



# Chemical composition of rainwater and the acid neutralizing effect at Beijing and Chizhou city, China



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## ABSTRACT

The chemical compositions were measured in rainwater samples collected during 2011–2012 from two representative cities, Beijing in north China and Chizhou city in south China. The rainwater was highly acidic with a volume-weighted mean (VWM) pH of 4.56, ranging from 3.77 to 5.67, and about 94% of the samples had pH below 5.0 in Chizhou. The pH values of rainwater in Beijing ranged from 3.78 to 6.62, with a VWM value of 4.85. The predominant ions in the precipitation were  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  at both sites. The VWM concentrations of ions in rainwater were higher in Beijing, and the  $\text{SO}_4^{2-}$  concentration of rainwater in Beijing was about twice that in Chizhou. However, due to the weaker neutralization of acidity, the rainwater from Chizhou had relatively low pH values. According to the results of linear regression analysis, the percentage of the potential acidity counteracted by  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  was higher in rainwater in Beijing (90.7%) than that in Chizhou (70.8%). Using Na as an indicator of marine origin, and Al for the terrestrial inputs, the proportions of sea salt and terrestrial elements were estimated from elemental ratios. More than 98% of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in rainwater samples are non-sea-salt origin at both sites. Coal combustion may be the main source of  $\text{SO}_4^{2-}$ , and local and remote soil dust may be an important source of  $\text{Ca}^{2+}$  in Beijing rainwater. The high concentrations of alkaline ions ( $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ ) have played an important role to neutralize the acidity of rainwater in Beijing.

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## 1. Introduction

In the past several decades, China has become the third region in the world seriously affected by acid rain (after Northeast America and Central Europe). This is mainly caused by strong acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  originating from combustion of fossil fuels. Moreover, the regions affected by acid rain are gradually expanding due to rapid economy growth and increasing fossil fuel consumption in China (Wang, 1994; Zhang et al., 2007). According to the Administration of Environmental Protection of the People's Republic of China (2013), acid precipitation had affected about 30% of areas across this country (Fig. 1). Furthermore, the seriously affected regions are mainly located in the economically developed areas in southeastern China.

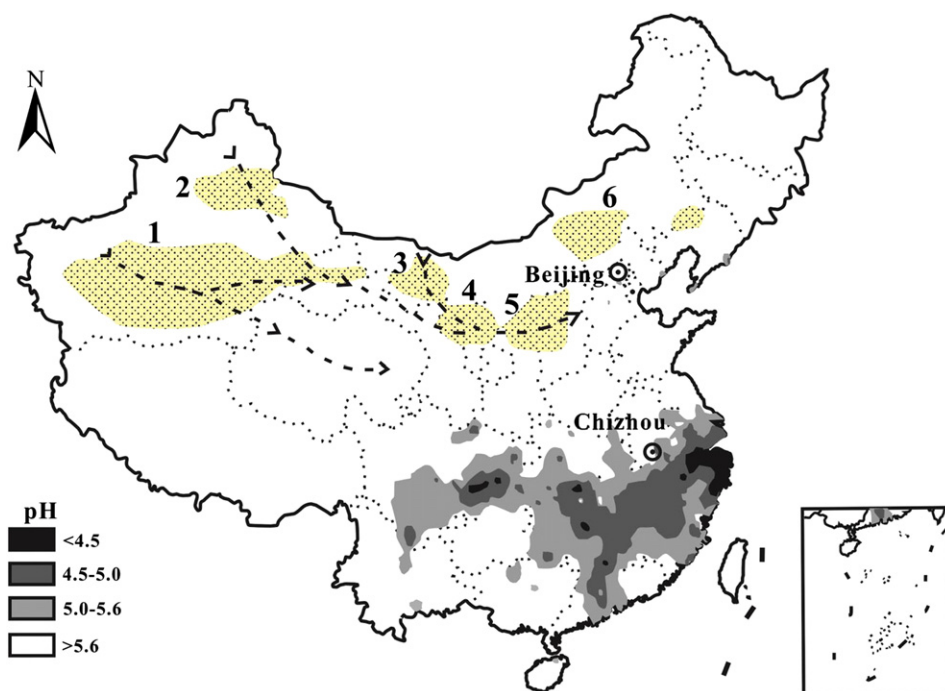
Previous studies have suggested that rainwater has played an important role in removing aerosols and their components from the atmosphere (Négre et al., 2007; Tang et al., 2005; Wang and Wang, 1995). Since, it can absorb both gases and particles from the atmosphere, rainwater composition can be used to define the level of acid deposition and

to understand the relative contribution of different sources of atmospheric pollutants (Zhang et al., 2007). During the last three decades, chemistry of precipitation has been widely investigated in many areas of China. These studies argued that even though the emissions of precursors of acid deposition come predominantly from northern China, acid rain occurs mainly in the south (Feng et al., 2001; Larssen and Seip, 1999; Tang et al., 2005). In northern China, acid deposition is heavily influenced by alkaline dust from desert and semi-arid areas. Despite high sulfur emissions and large quantities of sulfuric acid in the precipitation, pH values of rainwater in northern China still remain relatively high (Larssen and Carmichael, 2000; Xu and Han, 2009; Xu et al., 2009). This is mainly due to high levels of neutralizing effect of alkaline soil dust aerosols in the atmosphere. On the contrary, because of the low buffering capacity of aerosols in the atmosphere of southern China, the annual pH values of precipitation are generally low (Lei et al., 1997; Xiao et al., 2013; Zhang et al., 2007). However, previous studies on acid rain always observed and elaborated chemistry of precipitation at one site in China. To date, few studies contrast chemical composition of precipitation between northern and southern China during the same period.

