



# $\delta^{15}\text{N}\text{-NH}_4^+$ variations of rainwater: Application of the Rayleigh model



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## ABSTRACT

It is generally difficult to measure atmospheric gaseous ammonia concentration and to identify its sources by isotopic technique due to the isotopic fractionation after it enters the atmosphere. In this study, Rayleigh model was successfully used to quantify atmospheric concentration and isotopic composition of gaseous ammonia based on sampling of 20 rain events from October 1st, 2008 to September 30, 2009 in Guiyang, southwest China. The estimated gaseous ammonia concentration was  $25.7 \pm 36.3 \mu\text{g}/\text{m}^3$  and estimated isotopic composition was  $-16.8 \pm 4.9\%$  in Guiyang. The study also showed that estimated enrichment factor was  $+10.4 \pm 4.3\%$ , inferring that large nitrogen isotopic fractionation occurred during exchange reactions in most of the rain events. The atmospheric ammonium deposition was further estimated to be  $38.1 \text{ kg}/\text{ha}/\text{year}$ . However, there is no validation for the approach from an actual gas phase  $\text{NH}_3$  measurement to examine the model in this study.

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## 1. Introduction

Ammonia volatilization is an important pathway to account for atmospheric ammonia in many Chinese agricultural areas, particularly those with calcareous soils (Lin and Liang, 1992). The contribution of ammonia volatilization is higher from wastes of domestic animal than from fertilizer use in China because domestic animal production has increased greatly since the late 1980s (Bouwman et al., 2002; Xiao et al., 2012, 2013; Liu et al., 2013). In Guiyang, southwest China, for example, the ammonium concentration has increased about for 1.8 times from 1984 to 2009 in rainwater (Galloway et al., 1987; Xiao et al., 2012). Excessive nitrogen inputs have led to debate on the nitrogen balance between aquatic and terrestrial ecosystems, and many negative effects on atmospheric environment and human health (Krupa, 2003; Huang et al., 2011; Hu et al., 2014).

Knowledge of the sources and behaviors of ammonia is a key for pollution control. However, it is difficult to understand the ammonia sources and behaviors only by the traditional analysis of ammonia concentration. Stable nitrogen isotopic [ $\delta^{15}\text{N}$  (‰ vs at-air) =  $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$ ] analysis has become a robust tool in atmospheric environment research.  $\delta^{15}\text{N}\text{-NH}_4^+$  has been used to investigate the sources of nitrogen in many areas (Freyer, 1978; Heaton, 1987; Garten, 1992; Xiao et al., 2012). The nitrogen isotopic composition in rainwater can be affected by in-cloud and below-cloud chemical-physical processes (Heaton, 1987; Xiao et al., 2012). The exchange reaction and unidirectional reaction have been both observed in rain process (Freyer, 1978; Heaton, 1987), but the reasons for these phenomena are not clear.

In this study, we report the ammonium  $\delta^{15}\text{N}$  trend of 20 sequentially sampled rain events from October 1st, 2008 to September 30, 2009 in Guiyang, southwest China. The main objective of our investigation is to study whether the Rayleigh model can be used to estimate atmospheric concentration and source of ammonia, and to trace the isotopic processes during rain events.

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## 2. Materials and methods

### 2.1. Sample collection and chemical and isotopic analysis

The sampling location is in the Institute of Geochemistry, Chinese Academy of Sciences, which locates in a typical urban area. The sequential sampling of rainwater was carried out by a custom sampler, made up of two aluminum sheets (projection area: about 7.2 m<sup>2</sup>), and fixed at 1.5 m above the roof of a 3 m building. The sheets were cleaned by Milli-Q water and dried in air before use. 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, the clean large polyethylene sheet was removed and sequential sampling rainwater was collected from the aluminous sheet into 1.5 L pure plastic bottles (some were more or less than 1.5 L, more information in Table S1).

