Seasonal pattern of ammonium $^{15}$N natural abundance in precipitation at a rural forested site and implications for NH$_3$ source partitioning*

Shaonan Huang $^{a,g,h}$, Emily M. Elliott $^{b}$, J. David Felix $^{c}$, Yuepeng Pan $^{d}$, Dongwei Liu $^{a,g}$, Shanlong Li $^{a,g}$, Zhengjie Li $^{a,h}$, Feifei Zhu $^{a,g}$, Na Zhang $^{f}$, Pingqing Fu $^{d,e}$, Yunting Fang $^{a,g,*}$

$^a$ CAS Key Laboratory of Forest Ecology and Management, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, Liaoning, 110164, China
$^b$ Department of Geology & Environmental Science, 4107 O’Hara Street, University of Pittsburgh, Pittsburgh, PA, 15260, United States
$^c$ Department of Physical and Environmental Science, 6300 Ocean Drive, Texas A & M University – Corpus Christi, Corpus Christi, TX, 78414, United States
$^d$ State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100029, China
$^e$ Institute of Surface-Earth System Science, Tianjin University, Tianjin, 300072, China
$^f$ College of Resource and Environmental Sciences, Shijiazhuang University, Shijiazhuang, 050035, China
$^g$ Qingyuan Forest CERN, Chinese Academy of Sciences, Shenyang, Liaoning, 110014, China
$^h$ College of Resources and Environment, University of Chinese Academy of Sciences, Beijing, 100049, China

ARTICLE INFO

Article history:
Received 27 June 2018
Received in revised form 5 November 2018
Accepted 8 January 2019
Available online 22 January 2019

Keywords:
Nitrogen deposition
Stable nitrogen isotopes
Ammonium
Nitrogen isotope fractionation
Precipitation
Northeast China

ABSTRACT

Excess ammonia (NH$_3$) emissions and deposition can have negative effects on air quality and terrestrial ecosystems. Identifying NH$_3$ sources is a critical step for effectively reducing NH$_3$ emissions, which are generally unregulated around the world. Stable nitrogen isotopes ($^\delta^{15}$N) of ammonium (NH$_4^+$) in precipitation have been directly used to partition NH$_3$ sources. However, nitrogen isotope fractionation during atmospheric processes from NH$_3$ sources to sinks has been previously overlooked. Here we measured $^\delta^{15}$N values of NH$_4^+$ in precipitation on a daily basis at a rural forested site in Northeast China over three years to examine its seasonal pattern and attempt to constrain the NH$_3$ sources. We found that the NH$_4^+$ concentrations in precipitation ranged from 5 to 1265 $\mu$M, and NH$_4^+$ accounted for 65% of the inorganic nitrogen deposition (20.0 kg N ha$^{-1}$ yr$^{-1}$) over the study period. The $^\delta^{15}$N values of NH$_4^+$ fluctuated from $-24.6$ to $+16.2$‰ (average $-6.5$‰) and showed a repeatable seasonal pattern with higher values in summer (average $-2.3$‰) than in winter (average $-16.4$‰), which could not be explained by only the seasonal changes in the NH$_3$ sources. Our results suggest that in addition to the NH$_3$ sources, isotope equilibrium fractionation contributed to the seasonal pattern of $^\delta^{15}$N–NH$_4^+$ in precipitation, and thus, nitrogen isotope fractionation should be considered when partitioning NH$_3$ sources based on $^\delta^{15}$N–NH$_4^+$ in precipitation.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Atmospheric nitrogen (N) deposition has rapidly increased over the past 100 years as a result of the increasing anthropogenic emissions of reactive forms of N from fossil fuel combustion and fertilizer application (Galloway et al., 2004; Galloway et al., 2008; Fowler et al., 2013). Although enhanced N deposition can increase food production in N-limited regions, excess N loading can cause negative impacts on terrestrial ecosystems, such as soil acidification, eutrophication of water bodies and decreases in biodiversity (Vitousek et al., 1997; Stevens et al., 2004; Bowman et al., 2008). Deposition of N compounds mainly originates from either ammonia (NH$_3$) or nitrogen oxide (NO$_x$) sources that subject to transport in the atmosphere. While NO$_x$ emissions controls have been implemented in many regions, including North America, Europe and China, this is not the case for NH$_3$ emissions. NH$_3$
emissions are generally unregulated around the world although ammonium (NH$_4^+$) is the dominant form of inorganic N deposition globally (Galloway et al., 2008; Liu et al., 2013). NH$_3$ emissions also play an important role in aerosol formation during severe haze periods (Pan et al., 2016; Wang et al., 2016). However, it is difficult to make effective strategies for reducing NH$_3$ emissions without constraining and quantifying NH$_3$ sources.

