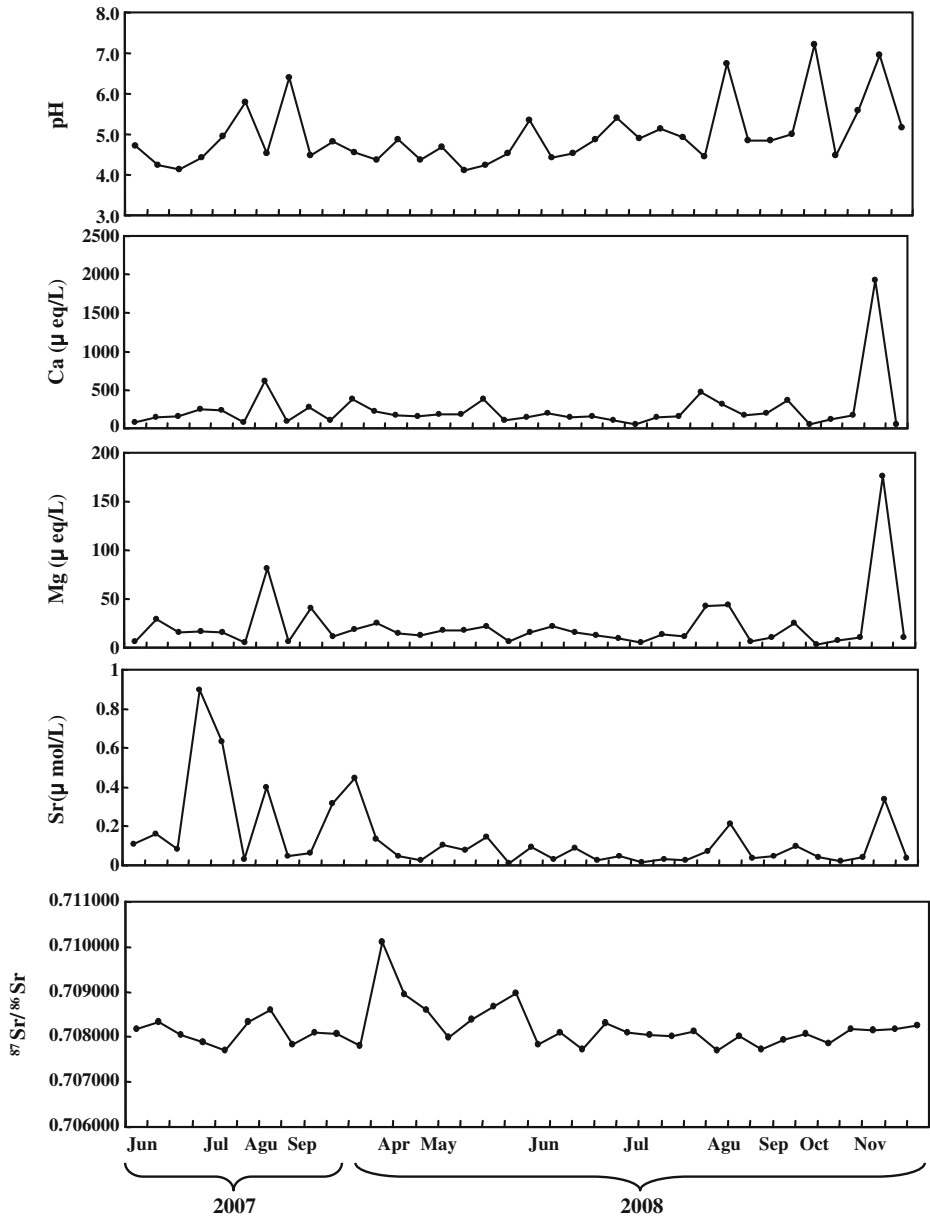


Fig. 4 The temporal variation of the pH, Ca, Mg and Sr content, and Sr isotopic ratios of the rainwater from Guiyang city

