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The effect of acidic solutions on the determination of the natural abundance of nitrogen isotopes in ammonia

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Abstract

Atmospheric ammonia (NH_3) contributes significantly to environmental pollution and human health once it reacts with atmospheric acidic species and deposits on soil and water surfaces. The natural abundance of nitrogen isotope ($\delta^{15}N$) can be used to trace the source of NH_3 for emission control. NH_3 is generally passively absorbed by acidic solutions, which can convert NH_3 to ammonium (NH_4^+). However, it remains unclear whether the passive collection process and the acidic solutions may influence recovery at different NH_4^+ levels and introduce isotope fractionation. Here, the recovery rate of NH_3 was evaluated using two acidic solutions, sulfuric, and boric acid. Then, these two solutions were used to passively absorb isotope reference materials to assess their effects on $\delta^{15}N$ measurements. Results showed that NH_3 absorbed by sulfuric acid solution achieved an average recovery of 95%, indicating that its influence on $\delta^{15}N$ values could be ignored. In contrast, the recovery rate of the boric acid solution was below 90%, which may induce isotope fractionation during absorption. Although both solutions provided acceptable accuracy for $\delta^{15}N$ determination, sulfuric acid was more suitable than boric acid, even at NH_4^+ concentrations as low as 20 μmol L^{-1}. Finally, this method was adopted to observe the $\delta^{15}N$ values of NH_3 emitted from croplands, livestock, orchards, and vegetables, and significant differences were found among these four sources.

Keywords: Acidic solution, NH_3 absorption, Natural isotope abundance in ammonia, Precision, Applicability

Highlights

- Sulfuric acid solution achieved over 95% NH_3 recovery rate.
- Sulfuric acid solution provided reliable $\delta^{15}N$ measurements even at low NH_3 concentration.
- The optimized method was successfully applied to the field measurement of $\delta^{15}N$-NH_3.

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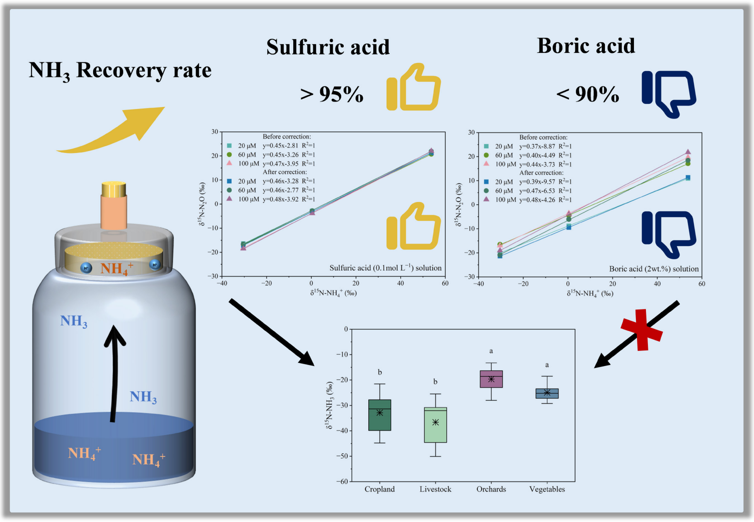
Graphical abstract



Introduction

Ammonia (NH_3) is the most important alkaline gas in the atmospheric environment, and plays a key role in the atmospheric nitrogen (N) cycle[1,2]. However, excess NH_3 in the atmosphere can react with acidic substances such as sulfur dioxide (SO_2), and nitrogen oxides (NO_x) to form ammonium sulfate ($(NH_4)_2SO_4$), and ammonium nitrate (NH_4NO_3)[3,4]. These N-containing compounds are important precursors for the formation of fine particulate matter ($PM_{2.5}$), which significantly affects air quality, solar radiation, and human health[5,6]. It can even be transported long distances through the atmosphere, thereby threatening the environmental security of downwind regions[7]. Therefore, accurate source identification of atmospheric NH_3 is essential for emission mitigation and air-quality management.

Natural abundance of nitrogen isotopes ($\delta^{15}N$) provides a promising tool for tracing NH_3 sources because different emissions exhibit distinct isotopic signatures, particularly among primary agricultural sources such as fertilizers and livestock waste[8−10]. Therefore, the $\delta^{15}N$-based source apportionment method has been successfully applied to quantify the relative contributions of various sources to atmospheric NH_3 and NH_x deposition in different regions[9,11,12].

