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Who controls the monthly variations of NH$_4^+$ nitrogen isotope composition in precipitation?

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ABSTRACT

Nitrogen isotopes of ammonium (δ^{15}N–NH$_4^+$) in precipitation have been analyzed, to study their monthly variations, from Oct. 2008 to Sep. 2009 at Guiyang, Southwest China. δ^{15}N–NH$_4^+$ values were higher in winter and lower in summer showing a strong sine curve. In summer (rainy season), raindrop may remove more light ammonia by washout process, because raindrop incorporated ^{15}NH$_3$ preferentially while left the ^{14}N in the atmosphere. At the same time, longer sunshine times imply more $h\nu$ for producing H$_2$SO$_4$ of SO$_2$ to H$_2$SO$_4$, which accelerates gaseous to particle conversion of NH$_3$ to (NH$_4$)$_2$SO$_4$ by unidirectional reactions for isotopic enriched ^{14}N. The above two aspects can somewhat cause the seasonal variation of nitrogen isotopic composition, but are not the main or direct reasons. The temperature has an opposite trend with seasonal variation of δ^{15}N values. The temperature not only causes seasonal variation of δ^{15}N values, but also increases the volatilization rate of NH$_3$ and microbial activities. And there is a robust linear relationship between temperature and δ^{15}N, showing that the temperature is the main factor to decide the monthly variation of δ^{15}N–NH$_4^+$.

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1. Introduction

Global nitrogen cycle is important for ecosystem, but has been modified by anthropogenic emissions. Ammonia, an important form of inorganic nitrogen, serves as a neutralizing agent in the atmosphere, suffering from acid rain and influencing the pH of aerosols (Galloway and Likens, 1981; Olivier et al., 1998). Ammonia can enhance the productivity of water bodies and soil after deposited as a role in fertilization in low nitrogen areas (Duce et al., 2008). However, excessive nitrogen loadings will cause negative effect on the ecosystems and atmospheric environment (Jung et al., 1997; Krupa, 2003) as well as human health (Townsend et al., 2003). Atmospheric nitrogen deposition showed a sharp increase in recent decades due to extensive human activities. For instance, Guiyang has increased 1.8 times from 1984 in wet deposition (Galloway et al., 1987; Xiao et al., 2010a), which has caused serious water pollution.

Information on the sources of NH$_x$ is important for pollution control. Yet, it is not easy to understand the NH$_x$ sources only by the measurement of NH$_x$ concentrations in gas, aerosol and precipitation. However, the stable nitrogen isotope (δ^{15}N) has been proved

to be important in examining the sources of nitrogen (Heaton, 1986; Xiao and Liu, 2002; Xie et al., 2008). δ^{15}N in precipitation has been used successfully to indentify ammonium sources in some sites shown in Table 1, such as Chengdu, China (Li et al., 2007), North China Plain, China (Zhang et al., 2008), Jülich, Germany (Freyer, 1978), Pretoria, South Africa (Heaton, 1987), Niigata Platin, Japan (Fukuzaki and Hayasaka, 2009). The ammonium sources in the atmosphere are mainly from animal excreta, fossil fuel combustion, and fertilizer use (Klaassen, 1991; Wiliam and Anne, 1992; Xiao et al., 2010b). The monthly variations of ammonium sources may affect the monthly variations of δ^{15}N–NH$_4^+$ values in precipitation (Jia and Chen, 2010), which can be also modified by chemical and physical process in atmosphere (Moore, 1977; Freyer, 1978). ^{15}N preferentially incorporated into raindrop by exchange reactions and left light isotope in the atmosphere, so that the δ^{15}N–NH$_4^+$ value in a rain event becomes more negative (Heaton, 1986; Xiao and Liu, 2002). And ammonium in atmospheric aerosol is enriched in ^{15}N compared to ammonium in precipitation and gaseous ammonia (Moore, 1977; Pavuluri et al., 2010). However, Freyer (1978) thought nitrogen isotopic fractionation during rain-out and washout is controlled by unidirectional reactions.

