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Changes of $\delta^{15}N$ values during the volatilization process after applying urea on soil *

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ABSTRACT

Ammonia (NH₃) volatilized from soils plays an important role in N cycle and air pollution, thus it is important to trace the emission source and predict source contributions to development strategies mitigating the environmental harmful of soil NH₃ volatilization. The measurements of ¹⁵N natural abundance ($\delta^{15}N$) could be used as a complementary tool for apportioning emissions sources to resolve the contribution of multiple NH₃ emission sources to air NH₃ pollution. However, information of the changes of δ^{15} N–NH₃ values during the whole volatilization process under different N application rates are currently lacking. Hence, to fill this gap, we conducted a 15-day incubation experiment included different urea-N application rates to determine δ^{15} N values of NH₃ during volatilization process. Results showed that volatilization process depleted 15 N in NH₃. The average δ^{15} N value of NH₃ volatilized from the 0, 20, 180, and 360 kg N ha⁻¹ treatment was -16.2 ± 7.3 %, -26.0 ± 5.4 %, -34.8 ± 4.8 %, and $-40.6 \pm 5.7\%$. Overall, δ^{15} N-NH₃ values ranged from -46.0% to -4.7% during the whole volatilization process, with lower in higher urea-N application treatments than those in control. δ^{15} N–NH₃ values during the NH₃ volatilization process were much lower than those of the primary sources, soil $(-3.4 \pm 0.1\%)$ and urea $(-3.6 \pm 0.1\%)$. Therefore, large isotopic fractionation may occur during soil volatilization process. Moreover, negative relationships between soil NH⁴₄-N and NH₃ volatilization rate and δ^{15} N–NH₃ values were observed in this study. Our results could be used as evidences of NH₃ source apportionments and N cycle.

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1. Introduction

Ammonia (NH₃) is the most abundant basic gaseous species in the atmosphere and it plays an important role in the global nitrogen (N) cycle (Aneja et al., 2000; Erisman et al., 2007; Galloway et al., 2008). However, excessive NH₃ emitted from sources such as animal waste and synthetic fertilizers, biomass burning, human excreta and fossil fuel combustion has contributed significantly to air pollution, soil acidification, water eutrophication, biodiversity loss, and declining human health (Behera et al., 2013; Krupa, 2003; Stokstad, 2014). In addition, NH₃ volatilization from agricultural soils and crops has been identified as an important source of atmospheric NH₃, it accounts for 43.3% of total global NH₃ emissions estimated by an agricultural emissions model (Paulot et al., 2014). Thus a better understanding of the relative contribution of different emission sources is necessary for effective NH₃ management and abatement.

The ¹⁵N natural abundance (expressed by δ^{15} N) is a potential tool for identifying and quantifying the origin and environmental dynamics of atmospheric NH₃ and N cycle because different sources have relatively distinct and well-characterized N isotopic signatures (Denk et al., 2017; Freyer, 1978b; Heaton, 1987; Robinson, 2001). For example, the δ^{15} N of NH₃ emitted from agricultural sources ranged from –48 to +3‰ and –56 to –4‰ for fertilizer and livestock manure (Chang et al., 2016; Felix et al., 2013, 2014; Freyer,

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1978a; Ti et al., 2018), with an average of $-46 \pm 5\%$ and -28 ± 1.1 %, respectively, was much lower than those emitted from fossil fuel sources (-6%) and other natural NH₃ emission sources such as ocean $(-8\pm8\%)$ presented by Elliott et al. (2019). Based on the variations in $\delta^{15}N-NH_3$ in different sources, the contribution of soil NH₃ emission to N deposition, atmospheric NH₃, and aerosol ammonium was successful quantified recently (Chang et al., 2016; Felix et al., 2017; Pan et al., 2016; Ti et al., 2018). For instance, according to the field observations of $\delta^{15}N-NH_3$ values of major local emissions, estimated that volatilized fertilizer and animal excreta contributed more than 60% to wet and dry N deposition. However, NH₃ emission from soil is a complex process depending on factors such as soil pH, NH⁺₄ concentration, especially fertilizer application rate. Previous analyses showed that higher fertilizer N inputs along with higher NH₃ emission (liang et al., 2017). These factors may result in the produced NH_3 with different δ^{15} N values due to the fractionating process (Nikolenko et al., 2018). For example, Bedard-Haughn et al. (2003) indicated that actual fractionation could depend on the soil pH and temperature and when the supply of NH⁺₄ is unlimited, while the isotopic fractionation could results in the changes of the $\delta^{15}N-NH_3$ values which may impacts on the identify of emissions sources (Huang et al., 2019).

