

$\delta^{15}\text{N}$ -stable isotope analysis of NH_x : An overview on analytical measurements, source sampling and its source apportionment

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HIGHLIGHTS

- Challenges in sampling of NH_3 sources for $\delta^{15}\text{N}$ analysis are highlighted.
- Uncertainties in the isotope-based source apportionment of NH_3 and NH_4^+ are outlined.
- Characterizing dynamic isotopic fractionation may reduce uncertainties of NH_x science.

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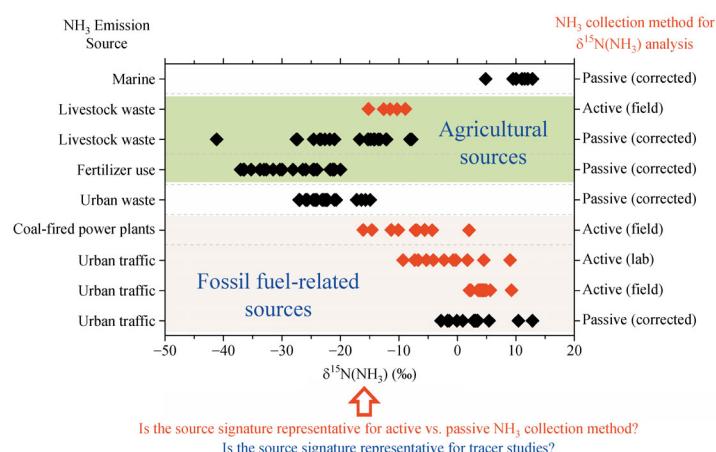
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ABSTRACT

Agricultural sources and non-agricultural emissions contribute to gaseous ammonia (NH_3) that plays a vital role in severe haze formation. Qualitative and quantitative contributions of these sources to ambient $\text{PM}_{2.5}$ (particulate matter with an aerodynamic equivalent diameter below $2.5\ \mu\text{m}$) concentrations remains uncertain. Stable nitrogen isotopic composition ($\delta^{15}\text{N}$) of NH_3 and NH_4^+ ($\delta^{15}\text{N}(\text{NH}_3)$ and $\delta^{15}\text{N}(\text{NH}_4^+)$, respectively) can yield valuable information about its sources and associated processes. This review provides an overview of the recent progress in analytical techniques for $\delta^{15}\text{N}(\text{NH}_3)$ and $\delta^{15}\text{N}(\text{NH}_4^+)$ measurement, sampling of atmospheric NH_3 and NH_4^+ in the ambient air and their sources signature (e.g., agricultural vs. fossil fuel), and isotope-based source apportionment of NH_3 in urban atmosphere. This study highlights that collecting sample that are fully representative of emission sources remains a challenge in fingerprinting $\delta^{15}\text{N}(\text{NH}_3)$ values of NH_3 emission sources. Furthermore, isotopic fractionation during NH_3 gas-to-particle conversion under varying ambient field conditions (e.g., relative humidity, particle pH, temperature) remains unclear, which indicates more field and laboratory studies to validate theoretically predicted isotopic fractionation are required. Thus, this study concludes that lack of refined $\delta^{15}\text{N}(\text{NH}_3)$ fingerprints and full understanding of isotopic fractionation during aerosol formation in a laboratory and field conditions is a limitation for isotope-based source apportionment of NH_3 . More experimental work (in chamber studies) and theoretical estimations in combinations of field verification are necessary in characterizing isotopic fractionation under various environmental and atmospheric neutralization conditions, which would help to better interpret isotopic data and our understanding on NH_x ($\text{NH}_3 + \text{NH}_4^+$) dynamics in the atmosphere.

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1 Introduction

Atmospheric ammonia (NH_3) plays a vital role in severe haze formation in the urban (Ye et al., 2011; Behera et al., 2013; Wang et al., 2015; Wei et al., 2015; Wang et al., 2016; Zhao et al., 2016; Ge et al., 2019; Jiang et al., 2021) and rural environment (Meng et al., 2018; Xu et al., 2020; Douglas et al., 2021). Despite the role of NH_3 in ion chemistry of $\text{PM}_{2.5}$ (particulate matter with an aerodynamic equivalent diameter below $2.5 \mu\text{m}$), which is due to the considerable contribution from NH_3 gas-to-particle conversion to inorganic secondary aerosol formation (Behera and Sharma, 2012; Behera et al., 2013; Huang et al., 2014), it is a largely unregulated pollutant in many regions of the world including China and the USA. Understanding the role of precursor (e.g., NH_3) in atmospheric chemistry and its contribution to fine particles is the key to designing effective air pollution control policies (e.g., Ding et al., 2019).

The stable nitrogen isotopic composition ($\delta^{15}\text{N}$) of $\text{NH}_3(\text{gas})$ and aerosol ammonium (NH_4^+) in the ambient air ($\delta^{15}\text{N}(\text{NH}_3)$ and $\delta^{15}\text{N}(\text{NH}_4^+)$, respectively) can yield valuable information about its sources and the processes they resulted from beyond what concentration alone could provide (Felix et al., 2014; Felix et al., 2017). For example, Pan et al. (2016) utilized isotope analysis method for source apportionment of NH_4^+ based on predicted initial NH_3 (calculated as initial $\delta^{15}\text{N}(\text{NH}_3) = \delta^{15}\text{N}(\text{NH}_4^+)$ (measured) $- \varepsilon_{\text{NH}_4^+ - \text{NH}_3} \times (1-f)$, where ε is the isotopic enrichment factor and f is the amount of NH_3 converted to NH_4^+ calculated as $(\text{NH}_4^+/(\text{NH}_4^+ + \text{NH}_3))$ for concurrently measured NH_3 and NH_4^+). Their study and an earlier study from Felix et al. (2014) highlighted the importance of fossil fuel related sources (e.g., vehicular exhaust, NH_3 slip from Selective Catalytic Reduction (SCR) equipped power plants, and coal combustion) based on isotope-based source apportionment of $\delta^{15}\text{N}(\text{NH}_4^+)$ and $\delta^{15}\text{N}(\text{NH}_3)$ values, respectively. Thereafter a number of studies suggested that fossil fuel related sources may be an important source of NH_4^+ and NH_3 in urban atmosphere in China based on source apportionment of $\delta^{15}\text{N}(\text{NH}_4^+)$ values (Liu et al., 2018; Pan et al., 2018a; Wu et al., 2019a; Wu et al., 2019b; Bhattacharai et al., 2020; Wu et al., 2020; Xiao et al., 2020; Zhang et al., 2020c) and $\delta^{15}\text{N}(\text{NH}_3)$ values (Chang et al., 2016; Chang et al., 2019; Bhattacharai et al., 2020; Zhang et al., 2020a; Zhang et al., 2020b), respectively.

