Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach

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Ammonia (NH3) emissions in the form of wet and dry atmospheric deposition are a substantial source of nitrogen pollution to sensitive terrestrial, aquatic, and marine ecosystems.1-4 Excess nitrogen loading to these ecosystems can lead to eutrophication (i.e., algal blooms, hypoxia) of surface waters, decreased biodiversity, and increased soil acidity.5 NH3 emissions are directly related to ammonium (NH4+1) deposition. In the USA, precipitation NH4+ concentrations have increased at 90% of the monitoring sites (National Trends Network, National Atmospheric Deposition Program (NADP)) from 1985 to 2002 with increases exceeding 50% occurring in a large area of central USA.6 Consequently, NH3 emissions and resulting deposition have become of particular concern to air quality managers, modelers, epidemiologists, and ecosystem scientists.

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(i.e., in vehicle engines and in electricity generation in power plants) accounts for less than 10% of NH₃ emissions in the USA. [4, 8]

Although the primary source of NH₃ in the USA is from agricultural activities, fossil-fuel combustion can be a major emission source in urban areas. [9] NH₃ is emitted from vehicles equipped with three-way catalytic converters (TWC) during the reduction of NO to reduce NOₓ emissions. [10] NH₃ emissions from road traffic have increased with increased implementation of TWCs since the 1980s. By 2000, ~95% of vehicles in the USA were equipped with TWCs. [11] NH₃ concentrations along heavily trafficked roads have been reported to be 3 to 5 times higher than background concentrations [10–13] and the concentrations near roadways are reported to decrease by 90% within 10 m from the road. [11]

NH₃ is also emitted as ‘NH₃ slip’ from electrical generating units equipped with selective catalytic reduction (SCR) and selective non-catalytic NOₓ reduction technologies. The SCR process injects NH₃ into the power plant flue gas stream where it is passed over a catalyst (V₂O₅) in the presence of oxygen. NOₓ and NH₃ react to form N₂ and water vapor:

\[ 4\text{NO} + 4\text{NH}_3 + O_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]  

(1)

If the entire NH₃ supplied does not react, this can lead to ‘NH₃ slip’ in the plant emissions. NH₃ in the emissions can also be present as ‘fuel NH₃’ formed from the combustion of N contained in the fossil fuel. However, data on the magnitude of this source are uncertain. [14] Other non-agricultural area sources of NH₃ emissions include oceans, human waste, soils, and vegetation. [5] These non-agricultural sources are difficult to quantify due to their diffuse spatial distribution and general lack of NH₃ emission data. [15]

Precise information on the stable isotopic composition of atmospheric δ¹⁵N-NH₃ values can aid in the quantification of NH₃ sources. NH₃ emitted from the most prevalent source, livestock waste, is reported to have negative values from livestock barns (−37 to −9‰) [16–19] and laboratory incubations of liquid manure (−43 to −37‰). [20] During NH₃ volatilization, the lighter ¹⁴N-NH₃ isotopologue volatilizes more readily causing low δ¹⁴N values in the emitted NH₃. In comparison, the reported δ¹⁴N values of NH₃ emitted from coal combustion (−7 to +2‰) [16] are considerably higher than those from livestock emissions. Together, these studies suggest that the isotopic composition of NH₃ from major emission sources may be helpful in source apportionment studies. However, to use this approach, a comprehensive characterization of isotopic compositions associated with various NH₃ sources is required; this task is complicated by the challenge of analyzing isotopic compositions of NH₃ sources, particularly those with low concentrations.

In the present study, we: (1) develop a new approach for the isotopic analysis of low concentration NH₃ samples, and (2) build on the published δ¹⁵N-NH₃ inventory of agricultural and fossil fuel-based NH₃ sources using this approach.

**EXPERIMENTAL**

**NH₃ emission collection methods for concentration and isotope analysis**

Passive samplers are ideal for the collection of dry nitrogen deposition as they are less expensive than active samplers, easy to use, and do not require electricity. [21–23] These advantages allow for multiple deployments of passive samplers at a single site. Passive samplers, either Ogawa (Ogawa & Co., USA, Inc., Pompano Beach, FL, USA) or Adapted Low-Cost Passive High Absorption (ALPHA) (Centre for Ecology and Hydrology, Edinburgh, UK), have been used in previous studies to collect NH₃ emissions and monitor NH₃ concentrations. [15, 24–30] The Ogawa is a double-sided passive diffusion sampler equipped with a diffusive end cap, followed by a stainless steel screen, and a 14 mm quartz filter impregnated with phosphoric acid. The ALPHA is a circular polyethylene vial (26 mm height, 27 mm diameter) with one open end. The vial contains a position for a 25 mm phosphorous acid-impregnated filter and a PTFE membrane for gaseous NH₃ diffusion. [31]

