

Rapid Commun. Mass Spectrom. 2013, 27, 2239–2246
(wileyonlinelibrary.com) DOI: 10.1002/rcm.6679

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

J. David Felix^{1*}, Emily M. Elliott¹, Timothy J. Gish², Laura L. McConnell³ and Stephanie L. Shaw⁴

¹Department of Geology & Planetary Science, 4107 O'Hara Street, University of Pittsburgh, Pittsburgh, PA 15260, USA

²USDA-ARS, Hydrology and Remote Sensing Laboratory, Beltsville, MD 20705, USA

³USDA-ARS, Environmental Management and Byproducts Utilization Laboratory, Beltsville, MD 20705, USA

⁴Electric Power Research Institute, 3420 Hillview Avenue, Palo Alto, CA 94304, USA

RATIONALE: Ammonia (NH₃) emissions are a substantial source of nitrogen pollution to sensitive terrestrial, aquatic, and marine ecosystems and dependable quantification of NH₃ sources is of growing importance due to recently observed increases in ammonium (NH₄⁺) deposition rates. While determination of the nitrogen isotopic composition of NH₃ ($\delta^{15}\text{N-NH}_3$) can aid in the quantification of NH₃ emission sources, existing methods have precluded a comprehensive assessment of $\delta^{15}\text{N-NH}_3$ values from major emission sources.

METHODS: We report an approach for the $\delta^{15}\text{N-NH}_4^+$ analysis of low concentration NH₄⁺ samples that couples the bromate oxidation of NH₄⁺ to NO₂⁻ and the microbial denitrifier method for $\delta^{15}\text{N-NO}_2^-$ analysis. This approach reduces the required sample mass by 50-fold relative to standard elemental analysis (EA) procedures, is capable of high throughput, and eliminates toxic chemicals used in a prior method for the analysis of low concentration samples. Using this approach, we report a comprehensive inventory of $\delta^{15}\text{N-NH}_3$ values from major emission sources (including livestock operations, marine sources, vehicles, fertilized cornfields) collected using passive sampling devices.

RESULTS: The $\delta^{15}\text{N-NH}_4^+$ analysis approach developed has a standard deviation of $\pm 0.7\%$ and was used to analyze passively collected NH₃ emissions with a wide range of ambient NH₃ concentrations (0.2 to 165.6 $\mu\text{g}/\text{m}^3$). The $\delta^{15}\text{N-NH}_3$ values reveal that the NH₃ emitted from volatilized livestock waste and fertilizer has relatively low $\delta^{15}\text{N}$ values (-56 to -23%), allowing it to be differentiated from NH₃ emitted from fossil fuel sources that are characterized by relatively high $\delta^{15}\text{N}$ values (-15 to $+2\%$).

CONCLUSIONS: The isotopic source signatures presented in this emission inventory can be used as an additional tool in identifying NH₃ emission sources and tracing their transport across localized landscapes and regions. The insight into the transport of NH₃ emissions provided by isotopic investigation is an important step in devising strategies to reduce future NH₃ emissions, a mounting concern for air quality scientists, epidemiologists, and policy-makers. Copyright © 2013 John Wiley & Sons, Ltd.

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⁺) 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.

Pinpointing NH₃ emission sources and quantifying NH₃ contributions from individual sources is important for management strategies designed to reduce adverse impacts from NH₃ emissions. Global NH₃ emissions are dominated by agricultural activities (livestock operations and fertilizer application) and it is estimated that in 2008, agricultural sources contributed 80% of NH₃ emissions in the USA.^[4] The primary agricultural source, urea in livestock waste, is quickly hydrolyzed to NH₃, which is then volatilized to the atmosphere.^[7] In addition to waste sources, urea present in fertilizers can hydrolyze and volatilize as NH₃; this is also the case with NH₃ (or NH₄⁺) in fertilizer subject to direct volatilization after application.

While these agricultural sources emit the bulk of NH₃ emissions, NH₃ produced as a byproduct of technologies used to reduce NO_x emissions from fossil fuel combustion

* Correspondence to: J. D. Felix, Department of Geology & Planetary Science, 4107 O'Hara Street, University of Pittsburgh, Pittsburgh, PA 15260, USA.
E-mail: felixj@uncw.edu

(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 NO_x 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 NO_x 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. NO_x and NH₃ react to form N₂ and water vapor:



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 δ¹⁵N values in the emitted NH₃. In comparison, the reported δ¹⁵N 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 NH₄⁺ 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, Edinburg, 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 phosphorous 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 samplers (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 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 phosphorous 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 NH_3 samplers were deployed in the ventilation portion of a tunnel (Squirrel Hill Tunnel, ~100,000 vehicles a day) in Pittsburgh, PA, USA to collect NH_3 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 $\delta^{15}\text{N}$ values of power plant NO_x 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 NH_3 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 NH_3 source.