In this study, we investigated the ammonium concentrations and the δ^{15}N signatures of precipitation from Oct. 2009 to Sep. 2010 at Guiyang, Southwest China, aiming to investigate the sources of atmospheric ammonium. By analyzing the monthly average

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Table 1
Mean $\delta^{15}N$ values of ammonium in precipitation at different sites.

sites	Information	Period	$\delta^{15}NH_4^+$ (‰)	Refs.
Guiyang, China	Urban	Oct. 2008 to Sep. 2009	−15.9	This study
Beijing, China	Suburban	Apr. to Dec. 2005	+0.5	Zhang et al., 2008
Yangtze River Delta, China	Rural (agriculture)	Jun. 2003 to Jul. 2005	+1.0	Xie et al., 2008
Chengdu, China	Urban	Dec. 2003 to Aug. 2004	−6.6	Li et al., 2007
Guangzhou, China	Urban	Jan. to Dec. 2008	−5.1	Jia and Chen, 2010
Colorado, USA	Urban	–	−1.4	Moore, 1977
Julich, Germany	Urban	Winter 1974 to autumn 1976	−12.1	Freyer, 1978
Pretoria, South Africa	Suburban	Mar. 1980 to Aug. 1984	−3.8	Heaton, 1987
Tennessee and Virgina, USA	Rural	Jul. 1987 to May 1988	−3.4	Garten, 1992
Lewes, USA	Coastal	May 1993 to Dec. 1994	−0.5	Russell et al., 1998
Niigata Platin, Japan	Rural (mountain)	May 2001 to Nov. 2002	−3.7	Fukuzaki and Hayasaka, 2009

$\delta^{15}N–NH_4^+$ values in precipitation, we also attempt to know who controls the monthly variations of NH_4^+ nitrogen isotope composition in precipitation.

2. Materials and methods

2.1. Description of study area

The Guiyang City, the capital of Guizhou Province, surrounded by mountains (Fig. 1), has a subtropical monsoon climate with an annual average temperature of 15.3 °C, annual rainfall of 1174 mm, and the relative humidity (RH) of about 77%. The concentration of SO_2 in atmosphere is 0.064 mg m^{-3} in 2008 and 0.058 mg m^{-3} in 2009, respectively (Xiao et al., 2011).

The possible anthropogenic sources of air pollutants over Guiyang city, include emissions from industrial processes, transportation and biomass combustion in the northwest, and domestic and commercial sewage in Nanming River in the south (Fig. 1), which has been believed to be the main source for NH_x (Xiao et al., 2010b). Atmospheric N deposition at Guiyang is characterized by a low NO_x concentration and high NH_x concentration due to low traffic intensity and high ammonia emission of sewage (Liu et al., 2008). Atmospheric NH_x is usually rapid deposited within 500m of release source (Sutton et al., 1998) and has a short resident of less than 2 days in the atmosphere at Guiyang (Xiao and Liu, 2002). Furthermore, there are no significant correlation between

$\delta^{15}N–NH_4^+$ and wind direction at Guiyang (Table 2). So, the main ammonium sources of our sampling site are believed to be the sewage in Nanming River (Fig. 1).

2.2. Methodology

2.2.1. Sampling and chemical analysis

The sampling site is located in the State Key Laboratory of Environmental Geochemistry, CAS, about 500 m far away from the downtown of Guiyang city. Rainfall samples were collected by using two aluminous sheets (projection area: 2.1 m × 1.7 m), which was fixed 1.5 m above the roof of a building by aluminous-alloy bracket. Prior to use, the aluminous sheets were cleaned with Milli-Q water and dried. Between rain events, the collection device was covered with a clean large polyethylene sheet in order to avoid the dry deposition and other pollutants. When it begins to rain, a clean large polyethylene sheet was removed and rainwater was collected from the aluminous sheet into 1.5 L pure plastic bottles. The bottles were acid-cleaned prior to use. The number of all the rainwater samples was 1235.