ALPHA samplers, designed for use in a nationwide NH₃ monitoring network in the UK, have a reported detection limit of 0.02 μg/m³ [32] and studies using Ogawa samplers have reported detection limits of 0.18 to 0.26 μg/m³. A previous study reported that the NH₃ concentrations collected using an ALPHA sampler more accurately reflected a reference method (annual denuder sampling (URG Corp., Chapel Hill, NC, USA)) than those using an Ogawa sampler (−2.4% and −37% median percent difference, respectively). [21] In this study, to examine the reproducibility of δ¹⁵N-NH₃ values obtained using ALPHA samplers, six sets of triplicate samples (n = 18) were deployed at different field sites.

ALPHA samplers were used at all sites for this study, with the exception of a small dairy barn where Ogawa samplers were employed. After an initial deployment of the Ogawa samplers at the small dairy operation, ALPHA samplers were used due to lower detection limits, greater accuracy, and a larger surface area that allows for a larger capacity for greater NH₃ collection. The larger collection capacity is important to ensure adequate sample mass for isotopic analysis. Prior to deployment, the ALPHA samplers were transported to the field sites in sealed mason jars containing ammonia-absorbing packets (API Ammo-Chips). The jars were placed in coolers with ice until deployment. ALPHA blanks in a sealed mason jar were transported with the deployed ALPHA samplers were used at all sites for this study, with the exception of a small dairy barn where Ogawa samplers were employed. After an initial deployment of the Ogawa samplers at the small dairy operation, ALPHA samplers were used due to lower detection limits, greater accuracy, and a larger surface area that allows for a larger capacity for greater NH₃ collection. The larger collection capacity is important to ensure adequate sample mass for isotopic analysis. Prior to deployment, the ALPHA samplers were transported to the field sites in sealed mason jars containing ammonia-absorbing packets (API Ammo-Chips). The jars were placed in coolers with ice until deployment. ALPHA blanks in a sealed mason jar were transported with the deployed ALPHA samplers and were later analyzed for [NH₃] to allow for a ‘blank correction’. After collection, the ALPHA samplers were placed back in mason jars, sealed, transported in coolers with ice, and frozen at −20°C until subsequent analysis of the samples.

In addition to the use of passive sampling, for the collection of NH₃ emissions from a coal-fired power plant, we used a modified EPA Method 7 [33, 34] in which a phosphoric acid absorbing solution was used instead of a H₂SO₄/H₂O₂ solution.

**NH₃ emission source sampling**

**Livestock waste volatilization emissions**

Ogawa passive samplers were deployed inside a 150-head dairy barn in Western Pennsylvania and directly outside the barn’s ventilation fans. The samplers were deployed for 1 month (28 June 2009 to 28 July 2009). Additional characterization of livestock waste emissions occurred at the USDA ARS, Beltsville Agricultural Research Center (BARC), Beltsville, MD, USA. ALPHA samplers were deployed in spring/summer 2010 and 2011 (21 May 2010 to 9 June 2010, and 24 June 2011 to 22 July 2011) in an open-air,
150 dairy cow barn equipped with ventilation fans. ALPHA samplers were also deployed in spring/summer 2010 and 2011 (21 May 2010 to 9 June 2010, and 24 June 2011 to 22 July 2011) in a closed room fitted with ventilation fans containing ~60 Tom turkeys. Lastly, in summer 2010 (6 August 2010 to 21 August 2010), ALPHA passive samplers were deployed at a concentrated animal feeding operation (CAFO) in central Kansas that contained 30 000 head of beef cattle in ~59 ha.

Vehicular emissions

ALPHA NH3 samplers were deployed in the ventilation portion of a tunnel (Squirrel Hill Tunnel, ~100,000 vehicles a day) in Pittsburgh, PA, USA to collect NH3 emitted from a diversity of personal and commercial vehicles, engines and fuel types, and emission controls. Samplers were deployed monthly from April 2010 to May 2010, and from May 2010 to June 2010.