Nitrogen isotopic analysis of low $[\text{NH}_4^+]$ 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 N_2 as the end product and generally requires greater than 1 μmol N. This relatively large amount of N_2 is required because of interferences that arise from the abundance of atmospheric N_2 .^[36] To resolve this problem, we developed a new approach for $\delta^{15}\text{N}$ - NH_3 isotopic analysis that combines two existing methods (Fig. 1). After collection on the passive sampler filters, NH_3 was eluted with Milli-Q (EMD Millipore, Billerica, MA, USA) water and analyzed as NH_4^+ using the phenolate method^[37] and a Thermo Evolution 60S UV-vis

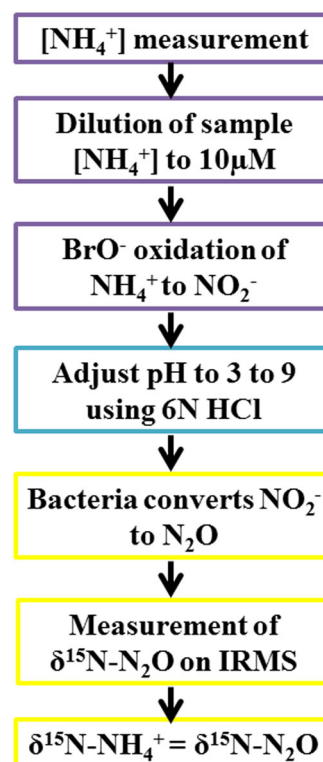


Figure 1. Method schematic for the isotopic analysis of NH_4^+ that combines bromate oxidation of NH_3 (purple),^[36] pH adjustment (blue), and the microbial denitrifier method (yellow).^[39]

instrument (Thermo Scientific, Waltham, MA, USA). NH_3 air concentrations were calculated according to Ogawa or ALPHA sampler protocols.^[31,38] An oxidation method^[32] employing a hypobromite oxidation solution was used to oxidize the NH_4^+ in the sample to nitrite (NO_2^-). 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.^[36] 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.^[36] 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.^[36] NH_4^+ samples were diluted to 10 μM NH_4^+ and 20 mL of the sample was transferred to acid-washed 50 mL centrifuge vials. To oxidize sample NH_4^+ to NO_2^- , 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 NO_2^- was converted into N_2O using the bacterial denitrifier *Pseudomonas aureofaciens* and introduced into an isotope ratio mass spectrometer.^[39]

N_2O is the final product analyzed using this method; as it is much less abundant in the atmosphere than N_2 , 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 $\delta^{15}\text{N}$ values using a Trace Gas pre-concentrator (Isoprime, Cheadle

Hulme, UK) 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:

$$\delta^{15}\text{N}(\text{‰}) = \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{standard}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} \times 1000 \quad (2)$$

International reference $\delta^{15}\text{N}-\text{NO}_3^-$ standards (USGS34, USGS32) and $\delta^{15}\text{N}-\text{NH}_4^+$ (USGS25, USGS26) were used for data correction by first correcting to the NO_3^- standards, then to the NH_4^+ standards. All samples were analyzed using this approach except the power plant NH_3 sample that also contained nitrate. For this sample, the $\delta^{15}\text{N}-\text{NO}_3^-$ value was initially determined using the denitrifier method. The sample NH_4^+ was then oxidized to NO_2^- and the resulting sample was analyzed for $\delta^{15}\text{N}-\text{NO}_2^-$ using the denitrifier method. The $\delta^{15}\text{N}-\text{NH}_4^+$ value of the sample was calculated using the mixing equation:

$$(\delta^{15}\text{N} - \text{NO}_3^- + \delta^{15}\text{N} - \text{NO}_2^-) = f * \delta^{15}\text{N} - \text{NO}_3^- + (1-f) * \delta^{15}\text{N} - \text{NH}_4^+ \quad (3)$$

