**Abstract:** Ammonia (NH$_3$) volatilized from cropland significantly impacts the ecological environment and human health. The identification and quantification of atmospheric sources of NH$_3$ from cropland are therefore important for NH$_3$ emission reduction and air pollution control. Choosing appropriate nitrogen (N) fertilizer types is one of the key ways to reduce NH$_3$ emissions from agricultural systems due to different N fertilizers with different emission factors. The natural abundance isotope of N ($\delta^{15}$N) values can well identify the source of NH$_3$ volatilization, although there is rare research on $\delta^{15}$N-NH$_3$ values volatilized when applying different types of N fertilizers. Here, we conducted an incubation experiment to study the characteristics of $\delta^{15}$N-NH$_3$ values during the whole volatilization process after different N fertilizers were applied to the soil. The results show that the cumulative NH$_3$ volatilization from urea (U), urease inhibitor fertilizer (UI), compound fertilizer (CF) and ammonium nitrate phosphate fertilizer (AP) treatment was 5.25 ± 0.00, 3.11 ± 0.00, 3.22 ± 0.19 and 1.38 ± 0.12 kg N ha$^{-1}$ at the end of the 15-day incubation period, respectively. The average $\delta^{15}$N value of NH$_3$ volatilized from the U, UI, CF and AP treatments was −36.02 ± 4.95, −29.08 ± 9.70, −35.18 ± 4.98 and −29.42 ± 4.33‰, respectively. Generally, the $\delta^{15}$N-NH$_3$ values ranged from −41.33 to −6.30‰ during the NH$_3$ volatilization process. The $\delta^{15}$N-NH$_3$ value was lower in the U treatment than in the UI and AP treatments ($p < 0.05$), which suggests that N forms and the slow-release additions of different fertilizers, such as NO$_3^-$-N and urease inhibitors, can delay or slow down NH$_3$ volatilization, resulting in relative isotopic enrichment. Therefore, the basic properties of different N fertilizers, the changes in soil NH$_4^+$-N and cumulative NH$_3$ during the volatilization process significantly impacted the $\delta^{15}$N-NH$_3$ values.

**Keywords:** fertilizer types; soil NH$_3$ volatilization; variation in $\delta^{15}$N-NH$_3$; nitrogen cycle; source tracing

**1. Introduction**

Ammonia (NH$_3$) is an important alkaline gas and one of the main reactive nitrogen (N) compounds in the atmosphere, and it plays a key role in atmospheric transport and the global N cycle [1,2]. However, excessive NH$_3$ emission exerts negative influences on the ecological environment and human health, with effects such as soil acidification, water eutrophication and secondary particulate pollution [3–8]. NH$_3$ emitted from fertilizer applications and livestock waste, accounting for approximately 90% of total NH$_3$ emissions in China, has been recognized as a major source of atmospheric NH$_3$ [9,10]. Globally, the total agricultural NH$_3$ emissions from the use of synthetic N fertilizer were considerable,
especially in China; the proportion reached approximately 34% [11]. However, the above estimations of the sources of contributions of NH₃ emission from agriculture or cropland were focused on the “bottom-up” emission inventory methodology and model simulation method [12,13]. Bottom-up statistical methods require detailed spatiotemporal information on local agricultural practices and environmental conditions to ensure the accuracy of activity data and emission factors, and there are large uncertainties in using these methods because it is difficult to obtain real-time NH₃ emission factors, activity data, etc. [10,14]. Moreover, the results of model simulations are difficult to verify due to the limitation of long-term observations of atmospheric NH₃ and the uncertainty of atmospheric transport [10].