Isotope-based source apportionment of NH_4^+ and NH_3 utilizing $\delta^{15}\text{N}(\text{NH}_4^+)$ values or $\delta^{15}\text{N}(\text{NH}_3)$ values would require relatively distinct source signature of NH_3 emission sources. After early research by Moore (1974), a number of studies (e.g., Freyer, 1978; Felix et al., 2013; Chang et al., 2016) have been carried out on characterizing $\delta^{15}\text{N}(\text{NH}_3)$ source signature of gaseous NH_3 . However, variability and

overlapping exist between previously reported $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for agricultural sources (e.g., livestock waste, fertilizer application), thus this study tries to answer if those source signatures (e.g., livestock waste (-56.1‰ to -8.9‰) (Freyer, 1978; Heaton, 1987; Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020)) are representative of the original emission sources for different NH_3 collection methods (e.g., active vs. passive). Moreover, this study investigates if previously reported source signatures of NH_3 emission sources are representative for tracer studies.

Source apportionment of NH_4^+ from $\delta^{15}\text{N}(\text{NH}_4^+)$ values requires consideration of equilibrium isotope effect of NH_3 (gas) to NH_4^+ (particle) in the air (Altieri et al., 2014; Pan et al., 2016). Notably, some progresses have been made in the past years, including but not limited to analytical techniques for $\delta^{15}\text{N}(\text{NH}_4^+)/\delta^{15}\text{N}(\text{NH}_3)$ measurement (Zhang et al., 2007; Felix et al., 2013; Liu et al., 2014), characterizing source signature of NH_3 emissions sources (e.g., fertilizer use vs. vehicular emissions reported by Felix et al. (2013)) and theoretical estimation of temperature dependent equilibrium isotopic enrichment factor ($\varepsilon_{\text{NH}_4^+ - \text{NH}_3} (\%) = 1000 \times (\alpha_{\text{NH}_4^+ - \text{NH}_3} - 1)$, where $\alpha_{\text{NH}_4^+ - \text{NH}_3}$ is the isotopic fractionation factor) for phase specific NH_3 (gas) to NH_4^+ (solid or aqueous) conversion in the atmosphere (Urey, 1947; Walters et al., 2019b). Research by Pan et al. (2016) and Chang et al. (2016) has enabled isotope-based source apportionment of ambient NH_4^+ utilizing $\delta^{15}\text{N}(\text{NH}_4^+)$ values (e.g., Pan et al., 2018a; Wu et al., 2019a), and of ambient NH_3 utilizing $\delta^{15}\text{N}(\text{NH}_3)$ values (e.g., Chang et al., 2019; Zhang et al., 2020a), respectively. However, there are some potential uncertainties in the current approach of isotope-based source apportionment of NH_4^+ and NH_3 , which are highlighted in this study.

In short, we review the recent isotope related progress that has been made in collection of NH_x ($\text{NH}_3 + \text{NH}_4^+$) for $\delta^{15}\text{N}(\text{NH}_4^+)/\delta^{15}\text{N}(\text{NH}_3)$ analysis (second section), isotope source signature of major NH_3 emissions sources (third section), and potential uncertainties in current approach of isotope-based source apportionment of NH_4^+ and NH_3 (fourth section). Outlook for further research needs including suggestions on reducing potential uncertainty are provided in the fifth section.

2 Collection of NH_x for $\delta^{15}\text{N}(\text{NH}_4^+)/\delta^{15}\text{N}(\text{NH}_3)$ analysis

2.1 Collection of NH_x for isotope studies

A summary of advancement in the concentration measurement of NH_3 from the use of the bubbler sampling method to recent online methods can be found in Sutton et al.

(2008). This section only describes recent methods for capturing NH_3 (passive sampling device or active sampling device for simultaneous collection of NH_3 and NH_4^+) for $\delta^{15}\text{N}$ analysis.

Passive diffusion samplers operate on the principle of diffusion (e.g., Adapted Low-cost Passive High Absorption, ALPHA, or Ogawa) and are widely used for measurement of $\delta^{15}\text{N}(\text{NH}_3)$ values in ambient NH_3 (e.g., Felix et al., 2014; Chang et al., 2019) and $\delta^{15}\text{N}$ isotopic fingerprinting of NH_3 emission sources (e.g., Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020).

Replicate samples (e.g., triplicate) need to be collected in parallel with passive samplers to provide estimates of accuracy and precision of method (Tang et al., 2001; Puchalski et al., 2011). Thus, passive samplers can provide confidence in the reproducibility of collected samples. However, recent studies show that $\delta^{15}\text{N}(\text{NH}_3)$ values measured with the ALPHA passive sampler could be lower than actual values based on the comparison of weekly ALPHA sampling with denuder based active sampler (DELTA) (Pan et al., 2020b), and with honeycomb denuders in Walters et al. (2020). In this case, passive samplers may still supplement field sampling of NH_3 measurement for $\delta^{15}\text{N}(\text{NH}_3)$ analysis after correction by adding 15‰ for samples collected using passive diffusion samplers (Pan et al., 2020a). Moreover, a recent laboratory-validation study on passive diffusion samplers suggest that bias may vary depending upon the amount of NH_3 collected by the sampler (Kawashima et al., 2021).