After collection, pH, electrical conductivity and temperature were immediately measured by a WTW Multi 360i pH meter. Water samples were filtered with thoroughly cleaned 0.45 μm acetate membrane filters.

The data of NH<sub>4</sub><sup>+</sup> and δ<sup>15</sup>N were from our previous field data published earlier (Xiao et al., 2012) and shown in Table S1.

### 2.2. The Rayleigh model description

Gaseous ammonia that dissolves into raindrops and ammonium particles are both captured. Ammonium concentrations in particles were reduced only about 34% in rainy days in Guiyang (Xiao and Liu, 2004). The scavenging coefficients of gaseous ammonia and 0.5 μm ammonium particles are between 0.6 and 12 h<sup>-1</sup>, and 1 × 10<sup>-4</sup> h<sup>-1</sup> in below-cloud scavenging, respectively (Shimshock and Pena, 1988; Seinfeld and Pandis, 1998; Mizak et al., 2005), suggesting that the below-cloud scavenging of ammonium particles can be ignored. More than 88% of ammonium in rainwater comes from below-cloud scavenging of gaseous ammonia in agricultural or industrial areas (Oberholzer et al., 1993; Shen et al., 1993; Mizak et al., 2005). Further, the initial in-cloud ammonium concentration is also considered to be negligible because ammonium concentration was below detection limit in cloud water in Guiyang (Shen et al., 1993; Tanner et al., 1997; Xiao and Liu, 2002). The Rayleigh model can be described by equation below:

$$R_i = R_0 f^{\alpha-1} \quad (1)$$

where  $R_0$  is the nitrogen isotopic ratio of initial ammonia while  $R_i$  is instantaneous isotopic ratio of residual ammonia in the atmosphere; and  $f$  is the proportion of residual ammonia.

According to the hypothesis, rain drops only acquire ammonia from atmospheric gaseous ammonia and no new ammonia gas enters into the atmosphere during a rain event. So, there is a mass balance and an isotopic balance between atmospheric gaseous ammonia and ammonium in rainwater:

$$C_{g0}ZA_t - C_{gi}ZA_t = \sum_{i=1} C_{li}V_i \quad (2)$$

$$C_{g0}ZA_t \times \delta^{15}N_{g0} - C_{gi}ZA_t \times \delta^{15}N_{gi} = \sum_{i=1} C_{li}V_i \times \delta^{15}N_{li} \quad (3)$$

where  $C_{g0}$ (μg/m<sup>3</sup>),  $C_{gi}$ (μg/m<sup>3</sup>) and  $C_{li}$ (mg/L) are initial atmospheric ammonia concentration, instantaneous ammonia concentration after  $i$  rainwater sample, and ammonium concentration in  $i$  rainwater sample, respectively;  $\delta^{15}N_{g0}$ ,  $\delta^{15}N_{gi}$  and  $\delta^{15}N_{li}$  are initial atmospheric ammonia nitrogen isotopic composition, instantaneous ammonia nitrogen isotopic composition after  $i$  rainwater sample, and ammonium nitrogen isotopic composition in  $i$  rainwater sample, respectively;  $V_i$  (L) is the volume of  $i$  rainwater sample;  $Z$  (m) is the cloud base height calculated by temperature and relative humidity; and  $A_t$  is the projection area of sampler (7.2 m<sup>2</sup>).

The Rayleigh equation of ammonia in the atmosphere is:

$$\delta^{15}N_{gi} = \delta^{15}N_{g0} + \varepsilon \ln \left( \frac{C_{gi}}{C_{g0}} \right) \quad (4)$$

where  $\varepsilon$  is isotope enrichment factor.