However, published data on the δ^{15} N values of NH₃ volatilized from different application rates during the whole NH₃ emission processes is rare. Ti et al. (2018) indicated that factors such as NH₃ volatilization rates can influence the values of δ^{15} N–NH₃, and the isotopic compositions of NH₃–N from volatilized fertilizer after applications ranged from –17.6 to 3.3‰ for samples collected over the winter wheat season, and from –5.5 to –0.8‰ for samples collected over the summer rice season, with N fertilizer application rate of 180 and 300 kg N ha⁻¹, respectively. Thus using a constant δ^{15} N–NH₃ values to represent different N application rates and the detailed changes during the volatilization process could lead to the uncertainty of traceability results. Hence it is crucial to precisely determine isotopic signatures of fertilized soil NH₃ volatilization during the whole NH₃ emission processes under different N



Fig. 1. The schematic diagram of the incubation for the measurement of $\rm NH_3$ volatilization from soil in this study.

application rates to improve the use of stable isotopes for reliable source apportionment.

Here, we therefore aimed to 1) identify the values of $\delta^{15}N-NH_3$ during NH₃ volatilization process under different urea application rates from same soil; and 2) to discuss the factors causing variations in the $\delta^{15}N$ of volatilized NH₃. The major objectives are to contribute to further understanding of isotopic signatures of primary NH₃ sources and isotope fractionation of $\delta^{15}N-NH_3$ during soil NH₃ process.

2. Materials and methods

2.1. Soil sample

Surface soil (0–20 cm depth) samples for this study were collected in mid-November 2018 from Changshu Agro-ecological Experimental Station (31° 32′ 93″N, 120° 41′88″E), Jiangsu province in eastern China. The average annual precipitation in this region is 1038 mm, and the mean air temperature is 15.5 °C. The soil in this site is classified as Gleyi-Stagnic Anthrosol (CRGCST 2001) developed from lacustrine sediments. Roots and visible rocks in soil were carefully removed manually and then soil sample was airdried and ground to pass through a 2 mm stainless steel sieve to achieve a high degree of homogeneity.

2.2. Soil physical and chemical analysis

Soil texture was determined by the laser diffraction method, and soil bulk density of 0–20 cm soil layer was measured according to the cutting-ring method. Soil NH⁴₄–N and NO₃–N concentrations were extracted using 2 M KCl by agitating for 1 h on a mechanical shaker, and then filtered and measured using a Skalar San++ continuous flow analyzer (Breda, The Netherlands). Soil pH was measured at a 1:2.5 (v/v) soil:water suspension using a glass electrode. The TN and TC concentrations were determined by the dry combustion method using a Vario MAX CN analyzer (Elementar, Vario Max CN, Germany).