Coal-fired power plant emissions

Power plant emissions were sampled on 25 January 2011 from the stack of a coal-fired power plant equipped with SCR as part of a larger sampling effort to characterize δ15N values of power plant NOx emissions.34

Urea-ammonia-nitrate fertilizer volatilization

In summer 2010 and 2011 (19 June 2010 to 22 July 2010, and 23 June 2011 to 22 July 2011), ALPHA passive samplers were deployed at three sites over a field that had received two 135 kg N/ha applications of urea-ammonia-nitrate (UAN) fertilizer. The field was a conventionally managed cornfield that was part of a larger study ‘Optimizing Production Inputs for Economic and Environmental Enhancement’ (OPE3). This field represents traditional farming practices common in Midwestern United States, mainly corn row crops with a uniform application of urea-ammonia-nitrate (UAN) commercial fertilizer.35

Marine emissions

The National Atmospheric Deposition Program Ammonia Monitoring Network (AMoN) operates a NH3 passive sampling site located in the coastal Cape Romain National Wildlife Refuge, SC, USA. ALPHA passive samplers were deployed monthly at this site for a year (July 2009 to June 2010) to collect a primarily marine NH3 source.

Nitrogen isotopic analysis of low [NH4+] samples

One drawback to using passive samplers is that the amount of N collected is often insufficient for conventional isotope analysis via elemental analyzer (EA) combustion, which analyzes N2 as the end product and generally requires greater than 1 μmol N. This relatively large amount of N2 is required because of interferences that arise from the abundance of atmospheric N2.36 To resolve this problem, we developed a new approach for δ15N-NH3 isotopic analysis that combines two existing methods (Fig. 1). After collection on the passive sampler filters, NH3 was eluted with Milli-Q (EMD Millipore, Billerica, MA, USA) water and analyzed as NH4+ using the phenolate method37 and a Thermo Evolution 60S UV-vis instrument (Thermo Scientific, Waltham, MA, USA). NH3 air concentrations were calculated according to Ogawa or ALPHA sampler protocols.31,38 An oxidation method39 employing a hypobromite oxidation solution was used to oxidize the NH4+ in the sample to nitrite (NO2−). Briefly, a bromate/bromide stock solution was made by mixing 0.6 g of sodium bromate and 5 g of sodium bromide in 250 mL of Milli-Q water.39 A BrO working solution was prepared on each day of oxidation by adding 1 mL of the stock to 50 mL of Milli-Q water and 3 mL of 6 M HCl.39 The mixture was allowed to react in the dark for 5 min and 50 mL of 10 N NaOH was then added to the solution.39 NH4+ samples were diluted to 10 μM NH4+ and 20 mL of the sample was transferred to acid-washed 50 mL centrifuge vials. To oxidize sample NH4+ to NO2−, 2 mL of the BrO working solution was added to the sample vial. The vial was immediately capped and hand-shaken vigorously for ~30 s followed by shaking for ~1 h on a shaker table. After oxidation, the sample pH was adjusted to between 3 and 9 using 6 N HCl. If the pH was adjusted to below 3, it was readjusted to the 3 to 9 range using 10 N NaOH. Then 20 nmol of sample NO2− was converted into N2O using the bacterial denitrifier Pseudomonas aureofaciens and introduced into an isotope ratio mass spectrometer.39

N2O is the final product analyzed using this method; as it is much less abundant in the atmosphere than N2, it causes minimal atmospheric contamination. The pH adjustment is needed because the high pH created by the addition of the bromate oxidizing agent to the sample is toxic to the denitrifying bacteria. Samples were analyzed for δ15N values using a Trace Gas pre-concentrator (Isoprime, Cheadle...
The N₂O production is created from the addition of the bromate and a GX-271 autosampler (Gilson, Middleton, WI, USA) coupled with an Isoprime continuous flow isotope ratio mass spectrometer at the Regional Stable Isotope Laboratory for Earth and Environmental Research, University of Pittsburgh. Isotope ratio values are reported in parts per thousand relative to atmospheric N₂ as follows:

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

(2)