In this study, we collected rainwater samples systemically for almost one year from Beijing and Chizhou city in the north and south of China, respectively, and then analyzed the frequency of acid rain and chemical compositions of these rainwater samples, to present and contrast

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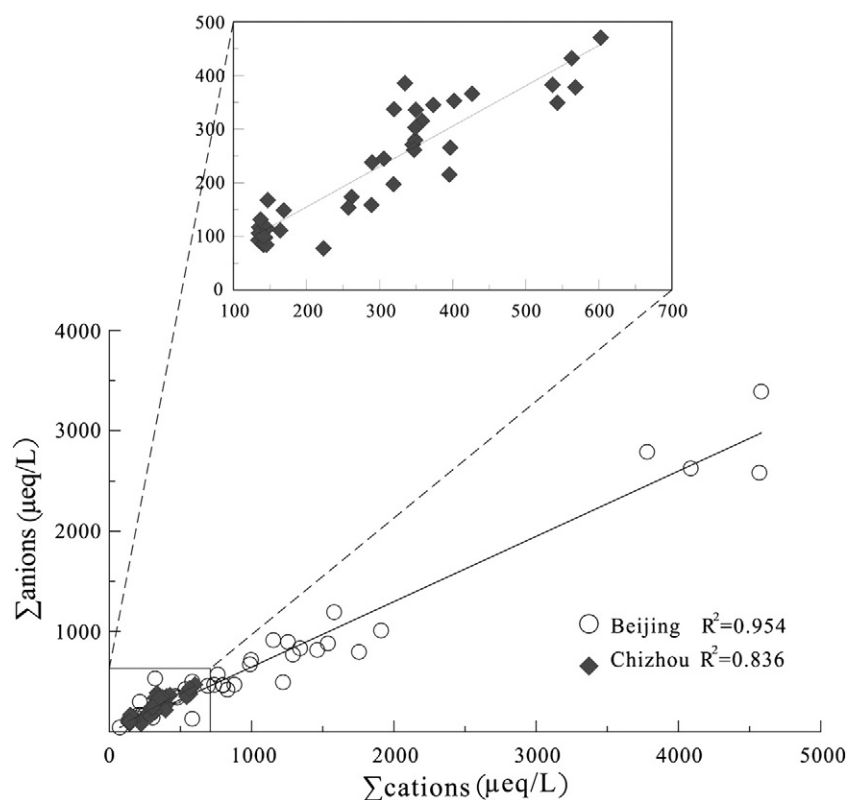
E-mail address: [zfxu@mail.iggcas.ac.cn](mailto:zfxu@mail.iggcas.ac.cn) (Z. Xu).



**Fig. 1.** Map showing the sampling stations, the desert areas in northern China and the distribution of rain water acidity during 2012 (according to State Environmental Protection Administration of China). 1. Taklamakan Desert; 2. Gurbantonggut Desert; 3. Badain Jaran Desert; 4. Tengeli Desert; 5. Muus Desert; 6. Hunshandake Desert. The arrows indicate the sources of soil dust and transportation routes. Modified after Xu and Han (2009).

chemical compositions of rainwater samples between northern and southern China. The purpose of this paper is to show and discuss the chemical features of precipitation at the two sampling sites, to gain a

primary understanding of the chemical compositions of the rainwater, to contrast the neutralizing capacities between them, and to finally identify possible sources that contribute to their chemical compositions.



**Fig. 2.** The correlation coefficients between the sum of anions and the sum of cations for rainwater samples from Beijing and Chizhou.

**Table 1**Summary statistics of pH, EC and major ion concentrations for rainwater samples collected from Beijing and Chizhou (concentrations in  $\mu\text{eq l}^{-1}$ , pH in unit, EC in  $\mu\text{S cm}^{-1}$ ).

	pH	EC	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>
<b>Beijing</b>												
Mean value	4.73	126	21.5	108	77.3	544	363	16.2	63.4	557	124	18.8
VWM <sup>a</sup>	4.85	82.0	12.0	50.9	42.6	357	346	9.17	21.5	273	53.3	10.2
VWSD <sup>b</sup>	1.00	18.1	3.42	11.1	8.48	72.5	84.1	2.47	5.37	62.2	11.9	3.43
Minimum	3.78	5.00	0.00	0.00	7.14	35.5	36.6	1.29	1.10	10.3	2.61	0.11
Maximum	6.62	503	158	1035	333	2736	1007	60.4	787	3214	955	208
<b>Chizhou</b>												
Mean value	4.45	26.0	5.46	13.8	13.2	197	47.8	4.02	4.10	196	8.59	3.49
VWM <sup>a</sup>	4.56	23.0	6.12	14.1	10.3	178	38.2	3.33	3.09	189	5.71	2.73
VWSD <sup>b</sup>	0.69	3.91	2.76	3.59	2.12	28.4	6.44	0.571	0.436	32.3	0.88	0.76
Minimum	3.77	6.00	0.00	0.00	1.14	64.8	11.3	0.711	0.522	105	0.98	0.10
Maximum	5.67	97.0	22.9	41.1	93.9	425	178	15.4	12.7	302	36.6	12.2

<sup>a</sup> Volume weighted mean.<sup>b</sup> Volume weighted Standard deviation.