Eqs. (2) and (3) are substituted into Eq. (4), we get:

$$\delta^{15}N_{g0} - \left( \frac{C_{g0}ZA_t}{\sum_{i=1} C_{li}V_i - 1} \right) \varepsilon \ln \left( 1 - \frac{\sum_{i=1} C_{li}V_i}{C_{g0}ZA_t} \right) = \frac{\sum_{i=1} (C_{li}V_i \times \delta^{15}N_{li})}{\sum_{i=1} C_{li}V_i} \quad (5)$$

Then,  $\delta^{15}N_{g0}$ ,  $C_{g0}$  and  $\varepsilon$  can be calculated by the software of 1stOpt, used the actual data of  $C_{li}$ ,  $V_i$  and  $\delta^{15}N_{li}$  in rainwater in Table S1 (detail calculated information in Supplementary Text S1). Because the calculated  $C_{g0}$  depends on cloud base height ( $Z$ ), which is calculated by temperature and relative humidity, it increases a propagation of error in calculated  $C_{g0}$ .

And the atmospheric ammonium deposition defined as:

$$\text{Annual atmospheric ammonium deposition} = \text{annual average concentration of NH}_3 \times \text{cloud base height} \times 365.$$

## 3. Results

### 3.1. Results of Rayleigh model

The estimated NH<sub>3</sub> concentrations ranged from 1.4 μg/m<sup>3</sup> to 129.5 μg/m<sup>3</sup>, with the average of 25.7 ± 36.3 μg/m<sup>3</sup> (Table 1). The average concentration of NH<sub>3</sub> was a little higher than those reported in many cities (Meng et al., 2011 and references within), because the ammonia emission is higher in Guiyang, and/or the error may come from both the calculation itself of software and cloud base height calculated by temperature and relative humidity. According to initial NH<sub>3</sub> concentrations and cloud base height, the atmospheric NH<sub>3</sub> deposition was estimated to be 38.1 kg/ha/year in Guiyang, close to the results of 30.2 kg/ha/year (maximum value of 44.7 kg/ha/year) reported by Liu et al. (2008). The contribution of wet deposition to the total ammonium deposition was 49% in Guiyang (Xiao and Liu, 2011), and the ammonium concentration in rainwater was 112.9 μeq/L and the amount of rainfall was 1174 mm (Xiao et al., 2012, 2013), resulting in an atmospheric NH<sub>3</sub> deposition of 36.7 kg/ha/year.

**Table 1**Precipitation event characteristics and application of the Rayleigh model to calculated initial  $\delta^{15}\text{N}$  value, concentration and enrichment factor ( $\epsilon$ ).

Date/order	Duration	Intensity (mm/h)	Precipitation (mm)	<sup>a</sup> Cloud base height (m)	Initial $\delta^{15}\text{N}$ (‰)	Initial $\text{NH}_3$ concentration ( $\mu\text{g}/\text{m}^3$ )	Enrichment factor $\epsilon$ (‰)
2008.10.31/01	01:16–02:24	1.44	2.08	611	−18.5	19.1	6.4
2009.01.05/02	03:00–18:33	0.12	1.93	419	−13.4	67.4	5.7
2009.02.26/03	18:00–22:00	0.44	1.78	116	−16.6	129.5	9.5
2009.02.27–1/04	00:00–00:55	5.00	4.58	352	−18.0	85.6	10.5
2009.02.27–2/05	19:00–21:36	3.19	8.31	479	−8.1	104.0	1.2
2009.03.29/06	21:00–23:25	1.18	2.85	1568	−14.1	9.3	11.3
2009.03.30/07	22:55–23:20	3.00	1.25	1409	−13.5	2.6	7.4
2009.04.08/08	22:10–01:21	1.45	4.06	1249	−18.7	19.7	11.0
2009.04.11–1/9	19:46–21:52	9.14	19.19	3055	−43.9	18.0	34.8
2009.04.11–2/10	23:00–00:20	5.19	6.92	668	−17.1	24.9	8.2
2009.04.15/11	19:46–20:18	3.80	2.15	2799	−14.5	4.1	8.0
2009.04.18/12	16:50–21:07	0.41	1.74	1897	−15.5	4.9	12.7
2009.04.28/13	22:00–00:43	2.61	7.08	446	−16.9	44.2	7.6
2009.05.05/14	20:50–22:30	5.22	8.79	1697	−13.2	32.2	1.1
2009.05.19/15	10:54–18:00	0.35	2.48	946	−33.8	8.9	14.9
2009.06.01/16	20:30–21:28	1.87	1.81	956	−17.5	7.4	15.7
2009.07.02/17	15:50–16:18	2.68	1.25	1660	−16.1	2.0	3.4
2009.09.15/18	02:00–03:09	1.57	1.81	1926	−11.5	1.5	8.9
2009.09.20/19	11:00–11:08	6.25	0.83	1660	−12.0	1.4	20.3
2009.09.27/20	03:00–03:42	3.98	2.92	1668	−18.7	3.6	15.2
Average	–	2.94	4.19	1279	$-16.8 \pm 4.9^b$	$25.7 \pm 36.3^b$	$10.4 \pm 4.3^b$
Max	–	9.14	19.19	3055	−8.1	129.5	34.8
Min	–	0.12	0.83	116	−43.9	1.4	1.1