2.3. Ammonia volatilization experiment

Ammonia volatilization experiment was carried out in the controlled laboratory conditions. One hundred g (dry weight basis) soil was weighed into 500 ml-mason jar. The N fertilizer treatments were: 1) control (0 N applied); 2) 7.04 mg urea (equivalent to 20 kg N ha^{-1} based on the soil surface area in the jar); 3) 63.36 mg urea (equivalent to 180 kg N ha^{-1}); and 4) 126.72 mg urea (equivalent to 360 kg N ha^{-1}), with three replicates. Urea with deionized water was uniformly applied on the soil surface with a micropipette, and the basic δ^{15} N value of urea used in this study was -3.6 ± 0.1 %. Then the soil water content in each jar was adjusted to 60% water-filled pore space (WFPS) by deionized water. Jars were then placed inside an incubator at 25 °C and 95% humidity; the soils were incubated for 1, 2, 3, 4, 5, 6, 7, and 15 days. A sponge-trapping and KCl-extraction method was used to capture the volatilized NH₃ described by Chen et al. (2013). Briefly, a sponge containing 4 mL trapping solution made by combining 75 mL concentrated H₃PO₄, 40 mL glycerol, and 715 mL deionized water (the amount of acid in the 4 ml solution was sufficient for absorption of NH₃ volatilized from the soil in this experiment) were used to absorb NH₃ gas. In this process, NH₃ can be converted to NH⁴, and then prepared for the N isotopic analysis. A small sponge was inserted into a tube which was inserted in the hole of the plastic lid. This small sponge piece was moistened with the above trapping solution to allow air exchange while trapping and

preventing any external ammonia from entering the system (Fig. 1).

After each sampling interval, NH_4^+-N in the acid traps was extracted with 50 mL of 1 M KCl and measured using the Skalar San++ continuous flow analyzer after each sampling date. Changes of soil NH_4^+-N , NO_3^--N , pH, total carbon (TC) and total N (TN) were also measured after each sampling date using the methods described in the below section.

2.4. Nitrogen isotopic analysis

The isotopic N concentrations of the volatilized NH₃ and soil NH₄⁺ at natural abundance were analyzed using the method of Liu et al. (2014). In brief, the method is based on the isotopic analysis of nitrous oxide (N₂O). The NH₄⁺ is oxidized to nitrite (NO₂⁻) and then quantitatively converted into N₂O by hydroxylamine (NH₂OH) under strongly acidic conditions. The produced N₂O is analyzed using an isotope ratio mass spectrometer. Isotope ratio values are reported in parts per thousand relative to atmospheric N₂ according to the following formula:

$$\delta^{15}N - NH_X(\%) = \frac{\left(\frac{15N}{14N}\right)sample - \left(\frac{15N}{14N}\right)s \tan dard}{\left(\frac{15N}{14N}\right)s \tan dard} \times 1000$$

The N isotopic compositions of all samples were analyzed using an isotope mass spectrometer (Isoprime 100, Isoprime, UK). In the present study, international reference $\delta^{15}N-NH_{\pm}^{4}$ standards (USGS25, -30.4%; USGS26, +53.7%; and IAEA N1, +0.4%) were used for data correction. The typical analysis size was 4 mL and produced 60 nmol N₂O, with a $\delta^{15}N$ standard deviation of less than 0.3‰ and often less than 0.1‰, based on six replicates.

2.5. Statistical analysis

Data were expressed as the mean and standard deviation. A oneway analysis of variance (ANOVA) was used to test for statistically significant differences among treatments and least significant difference (LSD) calculations was used to evaluate the mean comparison between treatments. Nonlinear curve fit analyses were used to examine the relationship among soil properties, NH₃ volatilization fluxes and δ^{15} N–NH₃ values. Throughout, *p* < 0.05 was considered statistically significant. All statistical analyses were performed using SPSS ver. 22.0 (IBM Corp., Chicago, IL, USA).

3. Results

3.1. Changes of soil properties

The soil has following basic properties: sand 9.93 \pm 1.69%, silt 58.42 \pm 1.09%, clay 31.65 \pm 0.70%, soil bulk density 1.01 g cm⁻³, pH 7.09 \pm 0.03 (1:2.5 soil:water), NH₄⁺-N 3.55 \pm 0.05 mg kg⁻¹ soil, NO₃⁻-N 6.10 \pm 0.27 mg kg⁻¹ soil, Total N 0.27 \pm 0.02%, and total C 2.99 \pm 0.15%, respectively. Different urea-N application rates caused different changes in soil properties. Throughout the experiment, soil NH₄⁺-N concentrations increased sharply from day 0 to day 1, while fast decrease afterward (Fig. 2a). The soil NH₄⁺-N levels in the treatments with 0 and 20 kg N ha⁻¹ application were much lower than those in treatments with 180 and 360 kg N ha⁻¹ (p < 0.05).