## 2. Materials and methods

### 2.1. Sampling sites

The two sampling sites are illustrated in Fig. 1. Beijing, the capital city of China, is located in the northern part of the North China Plain and spans an area of 16,427 km<sup>2</sup> with a population more than 20 million. It has a typical continental monsoon climate with hot and humid summers due to the influence of the East Asian monsoon, and cold and dry winters due to the Siberian anticyclone. Prevailing wind direction reveals obvious seasonal changes. In spring and winter the northwest wind prevails while in summer southeast wind prevails. As shown in Fig. 1, Beijing is under the influence of soil dust from desert and semi-arid areas in the northwest and north of China. Previous studies have suggested that pH values of rainwater in Beijing were always higher than 6.0 (Feng et al., 2001; Tang et al., 2005). However, during the last decade, the tendency of rain acidification is obviously linked to the rapidly increasing number of private cars and industrial activities (Xu and Han, 2009).

Chizhou, a city in Anhui province, lies at the northern edge of the acid rain area of South China (Fig. 1). With a subtropical monsoon climate, Chizhou has a high proportion of forest coverage. However, this city has experienced a rapid urbanization and industrialization in recent decades. According to the environmental bulletin of Anhui province, Chizhou is one of the regions that are seriously affected by acid rain.

### 2.2. Sampling and chemical analyses

At the two sampling sites, both of the sampling collectors were placed on the roof of a building about 10 m high from ground level. 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 of the building. Prior to use, the samplers were carefully washed with 2–3 N HCl acid, then rinsed with Milli-Q water and dried. In order to prevent contaminations from dry deposition, the collector was covered with a plastic lid, which was removed just before the onset of rainfall. A total of 76 rainwater samples were collected at both sites during Nov. 2011 and Oct. 2012. According to the records on China Meteorological Data Sharing Service System (cdc.cma.gov.cn), there were totally 669 mm and 1274 mm rainfall in Beijing and Anqing (the nearest meteorological station to Chizhou) during the sampling period, respectively. The precipitation occurred mainly in summer in Beijing and Chizhou. Only the major rainfall events were collected in this study, and the rainwater samples accounted for more than 50% of the total rainfall of both cities.

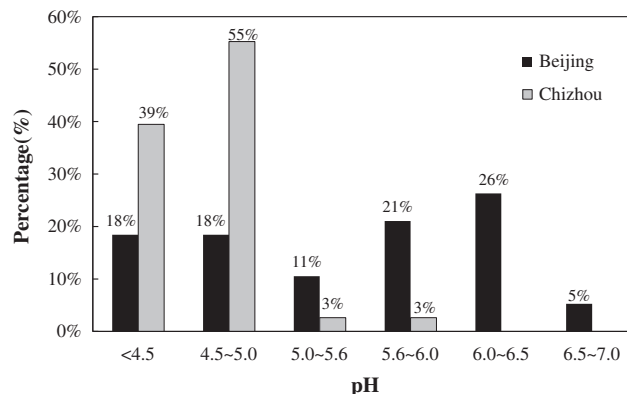
Values for pH and conductivity were measured immediately after sampling in the field with a portable pH and salt conductivity meter. The samples were then filtered through 0.22  $\mu\text{m}$  Millipore membrane filters using a pre-cleaned Nalgene filter apparatus to remove the

insoluble substances and the filtrate was divided into two aliquots. One was stored in polypropylene bottles for measuring the concentrations of anions and the other was acidified with ultra-purified nitric acid to pH < 2 for measuring cations. Major anions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>) were measured through an ionic chromatography (Dionex DX-120), and cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Al<sup>3+</sup>) were determined by using ICP-AES (Thermo's IRIS Intrepid II). NH<sub>4</sub><sup>+</sup> concentrations were measured by spectrophotometry using the Nessler method. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures and the analytical precision is better than  $\pm 5\%$ . For each ion, we calculated the volume-weighted mean concentration (VWM) and the volume-weighted standard deviation (VWMD). The VWM concentration was calculated using the formula:  $\bar{X} = \sum_{i=1}^n X_i P_i / \sum_{i=1}^n P_i$  (Sequeira and Lai, 1998) and VWMD was calculated as follows (Jain et al., 2000):

$$\text{VWSD} = \left[ \frac{N \sum_{i=1}^N P_i^2 [X_i]^2 - \left( \sum_{i=1}^N P_i [X_i] \right)^2}{\left( \sum_{i=1}^N P_i \right)^2 (N-1)} \right]^{1/2}$$

where  $P_i$  is the rainwater amount corresponding to the  $i$ th sample,  $X_i$  is the concentration of the species, and  $N$  is the number of samples. The average of pH in a period was calculated from the volume-weighted mean concentration of H<sup>+</sup>.