After collection, portions of the samples were immediately used for pH, electrical conductivity (EC) and temperature (T) determination with a pH meter. After the samples were passed through a 0.45 μm acetate membrane filters, a small aliquot was stored in two clean 10 ml-centrifuge tubes for anion and cation (acidification with HCl) determination, while the other aliquots were stored in
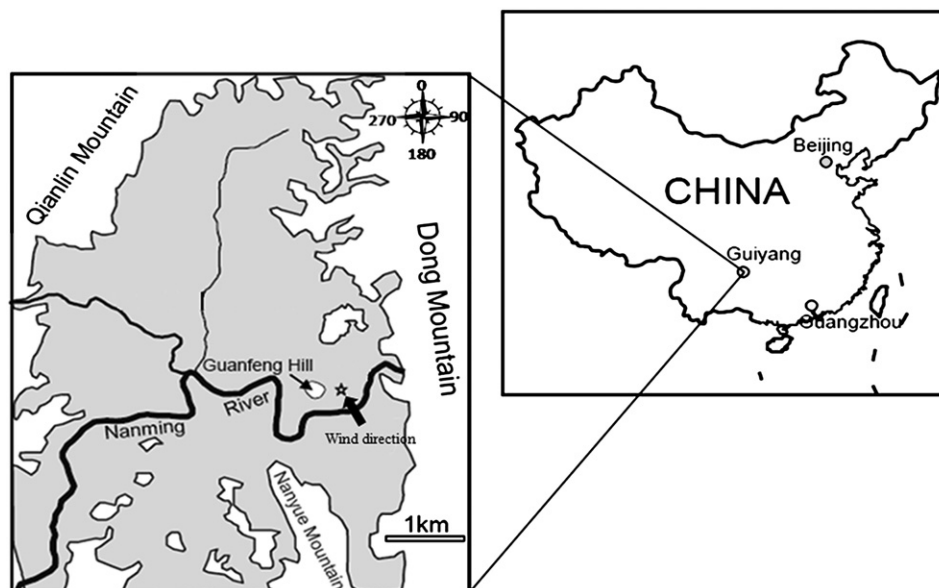

Fig. 1. Map showing sampling location in Guiyang.

Table 2
Temporal variations of weather conditions at Guiyang.

Month	Temperature, °C	Humidity, %	Precipitation, mm	Wind direction	Wind speed, m s^{-1}	Sunshine, h
2008.10	16.6	82	57.1	105	2.4	2.1
2008.11	10.5	72	61.6	111	2.4	2.3
2008.12	6.4	76	14.0	132	2.3	1.9
2009.1	3.8	73	11.2	101	2.5	1.5
2009.2	7.7	77	24.2	113	3.0	2.3
2009.3	11.4	71	31.5	129	2.8	2.6
2009.4	14.6	77	225.0	122	2.4	1.4
2009.5	18.6	76	81.8	136	2.6	2.3
2009.6	21.6	73	116.2	161	2.1	2.1
2009.7	22.8	76	158.5	140	2.5	3.1
2009.8	23.7	69	80.7	141	2.5	4.9
2009.9	21.7	67	31.7	130	2.5	5.3
Average	15.0	74	74.5	126	2.5	2.6
R value[a]	0.83[b]	0.17	0.73[c]	0.19	0.45	0.08
P value[a]	0.002[b]	0.6	<0.01[c]	0.6	0.1	0.8

The data of temperature, humidity, wind direction and wind speed is from Guizhou Meteorological Bureau, the data of sunshine is from Guiyang Statistical Yearbook 2009 and 2010.

[a] R and P value between $\delta^{15}N-NH_4^+$ and different weather conditions.
[b] Not included Aug.
[c] R and P value of logarithm.

a refrigerator at 4 °C for isotopic analysis after poisoned by adding HgCl$_2$. NH$_4^+$ concentrations were determined by spectrophotometry after treatment with Nessler's reagent, and the detection limit was better than 0.1 mg L^{-1}.

2.2.2. Isotopic analysis

$\delta^{15}N-NH_4^+$ was analyzed after NH$_4^+$ was separated from rainwater by cation exchange using cation resin (Dowex® 50W-X8, 50-mesh H$^+$ form) at the laboratory according to the modified methods reported by Garten (1992). Ion exchange resins were loaded into glass columns (15 mm diameter × 100 mm long) which contained glass wool plugs at the bottom and the top of the resin column. During the separation, the filtered rainwater sample was siphoned into the columns without being exposed to the atmosphere. Then 45 mL of 2 mol L^{-1} KCl solution was used to elute ammonium from the columns and then the eluate was moved into a diffusion bottle (60 ml NALGENE®). The sorption efficiency of ammonium by Dowex® 50W-X8 is greater than 98% (Xiao and Liu, 2002). Recovery of ammonia from the columns during the elution step was about 100% (Garten, 1992). No significant fractionation effects were introduced during ion exchange (Garten, 1992).