Accurate $\delta^{15}N$ determination requires precise methods, particularly during sample collection and measurement. To date, passive collection of atmospheric NH_3 typically relies on acidic adsorbents, such as sulfuric acid, boric acid, phosphoric acid, and citric acid[13−16]. These solutions convert gaseous NH_3 to dissolved ammonium (NH_4^+) for subsequent $\delta^{15}N$ analysis. However, previous applications generally focused on quantifying NH_3 concentrations and did not investigate whether absorption solutions or collection efficiencies may introduce isotopic fractionation or be suitable for different kinds of NH_3 source collections, especially those with low concentrations. In fact, the $\delta^{15}N$ values of samples are highly sensitive to the properties and absorption efficiency of the collecting solution[9,17]. Strong and weak acidic absorbents differ substantially in their protonation capacity and NH_3-NH_4^+ conversion efficiency, which can directly influence $\delta^{15}N$ measurements[18]. For example, strong acids such as sulfuric acid provide abundant H^+ and rapidly convert gaseous NH_3 into stable $(NH_4)_2SO_4$, ensuring high trapping efficiency and reducing the possibility of isotope fractionation during collection[19]. In contrast, weak acids such as boric acid supply limited H^+, which may lead to incomplete NH_3 absorption, lower recovery rates, and a greater likelihood of kinetic isotope effects when the conversion from NH_3 to NH_4^+. Moreover, due to the influence of emission sources and meteorological conditions, NH_3 concentrations in the atmosphere vary significantly, which may also affect $\delta^{15}N$ determination[20,21]. At present, no systematic comparison has been conducted to evaluate the suitability of commonly used acidic solutions for $\delta^{15}N$ determination across different NH_3 concentration ranges.

To address this gap, two widely used acidic absorption solutions, sulfuric acid and boric acid, were selected to evaluate their performance in $\delta^{15}N$ determination using isotope reference materials (USGS25, USGS26, IAEA-N1) at different concentrations. Additionally, field sampling was conducted to demonstrate the applicability of the optimized method for characterizing $\delta^{15}N$-NH_3 signatures from primary agricultural emission sources. The objectives of this study were: (1) to determine the effect of acidic solutions on $\delta^{15}N$ measurements of NH_3; (2) to compare the accuracy and precision of different acidic solutions for determining $\delta^{15}N$ values; and (3) to observe $\delta^{15}N$ values of major NH_3 emission sources using the optimal acidic solutions.

Materials and methods

NH_3 emission collection and recovery rate of the two solutions

The sponge-trapping method described by Ti et al.[22] was used to determine NH_3 emission using sulfuric acid and boric acid solutions. Specifically, the NH_3 released from the substrate solution was sequentially absorbed by an acid-treated sponge. A 100 mL solution of $(NH_4)_2SO_4$ as the NH_4^+-N substrate was added to a 500 mL incubation bottle. To collect the emitted NH_3, a circular sponge (8.5 cm in diameter, 1 cm thick) impregnated with an acid-absorption solution was attached to the neck of the incubation bottle. The appearance of the culture bottle was described by Ti et al.[22]. A hole 1.4 cm in diameter was drilled in the bottle cap, and a rubber tube of the same diameter was inserted into it. The small sponge containing the acid-absorption solution was carefully inserted into the tube to prevent ambient air from affecting the experiment. Then, 5 mL of 0.1 mol L^{-1} sodium hydroxide (NaOH) solution was injected into the bottle through the circular sponge using a 5 mL syringe. The bottle was immediately sealed with the prepared cap. The emitted NH_3 was absorbed by the acid solution within the circular sponge. Using the syringe injection method, rather than removing the sponge to add NaOH directly, ensured that the internal atmosphere of the bottle remained isolated from external air and was not affected by ambient contamination.

After incubation at 25 °C and 95% relative humidity for 24 h, NH_3 emission was terminated by adding 0.8 mL of acid solution to neutralize excess NaOH. The circular sponge used for NH_3 absorption was extracted with 1 mol L^{-1} KCl solution at 25 °C and 200 r min^{-1} for 2.5 h, followed by filtration through Whatman 42 filter paper (2.5 μm). The pH of the filtrate was adjusted to approximately 6, and NH_4^+-N concentrations in both the extract and the residual solution were determined using a continuous-flow analyzer (Smartchem 200S/N1104238, WESTCO, France). The minimum detection limit for the NH_4^+-N concentrations was 0.03 mg N L^{-1}.

Moreover, the NH_3 recovery rate of this collection system was calculated by measuring the NH_4^+-N mass in the sponge and in the substrate before and after the reaction. The NH_3 recovery rate was determined using Eq. (1):

$$R\,(\%) = \frac{M_1 + M_2}{M_0} \times 100 \tag{1}$$

where, M_0 indicates the NH_4^+-N mass (mg N) in the standard solution before reaction. M_1 represents the NH_4^+-N mass (mg N) measured in the filtrate after sponge extraction, and M_2 means the NH_4^+-N mass (mg N) in the standard solution after reaction.