<sup>a</sup> Cloud base height was calculated by  $H_b = (T_{db} - T_{dew}) / 4.4 * 1000$  ( $H_b$ : cloud base height;  $T_{db}$ : try bulb temperature in Fahrenheit;  $T_{dew}$ : dew point temperature in Fahrenheit, <https://www.easycalculation.com/weather/cloud-base.php>).

<sup>b</sup> The average values were not included the rain events of 2009.02.27–2, 2009.04.11, 2009.05.05.

The estimated  $\delta^{15}\text{N}$  values ranged from  $-8.1\text{‰}$  to  $-43.9\text{‰}$ , with an average of  $-16.8 \pm 4.9\text{‰}$  in gaseous ammonia, close to the  $\delta^{15}\text{N}$  values ( $-15.9\text{‰}$ ) of ammonium in rainwater in Guiyang (Xiao et al., 2012). The enrichment factors ( $\epsilon$ ) range from  $+1.1\text{‰}$  to  $+34.8\text{‰}$ , with average value of  $+10.4 \pm 4.3\text{‰}$ . Xiao and Liu (2002) reported the isotope enrichment factor ( $\epsilon$ ) was about  $+7.8\text{‰}$  in summer in Guiyang. The  $\epsilon$  was calculated to be  $+5.0\text{‰}$  by Moore (1977),  $+7.6\text{‰}$ ,  $+15.3\text{‰}$ ,  $+15.7\text{‰}$  by Urey (1947), Scalan (1958), Hanschmann (1981) and Li et al. (2012). These indicated that  $^{15}\text{NH}_3$  was preferentially dissolved in rain by exchange reactions.