Modified from the methods described by Xiao and Liu (2002), diffusion was carried out to collect ammonia-N with an acid solution (10 mL tube with 1 mL 1 mol L^{-1} KHSO$_4$) from the eluate for nitrogen isotope analysis. 10 ml 2 mol L^{-1} NaOH was added into the diffusion bottle and the cap was tightened quickly. Then the diffusion bottles were putted into an oven (the temperature was about 55 °C) for 10 days and the diffusion liquid was ensured to be alkaline. The diffusing procedure reliably collect more than 95% N from the eluate and cause no significant fractionation of nitrogen isotopes. The solution of (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$ in 10 mL tube was transferred into a 3 mL tube and dried in a cool drier.

Nitrogen isotopes were measured in the State Key Laboratory of Environment Geochemistry at Institute of Geochemistry, Chinese Academy of Sciences. About 50 μg N of ammonium collected from the rainwater samples were weighed and folded into small tin cups (φ3.5 × 5). After combustion at 1030 °C and separation of N$_2$ on-line, nitrogen isotopes were analyzed by a GV Isoprime continuous flow isotope ratio mass spectrometer for $^{15}N/^{14}N$ analyses. Analysis of two potassium nitrate standard matter provided by the laboratory, gave a mean (±SD) $\delta^{15}N_{air}$ value of +21.38‰ and −1.89‰ with actual agreed values of +(21.17 ± 0.34)‰ ($n = 6$) and −(1.98 ± 0.16)‰ ($n = 6$), and ammonium sulfate standard (IAEA-N2) respectively gave a mean (±SD) $\delta^{15}N_{air}$ value of +20.3‰

with actual agreed values of +(20.24 ± 0.06)‰ ($n = 6$). The analytical precision was better than 0.1‰.

2.2.3. Statistical analysis

Statistical analysis was conducted by SPSS 17.0 statistical program, and graphs were mainly created with SigmaPlot 2000 software (both SPSS Science, Chicago, USA).

3. Results

The monthly volume-weighted average ammonium concentrations ranged from 0.03 to 0.46 mmol L^{-1} (Fig. 2a), with the average of 0.11 mmol L^{-1}. And the $\delta^{15}N-NH_4^+$ ranged from −19.8 to −10.4‰ (Fig. 3), with the average of −15.9‰. Relative to the reported data (Table 1), the $\delta^{15}N-NH_4^+$ values at Guiyang city were low suggestive of a source from domestic and commercial sewage. The ammonium concentrations and $\delta^{15}N-NH_4^+$ both showed lower values in summer and higher values in winter. Moreover, ammonium concentrations changed with precipitation in a logarithm decay (Fig. 2b), and a strong sine curve relationship was found between $\delta^{15}N-NH_4^+$ values and season ($y = -15.6 + 4.0 \sin(2\pi x/10.3 + 5.0)$, $R = 0.90$, $P = 0.005$). However, most of the $\delta^{15}N$ values in Aug. 2009 (−13.1‰) are higher than those in Jul. (−18.3‰) and Sep. (−17.3‰) (Fig. 3). There are good correlations between $\delta^{15}N-NH_4^+$ values and temperature or precipitation, but not between $\delta^{15}N-NH_4^+$ values and the other weather parameters (Table 2).