Preparation of NH_3 absorbent solution

Standard solutions of 20, 60, and 100 mmol L^{-1} NH_4^+N were prepared using $(NH_4)_2SO_4$ isotope reference materials (USG-S25, USG-S26, IAEA-N1) to simulate the process that NH_3 is converted into NH_4^+. A volume of 20 μL of standard solutions was sequentially added to 20 mL of sulfuric acid absorption solution (0.1 mol L^{-1}), and boric acid absorption solution (2 wt.%), respectively. The mixed solutions were reacted for 24 h. Then the solutions absorbed by sulfuric acid (0.1 mol L^{-1}) and boric acid (2 wt.%) were adjusted to pH 6.0 using boiled NaOH solution. After dissolution in an equal volume of ultrapure water, the pH was adjusted to 6.0 with a boiled NaOH solution. The $(NH_4)_2SO_4$ standard solutions were obtained at concentrations of 20, 60, and 100 μmol L^{-1} (calculated as N).

Before the formal experiments, standard solutions were prepared using $(NH_4)_2SO_4$ and N isotope reference materials USGS-25, USGS-26, and IAEA-N-1 at a concentration of 20 mg L^{-1}. These solutions were used to verify the systematic recovery rate of NH_3 emission measured in this study, ensuring the accuracy of the experimental data. Each treatment included three parallel replicates.

Natural abundance of isotopes analysis

The $\delta^{15}N$ values in the samples were analyzed using the chemical analysis method described by Liu et al.[23]. The N-isotopic composition of all samples was analyzed using an isotope mass spectrometer (Isoprime 100, Isoprime, UK). Briefly, NH_4^+-N in the samples was oxidized to NO_2^-, which was then converted to N_2O by NH_2OH under strongly acidic conditions. The natural variation in stable N isotopes is generally expressed using the $\delta^{15}N$ value of the heavy isotope. Internationally, N_2 is used as the standard, with its $\delta^{15}N$ defined as 0‰. Isotope ratio values are reported in parts per thousand relative to atmospheric N_2, as shown in Eq. (2):

$$\delta^{15}N_{sample}\,(‰) = \frac{\left({}^{15}N/{}^{14}N\right)_{sample} - \left({}^{15}N/{}^{14}N\right)_{standard}}{\left({}^{15}N/{}^{14}N\right)_{standard}} \times 1{,}000 \tag{2}$$

where, $\delta^{15}N_{sample}$ represents the $\delta^{15}N$ value of N_2O produced from the sample. $({}^{15}N/{}^{14}N)_{sample}$ and $({}^{15}N/{}^{14}N)_{standard}$ represent the abundance ratios of ${}^{15}N$ to ${}^{14}N$ in the sample and in the standard, respectively, and $({}^{15}N/{}^{14}N)_{standard}$ was $(3{,}676 \pm 8.1) \times 10^{-6}$.

Blank correction of mass spectrometry results is performed using the mass balance equation, as shown in Eq. (3):

$$\delta^{15}N_{blank\ corr} = \frac{\delta^{15}N_{sample} \times A_{sample} - \delta^{15}N_{blank} \times A_{blank}}{A_{sample} - A_{blank}} \tag{3}$$

where, $\delta^{15}N_{blank\ corr}$ denotes the $\delta^{15}N$ ratio of N_2O in the sample after blank correction, $\delta^{15}N_{sample}$ represents the $\delta^{15}N$ ratio of the sample measured by mass spectrometry, and $\delta^{15}N_{blank}$ indicates the $\delta^{15}N$ ratio of the blank. A_{sample} means the peak area of the sample, and A_{blank} means the peak area of the blank.

The two N atoms in N_2O molecules produced through chemical conversion originate from NO_2^- and NH_2OH, respectively. When NH_2OH reagents are from the same batch, $\delta^{15}N$-NH_2OH remains constant. Standard curves were established using isotope reference materials of different isotopic abundances to calibrate the system. The $\delta^{15}N$-N_2O of the generated N_2O can then be used to back-calculate the $\delta^{15}N$-NH_4^+ of the substrate[23,24].

Statistical analysis

Differences in $\delta^{15}N$ values were examined using the one-way analysis of variance, and Duncan's multiple range test. All statistical analyses were performed with SPSS version. 22.0 (IBM Corp., Chicago, IL, USA). The results were drawn using OriginPro 2025b (OriginLab Corporation, Northampton, MA, USA). A p-value of < 0.05 was considered statistically significant throughout the study.