The $\delta^{15}$N natural abundance (expressed by $\delta^{15}$N of NH$_4^+$ in precipitation can aid in the identification and quantification of atmospheric NH$_4^+$ sources (Freyer, 1978; Heaton, 1987; Xie et al., 2008; Zhang et al., 2008; Xiao et al., 2012; Hall et al., 2016; Liu et al., 2017; Ti et al., 2018), because NH$_3$ emissions associated with agricultural and fossil fuel activities have different N isotopic signatures (Fig. 1). The $\delta^{15}$N values of NH$_3$ volatilized from animal waste and fertilizer range from $-56.1$ to $-4.4$% and $-48.0$ to $-19.6$, respectively (Freyer, 1978; Felix et al., 2013; Felix and Elliott, 2014). The reported $\delta^{15}$N values of NH$_3$ emitted from coal combustion ($-14.6$ to $-11.3$%) and vehicle exhaust ($-4.6$ to $-2.2$%) are higher than the $\delta^{15}$N values of NH$_3$ volatized from animal waste and fertilizer (Felix et al., 2013).

However, N isotope fractionation during atmospheric secondary processes was often overlooked when using the $\delta^{15}$N–NH$_4^+$ in precipitation to constrain NH$_3$ sources in many previous studies (Zhang et al., 2008; Jia and Chen, 2010; Liu et al., 2017; Ti et al., 2018). The NH$_4^+$ in precipitation is a mixture of the dissolution of atmospheric NH$_3$ gas and the scavenging of aerosol NH$_4^+$ (Russell et al., 1998). Thus, the $\delta^{15}$N–NH$_4^+$ in precipitation reflects the combined results of the $\delta^{15}$N value of atmospheric NH$_3$ and N isotope fractionation during aerosol NH$_4^+$ formation processes. Without considering N isotope fractionation, incorrect NH$_3$ source apportionments are likely to be obtained (Pan et al., 2018). The formation processes of aerosol NH$_4^+$ from atmospheric NH$_3$ are associated with equilibrium (exchange) reactions and kinetic (unidirectional) reactions (Freyer, 1978; Heaton, 1987; Heaton et al., 1997). Equilibrium reactions between NH$_3$ gas and aerosol NH$_4^+$ will cause aerosol NH$_4^+$ to become enriched in $^{15}$N due to the stronger associative strength of $^{15}$N than $^{14}$N in aerosol NH$_4^+$ (Heaton et al., 1997; Kundu et al., 2010; Kawashima and Kurahashi, 2011). Kirshenbaum et al. (1947) and Heaton et al. (1997) reported N isotopic fractionation ($\epsilon_{\text{NH}, \text{NH}_3}$) of equilibrium reactions between NH$_3$ gas and aerosol NH$_4^+$ at $25^\circ\text{C}$ as +34% and $+$33%, respectively, which has been proposed as a major reason for generally higher $\delta^{15}$N values in aerosol NH$_4^+$ and precipitation NH$_4^+$ than the $\delta^{15}$N values in precursor NH$_3$ (Heaton et al., 1997; Yeatman et al., 2001; Kundu et al., 2010; Pavuluri et al., 2010; Kawashima and Kurahashi, 2011; Ciezka et al., 2016). The kinetic fractionation resulting from NH$_3$ dissolution in the acidic rain solutions is potentially important, as described by Heaton (1987). Atmospheric NH$_3$ can also react with acids (H$_2$SO$_4$, HNO$_3$) by kinetic reaction whereby the lighter isotope ($^{14}$N) is preferentially absorbed into the aerosol particles and rain solutions such as (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$ and NH$_4$NO$_3$ (Freyer, 1978; Heaton et al., 1997; Pavuluri et al., 2010), N isotope fractionation of kinetic reactions is of minor importance for the whole time scale of aerosol NH$_4^+$ formation and can be ignored (Heaton et al., 1997).

Influenced by precursor NH$_3$ sources and N isotope fractionation, $\delta^{15}$N values of NH$_3$ in precipitation show seasonal changes (Freyer, 1978; Heaton, 1987; Xie et al., 2008; Zhang et al., 2008; Xiao et al., 2012; Ciezka et al., 2016; Liu et al., 2017; Ti et al., 2018). The seasonal variations of $\delta^{15}$N–NH$_4^+$ in precipitation among different sites are not always consistent, and the factors controlling the temporal variations are not yet clear. Higher $\delta^{15}$N values in winter than in summer were observed at the urban sites (Guiyang and Guangzhou) in Southern China (Jia and Chen, 2010; Xiao et al., 2012). Xiao et al. (2012) proposed that seasonal trends of $\delta^{15}$N–NH$_4^+$ in rain were controlled by seasonal changes in NH$_3$ sources and NH$_3$ gas converted to aerosol NH$_4^+$ via kinetic reactions. Additionally, the $\delta^{15}$N–NH$_4^+$ in rain was negatively correlated with temperature and precipitation amounts but not with NH$_4^+$ concentrations. The opposite seasonal pattern was observed at some rural and suburban sites with higher $\delta^{15}$N values in summer than these in winter (Heaton, 1987; Xie et al., 2008; Ciezka et al., 2016). Heaton (1987) suggested that the isotopic effects of equilibrium reactions potentially altered the seasonal changes of $\delta^{15}$N–NH$_4^+$ in precipitation, this finding was based on his observation that the $\delta^{15}$N–NH$_4^+$ in a sequence of rain events at Pretoria, South Africa became progressively more depleted in $^{15}$N, implying that $^{15}$N from aerosol NH$_4^+$ was preferentially incorporated via exchange processes into aqueous solution. To explain the conflicting seasonal patterns among different sites, the $\delta^{15}$N–NH$_4^+$ in precipitation should be further investigated at more sites on a long-term basis.