The equivalence ratio of the sum of anions to the sum 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 correlation coefficients between the sum of anions and the sum of cations ( $\Sigma \text{anions} / \Sigma \text{cations}$ ) were 0.95 and 0.84 for the samples from Beijing and Chizhou, respectively (Fig. 2), suggesting that almost all major

**Fig. 3.** Frequency distribution of pH values of rainwater samples from Beijing and Chizhou.

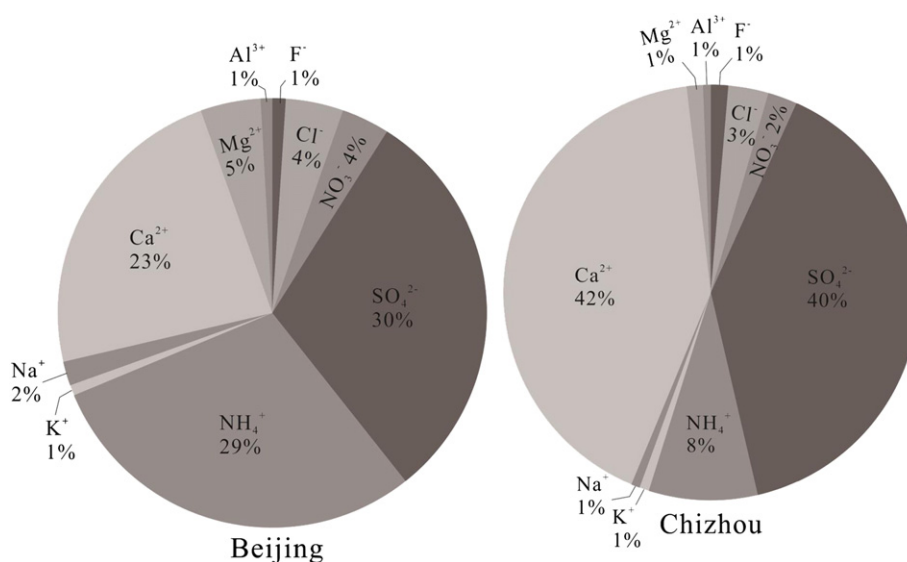


Fig. 4. Chemical composition percentages of rainwater in Beijing and Chizhou.

ions were measured. Given the large area of vegetation cover in Chizhou, the anion deficiency might be due to unmeasured organic anions in rainwater.

### 3. Results and discussion

#### 3.1. pH and conductivity

The pH values of the rainwater ranged from 3.78 to 6.62, with a VWM value of 4.85 in Beijing, and from 3.77 to 5.67, with a VWM value of 4.56 in Chizhou, respectively (Table 1). According to previous studies, water in equilibrium with an unpolluted atmosphere containing  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{SO}_2$  is slightly acidic with a pH between 5.0 and 5.6 (Charlson and Rodhe, 1982; Galloway et al., 1993). Thus precipitation with a pH of less than 5.0 is commonly classified as acid rain (Drever, 1997), and may have been influenced by anthropogenic emissions. The samples with pH values greater than 6.0 may indicate inputs of alkaline substances into rainwater (Wang and Han, 2011). The percentage frequency distribution of pH values for the rainwater samples from Beijing and Chizhou is presented in Fig. 3. The distribution indicates a higher acidity level of rainwater in Chizhou, about 94% of the samples had pH values below 5.0 in Chizhou, while only 36% of the samples had pH values less than 5.0 in Beijing.

The conductivity values of all the samples ranged from 5 to  $503 \mu\text{S cm}^{-1}$  in Beijing, while in Chizhou, conductivity values ranged from 6 to  $97 \mu\text{S cm}^{-1}$  (Table 1). Generally, conductivity reflects the total soluble components (Gioda et al., 2013). Rainwaters from Chizhou had conductivities lower than those from Beijing, which reflect better atmospheric environmental quality in Chizhou area. That may also

indicate a preferable dilution effect of atmospheric pollution due to the relatively abundant rainfall in Chizhou (Zhang et al., 2007).

#### 3.2. Chemical composition

The descriptive statistics of the rainwater compositions are shown in Table 1. Almost all the ions in rainwater in Beijing were more concentrated than those in rainwater in Chizhou. Moreover, the volume-weighted mean (VWM) concentration of  $\text{SO}_4^{2-}$  in rainwater in Beijing was about twice as high as in Chizhou. These results are unsurprisingly due to the lower rainfall and heavy anthropogenic pollution in Beijing. However, Chizhou rainwater showed a relatively low pH value compared with that of Beijing. This may be due to the neutralizing effects of high concentrations of calcium and ammonium in precipitation in Beijing, and the alkaline soil dusts transported from deserts and loess soils is likely the main cause (Fig. 1).

The relative dominance of ions was quite similar between the two sites (Fig. 4), and the predominant ions in the precipitation were  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ . Similar results were also observed by previous studies (Huang et al., 2009; Lu et al., 2011; Xiao et al., 2013). In detail,  $\text{SO}_4^{2-}$  accounted for 79.1% and 85.4% of the total measured anions in Beijing and Chizhou, respectively, suggesting that sulfate acid rain prevailed at both sites.  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  cations accounted for 86.8% and 93.9% of the total measured cations in Beijing and Chizhou, respectively. As shown in Fig. 4,  $\text{NH}_4^+$  made a greater contribution to the total ions in Beijing than Chizhou. Generally, atmospheric  $\text{NH}_4^+$  is derived from heterogeneous reactions involving  $\text{NH}_3$ .  $\text{NH}_3$  is mainly produced from fertilizers, animal waste, human activity, industrial facilities, and wastewater treatments (Dentener and Crutzen, 1994). The ammonia emission survey in Beijing suggested that the contribution values of  $\text{NH}_3$

Table 2  
Seasonal variations of VWM concentrations of the major ions and pH in Beijing and Chizhou rainwater.