Therefore, complementary tools for accurately apportioning emissions sources that contribute to atmospheric NH₃ are needed for NH₃ pollution control. The natural abundance of N (^{15}N/^{14}N, expressed as $\delta^{15}$N), which can characterize the distinct $\delta^{15}$N signatures of each source [15–18], was used to trace the sources of atmospheric NH₃. A previous study indicated that the $\delta^{15}$N-NH₃ values between agricultural sources and non-agricultural sources were significantly different [19]. For example, Bhattachar et al. (2021) indicated that $\delta^{15}$N-NH₃ emitted from fertilizer use (i.e., $-28.3 \pm 5.8\%$) and livestock manure (i.e., $-35.4 \pm 11.5\%$) was significantly lower than from fossil fuel (i.e., $0.7 \pm 6.5\%$) [18]. In addition, according to the relatively distinct isotopic signature of NH₃ emission sources, the contributions of different sources to sinks can be estimated by the isotope traceability model [18,20]. For instance, Ti et al. (2018) identified that the N deposition contribution from agricultural sources (volatilized fertilizer and animal excreta) was more than 60% through field observation data of $\delta^{15}$N-NH₃ [21]. However, currently, there is insufficient research on the $\delta^{15}$N values of NH₃ volatilization from different N fertilizers applied to soils [22]. Previous research has mainly focused on $\delta^{15}$N-NH₃ values from urea application, lacking comparison with $\delta^{15}$N values of NH₃ volatilized from other N fertilizers and the observations of $\delta^{15}$N-NH₃ variation throughout the whole volatilization process [23–25].

A meta-analysis showed that the fertilizer source, the use of enhanced efficiency fertilizer and the field application method are the most effective for abating NH₃ emissions effectively in the cropland system [26]. Different fertilizer types have different effects on reducing NH₃ emission, which may cause the emitted NH₃ to have different $\delta^{15}$N values. Hence, using a constant $\delta^{15}$N-NH₃ value to represent different types of N fertilizers and the detailed volatilization processes may enlarge the uncertainties in atmospheric NH₃ apportionment, and studies on $\delta^{15}$N-NH₃ values of different N fertilizer applications are limited. Given the lack of isotopic signatures of detailed NH₃ sources of different fertilizers, here, we hypothesized that (1) the $\delta^{15}$N-NH₃ values of different N fertilizers are different due to the forms of N contained in fertilizers, and (2) soil properties have different effects on the $\delta^{15}$N-NH₃ values of different fertilizers. The specific objectives of this study were to (1) clarify the characteristics of $\delta^{15}$N-NH₃ during NH₃ volatilization from different N fertilizer types applied to soils and to (2) explore the influencing factors of $\delta^{15}$N-NH₃ values in the process of NH₃ emission. Our findings can provide scientific support for the source apportionment and quantitative traceability of atmospheric NH₃.

2. Materials and Methods
2.1. Soil Sample and N Fertilizer Types

This study was conducted on soils collected from 0–20 cm topsoil sampled from Changshu Agro-ecological Experimental Station (31°32′93″ N, 120°41′88″ E) in mid-November 2018. The soil was categorized as Gleyi-Stagnic Anthrosol (CRGCST 2001), developed from lacustrine sediments. All soil samples were air-dried and passed through a 2 mm sieve after removing visible plant roots and impurities. The basic soil properties analyzed before incubation are shown in Table 1.

Four types of N chemical fertilizers—urea (U) (N, 46.33%), urease inhibitor fertilizer (UI) (N, 46.62%), compound fertilizer (CF) (N: P₂O₅: K₂O for 25: 15: 5) and ammonium nitrate phosphate fertilizer (AP) (N, 31.68%)—were selected in this study. The $\delta^{15}$N values of U, CF and AP were $-3.6 \pm 0.1$, $-3.0 \pm 0.4$ and $-0.8 \pm 0.7\%$, respectively.
Table 1. Basic soil properties.

|                     | pH  | Total N (g/kg) | SOC (g/kg) | NH₄⁺-N (mg/kg) | NO₃⁻-N (mg/kg) | Clay (%) | Silt (%) | Sand (%) | δ¹⁵N-NH₄⁺ (%) |
|---------------------|-----|----------------|------------|----------------|----------------|----------|----------|----------|---------------|
| Average             | 7.09| 0.27           | 2.99       | 3.55           | 6.10           | 31.70    | 58.40    | 9.90     | −3.4          |
| SD *                | 0.03| 0.02           | 0.15       | 0.05           | 0.27           | 0.7      | 1.1      | 1.7      | 0.1           |

* SD: standard deviation of each soil property.