While most prior studies focused on $\delta^{15}$N–NH$_4^+$ in precipitation at urban and agricultural sites, measurements of $\delta^{15}$N–NH$_4^+$ in precipitation at rural forested sites are lacking. Given that soil NH$_3$ emissions from rural forested sites are low due to low soil pH (Li et al., 2012; Xi et al., 2016; Li et al., 2017), scavenging of local air NH$_3$ and aerosol NH$_4^+$ is of minor importance to precipitation NH$_4^+$. As a result, the $\delta^{15}$N–NH$_4^+$ in precipitation at rural forested sites should mainly reflect the $\delta^{15}$N of regional aerosol NH$_4^+$. We hypothesized that the $\delta^{15}$N–NH$_4^+$ in precipitation would show higher values in winter than in summer (proportionally more from agricultural activities) if no N isotopic fractionation during atmospheric processes was considered. In the present study, we measured the $^{15}$N natural abundance of NH$_4^+$ in precipitation on a daily basis for a rural forested site in Northeast China over three years. The objectives of this study were: (1) to examine seasonal variations in the $\delta^{15}$N–NH$_4^+$ in precipitation, (2) to evaluate the influence of nitrogen isotope fractionation on $\delta^{15}$N–NH$_4^+$ in precipitation, and (3) to attempt to partition NH$_3$ sources with consideration of N isotopic fractionation.

![Fig. 1. The values (%o) of $\delta^{15}$N in ammonia sources and ammonia and ammonium in the atmosphere. Moore (1977), red closed triangle; Freyer (1978), red closed circle; Heaton (1987), blue open circle; Watmam (2001), blue open triangle; Felix et al. (2013), red open circle; Felix and Elliott (2014), red open triangle; Chang et al. (2016), blue closed circle; Savard et al. (2017), green closed triangle; and this study, red cross. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)
2. Materials and methods

2.1. Study site and sample collection

Precipitation samples were collected at the Qingyuan Forest Chinese Ecosystem Research Network (CERN), Chinese Academy of Sciences, which is located in Pingyuan County, Liaoning Province, Northeastern China (41°51’N, 124°54’E) (Fig. 2). The main land use types within a 50-km radius of this region are forestland (80%) and cropland (18%) (Fig. 2c). The study site has a continental monsoon climate (Zhu et al., 2007). Over the three-year study period, the annual precipitation ranged from 484 to 874 mm, and the annual mean air temperature was 4.6°C with a minimum of −27.1°C in January and a maximum of 27.0°C in July (Fig. 3a).

A total of 108 rain samples and 48 snow samples were collected on a daily basis from April 2014 to December 2016. Bulk deposition samples were collected because the precipitation samplers were always open to the air. Precipitation samples were filtered through 0.22-μm nylon membrane filters and then stored at −18°C until chemical and isotopic analyses could be conducted.

2.2. Chemical and isotopic analysis

The concentrations of NH₄⁺ and other inorganic ions in filtered precipitation samples were determined by an ion chromatograph (Dionex ICS-600; USA). Nitrogen isotopic analysis was conducted following a chemical method as described by Liu et al. (2014). Briefly, the method was based on nitrogen isotopic analysis of nitrous oxide (N₂O). NH₄⁺ was initially oxidized to nitrite (NO₂⁻) by hypobromite (BrO⁻) and then NO₂⁻ was quantitatively converted into N₂O by hydroxylamine (NH₂OH) under strongly acidic conditions. Subsequently, the produced N₂O was analyzed by a commercially available purge and cryogenic trap system coupled to an isotope ratio mass spectrometer (PT-IRMS, IsoPrime Ltd., UK). The δ¹⁵N values are reported in parts per mil relative to the standard (atmospheric N₂) as follows:

\[
\delta^{15}N(\%o) = \frac{\left(^{15}N/^{14}N\right)_{\text{sample}} - \left(^{15}N/^{14}N\right)_{\text{standard}}}{\left(^{15}N/^{14}N\right)_{\text{standard}}} \times 1000
\]

The natural abundances of ¹⁵N were not measured for five precipitation samples with NH₄⁺ concentrations less than 12 μM (μmol L⁻¹), below which the conversion efficiency was imperfect when converting NH₄⁺ to N₂O. Nitrite (NO₂⁻) was not detectable in most samples. There were eight samples with NO₂⁻ concentrations higher than 2 μM but NO₂⁻ accounted for only 1%–5% of the total NH₄⁺ + NO₂⁻ in the corresponding samples. Thus NO₂⁻ was not removed prior to isotopic analyses. Three international standards, IAEA-N-1 (δ¹⁵N = +0.4‰), USGS25 (δ¹⁵N = −30.4‰) and USGS26 (δ¹⁵N = +53.7‰), were used for the calibration of δ¹⁵N–NH₄⁺ in precipitation samples. The typical reaction volume was 4 mL and produced 60 nmol N₂O, with a δ¹⁵N standard deviation of less than 0.3‰ (based on 3 to 5 replicate analyses of the international standards).