RESULTS AND DISCUSSION

Validation using reference materials

The bromate oxidation-denitrifier method developed herein is for $\delta^{15}\text{N}$ analysis of low concentration NH_4^+ samples. The conversion of NH_4^+ into NO_2^- 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 NH_4^+ USGS standards USGS25 and USGS 26 are $\pm 0.7\text{‰}$ ($n = 45$) (Fig. 2). This approach is capable

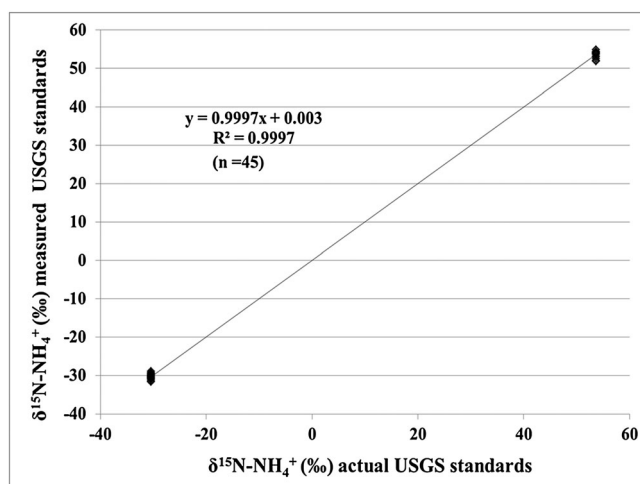


Figure 2. Actual $\delta^{15}\text{N}-\text{NH}_4^+$ USGS25 and USGS26 values vs USGS25 and USGS26 $\delta^{15}\text{N}-\text{NH}_4^+$ values measured using the presented approach.

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 NH_4^+ samples. It should be noted that the range in isotopic values of USGS $\delta^{15}\text{N}-\text{NH}_4^+$ standards (-30.4 to $+53.7\text{‰}$) 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 $\delta^{15}\text{N}-\text{NH}_4^+$ standard values, 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 $\delta^{15}\text{N}-\text{NH}_4^+$ value so that the $\delta^{15}\text{N}-\text{NH}_4^+$ values of the standard can bracket those of samples. The standard deviation of the power plant NH_3 sample is reported as 0.9‰ as it represents the standard deviation for both the $\delta^{15}\text{N}-\text{NO}_3^-$ and the $\delta^{15}\text{N}-\text{NH}_4^+$ analyses.

$\delta^{15}\text{N}$ values of major NH_3 emission sources

$\delta^{15}\text{N}$ values of NH_3 sources ranged from -56.1 to -2.2‰ where the NH_3 concentration ranged from 0.2 to $147 \mu\text{g}/\text{m}^3$ (Fig. 3). There was no significant correlation between the $\delta^{15}\text{N}$ values and the NH_3 concentration.

The $\delta^{15}\text{N}-\text{NH}_3$ values of livestock waste emissions collected in this study (-56.1 to -22.8‰) are similar to the range of $\delta^{15}\text{N}-\text{NH}_3$ values previously determined at livestock operations and during laboratory incubations (-43 to -9‰).^[16–20] This range in $\delta^{15}\text{N}$ values is a function of the initial $\delta^{15}\text{N}$ values of livestock waste, variations in the bacteria populations that hydrolyze urea in the waste and allow release of NH_3 , as well as factors that influence kinetic fractionation rates associated with NH_3 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 NH_3 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 NH_3 from volatilized fertilizer ranged from -48.0 to -36.3‰ for samples collected over the cornfield after fertilizer applications. The ambient NH_3

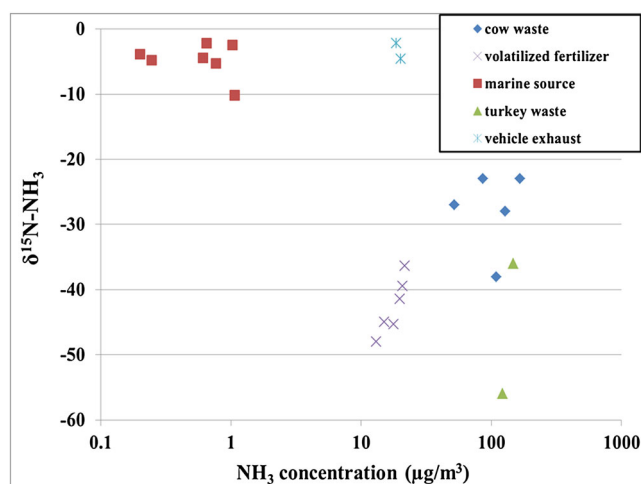


Figure 3. $\delta^{15}\text{N}-\text{NH}_3$ values of emission sources spanning a large range in ambient NH_3 concentrations.