2.2. Measurements of NH₃ Volatilization

The sponge-trapping method described by Ti et al. (2021) was used to measure NH₃ volatilization of different fertilizer treatments in this study [27]. Briefly, NH₃ volatilized from soils was absorbed in a sponge with the acid solution for staged cultivation. Each 100 g dry-weight soil was put into a 500 mL incubation bottle, adjusting soil moisture to 60% of water-filled pore space (WFPS) by adding deionized water. Four fertilizer treatments, (1) 63.36 mg U; (2) 63.36 mg UI; (3) 116.58 mg CF; and (4) 91.08 mg AP, equivalent to 180 kg N ha⁻¹, were applied to the soil. A sponge with a diameter of 8.5 cm and a thickness of 1 cm was placed on the neck of the incubation bottle to absorb NH₃ emissions from the soil. The sponge contained 4 mL of glycerol phosphate absorbent, sufficient for NH₃ absorption volatilized from the soil in the experiment. The bottle cap was punched with a 1.4 cm diameter hole, and a 1.2 cm diameter rubber tube was inserted into the hole. A small sponge containing the above absorbent was inserted into the hole to prevent NH₃ loss to air from the bottle (Figure 1). This experiment was designed for non-destructive sampling with three replicates to ensure experimental data accuracy. A total of 96 incubation bottles were then placed inside an incubator at a constant temperature of 25 ± 3 °C and a humidity of 95 ± 5%. The trapping sponges and incubated soils were sampled after 1, 2, 3, 4, 5, 6, 7 and 15 days. At each sampling interval, the removed trapping sponges were plunged into 50 mL of 1 mol L⁻¹ KCl and were shaken for 2.5 h at 100 rotations per minute for NH₄⁺-N sample extraction. The NH₄⁺-N in the solution was analyzed using a continuous-flow analyzer, described below.

![Figure 1. The schematic diagram of the incubation for the measurement of NH₃ volatilization from soil in this study.](image-url)
2.3. Physical and Chemical Soil Analysis

Concentrations of soil NH$_4^+$-N and NO$_3^-$-N were extracted with 50 mL of 2 mol L$^{-1}$ KCl, shaken for 1 h and determined by a continuous-flow analyzer (Skalar San$^{++}$ System, Breda, Netherlands). The minimum detection limits for determining the NH$_4^+$-N and NO$_3^-$-N concentrations were 0.046 and 0.015 mg N L$^{-1}$. Several soil samples from each bottle were taken for air-drying. The laser diffraction method was used to determine the soil texture. The soil was passed through a 20-mesh sieve and was measured at a 1:2.5 ($v/v$) soil:water suspension using a glass electrode to achieve soil pH. The dry combustion method was used to determine the TN and TC concentrations using a Vario Max CN analyzer (Elementar, Vario Max CN, Hanau, Germany).

2.4. Nitrogen Isotopic Analysis

Values of $\delta^{15}$N were measured from sponge extracts. The $\delta^{15}$N-NH$_4^+$ values were analyzed using the method of Liu et al. (2014) [28]. In short, the method is based on the isotopic analysis of nitrous oxide (N$_2$O). Based on the linear relationship between the $\delta^{15}$N of the substrate (NH$_4^+$) and the generated gas (N$_2$O), a standard curve is established, and the substrate $\delta^{15}$N-NH$_4^+$ is deduced. Isotope ratio values are reported in parts per thousand relative to atmospheric N$_2$ according to Equation (1).

$$\delta^{15}N - \text{NH}_4^+(\%) = \frac{(15N/14N)_{\text{sample}} - (15N/14N)_{\text{standard}}}{(15N/14N)_{\text{standard}}} \times 1000 \quad (1)$$

The N isotopic compositions of all samples were analyzed by an isotope mass spectrometer (Isoprime 100, Isoprime, Cheadle, UK). USGS25 ($-30.4\%$), USGS26 (+53.7\%) and IAEAN1 (+0.4\%) were selected as international reference $\delta^{15}$N-NH$_4^+$ standards for data correction. The typical analysis size was 4 mL and produced 60 nmol of N$_2$O with a $\delta^{15}$N standard deviation less than 0.3\% and often less than 0.1\%, based on six replicates.