2.3. NH₃ source apportionment

Precipitation NH₃ is mainly a result of the scavenging of in-cloud aerosol NH₄⁺ and dissolution of NH₃ in an acidic solution transported from outside the study region. The local NH₃ emissions in this forest region can be ignored due to the low soil pH of 4.8–6.0 (Xi et al., 2016) because under these conditions soil NH₄⁺ is stable and difficult to volatilize as degassing of NH₃ product (Li et al., 2012; Li et al., 2017). Therefore, in this study, we consider precipitation NH₃ to mainly result from scavenging of in-cloud aerosol NH₄⁺ and dissolved NH₃ transported from outside the study region. Thus, the δ¹⁵N of precipitation NH₃ is equivalent to the δ¹⁵N of the mixed aerosol NH₄⁺ transported from outside the study region. The
formation processes of aerosol NH$_4$$^+$ from NH$_3$(g) are both associated with kinetic reactions (e.g., with H$_2$SO$_4$) and equilibrium reactions, respectively:

\[ ^{14}\text{NH}_3(g) + H_2\text{SO}_4 \rightarrow (^{14}\text{NH}_4)\text{SO}_4 \] (2)

\[ ^{15}\text{NH}_3(g) + ^{14}\text{NH}_4(p) \leftrightarrow ^{14}\text{NH}_3(g) + ^{15}\text{NH}_4(p) \] (3)

Dissolution of NH$_3$ in an acidic solution (2) is a unidirectional process, and N isotopic fractionation for the unidirectional reaction is always invariably negative. The kinetic reactions were fast within a few minutes so that the $\delta^{15}$N value of produced NH$_4$$^+$ is close to the $\delta^{15}$N value of NH$_3$ gas (Heaton et al., 1997); then, we modestly assumed that the N isotopic fractionation of the kinetic reaction (2) was 0‰. The N isotope fractionation factor ($\varepsilon_{\text{NH}_4+-\text{NH}_3}$) of equilibrium reactions (3) was measured to be +33‰ at 25°C (Heaton et al., 1997). In addition to the value for $\varepsilon_{\text{NH}_4+-\text{NH}_3}$, the relationship between the $\delta^{15}$N values of aerosol NH$_4$$^+$ and the original precursor NH$_3$ gas from which aerosol NH$_4$$^+$ formed will depend on the aerosol/gas distribution in the final mixture. Therefore, the $\delta^{15}$N values of the original NH$_3$ were calculated using an isotopic mass balance in a well-mixed closed system as follows:

\[ \delta^{15}\text{N}_{\text{NH}_3(g)} = \delta^{15}\text{N}_{\text{NH}_4(p)} - \varepsilon_{\text{NH}_4+-\text{NH}_3} (1 - f) \] (4)

where $\delta^{15}$N$_{\text{NH}_3(g)}$ and $\delta^{15}$N$_{\text{NH}_4(p)}$ are the N isotopic compositions of the precursor NH$_3$ gas and the final ion phase in the aerosols, respectively. We used the $\varepsilon_{\text{NH}_4+-\text{NH}_3}$ value of 33‰, which was determined experimentally (Heaton et al., 1997). The $f$ value is the fraction of the initial NH$_3$ gas coveted to aerosol NH$_4$$^+$. To obtain $f$, the concurrent measurement of the aerosol NH$_4$$^+$ and NH$_3$ concentrations at the regional scale is needed (Hall et al., 2016; Pan et al., 2018) However, it is difficult to constrain $f$ values due to the large regional-scale measurements of these concentrations. Therefore we performed a sensitivity analysis in which we modeled $f$ values ranging from 0 to 100% and calculated the $\delta^{15}$N values of precursor NH$_3$ based on equation (4).

Then we used a Bayesian mixing model and attempted to partition the NH$_3$ sources. Atmospheric NH$_3$ mainly originates from volatilized fertilizer, animal waste, coal combustion and vehicle
exhaust (Sutton et al., 2000; Reis et al., 2009; Huang et al., 2012; Kang et al., 2016). The $^{15}$N signatures for each NH$_3$ source of coal combustion, vehicle exhaust, volatilized fertilizer and animal waste was reported in previous studies, with means and standard deviations of $-13.0 \pm 2.3\%$, $-3.4 \pm 1.7\%$, $-37.0 \pm 7.8\%$, and $-23.7 \pm 14.5\%$, respectively (Freyer, 1978; Heaton, 1987; Felix et al., 2013; Felix and Elliott, 2014; Chang et al., 2016). The model explicitly considered the uncertainty associated with multiple sources, fractionation and isotopic signatures and was recently used in atmospheric pollutant source partitioning (Liu et al., 2017; Zong et al., 2017; Ti et al., 2018).

The model was implemented in the software package Stable Isotope Analysis in R (SIAR) where proportional source contributions were the goal and these proportions were assigned a Dirichlet Distribution. For a detailed model framework and computational methods, readers should refer to Moore and Semmens (2008).