Site	Season	pH	$\text{F}^-$ $\mu\text{eq l}^{-1}$	$\text{Cl}^-$ $\mu\text{eq l}^{-1}$	$\text{NO}_3^-$ $\mu\text{eq l}^{-1}$	$\text{SO}_4^{2-}$ $\mu\text{eq l}^{-1}$	$\text{NH}_4^+$ $\mu\text{eq l}^{-1}$	$\text{K}^+$ $\mu\text{eq l}^{-1}$	$\text{Na}^+$ $\mu\text{eq l}^{-1}$	$\text{Ca}^{2+}$ $\mu\text{eq l}^{-1}$	$\text{Mg}^{2+}$ $\mu\text{eq l}^{-1}$	$\text{Al}^{3+}$ $\mu\text{eq l}^{-1}$
Beijing	Spring	5.73	22.2	71.1	78.4	550	545	11.1	31.7	347	78.9	14.7
	Summer	5.62	8.55	34.9	28.4	231	338	7.54	9.06	138	32.4	7.12
	Autumn	4.58	8.28	32.5	40.8	406	259	7.82	14.3	339	41.9	11.2
	Winter	4.94	27.5	172	86.0	798	250	20.5	109	949	185	22.1
Chizhou	Spring	4.79	9.37	18.8	12.8	178	40.9	3.67	2.79	218	5.39	3.21
	Summer	4.80	0.00	5.50	1.83	114	15.3	1.36	2.19	115	1.48	0.51
	Autumn	3.93	12.1	29.2	18.4	322	85.8	8.07	11.9	276	36.0	8.12
	Winter	4.40	7.66	15.3	16.7	258	61.2	5.03	4.27	226	9.97	4.45



**Table 3**  
Fractions of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  variance explained by  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ .

	% explained by $\text{Ca}^{2+}$	% explained by $\text{NH}_4^+$	% total explained
<i>Beijing</i>			
$\text{SO}_4^{2-}$	84.9%	7.6%	92.5%
$\text{NO}_3^-$	75.6%	–	75.6%
<i>Chizhou</i>			
$\text{SO}_4^{2-}$	72.2%	3.5%	75.7%
$\text{NO}_3^-$	26.8%	–	26.8%

from the five sources mentioned above are 41%, 34%, 22%, 2%, and 1%, respectively (Peng et al., 2000). Furthermore, the pH values of soils in the Beijing region are around 7–8 (Zhao et al., 1988), the alkaline soil is more beneficial to the volatilization of ammonia.

Seasonal variations of VWM concentrations of major ions and pH values in rainwater from Beijing and Chizhou are shown in Table 2. For Beijing, it can be observed that the concentrations of almost all ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , etc.) are relatively high in winter and spring rainwater samples. As shown in Fig. 1, soil dust in the loess and desert areas could be transported to Beijing by the prevailing northwest wind during the winter and spring period. These elements (Ca, Mg, K, and Na) are a common constituent of soil dust in the arid and semi-arid regions in northern China (Feng et al., 2001; Yokoo et al., 2004; Xu and Han, 2009). Therefore, the rainwater samples had high concentration of cations during the winter and spring period when the northwest wind prevails. Winter and spring rainwater samples also showed higher concentration of  $\text{SO}_4^{2-}$ , which was due to the heavy emissions of  $\text{SO}_2$  originated from coal combustion. This is consistent with the fact that most homes burn more coal for heating during winter and spring period in most northern parts of China. Compared with Beijing, the chemical composition of Chizhou rainwater was not an obvious seasonal variation.

### 3.3. Acid neutralization and rain alkalization

Generally, the acidification potential of rainwater is controlled by the presence of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and organic acids (Kaya and Tuncel, 1997). However, the presence of alkaline material (mainly  $\text{NH}_3$  and  $\text{CaCO}_3$ ) can neutralize these acid species. According to previous studies, the neutralization percentage evaluated by using neutralization factors might be to some extent overestimated, as the impact of those basic ions associated with anions was not considered (soil-derived evaporates consisting of sulfate and chlorides will be relatively abundant) (Draaijers et al., 1997; Huang et al., 2008). The neutralization efficiency of basic ions on acidic ions could be quantified by using the linear regression analysis (Anatolaki and Tsitouridou, 2009; Migliavacca et al., 2005; Niu et al., 2014).  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are used as dependent variables while  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  as independent variables in the model of linear regression.