Soil NO₃-N concentrations continuously increased over time (Fig. 2b). Soil NO₃-N concentrations in the treatments with 0 and 20 kg N ha⁻¹ had significantly (p < 0.05) lower values than those in the 180 and 360 kg N ha⁻¹ treatments. Furthermore, soil NO₃-N concentrations in the treatment with 180 kg N ha⁻¹ urea



Fig. 2. Changes of soil NH_4^+ -N (a), NO_3^- -N concentrations (b), and pH(c) during incubation period. Error bars indicate standard errors of triplicate samples.

application was also much lower than that in the 360 kg N ha⁻¹ treatment (p < 0.05), while there were no significant differences among the treatment with 0 and 20 kg N ha⁻¹ during the whole incubation period.

Across all treatments, soil pH followed very similar variation trends to those of soil NH⁴₊ concentrations. One day after urea addition, soil pH raised above 7 of all treatments, while gradually decreased from day 1 to day 15 (Fig. 2c). Soil pH peaked at 8.24 ± 0.03 on day 1 for 360 kg N ha⁻¹ treatment, which was higher than those of the soils with lower urea application rates. The pH values treated with 0 and 20 kg N ha⁻¹ fertilizer were significantly different from that observed under 360 kg N ha⁻¹ treatments (p < 0.05). However, significant difference was not observed between 180 and 360 kg N ha⁻¹ treatments.

Initial soil $\delta^{15}N-NH_4^+$ value was $-3.4 \pm 0.1\%$, while by the final sampling on day 15, it was $-6.6 \pm 5.4\%$, $-2.8 \pm 2.3\%$, $21.0 \pm 4.0\%$, and $14.4 \pm 1.8\%$ for 0, 20, 180 and 360 kg N ha⁻¹ treatments, respectively. Soil $\delta^{15}N-NH_4^+$ value ranged from $-24.8 \pm 1.8\%$ to $30.6 \pm 1.3\%$, $-41.0 \pm 1.8\%$ to $11.7 \pm 3.4\%$, $-4.8 \pm 2.3\%$ to $21.0 \pm 4.0\%$, and $-4.8 \pm 2.3\%$ to $14.4 \pm 1.8\%$ for the above four treatments, respectively. Observed results showed that the soil $\delta^{15}N-NH_4^+$ values of 0 and 20 kg N ha⁻¹ treatments were increased at first, then decreed, and finally increased again (Fig. 3). However, the soil $\delta^{15}N-NH_4^+$ value of 180 and 360 kg N ha⁻¹ treatments increased continuously over time.

3.2. Ammonia volatilization

NH₃–N volatilization rate varied with urea-N application rate and sampling time. The peak of daily NH₃–N volatilization was observed on day 3. NH₃–N volatilization from the 0 and 20 kg N ha⁻¹ treatment remained low and changed slightly across the incubation period, while the cumulative NH₃ volatilization increased steadily from day 1 to day 15 in the 180 and 360 kg N ha⁻¹ treated soils during the 15 days incubation period (Fig. 4). At the end of the measurement period, the cumulative NH₃ losses from treatment of 0, 20, 180, and 360 kg N ha⁻¹ urea application was 0.13 \pm 0.01, 0.23 \pm 0.04, 3.37 \pm 0.18, and 17.01 \pm 1.49 kg N ha⁻¹, respectively. Cumulative NH₃ volatilization in 360 kg N ha⁻¹ application treatment was significantly higher than other treatments across the study (p < 0.05). However, no significant differences in NH₃–N



Fig. 3. Changes of soil $\delta^{15}N-NH_4^+$ values after urea application during incubation period. Error bars indicate standard errors of triplicate samples.



Fig. 4. Cumulative NH₃–N volatilization after urea application during incubation period. Error bars indicate standard errors of triplicate samples.

volatilization were observed between 0 and 20 kg N ha^{-1} treatment.