2.5. Statistical Analysis

The data obtained in these experiments were sorted by Excel 2016. The analysis of variance was calculated by SPSS ver. 22.0 (IBM Corp., Chicago, IL, USA). The significant difference in cumulative NH$_3$ volatilization, NH$_4^+$-N and NO$_3^-$-N in soil among different treatments were tested using a one-way ANOVA and LSD (Least Significant Difference) methods. The correlogram of impact factors was drawn using R software. Within the text, all values are reported as mean $\pm$ SD, and significance is defined as $p < 0.05$.

3. Results

3.1. NH$_3$ Volatilization of Different Fertilizers

Cumulative NH$_3$ volatilization varied significantly with different types of N fertilizers at the 180 kg N ha$^{-1}$ level over time (Figure 2). Daily NH$_3$-N volatilization of U and CF treatments peaked on day 2 after fertilizer application, whereas UI and AP treatments were delayed to day 4 and day 7, respectively. NH$_3$-N volatilization from the AP treatment varied little and remained low throughout the incubation period, whereas cumulative NH$_3$ volatilization increased rapidly in the U treatment. The cumulative NH$_3$ losses from the UI and CF treatments were at the medium level compared with the U and AP treatments, and NH$_3$-N volatilization from the CF treatment increased faster than from the UI treatment at the initial stage (day 1 to day 3). The cumulative NH$_3$ volatilization from the U, UI, CF and AP treatments was 5.25 $\pm$ 0.00, 3.11 $\pm$ 0.00, 3.22 $\pm$ 0.19 and 1.38 $\pm$ 0.12 kg N ha$^{-1}$ at the end of the 15-day incubation period, respectively. There were significant differences in cumulative NH$_3$ volatilization in soils with different N fertilizers applied in all the treatments ($p < 0.05$).
3.2. \( \delta^{15}N \) Values of NH\(_3\) Volatilized from Soils

The \( \delta^{15}N \) values of NH\(_3\) volatilized from soils with different N fertilizers applied changed with time during the whole incubation period. They decreased from day 1 to day 4 and then increased after day 4 (Figure 3). Across the incubation period, the \( \delta^{15}N \) values of U, UI, CF and AP treatment ranged from \(-41.33\) to \(-26.99\)‰, \(-36.57\) to \(-6.30\)‰, \(-40.73\) to \(-27.69\)‰ and \(-33.78\) to \(-21.77\)‰, with an average of \(-36.02 \pm 4.95\), \(-29.08 \pm 9.70\), \(-35.18 \pm 4.98\) and \(-29.42 \pm 4.33\)‰, respectively. The \( \delta^{15}N \) values of NH\(_3\) volatilized from the U treatment were significantly lower than those from the UI and AP treatments during the 15-day incubation \((p < 0.05)\). However, there were no significant differences between other treatments.

Figure 3. The \( \delta^{15}N \) values of NH\(_3\) volatilized after different N fertilizers were applied to soils during 15-day incubation (all values are mean ± SD).
3.3. Variation in Soil Properties

Different N fertilizer applications created different variations in soil properties during the 15-day incubation period. Soil \( \text{NH}_4^+\)-N concentrations increased rapidly throughout the experiment and then decreased for all treatments (Figure 4a). Soil \( \text{NH}_4^+\)-N concentrations in the U, CF and AP treatments peaked on day 2 after N application, whereas those in the UI treatment peaked on day 4 (131.79 ± 3.61 mg N kg\(^{-1}\)). On day 15, the soil \( \text{NH}_4^+\)-N concentrations in the U, UI, CF and AP treatments, tending to the soil background value, were 10.00 ± 1.34, 9.59 ± 2.65, 5.56 ± 0.94 and 8.46 ± 0.81 mg N kg\(^{-1}\), respectively. Soil \( \text{NH}_4^+\)-N concentrations in the U treatment were much higher than those in the AP treatment (\( p < 0.05 \)), and there were no significant differences between the CF and UI treatments across the whole incubation period.