Results and discussion

Recovery rate of NH_3 emission from different solutions

Experiments were conducted using $(NH_4)_2SO_4$ and N isotope reference materials (USGS-25, USGS-26, IAEA-N1) as reaction substrates to determine the systematic recovery rate of NH_3 in the experimental apparatus. The initial NH_4^+-N mass of the emission substrate was 2.00 mg. For the $(NH_4)_2SO_4$ substrate, the NH_4^+-N mass values from the three replicates were 0.94, 0.95, and 0.83 mg after the reaction, with an average of 0.91 mg, and a coefficient of variation (CV) of 7.58% (Table 1). The NH_4^+-N mass measured in the filtrates extracted from the sponges containing sulfuric acid absorption solution was 0.99, 0.98, and 1.09 mg, with an average of 1.02 mg and a CV of 5.96%. The slightly higher CV compared with the ideal threshold of 5% was mainly due to minor analytical variation in the third replicate, which showed a lower NH_4^+-N mass in the reacted $(NH_4)_2SO_4$ solution, and a higher content in the sponge extract. This deviation was attributed to minor systematic errors in continuous-flow analysis but had little influence on overall recovery efficiency. When the sponge containing the boric acid absorption solution was used, the NH_4^+-N mass from the three replicates was 0.94, 0.91, and 0.86 mg after the reaction, with an average of 0.90 mg and a coefficient of variation (CV) of 4.51%. The NH_4^+-N mass measured in the filtrates extracted from the circular sponges was 0.79, 0.78, and 0.75 mg, with an average of 0.78 mg and a CV of 2.72%. The NH_4^+-N masses in the sponge extract were lower for the boric acid absorption solution than for the sulfuric acid solution.

When NH_3 was collected using the sulfuric acid absorption method, the recovery rate of NH_4^+-N ranged from 95.98% to 96.88%

Table 1 Recovery rate of NH_3 emission from $(NH_4)_2SO_4$ solution

Replicate	NH_4^+-N mass before reaction (mg)	NH_4^+-N mass after reaction (mg)	NH_4^+-N mass absorbed by sponge (mg)	Recovery rate (%)
Sulfuric acid	2.00	0.94	0.99	96.45
	2.00	0.95	0.98	96.88
	2.00	0.83	1.09	95.98
Mean	2.00	0.91	1.02	96.43
CV%	0.00	7.58	5.96	0.47
Boric acid	2.00	0.94	0.79	86.48
	2.00	0.91	0.78	84.74
	2.00	0.86	0.75	80.47
Mean	2.00	0.90	0.78	83.90
CV%	0.00	4.51	2.72	3.68

Table 2 Recovery rate of NH_3 emission from different N isotope standard solutions

Standard solutions	NH_4^+-N mass before reaction (mg)	NH_4^+-N mass after reaction (mg)	NH_4^+-N mass absorbed by sponge (mg)	Recovery rate (%)
Sulfuric acid				
USGS-25	2.00	0.89	1.09	99.09
CV%	0.00	8.64	6.77	0.16
USGS-26	2.00	0.89	0.99	97.72
CV%	0.00	2.83	5.00	1.24
IAEA-N1	2.00	0.83	1.09	96.03
CV%	0.00	4.89	4.05	0.17
Boric acid				
USGS-25	2.00	0.90	0.97	93.41
CV%	0.00	4.61	0.55	1.93
USGS-26	2.00	0.82	0.94	90.27
CV%	0.00	2.15	2.35	2.20
IAEA-N1	2.00	0.83	0.93	88.45
CV%	0.00	2.02	0.45	0.71

(mean = 96.43%, CV = 0.47%), while the recovery rate of NH_4^+-N ranged from 80.47% to 86.48% (mean = 83.90%, CV = 3.68%) for the boric acid absorption method. Results indicated that the sulfuric acid absorption method had high accuracy and reproducibility of the experimental system for NH_3 emission measurements.

For isotopic measurements, the influence of recovery rate on δ^{15}N accuracy mainly depends on isotope fractionation (ε) during the isolation process. When the system recovery rate is greater than 95%, the resulting deviation in δ^{15}N (approximately 3‰ under extreme conditions, ε = 20‰) is relatively small and exerts minimal influence on isotope precision[17]. Therefore, using sulfuric acid absorption to capture NH_3 can effectively preserve δ^{15}N values, whereas boric acid is less effective at maintaining isotopic integrity. The NH_3 collection apparatus and determination method developed in this study achieved higher recovery rates than those reported by Camargo Valero & Mara[25] and Zhou et al.[26]. For example, Zhou et al.[26] conducted laboratory experiments using sulfuric acid and boric acid as absorption solutions to evaluate NH_3 emission recovery rates under three pH gradients. They indicated that the NH_3 recovery rate for sulfuric acid (89.7%) was higher than that for boric acid (69.8%).