3.3. $\delta^{15}N$ values of volatilized NH₃ from soils

The δ^{15} N values of volatilized NH₃–N varied with treatments and incubation times during the whole observation period. Along with the increase of NH₃ volatilization, the δ^{15} N decreased from day 1 to day 4, and then increased over the following days (Fig. 5). During the 15-day incubation, the δ^{15} N–NH₃ values for the 0, 20, 180, and 360 kg N ha⁻¹ treatment ranged from –11.1 to –4.5‰, –32.7 to –18.4‰, –40.6 to –27.4‰, and –46.0 to –32.2‰, respectively. Across all treatments, δ^{15} N–NH₃ was lower in higher urea-N treatments than those in control. Mean δ^{15} N values of NH₃ volatilized from the 0, 20, 180, and 360 kg N ha⁻¹ treatment was –16.2 ± 7.3‰, –26.0 ± 5.4‰, –34.8 ± 4.8‰, and –40.6 ± 5.7‰, respectively. Significant differences (p < 0.05) in δ^{15} N–NH₃ values were observed among all treatments.



Fig. 5. δ^{15} N values of volatilized NH₃ with days after urea was added to soil. Error bars indicate standard errors of triplicate samples.

4. Discussion

4.1. Characterizes of $\delta^{15} N$ values in NH_3 during volatilization process

Soil NH₃ volatilization is a major source of air pollutant that could result in negative impacts on the environment and human health (Paulot et al., 2014; Ti et al., 2019). Although isotopic signature investigation of NH₃ emission from soils through stable isotope technique can be used to quantify and characterize the contribution of soil NH₃ in the air, much more detailed characterizes of $\delta^{15}N-NH_3$ values under different N applications should be studied to explored more accurate traceability results. Observed results in this study showed wide variations in the δ^{15} N values of NH₃ volatilized from different rates of urea N applied to soils. The average δ^{15} N–NH₃ for the urea-N application treatments in this study ranged from $-40.6 \pm 5.7\%$ (360 kg N ha⁻¹) to $-26.0 \pm 5.4\%$ $(20 \text{ kg N ha}^{-1})$, which were much lower than those values of basic soil and urea. With the increase of urea application rate, the average δ^{15} N–NH₃ values decreased during the whole incubation period (Fig. 6). In addition, there were large variations of $\delta^{15}N-NH_3$ during volatilization process due to sampling time (Fig. 5).

Although our results falling within the range of previously reported values ranges from -52% to 3.3% (Chang et al., 2016; Felix et al., 2013; Ti et al., 2018; Wells et al., 2015), similar/same $\delta^{15}N-NH_3$ values were investigated with different N application rates. For example, the $\delta^{15}N-NH_3$ from volatilized fertilizer ranged from -48.0 to -36.3% for samples collected over a cornfield after 135 kg N ha⁻¹ urea applications from a field observation (Felix et al., 2013), while similar $\delta^{15}N-NH_3$ values were observed under 360 kg N ha⁻¹ urea application in this study. Therefore, it is important to use local data to trace the sources of air NH₃. Furthermore, the trends of $\delta^{15}N-NH_3$ through the experiment after N application could indicate that there were large variations of $\delta^{15}N-NH_3$ values during the volatilization process (Frank et al., 2004; Wells et al., 2015).

4.2. Factors controlling NH₃ volatilization and their impact on $\delta^{15}N$

Soil NH₃ volatilization affects by several factors such as temperature, N application rate, and soil pH. These factors can affect the NH₃ volatilization rate and amount as well as isotopic fractionations and δ^{15} N values (Bussink and Oenema, 1998; Felix et al.,



Fig. 6. δ^{15} N values of the sources of soil, urea, and NH₃ volatilized of the whole volatilization process from different urea application rates in this study (mean \pm SD).