concentrations ($[\text{NH}_3]$) 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 NH_3 being sampled was from volatilized fertilizer. Similar factors to those influencing livestock NH_3 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 NH_3 . Vegetation (via stomatal or cuticular processes) is a source or sink of NH_3 depending on atmospheric NH_3 concentration, meteorology and surface characteristics.^[41,42] This suggests that the $\delta^{15}\text{N-NH}_3$ values collected over the cornfield may partially reflect the $\delta^{15}\text{N}$ values of NH_3 produced from air-surface exchange processes. The range in $\delta^{15}\text{N}$ values of volatilized fertilizer NH_3 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 $\delta^{15}\text{N}$ values. For example, cattle urine, feces and diet are reported to have $\delta^{15}\text{N}$ values of +0.5 to +1.9‰, +2.3 to +3.0‰ and +1.1 to +4.2‰, respectively.^[18] Likewise, fertilizer has average $\delta^{15}\text{N}$ values of $0 \pm 2\%$,^[43] thus, comparable fractionation factors (30 to 60‰)^[44] from volatilization would result in an overlapping $\delta^{15}\text{N-NH}_3$ range.

In comparison, the $\delta^{15}\text{N-NH}_3$ 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 NH_3 production during high-temperature combustion and associated fractionation. Vehicles equipped with TWCs form NH_3 as a secondary pollutant from the NO_x reduction process. Catalyst temperatures and air-to-fuel ratios are reported to be primary factors in the formation of NH_3 in vehicle exhaust.^[45] NH_3 from coal combustion is due to 'fuel NH_3 ' or ' NH_3 slip' from NO_x reduction technology. The $\delta^{15}\text{N-NH}_3$ values from coal combustion reported previously (−7 to +2‰) probably represent 'fuel NH_3 ' rather than ' NH_3 slip' because NH_3 was sampled from coal furnaces and factories prior to the advent of SCR NO_x reduction technology.^[16] The $\delta^{15}\text{N-NH}_3$ values from coal combustion

reported in this study (−11.3, −14.6‰) are probably from ' NH_3 slip', attributed to unreacted anhydrous NH_3 from the SCR unit, as samples collected from non-SCR equipped power plant had undetectable NH_3 concentrations. Anhydrous NH_3 is reported to have a $\delta^{15}\text{N}$ value of −1 to −2‰^[46] but undergoes reaction with NO_x in the SCR unit and any ' NH_3 slip' can react with SO_3 or H_2SO_4 ^[47] potentially causing further fractionation. In summary, the results of this $\delta^{15}\text{N-NH}_3$ source inventory reveal that NH_3 gases emitted from volatilized livestock waste and fertilizer have relatively low $\delta^{15}\text{N}$ 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 NH_3 source is generally expected to be insignificant relative to major NH_3 emission sources, in a coastal or open ocean environment not directly exposed to major NH_3 sources, marine NH_3 can be significant. The $\delta^{15}\text{N-NH}_3$ values from the Cape Romain coastal site ranged from −10.2 to −2.2‰ with a mean of $-4.7 \pm 2.7\%$ (n = 7). This range is similar to the $\delta^{15}\text{N-NH}_4^+$ range (−8 to −5‰) of aerosols collected over the Atlantic Ocean, assumed to be of marine-biogenic NH_3 origin.^[48] The range in marine source $\delta^{15}\text{N-NH}_3$ values may be due to fractionation occurring during air-sea NH_3 flux that is dependent on temperature and pH.^[48] It is also important to note that the Cape Romain site $\delta^{15}\text{N-NH}_3$ values may also represent a mix of terrestrial NH_3 sources and therefore may not represent solely a marine NH_3 source.