Walters and Hastings (2018) and Walters et al. (2019a) showed the suitability of the honeycomb denuder system combined with a filter pack to characterize $\delta^{15}\text{N}(\text{NH}_3)$ and $\delta^{15}\text{N}(\text{NH}_4^+)$ values when the aim is to determine both NH_3 gas and particles in the atmosphere. Honeycomb denuder combined with a filter pack sampling system has been widely used for inorganic gas and particle speciation in previous studies (Koutrakis et al., 1993; Pathak et al., 2003; Wei et al., 2015; Zhao et al., 2016). Walters et al. (2019a) indicates that a Nylon filter with an acid-coated back up filter can be used for collection to determine complete inorganic particulate concentrations for thermodynamic modeling with additional $\delta^{15}\text{N}$ measurement of speciated NH_x , whereas only an acid-coated filter could be used if $\delta^{15}\text{N}(\text{NH}_x)$ measurement were to be the primary goal. A challenge remains in field deployment of active samplers if the site is located far away due to their requirement for electricity.

2.2 Analytical techniques of $\delta^{15}\text{N}(\text{NH}_4^+)/\delta^{15}\text{N}(\text{NH}_3)$

The isotopic analysis of N relies on the generation of a stable gas as the analyte for isotope ratio mass spectrometry (IRMS). For atmospheric NH_3 samples collected using passive diffusion samplers, the sample concentration is often insufficient to satisfy conventional isotope analysis via Elemental Analyzer combustion which analyzes N_2 as an end product and requires greater than 1000 nmol N per sample for $\delta^{15}\text{N}$ analysis. Thus, this review focuses on recent progress in isotope analysis methods for small concentration (10–20 $\mu\text{mol/L}$) and low volume ($< 20 \text{ mL}$) atmospheric $\text{NH}_3/\text{NH}_4^+$ samples. Recently, more sensitive isotope analysis methods (requiring only 10–60 nmole of N per analysis) have been developed to determine $\delta^{15}\text{N}(\text{NH}_4^+)$ values for atmosphere, seawaters and soil water samples (Table 1). These methods analyze nitrous oxide (N_2O) as an end product using continuous flow purge and a cryogenically trapped system coupled with IRMS (PT-IRMS) and are: 1) bromate oxidation and azide reduction method (Zhang et al., 2007), 2) coupled bromate oxidation and denitrifier method (Felix et al., 2013), and 3) bromate oxidation and hydroxylamine reduction method (Liu et al., 2014). Briefly, NH_4^+ in the sample are oxidized to nitrite (NO_2^-) using hypobromite (BrO^-) (Zhang et al., 2007), which is then converted to N_2O using either sodium azide (NaN_3) (Method 1) or denitrifying bacteria (Sigman et al., 2001) (Method 2) or hydroxylamine (NH_2OH) (Method 3) (Liu et al., 2014) under strongly acid conditions. The principle of each method can be found in the respective references and so they are not elaborated here.

The ‘isotopic composition’ of a sample relative to a reference standard (atmospheric N_2) are reported using delta notation (δ) in units of per mil (‰) as follows (Eq. (1)):

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

Samples should be diluted to optimum NH_4^+ concentration for precise oxidation and reduction yields if NH_4^+ concentration is above the selected experimental method’s working concentration range (Table 1). The dilution is necessary to reduce undesirable isotope fractionation (Zhang et al., 2007). All three methods greatly facilitate

Table 1 Summary of the parameters of $\delta^{15}\text{N}(\text{NH}_3)/\delta^{15}\text{N}(\text{NH}_4^+)$ laboratory experimental methods

No.	Method	NH_4^+ ($\mu\text{mol/L}$)	N_2O (nmole)	Volume (mL)	Standards replicates ($\pm 1\sigma$ ‰)	References
1	Hypobromite-azide	0.5–10	10	20	0.3	Zhang et al. (2007)
2	Coupled denitrifier	10	20	20	0.7	Felix et al. (2013)
3	Hypobromite-hydroxylamine	10–20	60	4	0.3	Liu et al. (2014)

field sampling and in situ measurements due to its superiority in terms of low volume required (< 20 mL) and ability to measure low concentration (~10–15 μmol/L) samples with high throughput and precision. Overall, quantitative chemical transformation method of NH₄⁺ to N₂O (Method 3) seems more promising due to their main advantage over use of less dangerous reagent (i.e., NH₂OH) to reduce NO₂⁻ to N₂O instead of extremely toxic azide buffer reagent (e.g., Hydrazoic acid (HN₃)), and denitrifying bacteria, which may be impractical for most laboratories. When NH₄⁺ levels are too low (< 10 μmol/L), available methods can be tricky.

3 Isotope source signature of major NH₃ emission sources

3.1 Fossil fuel combustion related sources

$\delta^{15}\text{N}(\text{NH}_3)$ values of fossil fuel combustion-related sources (including emissions from coal-fired power plants and urban traffic) ($0.7\text{\textperthousand}\pm6.5\text{\textperthousand}$) and agricultural sources ($-21.9\text{\textperthousand}\pm8.7\text{\textperthousand}$) were significantly different (two-sample Welch's *t*-test, $p < 0.00001$) after correction of $\delta^{15}\text{N}(\text{NH}_3)$ values for systematic bias in passive diffusion samplers (Pan et al., 2020b; Walters et al., 2020), allowing its potential use in tracing fossil fuel-related sources and agricultural sources of NH₃ in the atmosphere. The heavier $\delta^{15}\text{N}(\text{NH}_3)$ from fossil fuel sources ($-17.8\text{\textperthousand}$ to $9.2\text{\textperthousand}$ (measured) or $-16.1\text{\textperthousand}$ to $12.8\text{\textperthousand}$ (after correction)) (Freyer, 1978; Heaton, 1987; Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020; Walters et al., 2020) is potentially due to NH₃ formation during high-temperature combustion and associated fractionation (Felix et al., 2013), compared to lighter $\delta^{15}\text{N}(\text{NH}_3)$ values observed in agricultural sources ($-56.1\text{\textperthousand}$ to $-8.9\text{\textperthousand}$ or $-41.1\text{\textperthousand}$ to $-7.8\text{\textperthousand}$ after correction) (Freyer, 1978; Heaton, 1987; Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020) (Fig. 1).