2.4. Air mass back trajectories

To analyze the origins of air mass transportation to the study site, 72-h air mass back trajectories were computed for all sampling days ($n = 156$) using NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) (http://ready.arl.noaa.gov/HYSPLIT_traj.php) at an altitude of 500 m above sea level (Draxler and Rolph, 2010). The 72-h backward trajectory was chosen since the lifetime of atmospheric NH$_4$ in each study period varied greatly from 5 to 1265 days ($n = 156$) using NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) (http://ready.arl.noaa.gov/HYSPLIT_traj.php) at an altitude of 500 m above sea level (Draxler and Rolph, 2010). The 72-h backward trajectory was chosen since the lifetime of atmospheric NH$_4$ and NH$_3$ in the boundary layer is approximately 2–4 days (Heaton, 1987; Xiao and Liu, 2002). Air mass sectors were categorized as being either continental origin (e.g. Western and Northern China) or marine origin (e.g. Bohai Bay and the Korean Peninsula) for each season according to the air mass origins (continental vs marine) on NH$_4$ concentrations among air mass origins (Table S2). During the three-year study period, annual dissolved inorganic nitrogen (DIN, NH$_4$ plus NO$_3$) deposition was 17.6–21.4 kg N ha$^{-1}$ yr$^{-1}$ and averaged 20.0 kg N ha$^{-1}$ yr$^{-1}$, whereby NH$_4$ accounted for 59–69% of DIN deposition (Table 1).

The equivalent ratio of NH$_4$/[SO$_4^{2-}$ + NO$_3^-$], an indicator of the degree of neutralization for acidic ions (H$_2$SO$_4$+HNO$_3$) by NH$_3$ gas, in the atmosphere, averaged 0.9, 1.1, 0.4 and 0.5 in spring, summer, autumn and winter, respectively (Table 2). NH$_4$/[SO$_4^{2-}$ + NO$_3^-$] was significantly higher in spring and summer than in autumn and winter. NH$_4$/[SO$_4^{2-}$ + NO$_3^-$] was not significantly different among air mass origins in each season (Table S2).

3. Results

3.1. NH$_4$ concentration and deposition in precipitation

The NH$_4$ concentrations in precipitation over three years exhibited a large fluctuation from $-24.6$ to $+16.2\%$ with an arithmetic average of $-6.5\%$ (Fig. 3c). The flux-weighted average of $^{15}$N–NH$_4$ was $-3.5\%$. We observed a seasonal pattern with significantly higher values in summer than in winter (Table 2, Fig. 3c). Arithmetic averages of $^{15}$N–NH$_4$ in spring, summer, autumn and winter were $-7.9$, $-2.3$, $-6.9$ and $-16.4\%$, respectively (Table 2). The $^{15}$N–NH$_4$ was not significantly different among years or air mass origins in any season (Table 1, Table S2). The $^{15}$N–NH$_4$ showed significant correlations with air temperature, precipitation amount and pH, but not with NH$_4$ concentrations (Fig. S1).

3.2. The $^{15}$N values of NH$_4$ in precipitation

The $^{15}$N values of NH$_4$ in precipitation were measured on a long-term scale at our study site. The annual mean $^{15}$N–NH$_4$ value at this rural site was higher than those monitored at urban sites, such as Jülich in Germany (Freyer, 1978) and Guiyang in Southern China (Xiao and Liu, 2002) but lower than those surveyed at agricultural and rural sites, such as the Tai Lake

### Table 1

<table>
<thead>
<tr>
<th>Year</th>
<th>Precipitation (mm)</th>
<th>NH$_4$ deposition</th>
<th>NO$_3$ deposition</th>
<th>Inorganic N deposition</th>
<th>NH$_4$ concentration ($\mu$mol L$^{-1}$)</th>
<th>$^{15}$N–NH$_4$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>37 472</td>
<td>14.4</td>
<td>6.5</td>
<td>20.9</td>
<td>182 ± 251 (143–1120)</td>
<td>$-7.9 \pm 7.4$</td>
</tr>
<tr>
<td>2015</td>
<td>64 723</td>
<td>14.1</td>
<td>7.3</td>
<td>21.4</td>
<td>148 ± 198 (49–1265)</td>
<td>$-5.2 \pm 7.9$</td>
</tr>
<tr>
<td>2016</td>
<td>55 827</td>
<td>10.4</td>
<td>7.2</td>
<td>17.6</td>
<td>111 ± 120 (49–586)</td>
<td>$-7.0 \pm 6.2$</td>
</tr>
</tbody>
</table>

$^a$ Calculated in kg N ha$^{-1}$ yr$^{-1}$.

$^b$ Numerical average ± 1SD (range).