4. Discussion

4.1. Isotopic effect of washout

Precipitation can remove various matters in the atmosphere (Xiao et al., 2010a), such as gaseous ammonia (NH$_3$) and aerosol ammonium (NH$_4^+$) (Fig. 2b), with different washout rate of change, 48% and 30%, respectively (Wang, 1999). The low precipitation amount results in low relative washout of ammonium and may affect nitrogen isotopic fractionation during NH$_3$-washout. The change of ammonium concentrations with precipitation presented a logarithm decay trend because atmospheric NH$_3$ is always in quasi-equilibrium with rainfall drop (Wang, 1999). Isotopic fractionation during the uptake of atmospheric ammonium by rain droplets has been studied by Freyer (1978), Heaton (1986) and Xiao and Liu (2002), which showed opposing results. In this study, $\delta^{15}N-NH_4^+$ shows higher values in winter than in summer (Fig. 3),
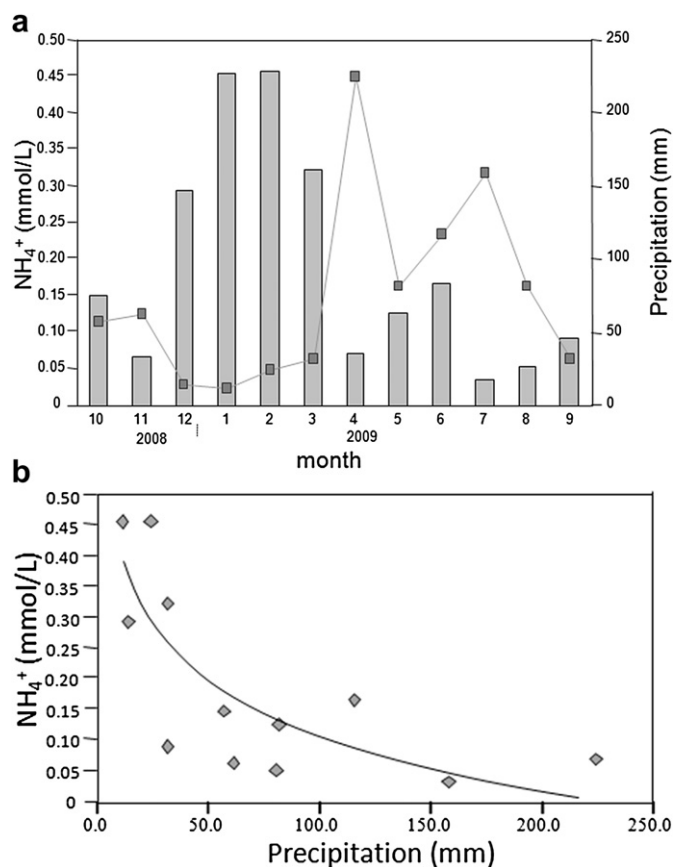
Fig. 2. Monthly variations of NH_4^+ and precipitation (a), and the relationship between NH_4^+ and precipitation (b).

and there is a logarithm relationship between $\delta^{15}N-NH_4^+$ and precipitation both at Guiyang and Guangzhou (Fig. 4a), suggested that ^{15}N is preferentially incorporated into aqueous solution, thus rendering the remaining free NH_3 depleted in ^{15}N. Apart from the above aspect, we note that the monthly variation of $\delta^{15}N-NH_4^+$ may be affected by other weather conditions as listed in Table 2.

Low precipitation intensity in precipitation can effectively scavenge atmospheric matters in different sizes, but rainstorm
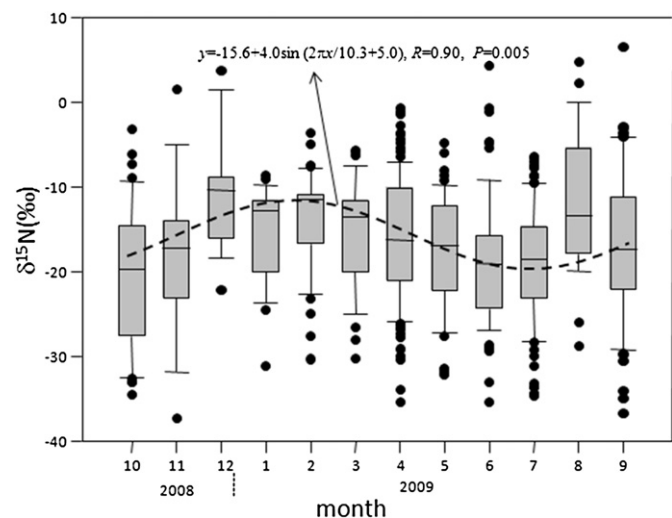