International reference \(\delta^{15}N-\text{NO}_3\) standards (USGS34, USGS32) and \(\delta^{15}N-\text{NH}_4^+\) (USGS25, USGS26) were used for data correction by first correcting to the NO₃⁻ standards, then to the NH₄⁺ standards. All samples were analyzed using this approach except the power plant NH₃ sample that also contained nitrate. For this sample, the \(\delta^{15}N-\text{NO}_3^-\) value was initially determined using the denitrifier method. The sample NH₄⁺ was then oxidized to NO₂⁻ and the resulting sample was analyzed for \(\delta^{15}N-\text{NO}_2^-\) using the denitrifier method. The \(\delta^{15}N-\text{NH}_4^+\) value of the sample was calculated using the mixing equation:

\[
(\delta^{15}N - \text{NO}_3^- + \delta^{15}N - \text{NO}_2^-) = f \delta^{15}N - \text{NO}_3^- + (1-f) \delta^{15}N - \text{NH}_4^+
\]  

(3)

RESULTS AND DISCUSSION

Validation using reference materials

The bromate oxidation-denitrifier method developed herein is for \(\delta^{15}N\) analysis of low concentration NH₄⁺ samples. The conversion of NH₄⁺ into NO₂⁻ is quantitative[36] and only 20 nmol N are required for analysis. No blank (extraneous N₂O production) is created from the addition of the bromate oxidizing agent or the 6 N HCl used for pH adjustment. Variation of final pH did not have an effect on the accuracy of the method, as long as the pH was between 3 and 9. Standard deviations of NH₄⁺ USGS standards USGS25 and USGS26 are ±0.7‰ (n = 45) (Fig. 2). This approach is capable of high-throughput (72 samples per 24 h) and eliminates the use of toxic chemicals (e.g. azide, arsenite) used in a prior method[36] for the analysis of low concentration NH₄⁺ samples. It should be noted that the range in isotopic values of USGS \(\delta^{15}N-\text{NH}_4^+\) standards (−30.4 to +53.7‰) does not encompass the range of isotopic values observed in this study (−56.1 to −2.2‰). To correct observed sample values outside the range of \(\delta^{15}N-\text{NH}_4^+\) standards, it is necessary to extrapolate calibration curves and this may lead to greater inaccuracy. Future work should focus on developing a standard with a lower \(\delta^{15}N-\text{NH}_4^+\) value so that the \(\delta^{15}N-\text{NH}_4^+\) values of the standard can bracket those of samples. The standard deviation of the power plant NH₃ sample is reported as 0.9‰ as it represents the standard deviation for both the \(\delta^{15}N-\text{NO}_3^-\) and the \(\delta^{15}N-\text{NH}_4^+\) analyses.

\(\delta^{15}N\) values of major NH₃ emission sources

\(\delta^{15}N\) values of NH₃ sources ranged from −56.1 to −2.2‰ where the NH₃ concentration ranged from 0.2 to 147 µg/m³ (Fig. 3). There was no significant correlation between the \(\delta^{15}N\) values and the NH₃ concentration.

The \(\delta^{15}N-\text{NH}_3\) values of livestock waste emissions collected in this study (−56.1 to −22.8‰) are similar to the range of \(\delta^{15}N-\text{NH}_3\) values previously determined at livestock operations and during laboratory incubations (−43 to −9‰).[16–20] This range in \(\delta^{15}N\) values is a function of the initial \(\delta^{15}N\) values of livestock waste, variations in the bacteria populations that hydrolyze urea in the waste and allow release of NH₃, as well as factors that influence kinetic fractionation rates associated with NH₃ volatilization. These factors include temperature, wind, pH, cation-exchange capacity of the substrate, and moisture availability (e.g. mitigation techniques).[7] For instance, increasing the ambient temperature increases the dissociation of ammonium to ammonia,[7] thus increasing NH₃ volatilization rates while decreasing fractionation factors. Li et al.[40] reported that higher temperatures led to less fractionation between ammonium and aqueous ammonia (e.g. 45.4‰ at 23°C and 33.5‰ at 70°C).

The isotopic compositions of NH₃ from volatilized fertilizer ranged from −48.0 to −36.3‰ for samples collected over the cornfield after fertilizer applications. The ambient NH₃

![Figure 2. Actual \(\delta^{15}N-\text{NH}_4^+\) USGS25 and USGS26 values vs USGS25 and USGS26 \(\delta^{15}N-\text{NH}_4^+\) values measured using the presented approach.](Image)