4. Discussion

4.1. Seasonal pattern of $^{15}$N–NH$_4$ in precipitation

Extensive sets of N isotopic signatures of NH$_4$ in precipitation were measured on a long-term scale at our study site. The annual mean $^{15}$N–NH$_4$ value at this rural site was higher than those monitored at urban sites, such as Jülich in Germany (Freyer, 1978) and Guiyang in Southern China (Xiao and Liu, 2002) but lower than those surveyed at agricultural and rural sites, such as the Tai Lake...
Region (Xie et al., 2008), the North China Plain in northern China (Zhang et al., 2008) and Niigata in central Japan (Fukuzaki and Hayasaka, 2009) (Table S1). We observed a large precipitation $^{15}$N fluctuation of 41‰ (from $-$24.6 to $+$16.2‰) at our study site. Similarly, such large ranges of $^{15}$N in precipitation were also found at the rural and suburban sites in previous studies such as Xie et al. (2008) ($-$16.0 to $+$22.0‰), Zhang et al. (2008) ($-$12.7 to $+$8.7‰) and Ti et al. (2018) ($-$23.6 to $+$8.3‰). In addition, the range of $^{15}$N in precipitation at our site exceeded the theoretical ranges of $^{15}$N of reported for NH$_3$ sources (Fig. 1).

We observed that the $^{15}$N in precipitation showed a clear seasonal pattern with higher values in summer and lower values in winter over the three-year study period, which was beyond our expectation. We expected to observe higher $^{15}$N in precipitation in winter than in summer at our study site due to the seasonal changes in NH$_3$ sources. NH$_3$ emissions from agricultural activities are temperature-dependent, and thus, the fraction of agricultural NH$_3$ sources should be higher in summer than in winter. As a result, we expected to observe low $^{15}$N values in summer corresponding to a larger proportion of NH$_3$ volatilized from agricultural activities (Fig. 1). Furthermore, in winter, the air temperature was very low (averaged $-$13°C) and the snow-covered soil was frozen. NH$_3$ emissions from agricultural activities should be of minor importance, and industrial NH$_3$ sources were expected to be more important. This seasonal pattern at our site was similar to that observed by Heaton (1987), Xie et al. (2008) and Ciezka et al. (2016) but not similar to those reported by Freyer (1978), Jia and Chen (2010) and Xiao et al. (2012). Ciezka et al. (2016) proposed

### Table 2
Seasonal comparison of concentrations and $^{15}$N values of NH$_4^+$ in precipitation at the study site. The letters on top of these values indicate the significant difference among seasons ($P$ < 0.05).

<table>
<thead>
<tr>
<th>Season</th>
<th>n</th>
<th>NH$_4^+$ concentration (µmol L$^{-1}$)</th>
<th>NO$_3^-$ concentration (µmol L$^{-1}$)</th>
<th>NH$_4^+$/(1/2SO$_4^{2-}$ + NO$_3^-$)</th>
<th>$^{15}$N–NH$_4^+$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>25</td>
<td>238 ± 301 (15.8–1210) $^A$</td>
<td>149 ± 161 (11–585) $^A$</td>
<td>0.9 ± 0.6 (0.3–2.8) $^A$</td>
<td>$-$7.9 ± 4.9 (18.3 to +1.4) $^A$</td>
</tr>
<tr>
<td>Summer</td>
<td>64</td>
<td>152 ± 194 (14.3–1265) $^AB$</td>
<td>65 ± 62 (13–385) $^B$</td>
<td>1.1 ± 0.9 (0.3–5.4) $^A$</td>
<td>$-$2.3 ± 6.2 (23.2 to +16.2) $^A$</td>
</tr>
<tr>
<td>Autumn</td>
<td>39</td>
<td>96 ± 121 (4.9–588) $^B$</td>
<td>88 ± 75 (0.6–312) $^B$</td>
<td>0.4 ± 0.2 (0.0–0.9) $^B$</td>
<td>$-$6.9 ± 5.2 (20.8 to +5.1) $^B$</td>
</tr>
<tr>
<td>Winter</td>
<td>28</td>
<td>105 ± 90 (7.3–393) $^B$</td>
<td>137 ± 104 (31–439) $^AB$</td>
<td>0.5 ± 0.3 (0.1–1.4) $^B$</td>
<td>$-$16.4 ± 4.1 (24.6 to –8.7) $^B$</td>
</tr>
</tbody>
</table>

P value: 0.003

$^A$ Numerical average ± 1SD (range).
$^B$ Equivalent ratio.

*Fig. 4.* The expected $^{15}$N values of NH$_3$ and NH$_3$ source apportionments in summer (a, c) and winter (b, d). The different squares represent the ranges of varied potential NH$_3$ sources (a, b).
that the seasonal pattern with higher $\delta^{15}\text{N} - \text{NH}_4^+$ values in summer than in winter was due to isotopic effects of equilibrium reactions. The isotopic effects of equilibrium reactions have proven to be a major reason for higher $\delta^{15}\text{N} - \text{NH}_4^+$ values in aerosol NH$_4^+$ and precipitation NH$_4^+$ (Heaton et al., 1997).

4.2. Isotopic effects of equilibrium reactions

In addition to NH$_3$ sources, the isotopic effects of equilibrium reactions potentially altered the $\delta^{15}\text{N} - \text{NH}_4^+$ in precipitation at our study site. The large range (-24.6% to +16.2%) and unexpected seasonal pattern at our site could not be explained by only the seasonal changes in NH$_3$ sources. To investigate the potential influence of isotopic effects of equilibrium reactions, different fractionation scenarios were conducted for summer and winter samples (Fig. 4).