The process that leads to NH₃ emissions from three-way catalytic convertors (TWC) in automobiles and from NH₃ slip from industrial/power plants could likely produce slightly depleted values of $\delta^{15}\text{N}(\text{NH}_3)$ due to fractionation similar to depletion found in NO produced by catalytic reduction (Walters et al., 2015). However, there is a lack of studies assessing potential fractionation in $\delta^{15}\text{N}(\text{NH}_3)$ during catalytic reductions, which means it is not possible to fully explain the mechanism. It is unknown whether or in what ways the reaction pathway and exhaust gas composition affect the $\delta^{15}\text{N}(\text{NH}_3)$ value for NH₃ emitted from automobiles. However, previous studies suggest that the amount of $\delta^{15}\text{N}$ depletion or enrichment could depend on the variations in combustion-related factors (e.g., temperature of the catalyst, catalytic converter efficiency) within each vehicle (Pan et al., 2016; Berner and Felix, 2020).

Importantly, two-sample Welch's *t*-test indicates ($p = 0.37$) and suggests $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for urban traffic samples collected in road tunnels with honeycomb denuders ($2.1\text{\textperthousand}$ to $9.2\text{\textperthousand}$) (Walters et al., 2020) falls within the range of $\delta^{15}\text{N}(\text{NH}_3)$ source signature for urban traffic characterized with passive samplers (corrected) ($-2.8\text{\textperthousand}$ to $12.8\text{\textperthousand}$) (Felix et al., 2013; Chang et al., 2016). The variability observed in $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for urban traffic ($-2.8\text{\textperthousand}$ to $12.8\text{\textperthousand}$) could be likely due to the difference in active and passive collection methods. However, there is still mismatch between $\delta^{15}\text{N}(\text{NH}_3)$ values of tailpipe emissions in field study ($-9.3\text{\textperthousand}$ to $9.0\text{\textperthousand}$, $-1.9\text{\textperthousand}\pm5.5\text{\textperthousand}$) (Berner and Felix, 2020) and validated sampling techniques using citric-acid coated honeycomb denuders ($2.1\text{\textperthousand}$ to $9.2\text{\textperthousand}$, $4.2\text{\textperthousand}\pm1.8\text{\textperthousand}$) (two-sample Welch's *t*-test, $p < 0.01$) (Walters et al., 2020) (Fig. 1). This suggests more experimental and field studies to ensure representativeness of $\delta^{15}\text{N}(\text{NH}_3)$ source signature for vehicular emissions are required in future studies.

3.2 Agricultural sources

Large variability and overlapping exist between $\delta^{15}\text{N}(\text{NH}_3)$ source signature of livestock waste that ranged from $-56.1\text{\textperthousand}$ to $-8.9\text{\textperthousand}$ ($-35.4\text{\textperthousand}\pm11.5\text{\textperthousand}$) which could be due to different collection methods (e.g., 0.01 M H₂SO₄ scrubber ($-12.6\text{\textperthousand}$ to $-10.3\text{\textperthousand}$) (Freyer, 1978), HCl scrubber ($-15.2\text{\textperthousand}$ and $-8.9\text{\textperthousand}$) (Heaton, 1987), and passive diffusion samplers ($-56.1\text{\textperthousand}$ to $-22.8\text{\textperthousand}$) (Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020)) utilized in NH₃ sampling. Indeed, $\delta^{15}\text{N}(\text{NH}_3)$ source signature for livestock waste ($-15.2\text{\textperthousand}$ to $-8.9\text{\textperthousand}$) collected using active collection methods (e.g., 0.01 M H₂SO₄ scrubber (Freyer, 1978) and HCl scrubber (Heaton, 1987)) were within the range of $\delta^{15}\text{N}(\text{NH}_3)$ values ($-41.1\text{\textperthousand}$ to $-7.8\text{\textperthousand}$) collected with passive diffusion samplers (Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020) that were corrected for systematic bias in passive diffusion samplers (Fig. 1). However, $\delta^{15}\text{N}(\text{NH}_3)$ source signature for livestock waste ($-15.2\text{\textperthousand}$ to $-8.9\text{\textperthousand}$, $-11.7\text{\textperthousand}\pm2.4\text{\textperthousand}$) collected using active collection methods were statistically significantly different from source signature ($-41.1\text{\textperthousand}$ to $-7.8\text{\textperthousand}$, $-18.3\text{\textperthousand}\pm7.7\text{\textperthousand}$) characterized with passive samplers (corrected) (two-sample Welch's *t*-test, $p < 0.01$).

For fertilizer use, $\delta^{15}\text{N}(\text{NH}_3)$ source signatures ranged from $-52.0\text{\textperthousand}$ to $-35.0\text{\textperthousand}$ (Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020) where NH₃ were collected using passive diffusion samplers. The variability between $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for fertilizer use ($-52.0\text{\textperthousand}$ to $-35.0\text{\textperthousand}$) could be due to the difference in urea fertilizer types (Bateman and Kelly, 2007), urea application rates (Ti et al., 2021) and potential equilibrium and kinetic fractionation (Elliott et al., 2019) during volatilization in those field studies (Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020). $\delta^{15}\text{N}(\text{NH}_3)$ source signature for