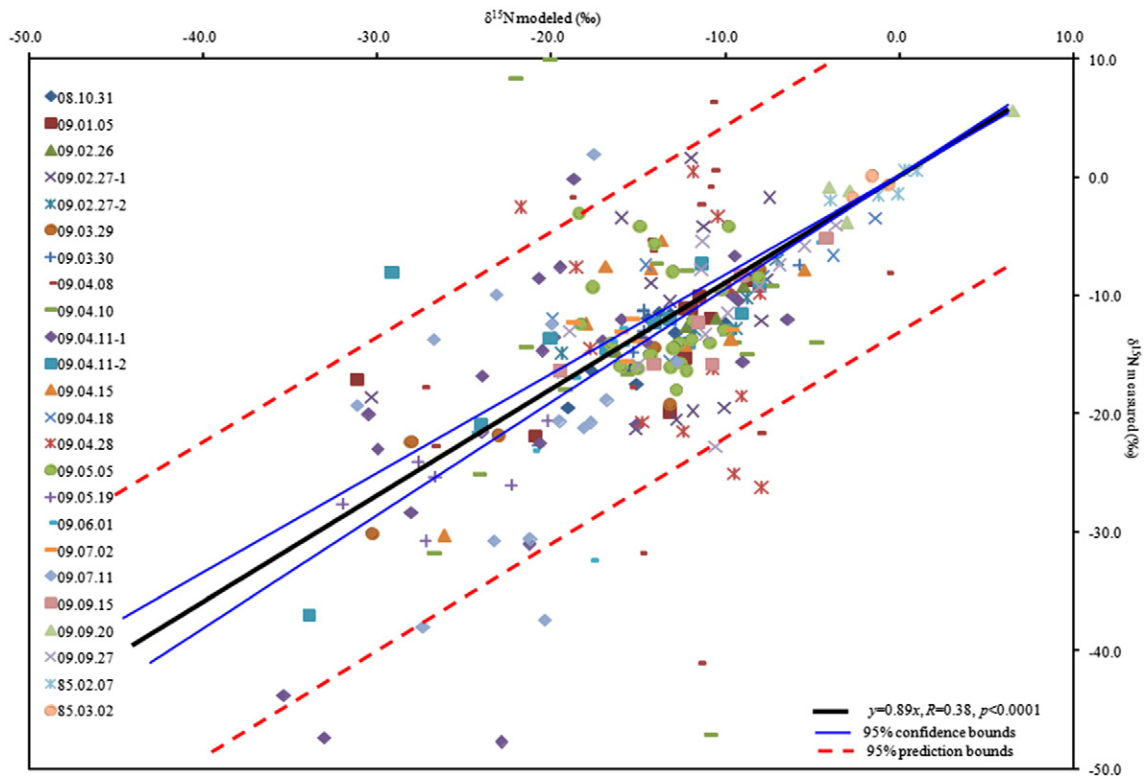
### 3.2. Comparisons between estimated and experimental results

By using atmospheric initial concentration ( $C_{g0}$ ),  $\delta^{15}\text{N}$  value ( $\delta^{15}\text{N}_{g0}$ ) and isotope enrichment factor ( $\epsilon$ ),  $\delta^{15}\text{N}$  value in every sequential sample ( $\delta^{15}\text{N}_{gr}$ ) was calculated by Rayleigh model (Eq. (4)). Those modeled results are shown in Fig. 1, consistent with the observed values ( $y = 0.89x$ ,  $R = 0.38$ ,  $p < 0.0001$ ), which includes the data reported by Heaton (1987). As shown in Fig. 2, the atmospheric initial  $\delta^{15}\text{N}$  values were slightly lower than average  $\delta^{15}\text{N}$  values in rainwater. The maximum value of the difference between  $\delta^{15}\text{N}$  in rainwater and that in the atmosphere was  $22.8\text{‰}$  in 2009.04.11–1 rain event and the minimum was close to  $0\text{‰}$  in 2009.02.27–2 and 2009.05.05 rain events. All  $f$  values in 8 rain events did not reach 0 as shown in Fig. 3, indicating that gaseous ammonia was not completely removed by rainwater.  $^{15}\text{NH}_3$  was preferentially incorporated into raindrops by exchange reactions whereas  $^{14}\text{NH}_3$  was preferentially left in the atmosphere, resulting in more negative  $\delta^{15}\text{N}$  value in the next rain event (Xiao et al., 2012). According to Heaton (1987), the  $\delta^{15}\text{N}$  value of rainwater is expected to decrease during the course of a single rain event. As shown in