Fig. 3. Monthly variations of $\delta^{15}N-NH_4^+$ values. The boundary of the box indicates the 25th and 75th percentile. The lines within the box mark the mean. Whiskers above and below the box indicate the 90th and 10th percentiles.

mainly scavenges soil-derived of high $\delta^{15}N-NH_4^+$ values because of different efficiency (Freyer, 1978). Freyer (1978) had found the $\delta^{15}N$ value in rainstorm (−9.7‰) was higher than that in other rainfalls (−12.6‰). In Aug. 2009, the mean precipitation intensity is more than 20 mm h^{-1}, higher than that in July and Sep. So the $\delta^{15}N-NH_4^+$ values of most samples in this month and the monthly average $\delta^{15}N-NH_4^+$ value are much higher than that of the other two months (Fig. 3).

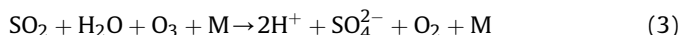### 4.2. Isotopic effect of sunshine hours and unidirectional reactions

The atmospheric NH_3 is absorbed by acid matter, such as H_2SO_4 and HNO_3 (Formula (4)). The reactions, during which ^{14}N is preferentially absorbed by H_2SO_4 into NH_4NO_3, $(NH_4)_2SO_4$ or NH_4HSO_4 (Freyer, 1978; Ottley and Harrison, 1992; Pavuluri et al., 2010), are unidirectional. SO_4^{2-} is the most abundant chemical component and accounts for 69.3% of anion in precipitation (Xiao et al., 2010a) and 86.5% of anion in TSP (Xiao and Liu, 2004). Therefore, the predominant SO_2 oxidation pathways may be considered as a driver for seasonal variations of $\delta^{15}N-NH_4^+$. There are three oxidation pathways of SO_2 in the atmosphere: photo-oxidation (Formula (1)), reaction with free radicals (Formula (2)), and heterogeneous chemical processes (Formula (3)) (Wang, 1999). The rate of photo-oxidation is about 1% SO_2/h (Formula (1)), so if the sunshine hour is longer, the oxidation products would be more. Moreover, because the formation of free radicals need sunshine, free radicals such as OH were found lower in winter and higher in summer. As can be seen from Table 2, the summer (May–July) is characterized by sunshine hours more than about 1.8 and SO_2 concentrations more than about 0.5 (Fig. 4b). Both the more sunshine hours and lower SO_2 concentration in summer increase the importance of absorbed reaction. Oxidation pathways due to different seasonal weather condition would lead to lower $\delta^{15}N-NH_4^+$ values in summer and higher values in winter, which is the case from our results (Fig. 4b). In addition the average value of $\delta^{15}N-NH_4^+$ in daytime is −2.4‰ lower than in nighttime. The same result was found in aerosols at Chennai (Indian), which $\delta^{15}N$ was higher in daytime than in nighttime during both early and late winter (Pavuluri et al., 2010). However, there is no significant correlation between sunshine hours and the $\delta^{15}N-NH_4^+$ values at Guangzhou ($R = 0.09$, $P = 0.8$) (Jia and Chen, 2010) and at Guiyang ($R = 0.08$, $P = 0.8$), meaning that sunshine is not the most important factor to affect the seasonal variations of the $\delta^{15}N-NH_4^+$ values.

$$SO_2 + h\nu(0.33 \sim 0.24\ \mu m) \rightarrow SO_2^* \rightarrow \cdots \rightarrow H_2SO_4 \quad (1)$$
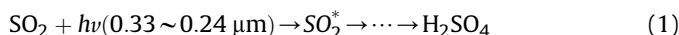
where * means that SO_2 is in the excited-state

$$SO_2 + 2OH + M \rightarrow H_2SO_4 + M \quad (2)$$

where M is catalyst, the same as Formula (3)

$$SO_2 + H_2O + O_3 + M \rightarrow 2H^+ + SO_4^{2-} + O_2 + M \quad (3)$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \quad (4)$$