![Figure 3. \(\delta^{15}N-\text{NH}_3\) values of emission sources spanning a large range in ambient NH₃ concentrations.](Image)
concentrations ([NH₃]) increased by an average of 7.3 times at the sampling sites over the cornfield after two separate 135 kg N/ha fertilizer applications. Therefore, it was assumed that the majority of the NH₃ being sampled was from volatilized fertilizer. Similar factors to those influencing livestock NH₃ volatilization (discussed in previous paragraph) will also influence fertilizer volatilization. In addition, during the volatilization process, fractionation can occur during air-surface (soil and vegetation) exchange of NH₃. Vegetation (via stomatal or cuticular processes) is a source or sink of NH₃ depending on atmospheric NH₃ concentration, meteorology and surface characteristics. This suggests that the δ¹⁵N-NH₃ values collected over the cornfield may partially reflect the δ¹⁵N values of NH₃ produced from air-surface exchange processes. The range in δ¹⁵N values of volatilized fertilizer NH₃ overlaps the range of livestock waste values; therefore, the results presented here do not differentiate between these two agricultural sources. This result was expected since the kinetic fractionation affecting both isotopic signatures is volatilization, and livestock waste and fertilizer are reported to have similar starting material δ¹⁵N values. For example, cattle urine, feces and diet are reported to have ⁰.5 to +1.9‰, +2.3 to +3.0‰ and +1.1 to +4.2‰, respectively. Likewise, fertilizer has average δ¹⁵N values of 0 ±2‰, thus, comparable fractionation factors (30 to 60‰) from volatilization would result in an overlapping δ¹⁵N-NH₃ range.

In comparison, the δ¹⁵N-NH₃ values in vehicle exhaust (−4.6 to −2.2‰) and SCR-equipped power plant emissions (−11.3, −14.6‰), are higher than those observed from livestock waste or fertilizer volatilization. This difference probably arises from NH₃ production during high-temperature combustion and associated fractionation. Vehicles equipped with TWCs form NH₃ as a secondary pollutant from the NOₓ reduction process. Catalyst temperatures and air-to-fuel ratios are reported to be primary factors in the formation of NH₃ in vehicle exhaust. NH₃ from coal combustion is due to ‘fuel NH₃’ or ‘NH₃ slip’ from NOₓ reduction technology. The δ¹⁵N-NH₃ values from coal combustion reported previously (−7 to +2‰) probably represent ‘fuel NH₃’ rather than ‘NH₃ slip’ because NH₃ was sampled from coal furnaces and factories prior to the advent of SCR NOₓ reduction technology. The δ¹⁵N-NH₃ values from coal combustion reported in this study (−11.3, −14.6‰) are probably from ‘NH₃ slip’, attributed to unreacted anhydrous NH₃ from the SCR unit, as samples collected from non-SCR equipped power plant had undetectable NH₃ concentrations. Anhydrous NH₃ is reported to have a δ¹⁵N value of −1 to −2‰ but undergoes reaction with NOₓ in the SCR unit and any ‘NH₃ slip’ can react with SO₃ or H₂SO₄ potentially causing further fractionation. In summary, the results of this δ¹⁵N-NH₃ source inventory reveal that NH₃ gases emitted from volatilized livestock waste and fertilizer have relatively low δ¹⁵N values, allowing these gases to be differentiated from other sources such as vehicle exhaust emissions and coal combustion (Table 1, Fig. 4).

While the marine NH₃ source is generally expected to be insignificant relative to major NH₃ emission sources, in a coastal or open ocean environment not directly exposed to major NH₃ sources, marine NH₃ can be significant. The δ¹⁵N-NH₃ values from the Cape Romain coastal site ranged from −10.2 to −2.2‰ with a mean of −4.7 ± 2.7‰ (n = 7). This range is similar to the δ¹⁵N-NH₃ range (−8 to −5‰) of aerosols collected over the Atlantic Ocean, assumed to be of marine-biogenic NH₃ origin.

The range in marine source δ¹⁵N-NH₃ values may be due to fractionation occurring during air-sea NH₃ flux that is dependent on temperature and pH. It is also important to note that the Cape Romain site δ¹⁵N-NH₃ values may also represent a mix of terrestrial NH₃ sources and therefore may not represent solely a marine NH₃ source.

### Deployment reproducibility and potential limitations

Sets of six triplicate ALPHA samplers deployed simultaneously had average δ¹⁵N-NH₃ standard deviation of ±2.6‰ (range from 1.4 to 4.5‰) which represents the field deployment reproducibility. Triplicate samplers were deployed on a single post and thus collected NH₃ at slightly varying heights and from varying wind directions. Thus, physical differences in deployment direction and height among the triplicate samplers may be partially responsible for the observed isotopic differences in triplicate samplers.