**Table 4**  
Chemical compositions in wet precipitation at different sites in China ( $\mu\text{eq l}^{-1}$ ).

Site	Year	pH	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	References
Beijing <sup>a</sup>	2011–2012	4.85	12.0	50.9	42.6	357	346	9.17	21.5	273	53.3	This study
Chizhou <sup>a</sup>	2011–2012	4.56	6.12	14.1	10.3	178	38.2	3.33	3.09	189	5.71	This study
Beijing <sup>b</sup>	1995–1998	6.87	26.9	97.2	54.5	359	135	33.3	57.2	464	86.0	Feng et al. (2001)
Beijing <sup>a</sup>	2008	5.32	10.5	67.8	139	270	174	6.69	8.51	291	38.5	Xu et al. (2012)
Lanzhou <sup>a</sup>	2007	7.70	13.6	27.9	74.4	208	57.2	7.26	12.3	886	46.5	Xu et al. (2009)
Xi'an <sup>a</sup>	2010	6.64	28.7	38.7	129	490	230	13.8	31.1	426	36.6	Lu et al. (2011)
Jinhua <sup>a</sup>	2004	4.54	9.05	8.51	31.2	95.2	81.1	4.73	6.27	47.9	3.45	Zhang et al. (2007)
Chengdu <sup>a</sup>	2008	5.10	6.60	1.40	156	213	151	6.60	1.40	197	16.2	Wang and Han (2011)
TGR <sup>a</sup>	2009–2010	4.85	–	11.8	63.2	177	90.6	7.50	11.7	143	18.3	Wu and Han (2015)
Guiyang <sup>a</sup>	2008–2009	4.23	14.5	20.7	7.30	266	113	9.60	13.9	183	10.5	Xiao et al. (2013)
Guangzhou <sup>a</sup>	2005–2006	4.49	12.0	21.0	51.8	202	66.2	9.00	18.0	131	9.00	Huang et al. (2009)

<sup>a</sup> Volume-weighted means.

<sup>b</sup> Arithmetic means.

The results of the regression analysis coefficients in this study are shown in Table 3. For the precipitation in Beijing, approximately 92.5% of the variance in  $\text{SO}_4^{2-}$  and 75.6% of the variance in  $\text{NO}_3^-$  was explained by the two independent variables ( $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ). While in Chizhou, approximately 75.7% of  $\text{SO}_4^{2-}$  variance and 26.8% of  $\text{NO}_3^-$  variance were explained by them. Thus, the percentage of the potential acidity counteracted by  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  in Beijing (90.7%) was higher than that in Chizhou (70.8%), which indicates stronger neutralization of acidity in the rainwater from Beijing than Chizhou.

The concentrations of ions in precipitation have different signatures between north and south China. The concentrations of major ions and pH values in rainwater of this study and the available data from other areas in China are presented in Table 4. The ionic compositions of rainwater in Beijing are quite close to those in Lanzhou and Xi'an which are located in northern China. The ionic compositions of Chizhou rainwater are more similar to those areas in southern China, such as Jinhua, Chengdu, the Three Gorge Reservoir (TGR), Guiyang, and Guangzhou. Comparing the data from this study with those from Feng et al. (2001) and Xu et al. (2012), obvious increasing acidity of Beijing precipitation can be seen in the last two decades. It is also observed that the concentrations of  $\text{SO}_4^{2-}$  did not exhibit a distinct increase, while the concentration of  $\text{Ca}^{2+}$  has decreased in rainwater. According to previous studies, the precipitation acidity is heavily controlled by the relative contribution of  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (Larssen and Carmichael, 2000; Xu and Han, 2009).  $\text{Ca}^{2+}$  in Beijing rainwater is mainly attributed to the dissolution of calcite in natural soil dust from arid and semi-arid areas in north China. Moreover, high concentration of alkaline soil dust is an important feature of the atmosphere in north China. The alkaline materials (mainly  $\text{CaCO}_3$  and  $\text{NH}_3$ ) in Beijing atmosphere have played an important role to neutralize the acidity of rainwater. In Beijing area, however, measures are being taken to reduce particle concentrations in air for human health, and these alkaline particles may have significant neutralizing properties. It is therefore possible that the acidification tendency of rainwater in Beijing can be attributed partly to the decrease of the alkaline ions (especially  $\text{Ca}^{2+}$ ) concentration.

### 3.4. Sources

#### 3.4.1. Correlation factors

Correlation analysis was applied to determine relationships between ionic species and to obtain the likely sources of ions. The Spearman correlation coefficients for ions and pH values in rainwater of Beijing and Chizhou are shown in Table 5. There was no association between free acidity and acidic anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) in rainwater from Beijing, while there was moderate association in Chizhou rainwater. This indicates that there are stronger neutralizing processes influencing the rainwater of Beijing. The  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions in samples from Beijing possibly originated from the ionization of sulfate and nitrate salts, which were produced from neutralizing processes (Al-Khashman et al., 2013). A strong correlation between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  is found at

both cities. It is due to the common source (fossil fuel combustion) of their precursors ( $\text{SO}_2$ ,  $\text{NO}_x$ ) as well as the similarity of their chemical behavior in rainwater and airborne particles (Al-Khashman, 2005). Significant correlations were also found between cations ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) indicating that these elements have a common source, which is soil dust. As  $\text{NH}_4^+$  mainly originates from agricultural activities, it has only moderate correlation with other cations. In addition,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are well correlated with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  at both sampling sites, suggesting that these cations could play an important role in neutralizing the acidity of rainwater.