4.3. Isotopic effect of temperature and exchange reactions

The reaction of NH_3 with H_2SO_4 is a kinetic process (unidirectional reactions), favoring ^{14}N in the product. Their product will stay long in the atmosphere, but stoichiometric equilibrium is attained within several minutes (Heaton et al., 1997). Moreover, NH_3 is in quasi-equilibrium with NH_4^+ in aqueous solution. Both exchange reactions occur such as Formulas (5) and (6) (Heaton et al., 1997). The $\delta^{15}N-NH_4^+$ values will become higher than
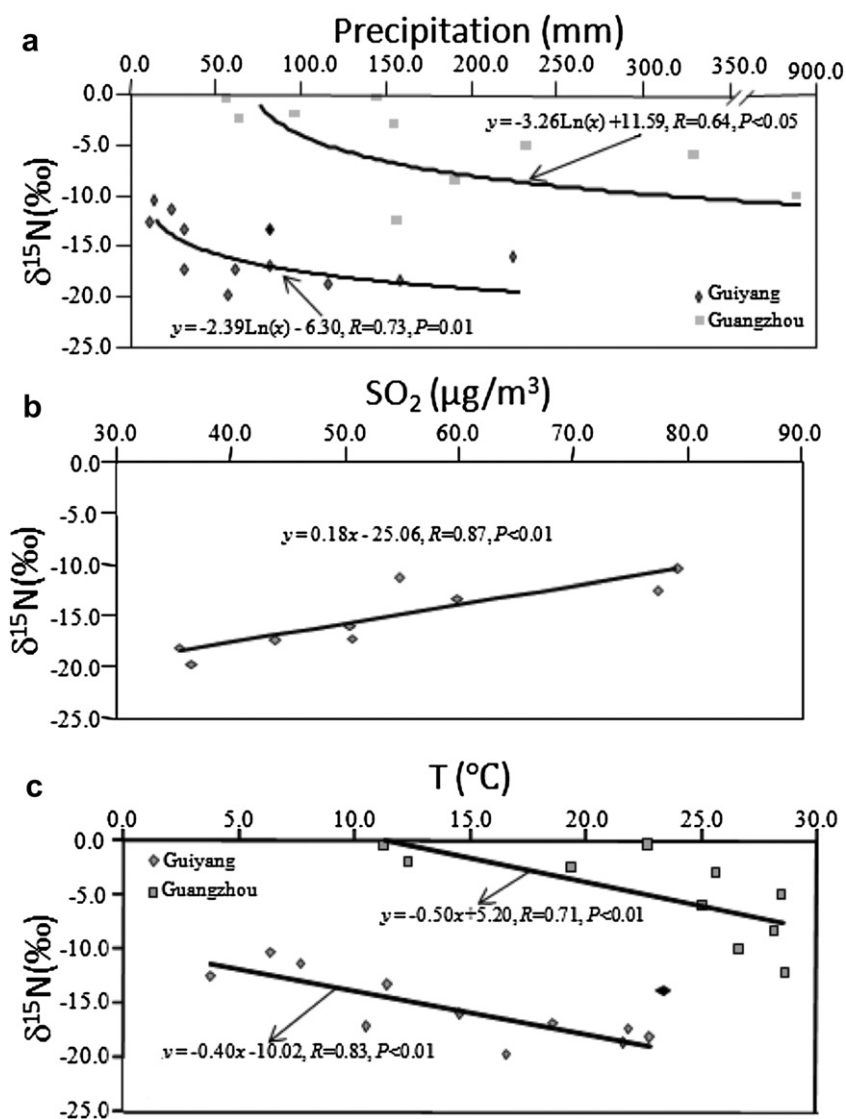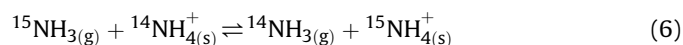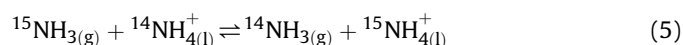
Fig. 4. Relationship between $\delta^{15}N$–NH_4^+ values and various weather conditions. (a) Monthly precipitation (Guangzhou precipitation data from Guangzhou Bureau of Statistics, http://www.gzstats.gov.cn/, and $\delta^{15}N$–NH_4^+ data of Guangzhou from Jia and Chen, 2010); (b) monthly SO_2 concentrations in atmosphere (SO_2 data from http://www.gygov.gov.cn/); (c) monthly temperature (Guiyang temperature data from Guizhou Meteorological Bureau, Guangzhou temperature data from Guangzhou Bureau of Statistics, http://www.gzstats.gov.cn/, and $\delta^{15}N$–NH_4^+ data of Guangzhou from Jia and Chen, 2010).