2013; Haynes and Williams, 1993; Sommer et al., 2004). Once urea is applied onto soil, NH₃ could be volatilized from urea hydrolysis under the high pH condition created by urea hydrolyses to NH⁴₄ and bicarbonate (Bedard-Haughn et al., 2003; Ferguson et al., 1984; Sherlock and Goh, 1985). Thus, increasing pH increases NH₃ volatilization rates while decreasing δ^{15} N–NH₃ and fractionation factors. A recent study also observed that higher pH along with higher N fractionation factor during NH₃ volatilization process (Cejudo and Schiff, 2018). The quadratic polynomial regression equation in this study demonstrated a statistically significant correlation between δ^{15} N–NH₃ values and soil pH (Fig. 7a).

In addition, soil NH[‡] availability is a dominant factor controlling NH₃ volatilization, NH₃ flux was positively correlated with the soil NH[‡] concentration (Malhi and Mcgill, 1982; Shang et al., 2014; Sommer et al., 2004); hence the increases of NH[‡]-N would lead to more light NH₃ molecules being released to the atmosphere from soils. The δ^{15} N–NH₃ observed in this study was significantly correlated with soil NH[‡]-N concentration (Fig. 7b). Furthermore, according to Jiang et al. (2017), NH₃ volatilization increase exponentially with N application rates, thereby the δ^{15} N–NH₃ value was significantly affected by urea-N rate. We found that higher NH₃ volatilization along with lower δ^{15} N–NH₃ value in this study (Fig. 7c). Similarly, there was a strong negative logarithmic correlation between the δ^{15} N–NH₃ values and the NH₃ volatilization rates observed from field experiment by Ti et al. (2018).

Moreover, NH₃ volatilization from soil is a highly fractionating process due to it involves several steps such as equilibrium fractionation between liquid-air interface, and molecular diffusion. which resulted in the produced NH₃ with depleted δ^{15} N (Nikolenko et al., 2018). The volatilization of NH₃ shows an isotope fractionation with a range from 24.5% to 60%, as described by Hogberg (1998), Robinson (2001), and Bedard-Haughn et al. (2003). However, published data on soil $\delta^{15}N-NH_4^+$ values was lack due to it is difficult to obtain the isotopic fractionation factors of NH₃ volatilizations from different N application rates. Wells et al. (2015) showed that the changes of soil $\delta^{15}\text{N}-\text{NH}_4^+$ increased from 1‰ to 16‰ by 80 kg urea \tilde{N} ha⁻¹ application during a 17-day in-situ observation. And based on direct measurements of fractionation during NH₃ volatilization linked with changes in the concentration and isotopic composition of the residual soil inorganic N pool, they indicated that following the addition of 80 kg N ha^{-1} urea fertilizer, NH₃ volatilization with a δ^{15} N fractionation factor of +40 ± 10‰. However, soil $\delta^{15}N-NH_4^+$ values changed from -41.0% to 30.6%over all treatments in our study (Fig. 3). Furthermore, trends of soil δ^{15} N–NH⁺ values depended on urea N application rates, for example, 0 and 20 kg N ha⁻¹ treatments were presented as inverted S-curves, while the values of 180 and 360 kg N ha⁻¹ treatments increased continuously over time (Fig. 3). In addition, $\delta^{15}N-NH_4^+$ would be influenced by nitrification because of NHx was converted to NO₃-N that can cause enrichment of the $\delta^{15}N-NH_4^+$ in soils as light isotopes are preferentially oxidized (Casciotti et al., 2003). Therefore, large isotopic fractionation factors may occur during our observation. However, the determined of the isotopic fractionation factors during volatilization process were not determined in this study due to the lack of observations on related values such as soil $\delta^{15}N-NO_{\overline{3}}$.

In addition, other factors such as temperatures and soil moisture could also impact on NH₃ volatilization and results in the changes of δ^{15} N–NH₃ value and isotopic fractionation. For example, temperature can increase the NH₃ volatilization rate and lead to more light NH₃ molecules being released to the atmosphere; hence, higher temperatures led to less fractionation between NH⁴₄ and aqueous NH₃ reported by Li et al. (2012) and Xiao et al. (2012). Moreover, there was a negative relationship between temperature and gaseous δ^{15} N–NH₃ values from field observation by Ti et al.