As shown in Table 2, when standard solutions of the N isotope reference materials USGS-25, USGS-26, and IAEA-N1 were used as volatilization substrates, the collection system exhibited consistently high NH_3 recovery rates. For all three standards, the initial NH_4^+-N mass was set at 2.00 mg. After reaction, the average residual NH_4^+-N masses for USGS-25, USGS-26, and IAEA-N1 were 0.89 mg (CV = 8.64%), 0.89 mg (CV = 2.83%), and 0.83 mg (CV = 4.89%), respectively. The average NH_4^+-N masses absorbed by the circular sponge using the sulfuric acid solution were 1.09, 0.99, and 1.09 mg for USGS-25, USGS-26, and IAEA-N1, with CV values of 6.77%, 5.00%, and 4.05%, respectively. The average recovery rates for NH_3 volatilization from USGS-25, USGS-26, and IAEA-N1 were 99.09%, 97.72%, and 96.03%, respectively, with CV values of 0.16%, 1.24%, and 0.17%, respectively. When the boric acid was used as an NH_3 absorption solution, the average residual NH_4^+-N masses after reaction for USGS-25, USGS-26, and IAEA-N1 were 0.90 mg (CV = 4.61%), 0.82 mg (CV = 2.15%), and 0.83 mg (CV = 2.02%), respectively. The average NH_4^+-N masses absorbed by the circular sponge were 0.97, 0.94, and 0.93 mg for USGS-25, USGS-26, and IAEA-N1, with CV values of 0.55%, 2.35%, and 0.45%, respectively. The average recovery rates for NH_3 volatilization from USGS-25, USGS-26, and IAEA-N1 were 93.41%, 90.27%, and 88.45%, respectively, with CV values of 1.93%, 2.20%, and 0.71%, respectively.

These results demonstrate that the system maintained stable, high recovery rates across all N-isotope reference solutions, comparable to those obtained with $(NH_4)_2SO_4$. The sulfuric acid absorption method also showed higher accuracy and reproducibility in the experimental system for NH_3 emission measurements than the boric acid solution method. The low CVs further confirm the high precision and reliability of the collection system for measuring NH_3 volatilization and its natural isotopic abundance.

Effect of different acid solutions on δ^{15}N measurement

The δ^{15}N-NH_4^+ vs δ^{15}N-N_2O conversion curves were established for different NH_4^+ concentrations absorbed by various acidic solutions. As shown in Fig. 1, δ^{15}N-NH_4^+ and δ^{15}N-N_2O exhibit excellent linear relationships (R^2 = 1) for sulfuric acid absorption solution across different NH_4^+ concentrations (20, 60, and 100 μmol L^{-1}). Mass balance equations were applied to correct δ^{15}N-N_2O measurements derived from the conversion of different acidic absorption solutions and different concentrations of $(NH_4)_2SO_4$ solutions. Before correction, the slope of the δ^{15}N-NH_4^+ vs δ^{15}N-N_2O conversion curves for sulfuric acid solution was 0.45 at 20 μmol L^{-1}, 0.45 at 60 μmol L^{-1}, and 0.47 at 100 μmol L^{-1}, respectively. After correction, the slope of the δ^{15}N-NH_4^+ versus δ^{15}N-N_2O conversion curves was 0.46 at 20 μmol L^{-1}, 0.46 at 60 μmol L^{-1}, and 0.48 at 100 μmol L^{-1}, respectively. The slight increase in the corrected slope indicates that after correction, the slopes of the δ^{15}N-NH_4^+ vs δ^{15}N-N_2O conversion curves approached the theoretical value of 0.5, improving the accuracy of isotope conversion. Besides, the minor variation in slope before and after correction suggests that NH_4^+ concentration has a weak influence on the isotope conversion relationship, so that sulfuric acid absorption solution exhibits good stability and consistency.

As shown in Fig. 2, δ^{15}N-NH_4^+ and δ^{15}N-N_2O exhibit distinct linear relationships (R^2 = 1) for boric acid absorption solution across different NH_4^+ concentrations (20, 60, and 100 μmol L^{-1}). Before correction, the slope of the δ^{15}N-NH_4^+ vs δ^{15}N-N_2O conversion curves for boric acid solution was 0.37 at 20 μmol L^{-1}, 0.40 at 60 μmol L^{-1}, and 0.44 at 100 μmol L^{-1}, respectively. After correction, the slope of the δ^{15}N-NH_4^+ vs δ^{15}N-N_2O conversion curves was 0.39 at 20 μmol L^{-1}, 0.47 at 60 μmol L^{-1}, and 0.48 at 100 μmol L^{-1}, respectively. The significant increase in the corrected slope indicates that the slopes of the δ^{15}N-NH_4^+ vs δ^{15}N-N_2O conversion curves approached the theoretical value of 0.5 after correction, especially at high concentrations of 60 and 100 μmol L^{-1}. However, the slope for the low-concentration solution (20 μmol L^{-1}) remains low, indicating that the isotope conversion efficiency of the boric acid absorption system is relatively weak at low NH_4^+ concentrations.

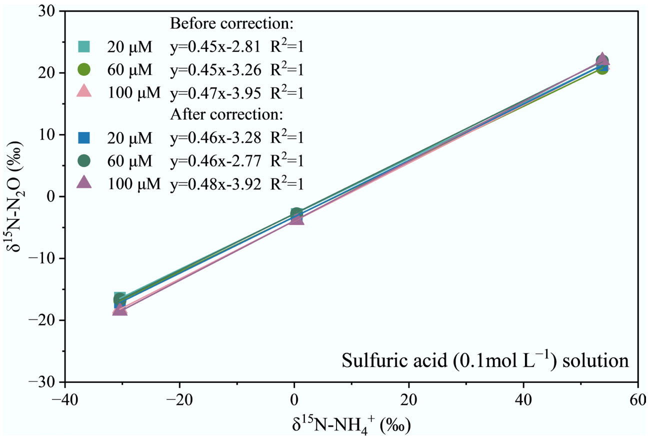


Fig. 1 Conversion curves of δ^{15}N-N$_2$O and δ^{15}N-NH$_4^+$ at different NH$_4^+$ concentrations in sulfuric acid (0.1 mol L^{-1}) solution.