Fig. 3, the  $\delta^{15}\text{N}$  value of gaseous ammonia in the atmosphere becomes more and more negative with decreasing residual atmospheric gaseous ammonia. Our model hypothesizes that no new gaseous ammonia is added during the scavenging process and the type of removal process is not changed (Heaton, 1987). However, some  $\delta^{15}\text{N}$  values in rainwater do not fit the curve very well, such as 5 May rain events. When standard deviation values of average rainfall intensity became higher (rainfall intensity became more variable), the model became less accurate to estimate the  $\delta^{15}\text{N}$  value in rainwater. As shown in Fig. 3, the  $\epsilon$  of 5 May ( $1.1\text{‰}$ ) was much lower than others because of large variation in rainfall intensity (standard deviation value of 5.2 of average rainfall intensity), suggesting that the Rayleigh model is not applicable in rain events with relatively large changes in rainfall intensity. Rayleigh model does not work well for large rainfall intensity either. For example, during the 11–1 April event with a rainfall intensity of 9 mm/h, the modeling result gave a value of  $+34.8\text{‰}$ , much larger than the other results modeled. Similar result was also observed in August in Guiyang with high rainfall intensity (Xiao et al., 2012). Freyer (1978) suggested that this phenomenon reflected kinetic solution of  $\text{NH}_3$  in which solution of the  $^{14}\text{NH}_3$  was favored.

## 4. Discussion

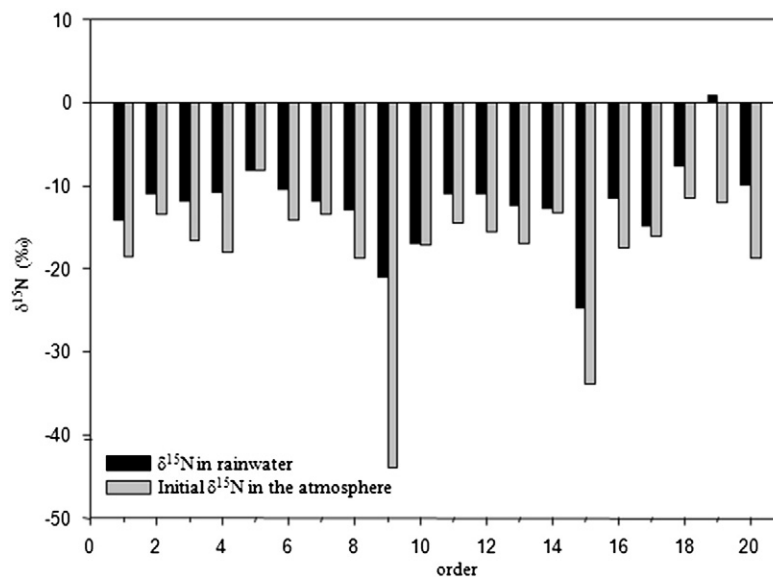
Variations of meteorological conditions (e.g. rainfall intensity, relative humidity, temperature and wind directions and speed) would affect the mass transfer (Adewuyi and Carmichael, 1982) or scavenging processes (Lim et al., 1991). Mass transfer model are based on the two-film theory proposed by Lewis and Whitman (1924), which highly soluble gases, such as ammonia, encounter the primary resistance to transfer from the gaseous film



**Fig. 1.** Modeled and measured  $\delta^{15}\text{N-NH}_4^+$  for different events at Guiyang and at Pretoria, South Africa (The data in 1985.02.07 and 1985.03.02 at Pretoria South Africa are from Heaton, 1987).

and  $\text{NH}_3$  absorption is gas phase controlled (Fig. S1; Adewuyi and Carmichael, 1982). Ammonia absorption behavior of raindrops is strongly dependent on rain drop size, cloud base height, atmospheric initial gaseous ammonia concentrations, and the chemical and physical properties of the constituents of the

mixture (Adewuyi and Carmichael, 1982). In the present study, significant correlations were observed between rainfall intensity and concentrations of  $\text{NH}_4^+$  ( $y = 5.1 - 12.1 \times \ln(x)$ ,  $R = 0.48$ ,  $p < 0.0001$ ), indicating rainfall intensity (relative to rain drop size) is important in controlling absorption of ammonia by rain water



**Fig. 2.** Atmospheric initial  $\delta^{15}\text{N}$  vs. weighted average  $\delta^{15}\text{N}$  in rainwater in different rain events.