### 3.4.2. Source contributions

Atmospheric aerosols, which include sea spray, terrestrial dust, and anthropogenic emissions, are the main sources of chemical constituents in precipitation (Chetelat et al., 2005; Négrel et al., 2007; Roy and Négrel, 2001). The chemical compositions of rainwater are expected to reflect the relative contribution of the ions from these reservoirs (Safai et al., 2004). Identifying the sea salt and non-sea salt contributions to the rainwater holds great importance to the study of the acid rain problem, as the calcium and sulfate originate from marine source are not produced by acid-base reactions and they have no significant effect on the acidity of rain (Losno et al., 1991). In order to quantify the contribution of sea salt (ss) and non-sea salt (nss) to precipitation chemistry, the sodium is assumed to be of marine origin and it is used as a reference element ( $\text{Na}_{\text{ref}}$ ). However, the selection of this element as a reference must be validated, particularly with regard to possible terrestrial influence. Since aluminum comes almost exclusively from terrestrial material, the non-sea salt Na ( $\text{Na}_{\text{nss}}$ ) can be calculated according to the following equation (Négrel and Roy, 1998):

$$\text{Na}_{\text{nss}} = \text{Al}_{\text{rw}} \times (\text{Na}/\text{Al})_{\text{nss}} \quad (1)$$

where  $\text{Al}_{\text{rw}}$  is the concentration measured in rainwater. Previous studies have shown that shale is more representative of average soils than rocks of the upper continental crust (Churc et al., 1984; Hoffman et al., 1977). Therefore, Négrel and Roy (1998) used shale as a terrestrial dust reference to correct the crustal Na with Al, and the Na/Al ratio of shale is 0.11. However, considering that the crustal Al-containing materials are mostly insoluble, the contribution of terrestrial Na could be

**Table 6**

Non-sea salt (nss) contributions (in %) for different ions in rainwater of Beijing and Chizhou.

	$\text{Cl}^-$ nss (%)	$\text{SO}_4^{2-}$ nss (%)	$\text{K}^+$ nss (%)	$\text{Na}^+$ nss (%)	$\text{Ca}^{2+}$ nss (%)	$\text{Mg}^{2+}$ nss (%)
<i>Beijing</i>						
Min	6.06	84.4	68.5	0.06	97.3	54.0
Max	93.1	99.8	99.0	30.1	99.9	95.8
Mean	55.1	98.3	94.9	7.94	99.3	84.4
<i>Chizhou</i>						
Min	43.7	98.9	94.2	0.46	99.6	30.9
Max	98.4	99.9	99.6	45.1	100	95.5
Mean	72.5	99.5	97.7	11.1	99.8	71.1

underestimated using Al concentration in soluble fractions only. According to the previous studies, the soluble Al accounted for approximately 30% of the total concentration of Al in rainwater in Mexico City and in a rural area of France (Báez et al., 2007; Colin et al., 1987). We thus correct the measured Na in rainwater ( $\text{Na}_{\text{rw}}$ ) for a non-sea salt contribution:

$$\text{Na}_{\text{ref}} = \text{Na}_{\text{rw}} - 0.11 \times \text{Al}_{\text{rw}}/0.3. \quad (2)$$

The contribution of non-sea salt components for a given element X ( $\text{X} = \text{Cl}^-, \text{SO}_4^{2-}, \text{K}^+, \text{Na}^+, \text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) is thus calculated as:

$$\text{X}_{\text{nss}} = \text{X}_{\text{rw}} - \text{Na}_{\text{ref}} \times (\text{X}/\text{Na})_{\text{sw}} \quad (3)$$

where  $(\text{X}/\text{Na})_{\text{sw}}$  is the elemental ratio of seawater.

The calculation results, expressed as percentages are shown in Table 6. The proportions of  $\text{Cl}^-$  originating from marine sources are 44.9% and 27.5% at the two sites.  $\text{SO}_4^{2-}$  is clearly dominated by non-marine sources, and as indicated by the correlation analysis above, both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in rainwater are directly associated with anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_x$ . In China, coal combustion accounts for about 70% of the commercial energy production (Aas et al., 2007), which contributes large amounts of atmospheric  $\text{SO}_2$ . Thus, coal combustion is the main source of  $\text{SO}_4^{2-}$  in rainwater. Several studies on sulfur isotope ratios for  $\text{SO}_2$  and sulfate in the atmosphere and rainwater in

**Table 5**

Spearman correlation matrix for rainwater samples collected from Beijing and Chizhou.