Fig. 7. Relationships between $\delta^{15}N-NH_3$ and soil pH (a), soil NH₄-N concentration (b), and soil NH₃ volatilization (c).

(2018), which indicates that the temporal variations of gaseous $\delta^{15}N-NH_3$ are also influenced by temperature.

4.3. Potential uses and limitations of $\delta^{15}N-NH_3$

N isotope of NH₃ volatilization can be used to investigate the source, flow and fate of N at different scales due to its unique features (Chalk et al., 2019: Choi et al., 2007: Robinson, 2001). For example, N isotopic compositions of NH₃ volatilized from soils were reported different from those from fossil fuel activities; NH₃ slip from fuel combustions was considerably higher than those from fertilizer emissions (Elliott et al., 2019). Moreover, because of the large isotope fractionation during NH₃ volatilization process, δ^{15} N of NH₃ emitted from soils was significantly lower than that of the primary agricultural sources, such as urea and soil. For instance, the primary δ^{15} N value of soil and urea was -3.4 ± 0.1 and -3.6 ± 0.1 % in this study, which was much higher than that of $\delta^{15}N-NH_3$ (Fig. 6). Thus, δ^{15} N values of NH₃ volatilization can aid in identifying emission sources contribution to air pollution (Felix et al., 2017). In fact, NHx isotopes have been successfully used to trace atmospheric reactive N sources on ecosystem, regional, and national scales (Chang et al., 2016; Felix et al., 2014; Ti et al., 2018). These results illustrate that isotope of NH₃ volatilization can aid in understanding emissions sources and N cycle.

However, some factors such as temperature, soil pH, and soil moisture could largely affect $\delta^{15}N-NH_3$ values. Although we provided the characterizes of $\delta^{15}N$ values in NH₃ during the whole volatilization process under different N application rates, it is still a big difficulty to quantify N sources and cycles using ^{15}N as a tracer. Therefore, the successful uses of N isotopic composition of NH₃ require a comprehensive database which includes $\delta^{15}N-NH_3$ values under different conditions and a quantification of its isotopic fractionation during N cycling processes in the future. Hence more research is needed in this area in relation to the factors that impact on isotopic signatures and mechanisms driving variations in these signatures.

5. Conclusion

It is the first time to study the changes of $\delta^{15}N$ values of NH_3 during the whole volatilization process under different N application rates. Our study concluded that the $\delta^{15}N$ values of primary sources such as soil and urea were $3.4 \pm 0.1\%$ and $3.6 \pm 0.1\%$. NH₃ volatilized from soils depleted in $\delta^{15}N$ values, and $\delta^{15}N-NH_3$ decreased with the increase of urea application rates. During the volatilization process, the $\delta^{15}N-NH_3$ decreased from day 1 to day 4, and then increased over the following days. In addition, volatilization process resulted in NH₃ has a lower δ^{15} N value than the residual NH[±] in soils. Our observations showed that across all the experiments, δ^{15} N values of NH₃ were significantly influenced by soil pH, soil NH⁺₄ concentration, and volatilization rate. This is the first comprehensive analysis of the changes of $\delta^{15}N$ values of NH_3 during the whole volatilization process. Our results could eventually help to trace emission sources and improve our current understanding of the N cycle. However, future efforts are needed to explore the mechanisms driving these variations and the utility of δ^{15} N–NH₃ in N source partitioning.

Author contributions

Huihui Zhou and Guijian Liu conceived the presented idea, and planned experiments. Huihui Zhou, and Liqun Zhang carried out the experiments. Huihui Zhou planned and carried out the analytic calculations. Huihui Zhou, Guijian Liu, Liqun Zhang and Chuncai Zhou and Md Manik Mian contributed to the interpretation of the results. Ayesha Imtiyaz Cheema and Md Manik Mian contributed to lanaguage checking. Huihui Zhou took the lead in writing the manuscript. All authors provided critical feedback and helped shape the research, analysis and manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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