$\delta^{15}N$–NH_3 after exchange reactions occur, the isotopic enrichment factor was estimated to be $+33\permil$ for Formula (6) (Heaton et al., 1997) and $+36\permil$ for Formula (5) (Moore, 1977) at 25 °C. Many previous studies have reported higher $\delta^{15}N$–NH_4^+ values of aerosol than those of gaseous ammonia in the atmosphere, such as in Niigata, Japan (Hayasaka et al., 2004) and in Chennai, India (Pavuluri et al., 2010). Moreover, the $\delta^{15}N$–NH_4^+ values in a sequence of rain events become more negative, suggesting that ^{15}N is preferentially incorporated into aqueous solution and led to the remaining NH_3 depleted in ^{15}N in the atmosphere (Fig. 4a) (Heaton, 1986; Xiao and Liu, 2002).

$$^{15}NH_{3(g)} + {}^{14}NH_{4(l)}^+ \rightleftharpoons {}^{14}NH_{3(g)} + {}^{15}NH_{4(l)}^+ \tag{5}$$

$$^{15}NH_{3(g)} + {}^{14}NH_{4(s)}^+ \rightleftharpoons {}^{14}NH_{3(g)} + {}^{15}NH_{4(s)}^+ \tag{6}$$

Light isotope molecules are usually enriched in vapor phase and enrichment factor depends on the temperature at which two cogenetic phases are in equilibrium (Richet et al., 1977). The temperature is high in summer and low in winter at Guiyang (Table 2) and has a strong sine curve relationship with season ($y = 15.0 + 9.1\ \sin(2\pi x/12.4 + 2.6)$, $R = 0.99$, $P < 0.0001$), which is opposite with the $\delta^{15}N$–NH_4^+ seasonal sine curve. From Fig. 4c, a decline linear relationship was found between $\delta^{15}N$–NH_4^+ and temperature, not only at Guiyang but also at Guangzhou, showing that the enrichment factor becomes low with increasing temperature. Furthermore, the temperature can increase the volatile rate of NH_3 from sewage (ammonia loss rate $= 23.6 + 1.19$ temperature) (Sommer et al., 1991; Song and Fan, 2003) and more light NH_3 molecules will release to the atmosphere as shown in Formula (5). With the temperature increased, microbial activity will increase and more organic matter will be decomposed (Formula (7)) (Hoefs, 2009). The higher temperature and stronger active biological activities facilitated organic N mineralization and NH_3 volatilization from excreta and N polluted water bodies (Xie et al., 2008).

$$\text{organic matter} \rightarrow NH_4 \tag{7}$$

Compared with precipitation amount effect on the $\delta^{15}N$–NH_4^+ values, we found that the relationship with temperature had

better R and P values (Table 2 and Fig. 4c), indicating temperature affects $\delta^{15}N-NH_4^+$ values greater than precipitation amount does. As shown in Figs. 2a and 3, the precipitation is highest in Apr., but it does not influence the sine curve, further evidencing that the seasonal variations of $\delta^{15}N-NH_4^+$ values are controlled by temperature.

5. Conclusions

The volume-weighted ammonium concentrations and $\delta^{15}N-NH_4^+$ in precipitation at Guiyang averaged 0.11 mmol L^{-1} and −15.9‰, respectively, showing that atmospheric NH_4^+ was mainly from domestic and commercial sewage. By combining variations in $\delta^{15}N-NH_4^+$ with different seasonal patterns of weather condition, we believed that temperature was the most important factor that led to the observed temporal isotopic changes. There are several reasons that higher temperature caused lower $\delta^{15}N-NH_4^+$ in summer: firstly, the temperature is an important factor that influences the isotopic fractionation factor; secondly, higher temperature increases the volatile rate of NH_3 (light isotope) from sewage and release; and thirdly, higher temperature increases the microbial activities. The other weather factors, such as sunshine hours and precipitation, may also affect the seasonal variation.

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