Soil \( \text{NO}_3^-\)-N concentrations increased continuously after N fertilizer applications over time (Figure 4b). Soil \( \text{NO}_3^-\)-N concentrations increased steadily in the U, UI and CF treatments, and the soil \( \text{NO}_3^-\)-N levels in the AP treatment increased sharply to 132.94 ± 0.96 mg N kg\(^{-1}\) and then increased relatively slowly. On day 15, soil \( \text{NO}_3^-\)-N concentrations in the U, UI, CF and AP treatments were 216.99 ± 15.88, 226.61 ± 6.84, 193.91 ± 1.92 and 233.21 ± 3.14 mg N kg\(^{-1}\), respectively. Soil \( \text{NO}_3^-\)-N concentrations in the AP treatment were significantly higher than those in the other treatments (\( p < 0.05 \)).

Soil pH had very similar variation trends to soil \( \text{NH}_4^+\)-N concentrations (Figure 4c). Soil pH peaked at 7.20 ± 0.02 in the AP treatment on day 1 after N fertilizer application and reached the greatest values at 7.83 ± 0.02 and 7.53 ± 0.05 on day 2 in the U and CF treatments, respectively, whereas the UI treatment peaked on day 4 (7.69 ± 0.04). At the end of the experiment, soil pH in the U, UI, CF and AP treatments was 6.56 ± 0.08, 6.37 ± 0.04, 6.62 ± 0.02 and 6.65 ± 0.01, respectively. Soil pH in the U treatment was significantly different from that in the AP treatment (\( p < 0.05 \)), with no significant differences between the other treatments.

3.4. Relationship between \( \delta^{15}\text{N-NH}_3 \) and Soil Properties

Throughout all treatments, \( \delta^{15}\text{N-NH}_3 \) was negatively correlated with soil \( \text{NH}_4^+\)-N and cumulative \( \text{NH}_3 \) volatilization (Figure 5). The soil \( \text{NH}_4^+\)-N concentration was positively correlated with the daily \( \text{NH}_3 \) volatilization, and the soil pH was positively correlated with the soil \( \text{NH}_4^+\)-N concentration. Moreover, the daily \( \text{NH}_3 \) volatilization negatively correlated with soil \( \text{NO}_3^-\)-N concentrations.
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Figure 4. Changes in soil NH$_4^+$-N concentrations (a), soil NO$_3^-$-N concentrations (b) and soil pH (1:2.5 soil:water) (c) after different N fertilizer applications to soils during the whole incubation process. Symbols and error bars denote mean ± SD.
Although our findings were within the range of previous studies from δ15N values of NH3 volatilized from different N fertilizer applications to soils is needed to support accurate traceability data. The results observed in this study indicate that the δ15N values of NH3 varied differently due to different types of N fertilizers applied to the soil. Although our findings were within the range of previous studies from −52.0‰ to −0.3‰, similar δ15N-NH3 values were obtained with different types of N fertilizers [21,23–25,30,31]. For example, δ15N-NH3 volatilized from urea was similar to the study of Wells et al. (2015) [23], but the N application rate was largely different. This is because the soils (Templeton Silt Loam) in the study of Wells et al. (2015) [23] have better aeration than the soils (Gleyi-Stagnic Anthrosol) in this study, which more easily emit NH3 [32]. In addition, other research on δ15N-NH3 volatilized from urea is quite different from this study due to the different research sites outside the laboratory with different N application rates [24,30].

According to previous studies, most of the observed δ15N-NH3 values were based on field monitoring of the urea application, and research on other types of N fertilizers is lacking (Figure 6). A notable finding in this study was that δ15N-NH3 values in the U treatment were significantly lower than those in the UI and AP treatments, which were distinctly different from previous research on δ15N-NH3 volatilized from soils with urea applied, as shown in Figure 6. Moreover, the sampling time caused changes in δ15N-NH3 values during the whole incubation process in this study. Similarly, prior researchers have reported a large variation in δ15N-NH3 values during the volatilization process [23,25,27].