Deployment reproducibility and potential limitations

Sets of six triplicate ALPHA samplers deployed simultaneously had average $\delta^{15}\text{N-NH}_3$ standard deviation of $\pm 2.6\%$ (range from 1.4 to 4.5‰) which represents the field deployment reproducibility. Triplicate samplers were deployed on a single post and thus collected NH_3 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. Ogawa passive samplers were only used during a pilot study at the small dairy operation because the sampling surface was smaller than that of the ALPHA, and this limited the amount of NH_3 collected for isotopic analysis. The $\delta^{15}\text{N-NH}_3$

Table 1. $\delta^{15}\text{N-NH}_3$ values of ammonia sources, source location, and sampling method

| Location | Source | $[\text{NH}_3]$ ($\mu\text{g}/\text{m}^3$) | $\delta^{15}\text{N-NH}_3$ (‰) | N = # samples | Sampling method |
|--|---|---|-----------------------------------|------------------|--------------------|
| Poultry facility, BARC | Turkey waste | 147.2, 121.4 | −56.1, −36.0 | 2 | ALPHA |
| Dairy barn, BARC | Cow waste | 86.0, 51.6 | −27.1, −23.1 | 2 | ALPHA |
| Cornfield, BARC | Volatilized fertilizer | 13.0 to 21.6 | −48.0 to −36.3 | 6 | ALPHA |
| Dairy barn, Western PA | Cow waste | 128.2, 165.6 | −28.5, −22.8 | 2 | Ogawa |
| Cattle CAFO, KS | Cow waste | 109.3 | −38.3 | 1 | ALPHA |
| Squirrel Hill Tunnel, Pittsburgh, PA (inside tunnel) | Vehicle exhaust | 20.2, 18.6 | −4.6, −2.2 | 2 | ALPHA |
| SCR equipped coal-fired power plant, US | Power plant emissions (NH_3 slip) | *NA | −11.3, −14.6 | 2 | EPA method 7 |
| Cape Romain National Wildlife Refuge | Marine source | 0.2 to 1.1 | −10.2 to −2.2 | 7 | ALPHA |

*Power plant emission sampling method did not allow for concentration calculation.

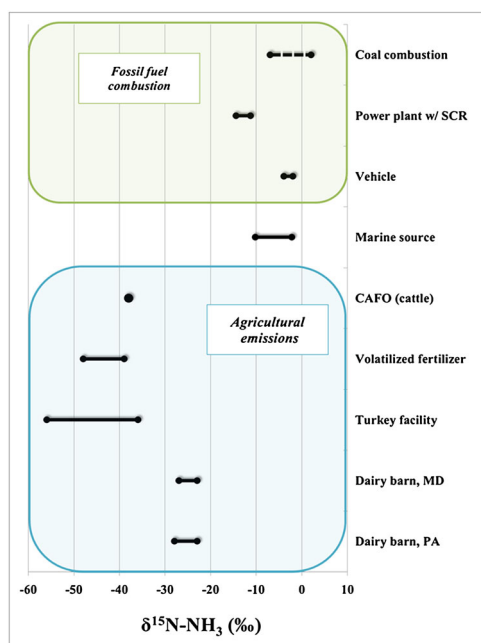


Figure 4. $\delta^{15}\text{N-NH}_3$ values of emissions sources from this study (solid lines) and from coal combustion (dashed line).^[16]

standard deviation among Ogawa samplers is not reported because one filter in the sampler was used for isotopic analysis and the other was used for NH_3 concentrations.

While quantification of isotope fractionation during NH_3 collection by the ALPHA sampler was beyond the scope of this study, prior studies have addressed potential 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 NH_3 concentrations.^[30] Furthermore, in a fumigation study, ALPHA samplers were exposed off and on for a 4-week period to an isotopically defined NH_3 fumigation source ($+2.8 \pm 0.5\text{‰}$).^[30] The $\delta^{15}\text{N}$ value of the NH_3 collected by an ALPHA sampler 1 m from the source was $-0.7 \pm 0.6\text{‰}$. This offset (3.5‰) was explained by the fact that the ALPHA sampler was 1 m from the source and was sampling ambient NH_3 ($-8 \pm 1.4\text{‰}$; measured 50 m upwind of the NH_3 fumigation source) during periods when the NH_3 fumigation source was turned off.^[30] Thus, while prior studies report the efficacy of the ALPHA sampler to collect representative $\delta^{15}\text{N}$ values of NH_3 sources, potential isotope fractionation during sample collection should be further investigated.

CONCLUSIONS

We report a new approach for the isotopic analysis of low concentration NH_4^+ samples and facilitate the investigation of NH_3 emissions across a large range of ambient conditions using low-cost passive diffusion sampling devices. Using this approach to characterize NH_3 emissions, we supplement the existing $\delta^{15}\text{N-NH}_3$ inventory of NH_3 sources. The results of this $\delta^{15}\text{N-NH}_3$ source inventory reveal that NH_3 gases emitted from volatilized livestock waste and fertilizer have relatively low

$\delta^{15}\text{N}$ values, allowing them to be differentiated from other sources of NH_3 , 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 NH_3 emission sources and tracing their transport across landscapes and regions. This insight into the transport of NH_3 emissions is an important step towards reducing future NH_3 emissions.