Table 1. δ¹⁵N-NH₃ values of ammonia sources, source location, and sampling method

<table>
<thead>
<tr>
<th>Location</th>
<th>Source</th>
<th>[NH₃] (µg/m³)</th>
<th>δ¹⁵N-NH₃ (%)</th>
<th>N = # samples</th>
<th>Sampling method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poultry facility, BARC</td>
<td>Turkey waste</td>
<td>147.2, 121.4</td>
<td>−56.1, −36.0</td>
<td>2</td>
<td>ALPHA</td>
</tr>
<tr>
<td>Dairy barn, BARC</td>
<td>Cow waste</td>
<td>86.0, 51.6</td>
<td>−27.1, −23.1</td>
<td>2</td>
<td>ALPHA</td>
</tr>
<tr>
<td>Cornfield, BARC</td>
<td>Volatilized fertilizer</td>
<td>13.0 to 21.6</td>
<td>−48.0 to −36.3</td>
<td>6</td>
<td>ALPHA</td>
</tr>
<tr>
<td>Dairy barn, Western PA</td>
<td>Cow waste</td>
<td>128.2, 165.6</td>
<td>−28.5, −22.8</td>
<td>2</td>
<td>Ogawa</td>
</tr>
<tr>
<td>Cattle CAFO, KS</td>
<td>Cow waste</td>
<td>109.3</td>
<td>−38.3</td>
<td>1</td>
<td>ALPHA</td>
</tr>
<tr>
<td>Squirrel Hill Tunnel, Pittsburgh, PA</td>
<td>Vehicle exhaust</td>
<td>20.2, 18.6</td>
<td>−4.6, −2.2</td>
<td>2</td>
<td>ALPHA</td>
</tr>
<tr>
<td>SCR equipped coal-fired power plant, US</td>
<td>Power plant emissions (NH₃ slip)</td>
<td>*NA</td>
<td>−11.3, −14.6</td>
<td>2</td>
<td>EPA method 7</td>
</tr>
<tr>
<td>Cape Romain National Wildlife Refuge</td>
<td>Marine source</td>
<td>0.2 to 1.1</td>
<td>−10.2 to −2.2</td>
<td>7</td>
<td>ALPHA</td>
</tr>
</tbody>
</table>

*Power plant emission sampling method did not allow for concentration calculation.
Fractionation during sample collection should be further considered for a 4-week period to an isotopically defined NH₃ fumigation study, ALPHA samplers were exposed off and NH₃ collected by an ALPHA sampler 1 m from the source. While prior studies have addressed potential isotope fractionations during passive collection associated with meteorological conditions or the collection mechanism itself,[29,30] These studies reported that passive samplers have minimal fractionation associated with variability in wind speed and NH₃ concentrations.[30] Furthermore, in a fumigation study, ALPHA samplers were exposed off and on for a 4-week period to an isotopically defined NH₃ fumigation source (+2.8 ± 0.5‰).[30] The δ¹⁵N value of the NH₃ collected by an ALPHA sampler 1 m from the source was -0.7 ± 0.6‰. This offset (3.5‰) was explained by the fact that the ALPHA sampler was 1 m from the source and was sampling ambient NH₃ (-8 + 1.4 ‰; measured 50 m upwind of the NH₃ fumigation source) during periods when the NH₃ fumigation source was turned off.[30] Thus, while prior studies report the efficacy of the ALPHA sampler to collect representative δ¹⁵N values of NH₃ sources, potential isotope fractionation during sample collection should be further investigated.

CONCLUSIONS
We report a new approach for the isotopic analysis of low concentration NH₃ samples and facilitate the investigation of NH₃ emissions across a large range of ambient conditions using low-cost passive diffusion sampling devices. Using this approach to characterize NH₃ emissions, we supplement the existing δ¹⁵N-NH₃ inventory of NH₃ sources. The results of this δ¹⁵N-NH₃ source inventory reveal that NH₃ gases emitted from volatilized livestock waste and fertilizer have relatively low δ¹⁵N values, allowing them to be differentiated from other sources of NH₃, such as vehicle exhaust emissions, coal combustion, and marine sources. The isotopic source signatures presented in this emission inventory can be used as an additional tool for identifying NH₃ emission sources and tracing their transport across landscapes and regions. This insight into the transport of NH₃ emissions is an important step towards reducing future NH₃ emissions.

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Improved method for isotope characterization of ammonia in air