Beijing	pH	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
pH	1									
$\text{F}^-$	0.03	1								
$\text{Cl}^-$	−0.03	0.88 <sup>a</sup>	1							
$\text{NO}_3^-$	−0.15	0.94 <sup>a</sup>	0.90 <sup>a</sup>	1						
$\text{SO}_4^{2-}$	−0.28	0.86 <sup>a</sup>	0.84 <sup>a</sup>	0.92 <sup>a</sup>	1					
$\text{NH}_4^+$	−0.23	0.53 <sup>a</sup>	0.59 <sup>a</sup>	0.57 <sup>a</sup>	0.56 <sup>a</sup>	1				
$\text{K}^+$	−0.09	0.84 <sup>a</sup>	0.88 <sup>a</sup>	0.89 <sup>a</sup>	0.83 <sup>a</sup>	0.49 <sup>a</sup>	1			
$\text{Na}^+$	−0.10	0.90 <sup>a</sup>	0.93 <sup>a</sup>	0.92 <sup>a</sup>	0.88 <sup>a</sup>	0.56 <sup>a</sup>	0.92 <sup>a</sup>	1		
$\text{Ca}^{2+}$	−0.20	0.82 <sup>a</sup>	0.80 <sup>a</sup>	0.86 <sup>a</sup>	0.88 <sup>a</sup>	0.45 <sup>b</sup>	0.89 <sup>a</sup>	0.90 <sup>a</sup>	1	
$\text{Mg}^{2+}$	−0.02	0.86 <sup>a</sup>	0.86 <sup>a</sup>	0.86 <sup>a</sup>	0.82 <sup>a</sup>	0.46 <sup>b</sup>	0.94 <sup>a</sup>	0.93 <sup>a</sup>	0.95 <sup>a</sup>	1
<i>Chizhou</i>										
pH	1									
$\text{F}^-$	−0.42 <sup>a</sup>	1								
$\text{Cl}^-$	−0.34 <sup>b</sup>	0.47 <sup>a</sup>	1							
$\text{NO}_3^-$	−0.50 <sup>a</sup>	0.67 <sup>a</sup>	0.65 <sup>a</sup>	1						
$\text{SO}_4^{2-}$	−0.67 <sup>a</sup>	0.59 <sup>a</sup>	0.61 <sup>a</sup>	0.85 <sup>a</sup>	1					
$\text{NH}_4^+$	−0.47 <sup>a</sup>	0.55 <sup>a</sup>	0.56 <sup>a</sup>	0.80 <sup>a</sup>	0.73 <sup>a</sup>	1				
$\text{K}^+$	−0.44 <sup>a</sup>	0.51 <sup>a</sup>	0.58 <sup>a</sup>	0.88 <sup>a</sup>	0.82 <sup>a</sup>	0.89 <sup>a</sup>	1			
$\text{Na}^+$	−0.30	0.36 <sup>b</sup>	0.44 <sup>a</sup>	0.69 <sup>a</sup>	0.63 <sup>a</sup>	0.79 <sup>a</sup>	0.84 <sup>a</sup>	1		
$\text{Ca}^{2+}$	−0.53 <sup>a</sup>	0.56 <sup>a</sup>	0.55 <sup>a</sup>	0.86 <sup>a</sup>	0.83 <sup>a</sup>	0.81 <sup>a</sup>	0.89 <sup>a</sup>	0.76 <sup>a</sup>	1	
$\text{Mg}^{2+}$	−0.45 <sup>a</sup>	0.50 <sup>a</sup>	0.52 <sup>a</sup>	0.82 <sup>a</sup>	0.77 <sup>a</sup>	0.76 <sup>a</sup>	0.87 <sup>a</sup>	0.78 <sup>a</sup>	0.93 <sup>a</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).

China have also confirmed a considerable contribution of coal combustion to the sulfur compounds in the atmosphere (Mukai et al., 2001; Xiao et al., 2014; Wu and Han, 2015).  $\text{NO}_3^-$  may attribute to traffic emissions, which is an increasing important source due rapidly expanding road networks and ownership of private vehicles.

From the results in Table 6, almost all the  $\text{Ca}^{2+}$  comes from non-sea salt source, and accounts for 99.3% and 99.8% in Beijing and Chizhou, respectively. Meanwhile,  $\text{K}^+$  and  $\text{Mg}^{2+}$  also mainly originate from terrestrial sources, which may be due to the contribution of natural soil dust. It is can be seen that Beijing is surrounded by deserts and loess areas (Fig. 1), and these elements (K, Ca, and Mg) are common constituents of soil dust in Beijing area and the arid and semi-arid regions in northern China. Therefore, local and remote soil dust may be an important source of  $\text{Ca}^{2+}$  in the rainwater of Beijing. While in Chizhou, anthropogenic sources may be another input of  $\text{Ca}^{2+}$  in the rainwater in addition to crustal sources. Anthropogenic  $\text{Ca}^{2+}$  in rainwater commonly originates from coal combustion and cement factories. Rapid urban expansion and the associated construction in Chizhou, may therefore account for some of the non-sea salt calcium in Chizhou rainwater.

#### 4. Conclusions

The rainwaters in Chizhou (with a VWM pH of 4.56) were more acidic than that in Beijing (with a VWM pH of 4.85) during the period of 2011 to 2012. About 94% of the samples had pH below 5.0 in Chizhou, while only 36% of the samples had pH less than 5.0 in Beijing. The concentrations of almost all species in Beijing rainwater were higher than those in Chizhou. In particular,  $\text{SO}_4^{2-}$  concentration in Beijing rainwater was about twice that in Chizhou. The dominated ions in the precipitation were quite similar between the two cities; they are  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ .  $\text{SO}_4^{2-}$  accounted for 79.1% and 85.4% of the total measured anions,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  accounted for 86.8% and 93.8% of the total measured cations in precipitation of Beijing and Chizhou, respectively. We attempt to identify the origins of major ions by using the combination of statistical analyses methods. It is suggested that  $\text{Cl}^-$  comes from both sea salt and non-sea salt sources.  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  mainly come from anthropogenic activities, while  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  mostly originate from terrestrial sources. Local and distal soil dust aerosol may be an important source of  $\text{Ca}^{2+}$  in Beijing rainwater. Despite the idea that the  $\text{SO}_4^{2-}$  concentration in Beijing rainwater was higher than that of Chizhou, the more acidic rainwater in Chizhou was due to the weaker neutralizing effects of  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ . The linear regression analysis indicated that the percentage of the potential acidity counteracted by  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  was 90.7% in Beijing, but only 70.8% in Chizhou.

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#### Appendix A. Supplementary data

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