Soil dust around the sampling site originating from carbonate weathering is considered to be a major source of non-sea-salt Sr, which play an important role in the chemical composition and acidity of precipitation (Nakano and Tanaka 1997; Yokoo et al. 2001; Nakano et al. 2006). The $^{87}\text{Sr}/^{86}\text{Sr}$ composition of soil dust can be estimated by studying the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of river waters and leaching experiment of soil in this region. Han and Liu (2004) reported $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7075–0.7080 for river water draining carbonate terrain. Accordingly, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$, high Ca and Sr content in the rainwater from Guiyang can all be attributed to the dissolution of carbonate in soil dust. We show the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ with Cl^-/Na^+ ratios in the rainwaters from Guiyang (Fig. 5). Cl^-/Na^+ ratio can be used as indicator of sources: marine source has Cl^-/Na^+ ratio of 1.17 and anthropogenic sources should have higher ratios. Compare to the previous data (Han and Liu 2006), there is almost no variation in Sr^{2+} concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Kanayama et al. (2002) suggested that the Ca-abundant urban aerosols are more affected by anthropogenic sources, such as road deposits or asphalts, and have an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio about 0.709. Recent study (Negrel et al. 2007) indicates that an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ranges between 0.7077 and 0.7083 for automobile exhaust, between 0.7083 and 0.73335 for urban heating, and between 0.7097 and 0.7100 for incinerators. We have estimated the $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl^-/Na^+ ratios together with the Sr and Na concentrations for the three end-members in rainwater arbitrarily according to the rainwater samples from our data. The first source is probable from calcite mineral dissolution, containing the lowest Cl^-/Na^+ and Na⁺ according to the rainwater samples GY1 (the estimated characteristic values of Cl^-/Na^+ , Na⁺ (μmol/L), $^{87}\text{Sr}/^{86}\text{Sr}$, Sr^{2+} (μmol/L) are 0.20, 3.21, 0.7082, 0.11, respectively). In contrast, other two end-members are characterized by high Cl^-/Na^+ ratio and high Na content, in accordance with signature of anthropogenic sources due to their high Cl^-/Na^+ ratio. We have estimated the values of Cl^-/Na^+ , Na⁺, $^{87}\text{Sr}/^{86}\text{Sr}$, Sr^{2+} for the urban heating end-member and fossil fuel

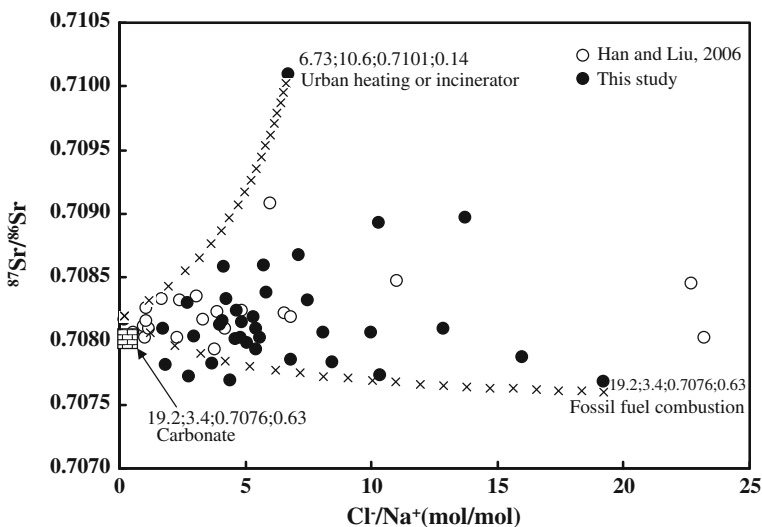


Fig. 5 Variation of Sr isotope ratios with Cl^-/Na^+ molar ratios in the rainwater samples. The binary mixing lines were calculated based on the isotope and element ratios estimated for each end-members (The mixing lines between calcite source end-member and fossil fuel combustion source end-member have been calculated, on which one mark (cross) stands for increase of 5% of end-member. Another non-sea-salt Sr source is probably made up of incinerator). The estimated characteristic values of Cl^-/Na^+ , Na⁺ (μmol/L), $^{87}\text{Sr}/^{86}\text{Sr}$, Sr^{2+} (μmol/L) for each end-members are also shown in the figure

combustion end-members according to the samples GY13 (the estimated characteristic values of Cl^-/Na^+ , Na^+ ($\mu\text{mol/L}$), $^{87}\text{Sr}/^{86}\text{Sr}$, Sr^{2+} ($\mu\text{mol/L}$) are 6.73, 10.60, 0.7101, 0.14, respectively) and GY5 (the estimated characteristic values of Cl^-/Na^+ , Na^+ ($\mu\text{mol/L}$), $^{87}\text{Sr}/^{86}\text{Sr}$, Sr^{2+} ($\mu\text{mol/L}$) are 19.22, 3.43, 0.7076, 0.63, respectively). Although natural soil dust and dust from construction activities probable have the same $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, it is clear that the most important origin of the Ca aerosols would be the calcite mineral dissolution (including carbonate weathering and secondary dust). Anthropogenic inputs (fossil fuel combustion and urban heating/incinerator) certainly cannot be ignored in Guiyang city.