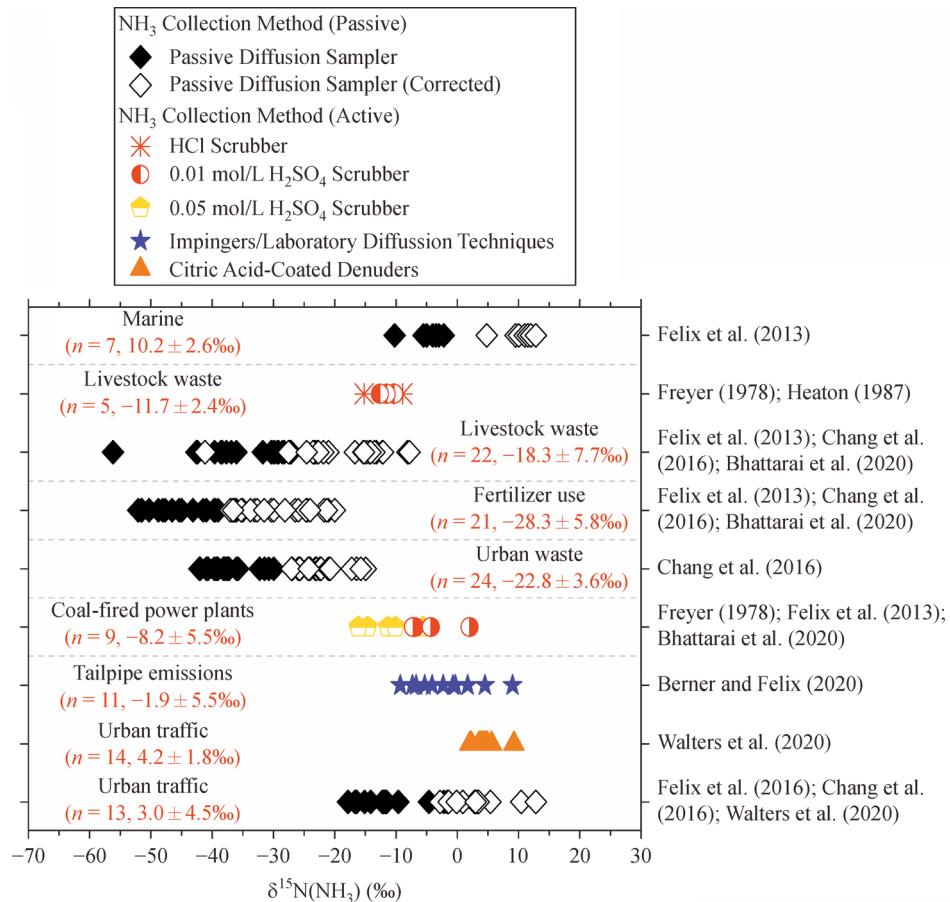


Fig. 1 Summary of previously reported $\delta^{15}\text{N}$ source signature of NH_3 ($\delta^{15}\text{N}(\text{NH}_3)$) that were collected with passive or active sampling techniques. Dashed horizontal lines classify major sources of NH_3 based on different sample collection methods utilized in previous studies. The $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for sources listed in the figure (from top to bottom) are as following: Marine (-10.2\% to 2.2\%) (Felix et al., 2013), livestock waste (active) (-15.2\% to -8.9\%), livestock waste (passive) (-56.1\% to -22.8\%), fertilizer use (passive) (-35.0\% to -35.0\%) (Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020), urban waste (passive) including human excreta (-39.6\% to -37.3\%), solid waste (-37.6\% to -29.9\%) and waste water (-42.0\% to -39.2\%) (Chang et al., 2016), coal-fired power plants (CFPP/active) which includes NH_3 slip from SCR equipped CFPP (-16.1\% to -5.6\%) (Felix et al., 2013; Bhattacharai et al., 2020) and coal combustion (-7.2\% to 2\%) (Freyer, 1978), tailpipe emissions (active) (-9.3\% to 9.0\%) (Berner and Felix, 2020), urban traffic (tunnel/active) (2.1\% to 9.2\%) (Walters et al., 2020), and urban traffic (tunnel/passive) (-17.8\% to -2.2\%) (Felix et al., 2013; Chang et al., 2016; Walters et al., 2020). $\delta^{15}\text{N}(\text{NH}_3)$ values of different sources were corrected for low bias in passive samplers by adding 15\% to measured $\delta^{15}\text{N}(\text{NH}_3)$ values (Pan et al., 2020b; Walters et al., 2020).

fertilizer use that were corrected for systematic bias in passive diffusion samplers (-37.0\% to -19.9\% , $-28.3\text{\%} \pm 5.8\text{\%}$) were significantly different from livestock waste collected using passive diffusion samplers (-41.1\% to -7.8\% , $-18.3\text{\%} \pm 7.7\text{\%}$) (two-sample Welch's t -test, $p < 0.00001$) or scrubbers (-15.2\% to -8.9\% , $-11.7\text{\%} \pm 2.4\text{\%}$) (two-sample Welch's t -test, $p < 0.00001$) (Fig. 1), allowing its potential use in tracing agricultural sources of NH_3 in the atmosphere.

Volatilization is the driving factor in deriving NH_3 from agricultural sources such as livestock waste and fertilizer application. Figure 2 shows the overlapping of instantaneous $\delta^{15}\text{N}(\text{NH}_3)$ values of liquid manure (-31.0\% to

-15.0\%) (Hristov et al., 2009) with the field-based $\delta^{15}\text{N}(\text{NH}_3)$ source signature for livestock waste (-41.1\% to -7.8\%) (Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020), characterized with passive diffusion samplers corrected for systematic bias during the initial stages of incubation (e.g., 14 days). $\delta^{15}\text{N}(\text{NH}_3)$ source signature for livestock waste are more depleted in ^{15}N during initial days of incubation as the lighter isotope molecules tend to react faster when volatilization of $\text{NH}_3\text{-N}$ is most intensive (Hristov et al., 2009; Lee et al., 2011).