In summer, if we assumed no N isotope equilibrium fractionation during the conversion of NH$_3$ gas to aerosol NH$_4^+$ in the atmosphere (i.e., $f = 100\%$), the expected $\delta^{15}\text{N}$ values of the initial NH$_3$ would have a range of -8.9 to +14.8% (Fig. 4a), which could not be explained by the range of NH$_3$ sources (Figs. 1 and 4a). When $f$ was assigned to <40%, the expected $\delta^{15}\text{N}$ values of NH$_3$ in summer were within the $\delta^{15}\text{N}$ theoretical bounds of potential NH$_3$ sources (Fig. 4a).

Here, we provide the potential mechanisms of how the isotopic effects of equilibrium reactions potentially altered the seasonal pattern of $\delta^{15}\text{N} - \text{NH}_4^+$ in precipitation. The degree of neutralization for acidic ions (H$_2$SO$_4$ and HNO$_3$) by NH$_3$ gas could provide a new perspective on the isotopic effects of equilibrium reactions and kinetic reactions in the atmosphere. The equivalent ratios of NH$_4^+$/(1/2SO$_4^{2-}$ + NO$_3^-$) could indicate the degree of neutralization for acidic ions (H$_2$SO$_4$ HNO$_3$) by NH$_3$ in the atmosphere. In summer, large amounts of NH$_3$ gas are released into the atmosphere because NH$_3$ emissions from agricultural activities increase with rising air temperature (Okita and Kanamori, 1971). Such large amounts of NH$_3$ gas could not be fully absorbed to the liquid phase, which contained acidic ions (H$_2$SO$_4$ HNO$_3$). The equivalent ratios of NH$_4^+$/ (1/2SO$_4^{2-}$ + NO$_3^-$) in summer averaged 1.1 (Table 2), reflecting an incomplete neutralization of NH$_3$ by H$_2$SO$_4$ and HNO$_3$. During the processes of equilibrium reactions between remaining NH$_3$ gas and aerosol NH$_4^+$, the $^{15}\text{N}$ of NH$_3$ preferentially exchanged with $^{14}\text{N}$ of aerosol NH$_4^+$ and caused significant $^{15}\text{N}$ enrichment in aerosol NH$_4^+$. In comparison, during winter, the importance of NH$_3$ emissions from agricultural activities relative to those from fossil fuel combustion decreased with decreasing air temperature and increasing fossil fuel combustion for the heating of buildings in this region. The equivalent ratios of NH$_4^+$/ (1/2SO$_4^{2-}$ + NO$_3^-$) in winter averaged 0.5 (Table 2), which indicated that NH$_3$ gas could not neutralize abundant acidic ions (H$_2$SO$_4$ HNO$_3$) by kinetic reactions. A small amount of air NH$_3$ gas would have the opportunity for isotopic exchange with aerosol NH$_4^+$ in winter (Garten, 1992; Yeatman et al., 2001; Kawashima and Kurahashi, 2011).

The influence of temperature on the N isotopic fractionation of equilibrium reactions was of slight importance for explaining the seasonal variations of $\delta^{15}\text{N} - \text{NH}_4^+$ in precipitation at our study site. Previous studies have shown that $\varepsilon_{\text{NH}_4+ - \text{NH}_3}$ decreases with increasing temperature (Kirshenbaum et al., 1947; Li et al., 2012; Savard et al., 2017). The dependence of $\varepsilon_{\text{NH}_4+ - \text{NH}_3}$ on temperature can be deduced from Urey (1947) as follows:

$$\varepsilon_{\text{NH}_4+ - \text{NH}_3} = 12.4678 \times 10^00\% (T+273.15) - 7.6694$$

where $T$ is temperature in degree Celsius. This equation (5) yielded an $\varepsilon_{\text{NH}_4+ - \text{NH}_3}$ value of ~34% at 25 °C, which is largely identical to the value determined experimentally (Heaton et al., 1997; Kirshenbaum et al., 1947). According to equation (5), the equilibrium fractionation factor decreases by an average of 0.15 per mill with every degree Celsius from 0 °C to 27 °C. As we assume equilibrium fractionation occurs only above 0 °C and the highest air temperature is 27 °C at the study site, the temperature explains only the $\delta^{15}\text{N}$ difference of approximately 4.1%. However, the seasonal difference in the $\delta^{15}\text{N}$ value for NH$_4^+$ in this study was 41%. Thus, the temperature dependence was much smaller relative to the seasonal difference. Furthermore, the air temperature influence on $\varepsilon_{\text{NH}_4+ - \text{NH}_3}$ would cause the opposite seasonal pattern of $\varepsilon_{\text{NH}_4+ - \text{NH}_3}$ with higher values in winter than in summer, which did not contribute to the seasonal pattern of $\delta^{15}\text{N} - \text{NH}_4^+$ in precipitation in our study site.