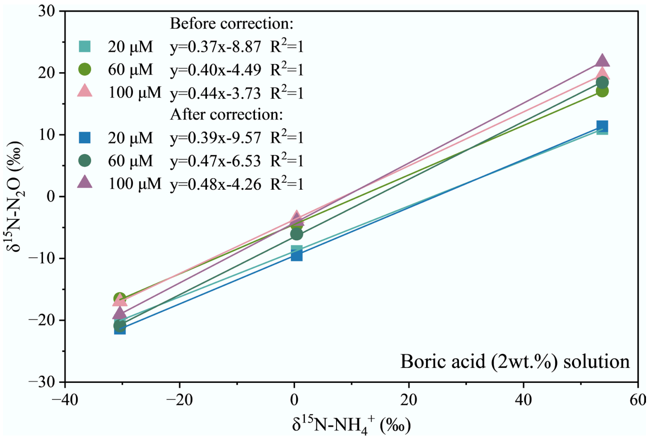


Fig. 2 Conversion curves of δ^{15}N-N$_2$O and δ^{15}N-NH$_4^+$ at different NH$_4^+$ concentrations in boric acid (2 wt.%) solution.

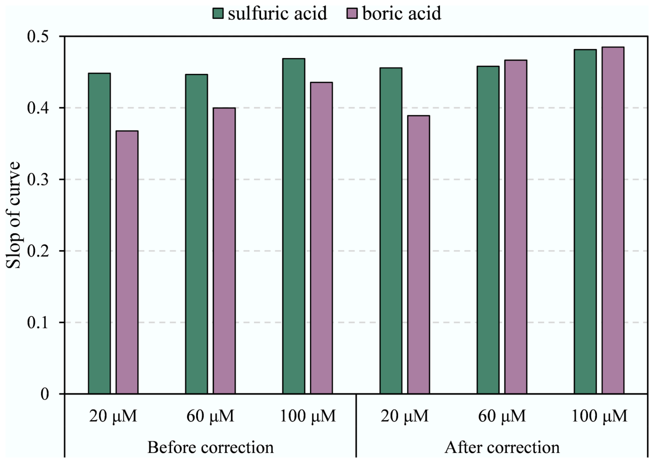


Fig. 3 Slope of conversion curves of δ^{15}N-N$_2$O and δ^{15}N-NH$_4^+$ at different NH$_4^+$ concentrations in sulfuric acid and boric acid solutions.

In this study, the NH$_4^+$-N concentration influenced the relationship between δ^{15}N-NH$_4^+$ and δ^{15}N-N$_2$O. When the concentrations of (NH$_4$)$_2$SO$_4$ standard solutions in acidic absorbents ranged from 20 to 100 μmol L^{-1}, the slopes of the δ^{15}N-NH$_4^+$ vs δ^{15}N-N$_2$O conversion curves increased with concentration, both before and after correction, gradually approaching the theoretical value of 0.5 (Fig. 3). Thus, the NH$_4^+$ concentration significantly affects the δ^{15}N value of volatilized NH$_3$. Similarly, previous studies observed that δ^{15}N-NH$_4^+$ generally decreases slightly with increasing NH$_4^+$-N concentration, attributed to rapid NH$_4^+$-N accumulation and^{15}N depletion[27−29].

Numerous studies have investigated the use of acidic solutions for atmospheric NH$_3$ absorption, and δ^{15}N values from different emission sources have also been widely examined[15,22]. However, few studies have addressed the applicability of acidic solutions for δ^{15}N measurement across different NH$_4^+$-N concentrations. In this study, the suitability of δ^{15}N measurements of NH$_3$ absorbed by various acidic solutions was analyzed. When the NH$_4^+$-N concentration in acidic solutions is identical, the slope of the relationship curve between δ^{15}N-NH$_4^+$ and δ^{15}N-N$_2$O before calibration is closest to the theoretical value of 0.5 for sulfuric acid absorption solution (Fig. 3). Compared to boric acid, sulfuric acid remains suitable for detecting δ^{15}N-NH$_4^+$ even at low NH$_4^+$-N concentrations in samples. The conversion curve of δ^{15}N-NH$_4^+$ in the sulfuric acid solution exhibited minimal influence from sample NH$_4^+$-N concentration before and after blank correction. Previous studies indicated that low concentrations of NH$_4^+$-N increased the proportion of blank contributions, leading to either underestimated or overestimated δ^{15}N values and resulting in poor reproducibility[30]. This explains the fact that when higher concentration standards are used in the conversion test, the resulting slope approaches the theoretical value of 0.5 more closely. The results indicated that sulfuric acid was more suitable for δ^{15}N-NH$_4^+$ determination when the NH$_4^+$-N concentration range in the sample is wide.