Notably, field-based $\delta^{15}\text{N}(\text{NH}_3)$ source signature for livestock waste were more depleted (-41.1\% to -7.8\%) than the instantaneous $\delta^{15}\text{N}(\text{NH}_3)$ values of liquid manure

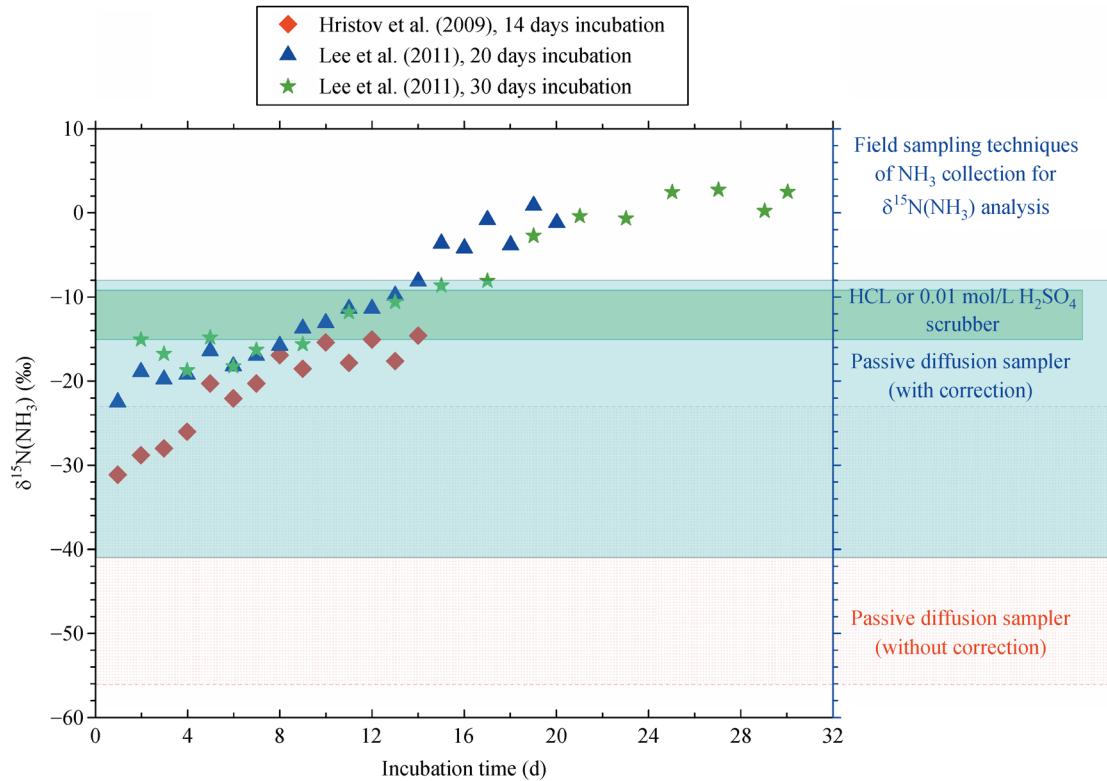


Fig. 2 Instantaneous $\delta^{15}\text{N}(\text{NH}_3)$ values in an NH_3 volatilization experiment with liquid manure during the incubation periods (14 to 30 days in total) (Hristov et al., 2009; Lee et al., 2011) and range of $\delta^{15}\text{N}(\text{NH}_3)$ values previously observed during field studies (-56.1 ‰ to -22.8 ‰ and -41.1 ‰ to -7.8 ‰ (corrected)) (Freyer, 1978; Heaton, 1987; Felix et al., 2013; Chang et al., 2016; Bhattacharai et al., 2020) for livestock waste (shaded area). During volatilization experiment, NH_3 released from liquid manure was incubated and absorbed in a $0.5\text{ mol/L H}_2\text{SO}_4$ scrubber to characterize $\delta^{15}\text{N}(\text{NH}_3)$ values in previous studies (Hristov et al., 2009; Lee et al., 2011).

(-31.0 ‰ (Hristov et al., 2009)/ -22.5 ‰ (Lee et al., 2011)/ -15.1 ‰ (Lee et al., 2011)) measured on the first or second day during various incubation experiments (Fig. 2) and, than $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for livestock waste collected with scrubbers (-15.2 ‰ to -8.9 ‰) (Freyer, 1978; Heaton, 1987). This discrepancy in $\delta^{15}\text{N}(\text{NH}_3)$ source signatures in previous studies is likely due to difference in sample collection intervals (e.g., (-27.5 ‰ to -12.1 ‰) 8–12 h (Chang et al., 2016; Bhattacharai et al., 2020)/(-41.1 ‰ to -7.8 ‰) two-four weeks (Felix et al., 2013)) because the dynamics of isotopic fractionation could affect $\delta^{15}\text{N}(\text{NH}_3)$ values due to volatilization during longer sampling periods (Högberg, 1997; Lee et al., 2011). Shorter sampling intervals could be appropriate to characterize $\delta^{15}\text{N}(\text{NH}_3)$ values in field conditions for livestock waste with either passive or active collection methods to reduce potential isotope effects. This requires further investigation with concurrent sampling of laboratory validated active sampler and passive sampler, which could additionally provide more understanding on representativeness of livestock waste sample for characterizing $\delta^{15}\text{N}(\text{NH}_3)$ values. This is because the sampling bias between the active collection method and passive sampler may vary depending upon the amount of NH_3 collected by

the sampler (Kawashima et al., 2021), which depends on sampling intervals.

4 Potential uncertainties in current approach of isotope-based source apportionment of NH_x

4.1 Source categories and their isotopic composition values in the stable isotope mixing model

Some studies have assumed three main sources of NH_3 or NH_4^+ (Pan et al., 2016; Pan et al., 2018a; Pan et al., 2018b; Berner and Felix, 2020; Xiao et al., 2020; Zhang et al., 2020c) to resolve measured $\delta^{15}\text{N}(\text{NH}_3)$ value or initial $\delta^{15}\text{N}(\text{NH}_3)$ value derived from $\delta^{15}\text{N}(\text{NH}_4^+)$ value in urban atmosphere. Other studies have assumed four main sources of NH_3 or NH_4^+ (Chang et al., 2016; Liu et al., 2018; Chang et al., 2019; Wu et al., 2019a; Wu et al., 2019b; Bhattacharai et al., 2020; Zhang et al., 2020a; Zhang et al., 2020b; Zhang et al., 2020c) in ambient atmosphere (see Supplementary data in Tables A1 and A2).