Acknowledgements

This project was supported by National Research Initiative Competitive (Grant No. 05-13204-6800-00000-404178) from the USDA Cooperative State Research, Education, and Extension Service Air Quality Program. We also acknowledge funding from NSF (Grant #0929182) and EPRI. We thank Katherine Redling for isotopic analysis at the University of Pittsburgh *Regional Stable Isotope Laboratory for Earth and Environmental Science Research*, the Sherry family for access to their property, John Cala for assistance in sample collection Sarah Dawsey at Cape Romain site for collecting samples, and PennDOT tunnel manager Tom Diddle for access to the Squirrel Hill Tunnel.

REFERENCES

- [1] J. T. Walker, V. P. Aneja, D. A. Dickey. Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmos. Environ.* **2000**, *34*, 3407.
- [2] C. T. Chimka, J. N. Galloway, B. J. Cosby. Ammonia and the Chesapeake Bay Airshed. Chesapeake Bay Program. *Scientific and Technical Advisory Committee*, Annapolis, MD, Publication, **1997**, 97–1.
- [3] D. Fowler, M. A. Sutton, R. I. Smith, C. E. R. Pitcairn, M. Coyle, G. Campbell, J. Stedman. Regional mass budgets of oxidized and reduced nitrogen and their relative contribution to the nitrogen inputs of sensitive ecosystems. *Environ. Pollut.* **1998**, *102*, 337.
- [4] E. A. Davidson, M. B. David, J. N. Galloway, C. L. Goodale, R. Haeuber, J. A. Harrison, R. W. Howarth, D. B. Jaynes, R. R. Lowrance, B. T. Nolan, J. L. Peel, R. W. Pinder, E. Porter, C. S. Snyder, A. R. Townsend, M. H. Ward. Excess nitrogen in the U.S. environment: trends, risks, and solutions. *ESA Issues Ecology* **2012**, *15*, 1.
- [5] J. N. Galloway, F. J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vorosmarty. Nitrogen cycles: Past, present, and future, *Biogeochemistry* **2004**, *70*, 153.
- [6] C. M. B. Lehmann, V. C. Bowersox, S. M. Larson. Spatial and Temporal Trends of Precipitation Chemistry in the United States, 1985–2002. *Environ. Pollut.* **2005**, *135*, 347.
- [7] A. N. Hristov, M. D. Hanigan, N. A. Cole, R. W. Todd, T. A. McAllister, P. M. Ndegwa, A. Rotz. Review: ammonia emissions from dairy farms and beef feedlots. *Can. J. Anim. Sci.* **2011**, *91*, 1.
- [8] National Emission Inventory. Available: <http://www.epa.gov/ttnchie1/net/2008inventory.html> (accessed January 2013).
- [9] M. Kirchner, G. Jakobi, E. Feicht, M. Bernhardt, A. Fischer. Elevated NH_3 and NO_2 air concentrations and nitrogen deposition rates in the vicinity of a highway in Southern Bavaria. *Atmos. Environ.* **2005**, *39*, 4531.