During isotope determination, systematic deviations arise from factors such as the absorber, conversion chemistry steps, sample quantity, reagent purity, and blank contributions[9]. Therefore, the slope of the relationship curve between δ^{15}N-NH$_4^+$ and δ^{15}N-N$_2$O was closer to 0.5 after black correction. Due to the simplicity of preparing sulfuric acid absorption solutions and the lower impurity content in sulfuric acid solutions compared with boric acid and citric acid solids, the impact on δ^{15}N-NH$_4^+$ mass spectrometry results was minimized[23]. Studies have also shown that acidic substances can influence NH$_3$ volatilization by regulating pH, with increased pH elevating NH$_3$ volatilization potential[31]. In acidic conditions, NH$_4^+$ remains predominantly in its ionic form, whereas in alkaline conditions, most NH$_4^+$ forms volatile NH$_3$[32]. A previous study also observed that higher pH, along with a higher N fractionation factor, occurred during the NH$_3$ volatilization process[33]. Sulfuric acid, being a strong inorganic acid, may exhibit greater NH$_4^+$ fixation capacity than weaker inorganic acids like boric acid or organic acids like citric acid during absorption and pH adjustment to 6.0[18]. This reduces the conversion of NH$_4^+$ to NH$_3$ and minimizes isotopic fractionation of both NH$_4^+$ and NH$_3$. Consequently, 0.1 mol L^{-1} sulfuric acid yields the most reliable results in δ^{15}N-NH$_4^+$ measurements.

Using the 100 μmol L^{-1} (NH$_4$)$_2$SO$_4$ standard solutions as an example, the accuracy and precision of δ^{15}N measurements obtained with different acidic solutions were evaluated, and the results are presented in Table 3. For the USGS-25 and USGS-26 standards, the measured δ^{15}N-NH$_4^+$ values using sulfuric acid and boric acid were all in close agreement with their certified reference values of −30.43‰ and 53.75‰, respectively. The deviations between measured and reference values were within ±0.5‰, indicating stable analytical performance. For the IAEA-N1, which has a relatively low δ^{15}N-NH$_4^+$ (reference value 0.41‰). The δ^{15}N-NH$_4^+$ values obtained with sulfuric acid and boric acid were 0.21‰ and 0.27‰, respectively. Although these results showed slightly greater relative

Table 3 The $\delta^{15}N$ values of 100 μmol L^{-1} $(NH_4)_2SO_4$ reference material in acidic solutions

Standard No.	Reference value (‰)	$\delta^{15}N$ values (‰)	
		Sulfuric acid (0.1 mol L^{-1})	Boric acid (2 wt.%)
USGS-25	−30.43 ± 0.40	−30.28 ± 0.78	−30.91 ± 0.91
USGS-26	53.75 ± 0.40	53.88 ± 0.13	53.71 ± 0.20
IAEA-N1	0.41 ± 0.20	0.21 ± 0.09	0.27 ± 0.20

variation, they remained within the reference uncertainty range and met analytical requirements.

Overall, the recovery rate of the boric acid solution was relatively low, which could lead to deviations in $\delta^{15}N$ values, particularly at low NH_4^+ concentrations. In contrast, 0.1 mol L^{-1} sulfuric acid provided consistent results across all standards. Considering its simple preparation and stability, sulfuric acid is recommended as the optimal absorbent for $\delta^{15}N$ determination, especially for samples with low or fluctuating NH_4^+ concentrations.

Case study of measurements for $\delta^{15}N$ values of major NH_3 emission sources

Since the sulfuric acid absorption solution provided excellent results for $\delta^{15}N$ determination of the two acid absorption solutions, it was used to conduct NH_3 absorption and $\delta^{15}N$ measurement of primary NH_3 emission sources, including cropland, livestock, orchards, and vegetables. The $\delta^{15}N$-NH_3 values for orchard and vegetable sources were obtained from Bai et al.[34], whose sampling setup and acidic absorption solution were identical to those in this study, thereby enabling a direct and valid comparison. As shown in Fig. 4, the mean $\delta^{15}N$ values of NH_3 emissions were −32.87‰ ± 7.41‰ (range: −44.79‰ to −21.56‰) for cropland, −36.64‰ ± 9.19‰ (range: −50.09‰ to −25.47‰) for livestock, −19.63‰ ± 5.09‰ (range: −27.98‰ to −13.29‰) for orchards, and −24.95‰ ± 3.29‰ (range: −29.26‰ to −18.52‰) for vegetables. The $\delta^{15}N$-NH_3 values for cropland and livestock were significantly lower than those for orchards and vegetables. Our obtained $\delta^{15}N$ values were within the range reported for agricultural sources in previous studies[24,35,36], which were obtained using passive adsorption samplers, supporting the effectiveness of the sampling results. However, the $\delta^{15}N$ values obtained with the passive sampler in this study were significantly lower than those measured with active samplers, due to isotope fractionation effects between different samplers[9]. For example, the $\delta^{15}N$ values for livestock measured using active sampling methods[15] were significantly higher than those obtained using passive samplers[24,35,36]. Previous studies have shown that $\delta^{15}N$ measurements from active and passive NH_3 samplers can differ by roughly 15‰, reflecting sampler-induced fractionation associated with diffusion limitations and incomplete absorption[9].