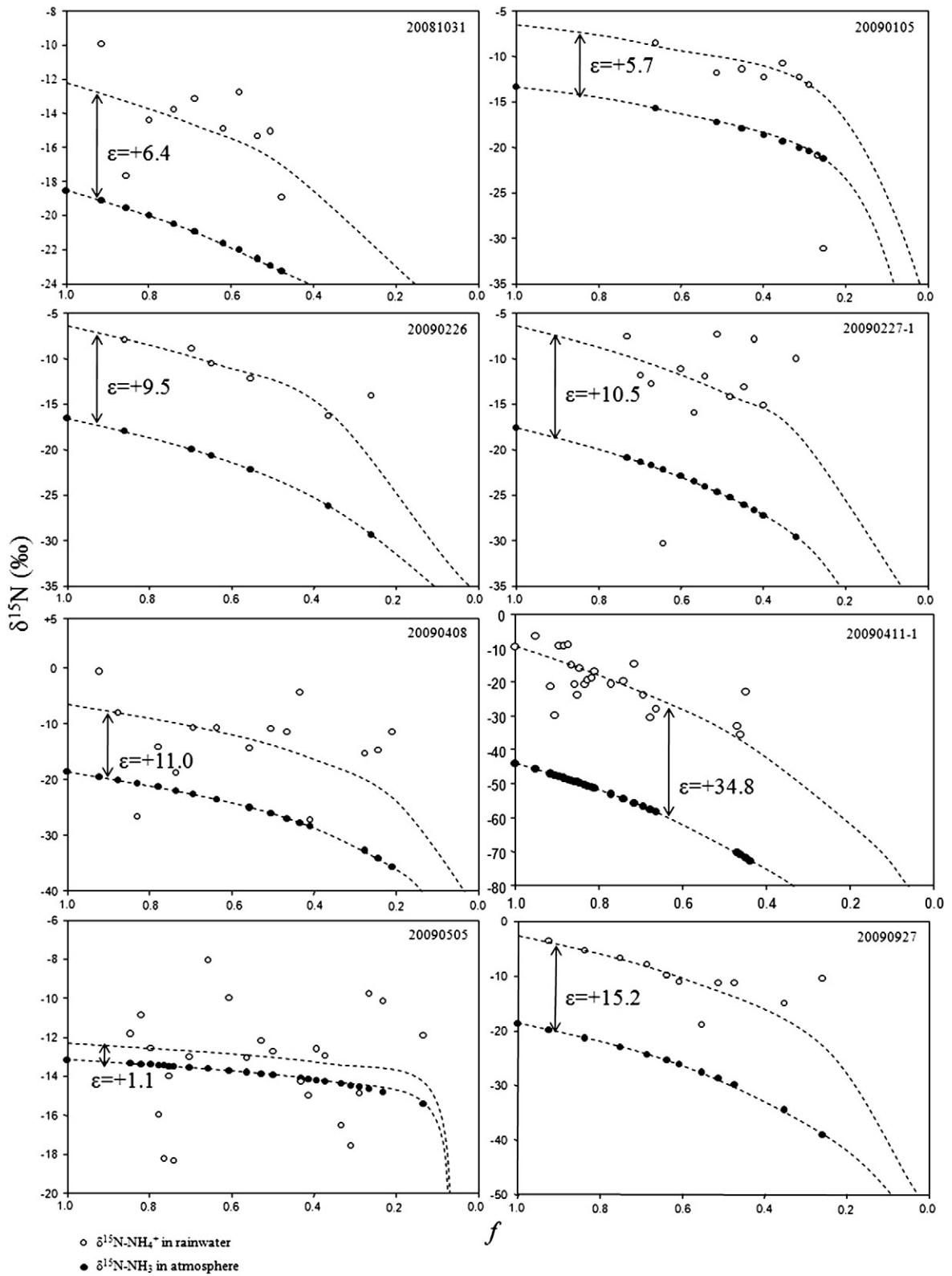


Fig. 3.  $\delta^{15}\text{N}$  value of modeled residual atmospheric gaseous ammonia and measured  $\text{NH}_4^+$  in rainwater versus the fraction of atmospheric gaseous ammonia ( $f$ ) in some rain events.