- [10] R. Matsumoto, N. Umezawa, M. Karaushi, S. Yonemochi, K. Sakamoto. Comparison of ammonium deposition flux at roadside and at an agricultural area for long-term monitoring: emission of ammonia from vehicles. *Water, Air, and Soil Pollution* **2006**, 173, 355.
- [11] J. N. Cape, Y. S. Tang, N. van Dijk, L. Love, M. A. Sutton, S. C. F. Palmer. Concentrations of ammonia and nitrogen dioxide at roadside verges, and their contribution to nitrogen deposition. *Environ. Pollut.* **2004**, 132, 469.
- [12] A. J. Kean, R. A. Harley, D. Littlejohn, G. R. Kendall. On road measurement of ammonia and other motor vehicle exhaust emissions. *Environ. Sci. Technol.* **2000**, 34, 3535.
- [13] C. Perrino, M. Catrambone, A. Di Menno Di Bucchianino, I. Allegrini. Gaseous ammonia in the urban area of Roma, Italy and its relationship with traffic emissions. *Atmos. Environ.* **2002**, 36, 5385.
- [14] A. Bouwman, D. Lee, A. Asman, F. Dentener, K. Van der Hoek, J. Olivier. A global high-resolution emission inventory for ammonia. *Global Biogeochem. Cycles* **1997**, 11, 561.
- [15] M. Roadman, J. Scudlark, J. Meisinger, W. Ullman. Validation of Ogawa passive samplers for the determination of gaseous ammonia concentrations in agricultural settings. *Atmos. Environ.* **2003**, 37, 2317.
- [16] H. D. Freyer. Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain collected at Jülich, Germany. *Tellus* **1978**, 30, 83.
- [17] T. H. E. Heaton. $^{15}\text{N}/^{14}\text{N}$ ratios of nitrate and ammonium in rain at Pretoria, South Africa. *Atmos. Environ.* **1987**, 21, 843.
- [18] A. N. Hristov, S. Zaman, M. Vander Pol, P. Ndegwa, L. Campbell, S. Silva. Nitrogen losses from dairy manure estimated through nitrogen mass balance or using markers. *J. Environ. Quality* **2009**, 38, 2438.
- [19] R. A. Skinner, P. Ineson, H. Jones, D. Sleep, R. Rank. Using $\delta^{15}\text{N}$ values to characterize the nitrogen nutrient pathways from intensive animal units. *Rapid Commun. Mass Spectrom.* **2006**, 20, 2858.
- [20] H. Schulz, M. Gehre, D. Hofmann, K. Jung. Nitrogen isotope ratios in pine bark as an indicator of N emissions from anthropogenic sources. *Environ. Monit. Assessment* **2001**, 69, 283.
- [21] M. A. Puchalski, M. E. Sather, J. T. Walker, C. M. B. Lelunann, D. A. Gay, J. Mathew, W. P. Robarge. Passive ammonia monitoring in the United States: Comparing three different sampling devices. *J. Environ. Monit.* **2011**, 13, 3156.
- [22] E. M. Elliott, C. Kendall, E. W. Boyer, D. A. Burns, G. Lear, H. E. Golden, K. Harlin, A. Bytnerowicz, T. J. Butler, R. Glatz. Dual nitrate isotopes in dry deposition: utility for partitioning NO_x source contributions to landscape nitrogen deposition. *J. Geophysical Research* **2009**, 114, doi:10.1029/2008JG000889.
- [23] H. E. Golden, E. W. Boyer, M. G. Brown, E. M. Elliott, D. K. Lee. Simple approaches for measuring dry atmospheric nitrogen deposition to watersheds. *Water Resources Res.* **2008**, 44, DOI: 10.1029/2008WR006952.
- [24] P. C. Rogers, K. Moore, R. Ryel. Aspen succession and nitrogen loading: a case for epiphytic lichens as bioindicators in the Rocky Mountains, USA. *J. Vegetation Sci.* **2009**, 20, 498.
- [25] M. E. Sather, J. Mathew, N. Nguyen, J. Lay, G. Golod, R. Vet, J. Cotie, F. Geasland. Baseline ambient gaseous ammonia concentrations in the Four Corners Area and eastern Oklahoma, USA. *J. Environ. Monit.* **2008**, 10, 1319.
- [26] R. L. Siefert, J. R. Scudlark, A. G. Potter, K. A. Simonsen, K. B. Savidge. Characterization of atmospheric ammonia emissions from a commercial chicken house on the Delmarva Peninsula. *Environ. Sci. Technol.* **2004**, 38, 2769.
- [27] Y. S. Tang, J. N. Cape, M. A. Sutton. Development and types of passive samplers for monitoring atmospheric NO_2 and NH_3 concentrations. *The Scientific World* **2001**, 1, 513.
- [28] M. A. Sutton, U. Dragosits, S. Hellsten, C. J. Place, A. J. Dore, Y. S. Tang, N. van Dijk, L. Love, N. Fournier, M. Vieno, K. J. Weston, R. I. Smith, M. Coyle, D. Roy, J. Hall, D. Fowler. Ammonia emission and deposition in Scotland and its potential environmental impacts. *The Scientific World Journal* **2004**, 4, 795.