NH_3 emission is affected by several factors, including fertilizer application rates, NH_4^+ substrate concentrations, and temperature[37,38]. These factors directly or indirectly cause significant variations in the $\delta^{15}N$ values of emitted NH_3[22,39]. Soil NH_4^+ and NH_3 volatilization rates exhibited a negative correlation with $\delta^{15}N$ values[40]. In general, molecules containing ^{14}N react faster than those containing ^{15}N because the energy required to break or form chemical bonds involving ^{15}N is greater than that for bonds involving ^{14}N[41]. However, partial overlap in $\delta^{15}N$ values among different emission sources may be influenced by variations in geography, season, and temperature[42]. Future research requires additional high-temporal-resolution field observation experiments to supplement $\delta^{15}N$ values.

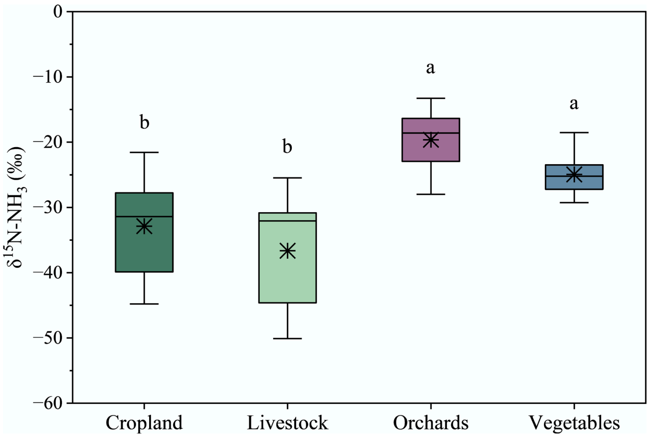


Fig. 4 $\delta^{15}N$ values for major NH_3 emission sources in sulfuric acid solution. The $\delta^{15}N$ values for cropland and livestock were measured in this study, and for orchards and vegetables were measured in the study of Bai et al.[34].

Therefore, the absorption and processing method for sulfuric acid solutions is highly suitable for determining the natural isotopic abundance of atmospheric NH_3 and its major emission sources in the field, which contributes to the source apportionment of atmospheric NH_3. In addition, NH_3 emitted from different emission sources exhibit unique $\delta^{15}N$ values, which have been successfully applied to explore N sources, transformation processes, and ultimate destinations under various scenarios[43−45]. $\delta^{15}N$-NH_3 values serve as a crucial tool for clarifying atmospheric NH_3 origins and provide precise data support for scientific and efficient fertilization in agricultural fields, as well as atmospheric haze management[46−48].

Conclusions

This study conducted a systematic investigation of recovery performance, isotope measurement stability, and field observations of NH_3 using sulfuric acid and boric acid absorption solutions by the sponge absorption method. Results indicated that sulfuric acid absorption solution achieved a significantly higher overall NH_3 recovery rate than the boric acid absorption solution, and exhibited excellent systematic stability for $\delta^{15}N$-NH_4^+ measurement when the NH_4^+-N concentration range in the sample is from 20 to 100 μmol L^{-1}. Therefore, sulfuric acid is identified as the optimal absorption for accurate $\delta^{15}N$ analysis across a wide range of NH_3 concentrations. This study also successfully applied the method to determine $\delta^{15}N$-NH_3 values for cropland, livestock, orchards, and vegetable emission sources. Therefore, the absorption method for sulfuric acid solutions is highly suitable for determining NH_3 emissions and $\delta^{15}N$-NH_3 values of major emission sources in the field, thereby contributing to the source apportionment of atmospheric NH_3.

Author contributions

The authors confirm their contributions to the paper as follows: Lingyun Peng: data curation, formal analysis, writing – original draft preparation, writing – review and editing; Chaopu Ti: conceptualization, methodology, writing – review and editing; Xiao Bai: data curation; Miao Li: data curation; Xi Wang: data curation; Bin Yin: conceptualization. All authors reviewed the results and approved the final version of the manuscript.

Data availability

The datasets used or analyzed during the current study are available from the corresponding author on reasonable requests.

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Declarations

Competing interests

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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