Isotopic mass balance approach would provide feasible mixing solutions when several sources of NH_3 are assumed

as possible sources and only a single isotope system (e.g., $\delta^{15}\text{N}$ of NH_3) is available (Phillips and Gregg, 2001, 2003). When there are too many sources, the $\delta^{15}\text{N}(\text{NH}_3)$ source signature of sources can be combined if they fall within a similar range and result from similar processes (Phillips et al., 2014). For example, NH_3 emitted from the volatilization process in livestock waste and fertilizer application may have similar $\delta^{15}\text{N}(\text{NH}_3)$ source signatures, so they can be combined. To ensure the qualitative representation of the major NH_3 emission sources, assumed sources and their $\delta^{15}\text{N}(\text{NH}_3)$ source signature should be carefully identified.

It should be noted that mean $\delta^{15}\text{N}(\text{NH}_3)$ source signature of sources may be derived from Keeling plots (Keeling, 1958, 1961), where y-intercept of linear regression between $\delta^{15}\text{N}$ values and 1/concentrations could characterize the mean $\delta^{15}\text{N}$ source signature. However, it is not certain whether mean $\delta^{15}\text{N}$ source signature values derived from Keeling plots (Phillips and Gregg, 2001) or the arithmetic mean of $\delta^{15}\text{N}(\text{NH}_3)$ values as adopted in various studies (Chang et al., 2016; Pan et al., 2016; Stratton et al., 2019; Berner and Felix, 2020) represent the true isotopic composition of NH_3 emissions sources, to be utilized in the isotopic mixing model for source apportionment. This might need further investigation as it has implication for source apportionment studies utilizing isotope-based method. Limited availability of $\delta^{15}\text{N}$ source signature of NH_3 emission sources and their corresponding concentration data may limit wide utilization of Keeling plots in determining the mean of $\delta^{15}\text{N}(\text{NH}_3)$ values for numerous sources.

4.2 Uncertainty from measured/corrected $\delta^{15}\text{N}(\text{NH}_3)$ values collected using passive samplers

Previous studies (Chang et al., 2016; Felix et al., 2017; Chang et al., 2019; Berner and Felix, 2020; Zhang et al., 2020a; Zhang et al., 2020b) have shown that non-agricultural sources such as fossil fuel sources (e.g., vehicle exhaust) and urban waste volatilized sources (human excreta, solid waste and wastewater) are important source of NH_3 in urban areas of China and the USA (Table 2). This is without consideration of potential fractionation in $\delta^{15}\text{N}(\text{NH}_3)$ values characterized for ambient NH_3 samples collected with passive diffusion samplers. Notably, based on recent studies (Pan et al., 2020b; Walters et al., 2020), the contribution of non-agricultural sources (e.g., fossil fuel related sources, urban waste) is likely underestimated with isotope-based source apportionment of NH_3 when $\delta^{15}\text{N}(\text{NH}_3)$ values in ambient NH_3 and $\delta^{15}\text{N}(\text{NH}_3)$ source signatures are corrected for systematic low bias (Bhattacharai et al., 2020; Pan et al., 2020a). However, it is not clear if the bias is significantly different in the shorter sampling intervals (e.g., few hours) for various sources when the concentration is high (e.g.,

livestock waste, urban wastes). For example, a recent study suggests that the bias can vary depending on amount of NH_3 collected by the passive diffusion sampler (Kawashima et al., 2021). Thus, $\delta^{15}\text{N}(\text{NH}_3)$ source signatures for some NH_3 emissions sources (e.g., livestock waste, urban wastes) probably need to be more carefully corrected for systematic bias before mean isotopic composition can be determined for tracer studies.

On the other hand, a recent study (Zhang et al., 2020a) suggested that the contribution of non-agricultural sources (e.g., vehicular emissions, NH_3 slip, urban waste) contribution might be underestimated with isotope-based source apportionment of NH_3 if the effect of isotopic fractionation due to $\text{NH}_3(\text{gas})$ to $\text{NH}_4^+(\text{particle})$ conversion on measured $\delta^{15}\text{N}(\text{NH}_3)$ values is not considered. Further investigation is needed to determine how atmospheric processing mechanisms will alter $\delta^{15}\text{N}(\text{NH}_3)$ values under various environmental (e.g., acidic environments) (Elliott et al., 2019) and atmospheric neutralization conditions (e.g., ammonium nitrate (NH_4NO_3) vs. ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) during NH_3 -rich or NH_3 -poor conditions) (Moore, 1977; Stratton et al., 2019), because this is unclear.

4.3 Uncertainty in isotope-based source apportionment of particulate NH_4^+

Isotope-based source apportionment of NH_4^+ derived from $\delta^{15}\text{N}(\text{NH}_4^+)$ values requires consideration of isotopic effects to trace back sources of NH_3 (Altieri et al., 2014) under NH_3 -rich conditions. Previous study utilized 33‰ (based on Heaton et al. (1997)) as an isotopic fractionation factor to estimate the sources of NH_4^+ from $\delta^{15}\text{N}(\text{NH}_4^+)$ values (Kawashima and Kurahashi, 2011) without consideration of temperature effects on isotopic fractionation factor (Urey, 1947; Savard et al., 2017) and ammonium partitioning ratio ($f = \text{NH}_4^+/(\text{NH}_4^+ + \text{NH}_3)$) (Pan et al., 2018a). Notably, concurrent measurements of NH_3 and NH_4^+ should be conducted to reduce uncertainty in isotope-based source apportionment of NH_4^+ that may derive from uncertainty in the f value (Pan et al., 2016; Huang et al., 2019).