**Figure 5.** Visualized correlation matrix of NH3-volatilization-related properties using correlogram drawing by R software (* and ** were defined as p < 0.05 and p < 0.01).
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4.2. Impacts of Fertilizer Types on $\delta^{15}$N-NH$_3$

A large amount of NH$_3$ is produced due to rapid urea hydrolysis by soil ureases (CO(NH$_2$)$_2$ + 3H$_2$O → CO$_2$ + 2NH$_3$ + 2H$_2$O) [33]. The high soil pH and NH$_4^+$ availability increase NH$_3$ volatilization rates, thus causing a decrease in $\delta^{15}$N-NH$_3$ values [27]. In this study, we found that soil pH and NH$_4^+$ concentrations were dominant factors controlling NH$_3$ volatilization, which negatively correlated with $\delta^{15}$N-NH$_3$ values. In addition, AP is produced by melting and granulating ammonium nitrate and monoammonium phosphate, a binary compound fertilizer containing NO$_3^-$N, NH$_4^+$-N and P [34]. Thus, the containing of NO$_3^-$N could result in lower soil NH$_4^+$-N and soil pH levels in the AP treatment than in the other three treatments, thereby leading to the lowest NH$_3$ volatilization and highest $\delta^{15}$N-NH$_3$ values in the four treatments. These results indicate that an increase in NO$_3^-$ in N applications can reduce NH$_3$ volatilization, thereby increasing the values of $\delta^{15}$N-NH$_3$.

Due to the addition of a urease inhibitor, the peak and amount of NH$_3$ volatilization was distinctly delayed or reduced for the UI treatment compared with the U treatment, and it was reduced by approximately 41% at the end of the experiment. These results are similar to those reported by Mariano et al. (2019) [35] and Silva et al. (2017) [32], in that cumulative NH$_3$ losses were reduced by around 50% relative to urea. The application of a urease inhibitor temporarily inhibits urease activity during urea hydrolysis [36], resulting in the prevention of a sudden increase in soil pH and avoiding the dominance of NH$_3$-N over NH$_4^+$-N in the soil [37]. Therefore, the soil pH of the UI treatment remained almost unchanged in the first four days, and NH$_4^+$-N accumulated in the soil. As a result, NH$_3$ volatilization in the UI treatment was lower than in the U treatment, and $\delta^{15}$N-NH$_3$ values were higher. These results indicate that applying a urease inhibitor can reduce NH$_3$ volatilization and subsequently increase $\delta^{15}$N-NH$_3$ to some extent. Moreover, CF used in this study was made of urea, ammonium phosphate and potassium chloride as the main raw materials. The part of N in CF existed in the form of urea, so cumulative NH$_3$ volatilization had similar trends with the U treatment in the first three days. Thereafter, NH$_3$ volatilization was dominated by ammonium phosphate (another form of N in the CF treatment), and NH$_3$ volatilization was minimal [38], resulting in $\delta^{15}$N-NH$_3$ values in the CF treatment characterized between the U and AP treatments. In conclusion, urease inhibition and increased NO$_3^-$-N can lead to a high value of $\delta^{15}$N-NH$_3$.

In general, cumulative NH$_3$ volatilization and soil NH$_4^+$-N concentrations made a direct impact on the $\delta^{15}$N-NH$_3$ emitted from N fertilizers applied to soils, whereas soil...
pH, soil NO$_3^-$-N concentrations and daily NH$_3$ volatilization affected $\delta^{15}$N-NH$_3$ indirectly. For example, the soil pH not only defines the intensity of microbiological reactions but also affects the NH$_3$ volatilization rate; it has been proved that this process is intensified under an alkaline soil pH [39,40]. With the growth of soil pH, soil NH$_4^+$-N concentrations increased, which facilitated the diffusion of NH$_3$ into the air, leading to a decrease in isotope values. Thus, soil pH affected $\delta^{15}$N-NH$_3$ indirectly in this study, and Wu et al. (2018) [41] demonstrated the negative effect of soil pH on $\delta^{15}$N-NH$_3$. Therefore, the $\delta^{15}$N-NH$_3$ volatilized from soils with different N fertilizers applied exhibited different patterns under various influencing factors.