- [29] R. A. Skinner, P. Ineson, W. K. Hicks, H. E. Jones, D. Sleep, I. D. Leith, L. J. Sheppard. Correlating the spatial distribution of atmospheric ammonia with $\delta^{15}\text{N}$ at an ammonia release site. *Water, Air, Soil Pollut.* **2004**, 4, 219.
- [30] R. A. Skinner, P. Ineson, H. E. Jones, D. Sleep, M. Theobald. Sampling systems for isotope-ratio mass spectrometry of atmospheric ammonia. *Rapid Commun. Mass Spectrom.* **2006**, 20, 81.
- [31] Y. S. Tang, N. van Dijk, M. A. Sutton. *Operation Manual for the CEH ALPHA (Adapted Low-cost Passive High Absorption) sampler*. Centre for Ecology & Hydrology Edinburgh Research Station Bush Estate, Penicuik, UK, **2009**.
- [32] UK National Ammonia Monitoring Network. Centre for Ecology & Hydrology (CEH). SID 5 Research Final Report, **2009**. Available: <http://pollutantdeposition.defra.gov.uk/>.
- [33] EPA, Determination of Nitrogen Oxide Emissions from Stationary Sources, **2010**. Available: <http://www.epa.gov/ttn/emc/promgate/m-07b.pdf>.
- [34] J. D. Felix, E. M. Elliott, S. L. Shaw. Nitrogen isotopic composition of coal-fired power plant NO_x : Influence of emission controls and implications for global emission inventories. *Environ. Sci. Technol.* **2012**, 46, 3528.
- [35] USDA OPE3 website. Available: <http://hydrolab.arsusda.gov/ope3/> (accessed October 2012).
- [36] L. Zhang, M. A. Altabet, T. Wu, O. Hadas. Sensitive measurement of $\text{NH}_4^+ \text{ }^{15}\text{N}/^{14}\text{N}$ ($\delta^{15}\text{NH}_4^+$) at natural abundance levels in fresh and saltwaters. *Anal. Chem.* **2007**, 79, 5297.
- [37] A. Eaton, L. Clecseri, E. Rice, A. Greenburg. *A method for the examination of water and wastewater*, (21 edn.). American Public Health Association, Port City Press, Baltimore, MD, **2005**.
- [38] Ogawa NO , NO_2 , NO_x and SO_2 Sampling Protocol, Edition 6, June, **2006**. Available: <http://www.ogawausa.com/passive.html>.
- [39] D. M. Sigman, K. L. Casciotti, M. Andreani, C. Barford, M. Galanter, J. K. Bohlke. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* **2001**, 73, 4145.
- [40] L. Li, B. S. Lollar, H. Li, U. G. Wortmann, G. Lacrampe-Couloume. Ammonium stability and nitrogen isotope fractionations for $\text{NH}_4^+ \text{--NH}_3(\text{aq})\text{--NH}_3(\text{gas})$ systems at 20–70°C and pH of 2–13: Applications to habitability and nitrogen cycling in low-temperature hydrothermal systems. *Geochim. Cosmochim. Acta* **2012**, 84, 280.
- [41] J. T. Walker, W. P. Robarge, Y. Wu, T. Meyers. Measurement of bi-directional ammonia fluxes over soybean using the modified Bowen-ratio technique. *Agric. Forest Meteorol.* **2006**, 138, 54.
- [42] J. T. Walker, P. Spence, S. Kimbrougha, W. Robarge. Inferential model estimates of ammonia dry deposition in the vicinity of a swine production facility. *Atmos. Environ.* **2008**, 42, 3407.
- [43] A. S. Bateman, S. D. Kelly. Fertilizer nitrogen isotope signatures. *Isot. Environ. Health Stud.* **2007**, 43, 237.
- [44] D. A. Frank, R. D. Evans, B. F. Tracey. The role of ammonia volatilization in controlling the natural ^{15}N abundance of a grazed grassland. *Biogeochemistry* **2004**, 68, 169.

- [45] N. V. Heeb, C. J. Saxer, A.M. Forss, S. Bruhlmann. Trends of NO, NO₂, and NH₃ emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars. *Atmos. Environ.* **2008**, *42*, 2543.
- [46] J. R. Gormly, R. E. Spalding. Sources and concentrations of nitrate-nitrogen in ground water of the central Platte region, Nebraska. *Ground Water* **1979**, *17*, 291.
- [47] R. T. Wilburn, T. L. Wright. SCR ammonia slip distribution in coal plant effluents and dependence on SO₃. *Power Plant Chem.* **2004**, *6*, 295.
- [48] T. D. Jickells, S. D. Kelly, A. R. Baker, K. Biswas, P. F. Dennis, L. J. Spokes, M. Witt, S. G. Yeatman. Isotopic evidence for a marine ammonia source. *Geophys. Res. Lett.* **2003**, *30*, 1374.