Previous research accounted for isotope effects due to NH_3 gas-to-particle conversion in predicting initial $\delta^{15}\text{N}(\text{NH}_3)$ derived from $\delta^{15}\text{N}(\text{NH}_4^+)$ values (e.g., Pan et al., 2018a; Wu et al., 2019a; Wu et al., 2020) whereas there could be other sink processes (e.g., NH_3 dry deposition, wet deposition) that could alter $\delta^{15}\text{N}(\text{NH}_3)$ values (Felix et al., 2017; Savard et al., 2017). The mechanism of these sink processes is unclear, which remains a challenge. Thus, there is an opportunity to further investigate the fractionation mechanisms that could alter $\delta^{15}\text{N}(\text{NH}_3)$ values in the atmosphere due to sink processes during various phase transformation of NH_3 and NH_4^+ to increase the scope of related research (Elliott et al., 2019).

Table 2 Summary of recent isotope-based source apportionment studies on gaseous NH₃ derived from measured $\delta^{15}\text{N}(\text{NH}_3)$ values observed in urban areas

Location	Sampling period	Measured $\delta^{15}\text{N}(\text{NH}_3)$ (‰)	Relative contribution (%)		References
			Agricultural ^{a)}	Non-agricultural ^{b)}	
Beijing (China)	18/10/2014 to 29/11/2014	-35.0±5.4 (n = 12)	54	46	Chang et al. (2016)
Indianapolis (USA)	07/2009 to 06/2010	-18.0 (n = 8)*	10	90	Felix et al. (2017)
Detroit (USA)	07/2009 to 06/2010	-14.3 (n = 11)*	4	96**	Felix et al. (2017)
Shanghai (China)	07/2015 to 08/2015	-31.7±3.4 (n = 10)	47	53	Chang et al. (2019)
Texas (USA)	09/2016 to 08/2017	-19.1±10.9 (n = 22)	45	55***	Berner and Felix (2020)
Beijing (China)	03/2016 to 03/2017	-33.2±8.6 (n = 73)	28	72	Zhang et al. (2020a)
Beijing (China)	03/2016 to 03/2017	-33.2±8.6 (n = 73)	34	66	Pan et al. (2020a)
Beijing (China)	13/09/2018 to 09/10/2018	-28.9±1.5 (n = 8)	37	63	Bhattarai et al. (2020)
Beijing (China)	03/01/2017 to 25/01/2017	-	26	74	Zhang et al. (2020b)
Beijing (China)	07/02/2020 to 13/02/2020 and 25/03/2020 to 01/04/2020	-	38	62	Zhang et al. (2020b)

Notes: a) Including livestock waste and fertilizer application. b) Including urban wastes and fossil fuel related sources. ** notes that measured $\delta^{15}\text{N}(\text{NH}_3)$ values were compared to relative proportion of emission inventory data. *** Including contribution from biomass burning and wild fire (1%). **** Include contribution from urban traffic. “_” Marked no information is available in the cell.

5 Conclusions and suggestions

In this article, we highlighted that the overlapping and large variability in source signatures of different sources (e.g., livestock waste, urban traffic etc.) were likely due to differences between NH₃ collection methods used in previous studies. Notably, discrepancies between $\delta^{15}\text{N}(\text{NH}_3)$ source signatures measured in the field and in the laboratory (e.g., for livestock waste or urban traffic) indicate that collecting a representative sample for multiple NH₃ emission sources remains a challenge. Moreover, this study highlights potential uncertainties in current approaches to isotope-based source apportionment of NH₄⁺ and NH₃. In this regard, the following suggestions could reduce uncertainties in future studies:

1) More field studies are necessary to refine the $\delta^{15}\text{N}(\text{NH}_3)$ source profile of NH₃ emission sources with parallel sampling where possible, with comparison between various active samplers (e.g., scrubbers, denuders) and passive samplers to verify if $\delta^{15}\text{N}(\text{NH}_3)$ measurements are representative of emission sources.

2) Nitrogen equilibrium isotope fractionation factors ($\epsilon_{\text{NH}_4^+ - \text{NH}_3}$, also known as isotopic enrichment factor) between NH₃(gas) and NH₄⁺(particle) ($\Delta\delta^{15}\text{N}_{\text{NH}_4^+ - \text{NH}_3}$ (%)) = $\delta^{15}\text{N}(\text{NH}_4^+) - \delta^{15}\text{N}(\text{NH}_3)$) (e.g., 10.7 ‰ to 31.4 ‰ (Walters et al., 2019a)) in a field study are not consistent

compared with modeled fractionation effects (31 ‰±4 ‰) (Walters et al., 2019b). More field and laboratory studies are necessary to validate field and theoretically predicted isotopic fractionation between NH₃ gas-to-particle conversions in the atmosphere (Elliott et al., 2019). With validation, prediction of initial $\delta^{15}\text{N}(\text{NH}_3)$ from $\delta^{15}\text{N}(\text{NH}_4^+)$ values can be conducted with more certainty, for isotope-based source apportionment of NH₄⁺.

3) Transport of air mass may alter $\delta^{15}\text{N}(\text{NH}_3)$ values in ambient atmosphere (Yeatman et al., 2001; Felix et al., 2017; Savard et al., 2017) under various environmental (e.g., T, RH, pH) and atmospheric neutralization conditions (e.g., NH₃-rich, NH₃-poor conditions). Simultaneous measurements of $\delta^{15}\text{N}(\text{NH}_3)$ and $\delta^{15}\text{N}(\text{NH}_4^+)$ values using validated sample collection method in a vertical tower (at varying heights) could be conducted to increase understanding of such effects on $\delta^{15}\text{N}(\text{NH}_3)$ values and their isotopic fractionation. The consideration of such effects during prediction of initial $\delta^{15}\text{N}(\text{NH}_3)$ values may not only help to improve the isotope-based method but also support our understanding of NH_x dynamics in the atmosphere.

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