Furthermore, changes in NH$_3$ species during NH$_3$ volatilization influenced by microbiological and physicochemical processes cause isotope fractionation effects, and the reaction product is enriched or depleted relative to the substrate [15,16]. Several studies have reported that the isotope composition of $^{15}$N during NH$_3$ volatilization varies due to isotope fractionation [42]. $^{14}$N-containing molecules react faster than those containing $^{15}$N, usually, because more energy is needed to break or form chemical bonds involving $^{15}$N than $^{14}$N [16,43,44]. NH$_3$ volatilization can strongly fractionate N isotopes ranging from 40% to 60% [16]. Thus, the isotope composition of NH$_3$ volatilization varied over time, decreasing first and then increasing. Furthermore, other factors such as soil moisture and temperatures can affect NH$_3$ volatilization and $\delta^{15}$N-NH$_3$. For example, Ti et al. (2018) [21] reported that, as the temperature increased in the field, the $\delta^{15}$N-NH$_3$ values decreased. In summary, the different types of N fertilizers, variations in soil NH$_4^+$-N and cumulative NH$_3$ during the volatilization process significantly affected $\delta^{15}$N-NH$_3$ values.

4.3. Application and Limitation of $\delta^{15}$N-NH$_3$

The distinct signature of the $\delta^{15}$N values of NH$_3$ volatilized from different emission sources has been successfully used to explore N sources, transformations, and fates in different scenarios [16,19,22]. For example, $\delta^{15}$N-NH$_3$ values in agricultural sources are significantly lower than in fossil fuel sources [19]. Moreover, $\delta^{15}$N-NH$_3$ values volatilized from soils are significantly lower than those of the background values of soils and N fertilizers because of the fractionation effect. Thus, the $\delta^{15}$N-NH$_3$ value can be an important tool to clarify the source of NH$_3$ in the atmosphere and can provide accurate data supporting the scientific and efficient fertilization of farmland and atmospheric haze control. In addition, the $\delta^{15}$N-NH$_3$ value can provide new research prospects for tracing atmospheric reactive N, such as the N deposition process, contributing to a better understanding of the N cycle in the ecosystem [19,21].

However, our study was conducted in incubation conditions. The $\delta^{15}$N values of NH$_3$ emitted from soils could be influenced by other factors, such as temperature, wind speed, moisture and land-use types [45]. NH$_3$ emitted from soils depends on multiple factors, such as soil properties, meteorological conditions and agricultural management, which may affect the $\delta^{15}$N-NH$_3$ values directly or indirectly [45,46]. The differences in chemical composition and production processes of different N fertilizers caused differences in soil properties and NH$_3$ volatilization after application to the soil, which in turn affected the differences in $\delta^{15}$N-NH$_3$ values. The use of $\delta^{15}$N as a tracer to quantify the sources and N cycling is still very difficult. Therefore, more detailed $\delta^{15}$N-NH$_3$ values in field conditions need to be quantified to improve the accuracy of atmospheric NH$_3$ traceability.

5. Conclusions

This study investigated variations in $\delta^{15}$N values of NH$_3$ volatilized from four types of N fertilizers applied to soils during a 15-day incubation process for the first time. Our observations show that the average $\delta^{15}$N-NH$_3$ volatilized from the U, UI, CF and AP treatments was $-36.02 \pm 4.95$, $-29.08 \pm 9.70$, $-35.18 \pm 4.98$ and $-29.42 \pm 4.33\%$, respectively. Our results conclude that urease inhibition and increased NO$_3^-$-N could lead to a high value of $\delta^{15}$N-NH$_3$. Furthermore, cumulative NH$_3$ volatilization and soil NH$_4^+$-N concentration were significantly correlated with $\delta^{15}$N-NH$_3$ values. Our results may ultimately help to
improve the accuracy of atmospheric NH3 traceability and enhance understanding of the N cycle. However, more mechanisms driving changes in δ15N-NH3 need to be explored in the future.

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