(Dijk, 2002; Duhanyan and Roustan, 2011). Rain drops absorb atmospheric gaseous ammonia by three processes (Fig. S1): process 1 is diffusion, which shows kinetic effect because a greater diffusion velocity of lighter isotope is expected by the kinetic energy equation; process 2 tends to have  $\text{NH}_3(\text{gas})/\text{NH}_3(\text{aq})$  and  $\text{NH}_3(\text{gas})/\text{NH}_4^+(\text{aq})$  equilibrium, which has a  $\epsilon$  value range between +20‰ and +27‰ in  $\text{NH}_3(\text{gas})/\text{NH}_4^+(\text{aq})$  equilibrium system and between +5‰ and 15.7‰ in  $\text{NH}_3(\text{gas})/\text{NH}_3(\text{aq})$  equilibrium system (Urey, 1947; Scalan, 1958; Moore, 1977; Hanschmann, 1981; Högberg, 1997; Tozer, 2006; Li et al., 2012). But the isotope fractionation in  $\text{NH}_3(\text{gas})/\text{NH}_4^+(\text{aq})$  equilibrium system is not important at less than pH 7 (Moore, 1977); and process 3 is ionization equilibrium and absorption process, which has small or negligible fractionation (Delwiche and Steyn, 1970; Högberg, 1997). In general, the diffusion rates are faster than droplet removal rates and hence equilibrium must be established and the diffusion process should be relatively unimportant (Moore, 1977). The combined isotopic effect of these factors is often large (Moore, 1977; Urey, 1947; Scalan, 1958; Hanschmann, 1981; Högberg, 1997; Li et al., 2012).  $\epsilon$  controlled by exchange reactions between gaseous  $\text{NH}_3$  and  $\text{NH}_3/\text{NH}_4^+$  in rainfall drops may be controlled by meteorological factors, such as temperature, relative humidity and pH (Högberg, 1997; Li et al., 2012; Schoonen and Xu, 2001; Xiao et al., 2012), which affect the rate of gaseous-liquid equilibrium (Lewis and Whitman, 1924). In the relatively lower rainfall intensity, rainfall drop has smaller diameter and thus larger surface area, so can stay longer in the atmosphere (Dijk, 2002), suggesting that the smaller rainfall drop can absorb more gaseous ammonia and have more time to reach the  $\text{NH}_3(\text{gas})/\text{NH}_3(\text{aq})$  and  $\text{NH}_3/\text{NH}_4^+$  equilibrium. On the other hand, when the rainfall intensity is large, the time for gaseous  $\text{NH}_3$  to diffuse into the bigger rain drop will be longer. Those may make kinetic isotope fractionation relatively more important in this rain process and lead to higher nitrogen isotopic value in rainwater. Therefore, the two-film theory explains well the mechanisms of ammonia absorption and isotope fractionation.

## 5. Conclusions

There was an inverse exponential relationship between the ammonium concentrations and cumulative rainfall for most of the samples. The isotopic composition of ammonium in rainwater shows decreasing trend with increase in some evaporation degree. Based on a Rayleigh model, we estimated the initial concentration of atmospheric ammonia to be  $25.7 \pm 36.3 \mu\text{g}/\text{m}^3$ , initial isotope value of the atmospheric ammonia to be  $-16.8 \pm 4.9\%$ , and the atmospheric ammonium deposition to be  $38.1 \text{ kg}/\text{ha}/\text{year}$ . The estimated enrichment factor was  $+10.4 \pm 4.3\%$ , indicating that  $^{15}\text{NH}_3$  was preferentially dissolved into rain water by exchange reactions.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.atmosres.2015.01.023>.

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