3.5 Acid neutralization and rain alkalization

The concentrations of major ion and pH values in rainwater in Guiyang city have been compared with the available data from other urban areas in the world, which are presented in Table 4. Compared with the monitoring data worldwide, the pH value was higher than those in Shanghai and Tokyo and close to those in Beijing and Istanbul, but much lower than those in Lhasa, Qinghai, Lanzhou and Ankara (Topcu et al. 2002; Basak and Alagha 2004; Zhang et al. 2003a, 2003b; Huang et al. 2008; Okuda et al. 2005; Xu and Han 2009; Xu et al. 2009; Xu et al. 2010). Compared with megacities in China, the data from Guiyang city show moderate ionic composition. The SO_4^{2-} and Ca of rainwater in Guiyang is higher than those from a lot of cities but similar to that of Chengdu, where is located in the acid rain central zone in China (Wang and Han 2011). Compared with some sites in worldwide, the ion concentrations of Guiyang rainwater, especially SO_4^{2-} , Ca^{2+} , exceed than those of reference cities in Europe, American and East Asia. And the problem of acid rain is not serious in Guiyang, whose neutralization is attributed to the presence of base cations (mainly Ca^{2+}).

Neutralization factors (NF) can be used to evaluate the neutralization of precipitation by Ca^{2+} , Mg^{2+} and NH_4^+ , which are calculated by the following equation (Possanzini et al. 1988; Zhang et al. 2007; Özsoy et al. 2008).

$$NF_{X_i} = \frac{[X_i]}{[\text{NO}_3^-] + [\text{SO}_4^{2-}]}$$

where X_i is the chemical component of interest, with all the ions expressed in $\mu\text{eq/L}$. The NF values for Ca^{2+} , Mg^{2+} , K^+ and NH_4^+ in rainwater of the study area are 0.78, 0.07, 0.05 and 0.28, respectively. The results reveal that Ca^{2+} and NH_4^+ are the dominant neutralization substances in the rainwater, whereas the neutralization by Mg^{2+} and K^+ is negligible. This is consistent with the fact that Guiyang city is surrounded by carbonate terrain.

The data of this present study can be compared with those suggested by Han and Liu (2006) (Table 4). It is noteworthy that the tendency of rain alkalization in precipitation in Guiyang is obvious, and the pH (mean) value has been increased by 0.5 units since 2002. It is also observed that the concentrations of NO_3^- (mean) have varied within a very limited range, whereas Ca^{2+} (mean) has increased greatly from 113 to 243 $\mu\text{eq/L}$, and SO_4^{2-} (mean) has increased from 188 to 268 $\mu\text{eq/L}$ during the same period. As previous discussion, Ca^{2+} is mainly attributed to the soil dust from weathering of carbonate or cement production/urban construction or coal burning. In order to improve air quality in Guiyang city, the Guiyang government has taken some powerful measures (e.g. cancelled the use of coal-fired household stoves) to control SO_2 emissions since 2004. These environmental protection and control measures have reduced greatly the SO_2 emissions of coal combustion. At the same time, Guiyang has undergone extensively urbanization and rapid industrial expansion. The concentrations of alkaline ions (especially Ca^{2+}) which may be caused by secondary dust in the atmosphere have been greatly

increased. So it can be concluded that urbanization has resulted the rain alkalization tendency of rainwater in Guiyang.

4 Conclusions

More than 30 years ago, the southwest region of China was considered as a potentially problematic area regarding acid deposition problems. In order to improve air quality in Guiyang city, the city government has taken some powerful measures to control SO₂ emissions from coal combustion since 2004. A decrease in the acidity could be observed. The mean pH value (5.0) in the rainwater measured in this study is higher than that of the mean pH value (4.5) measured between 1999 and 2001 (Han and Liu 2006). The nitrate content at all samples is rather similar or decrease slightly relative to previous study (Han and Liu 2006). The expected nitrate decrease through the decrease coal combustion emissions were compensated by increase NO_x traffic related emissions. The concentration of sulphate increased and calcium strongly increased, the nitrate remained slightly decrease, and in the acidity could be observed still decrease.

Guiyang city is surrounded by carbonate terrain and the soil dust from carbonate weathering and secondary dust can neutralize the acidic ions. The calcium-rich dust acts as a buffer, neutralizing sulfuric and nitric acid particles before they fall to Earth. It was clearly observed that the cations (mainly Ca²⁺) act as sulphate neutralizers in each rain event sample. Due to the substantial contribution of these cations to the sulphate neutralization action, the rain water of this region is only slight acidic, which showed that the air quality of the city improved. However, indeed the sulfur emissions from coal-fired power plants, and nitrogen oxide emitted from automobiles and airplanes have not been reduced, and urbanization results the calcium-rich dust increased, and the increase of calcium-rich dust masked the acid rain. So in future, an assessment of acid deposition in southwest China requires not only consideration of pH values and sulfur input, but also consideration of basic inputs and alkalization problem.

Acknowledgements This work was supported jointly by the Innovation Program of Chinese Academy of Sciences (No. KZCX2-YW-QN109) and the Chinese National Natural Science Foundation (No. 41021062, 40973088).

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