4.3. Implications for NH$_3$ source apportionment

We further attempt to conduct NH$_3$ source apportionment after consideration of N isotope fractionation. The contributions of various NH$_3$ sources to precipitation NH$_4^+$ were calculated for only summer and winter. Our results showed that NH$_3$ source apportionments were strongly dependent on the f-value. As mentioned in section 4.2, only when $f$ was set to <40% in summer was the range of expected $\delta^{15}\text{N} - \text{NH}_3$ values within the theoretical bounds of the $\delta^{15}\text{N}$ range of NH$_3$ sources. In summer when $f$ < 40%, the NH$_3$ emitted from agricultural activities accounted for 60-94% while fossil fuel combustion contributed 7-40% (Fig. 4c). Relative contributions of agricultural activities to NH$_3$ emissions in summer were similar to the results (80-90%) calculated by the high-resolution ammonia NH$_3$ emissions inventory in China at a national scale (Huang et al., 2012; Kang et al., 2016). High summer air temperatures (average 18 °C) could promote NH$_3$ emissions from agricultural activities. For instance, fertilizer application was conducted between May and August in Northeast China and high summer temperatures would enhance fertilizer NH$_3$ volatilization. Conversely, low winter air temperatures (average -13 °C) and snow-covered soil did not favor NH$_3$ emissions from agricultural activities. In winter, the relative contribution of NH$_3$ emissions from fossil fuel combustion would increase due to the heating of buildings in Northeast China. Hence, the contribution of fossil fuel combustion should be higher in winter than in summer. NH$_3$ emissions were mainly from fossil fuel combustion (44%-62%) when $f$ shifted to >80% in winter. Nevertheless, the NH$_3$ emissions from agricultural activities accounted for at least 38% in winter, suggesting that in such cold conditions NH$_3$ emissions from agricultural activities could not be ignored.

Although the relative contributions of NH$_3$ sources was simulated by the Bayesian model with consideration of N isotopic effects, there were still some uncertainties regarding the NH$_3$ source apportionments, which should be further investigated. First, there may be an uncertain difference between the simulated $\delta^{15}\text{N}$ values and the initial $\delta^{15}\text{N}$ values of atmospheric NH$_3$ for complex secondary atmospheric processes. Second, regional differences in the N isotopic signatures of different NH$_3$ sources were not considered in this study. For example, the $\delta^{15}\text{N}$ values of NH$_3$ emitted from coal combustion had not yet been measured in China. Third, the $\delta^{15}\text{N}$ of biomass burning has not been measured and was not included in our model, although wood materials might be used for heating the buildings in winter.

Additionally, plant uptake of atmospheric NH$_3$ was not considered in the study. Plant uptake of atmospheric NH$_3$ proved to be a significant sink for atmospheric NH$_3$ (Farquhar et al., 1980; Rogers and Aneja, 1980; Johnston and Berry, 2013). The uptake of atmospheric NH$_3$ is kinetic process that is affected by light, temperature and atmospheric NH$_3$ concentrations. In summer, increasing light, temperature and NH$_3$ concentrations promote uptake rates. During the process, $^{14}\text{NH}_3$ preferentially diffuses into the plant stoma and...
leads the remaining NH$_3$ to be $^{15}$N-enriched. Then atmospheric processes remove the remainder of $^{15}$N-enriched NH$_3$ and cause precipitation NH$_4^+$ with higher $^{15}$N values in summer and lower $^{15}$N values in winter. Therefore, plant uptake of atmospheric NH$_3$ may be a potential factor responsible for the seasonal pattern of $^{15}$N of precipitation NH$_4^+$ and should be given more attention in the future.

5. Conclusions

In this study, the daily $^{15}$N natural abundance of NH$_4^+$ in precipitation at a rural forested site in Northeast China over three years is presented. We found that the $^{15}$N–NH$_4^+$ in precipitation had a large range ($-24.6$ to $-16.2\%$) and showed a repeatable seasonal pattern with higher values in summer than in winter. However, the range and seasonal pattern of $^{15}$N–NH$_4^+$ in precipitation could not be explained solely by seasonal changes in NH$_3$ sources. Our results suggest that in addition to NH$_3$ sources, isotopic equilibrium fractionation played an important role in the seasonal variations of $^{15}$N–NH$_4^+$ in precipitation, and the relative importance of equilibrium reactions also varied seasonally. Therefore, $N$ isotope fractionation should be considered when partitioning NH$_3$ sources based on $^{15}$N–NH$_4^+$ in precipitation.

Acknowledgments

This research was financially supported by the National Key R&D Program of China (grant no. 2017YFC0212700, grant no. 2016YFA0600802), the Key Research Program of Frontier Sciences of Chinese Academy of Sciences (grant no. QYZDB-SSW-DQC002), the National Natural Science Foundation of China (grant no. 41773094), National Research Program for Key Issues in Air Pollution Control (grant number DQGG0105-02) and K.C.Wong Education Foundation. We are grateful for the experimental support provided by the Qingyuan Forest CENR, Chinese Academy of Sciences. The authors also acknowledge Daniel Bain, Department of Geology & Environmental Science, University of Pittsburgh, who assisted with the SIAR model in R language. We are also grateful for making the landuse figure by Yue Yu and Guiduo Shang, Institute of Applied Ecology, Chinese Academy of sciences. The authors declare no competing financial interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.01.023.

References