Examining the transport of ammonia emissions across landscapes using nitrogen isotope ratios

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HIGHLIGHTS

• We document the utility of δ15N-NH3 values for examining NH3 transport.
• We use an isotope mixing model to make approximations of NH3 source contributions.
• We relate modeled NH3 deposition flux to measured δ15N-NH3 values.

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ABSTRACT

The proportion of reactive nitrogen in wet deposition attributable to ammonium (NH4+) has increased over the last three decades in the U.S. due to steadily increasing NH3 emissions and concomitant reductions in NOx emissions. The importance of examining NH3 emission sources and transport is amplified as the fraction of NH3 contributing to reactive nitrogen budget increases. Presented here is a study illustrating how the nitrogen stable isotopic composition of NH3 (δ15N-NH3) can be used to characterize the transport of NH3 emissions at the landscape-scale. To accomplish this, ambient NH3 was sampled across varying land use types (e.g. conventionally managed corn field, tallgrass prairie, concentrated animal feeding operation (CAFO), dairy operation, urban setting) and analyzed for δ15N-NH3 values. Ambient δ15N-NH3 values at a conventionally managed corn field were used in an isotope mixing model to make first order approximations of NH3 source contributions to ambient air over the cornfield. Results suggest that while volatilized fertilizer is a primary contributor to ambient NH3 after fertilizer application, during periods of low or no fertilization, vehicle NH3 emissions can be a substantial contributor to ambient NH3 over cornfields that are adjacent to roadways. These source approximations can aid in evaluating NH3 emission abatement techniques to local landscapes. Modeled NH3 deposition flux at a CAFO was found to contribute a considerable amount of nitrogen to the landscape and δ15N-NH3 values were used to trace the livestock source contributing to this flux. Ambient NH3 concentrations and δ15N-NH3 values were measured across an urban region and δ15N-NH3 values indicated primarily fossil fuel-based emissions and large spatial variations in NH3 concentrations.

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1. Introduction

Ammonia (NH3) emissions lead to wet and dry atmospheric deposition of NH3 and ammonium (NH4+) that can be substantial sources of nitrogen pollution to sensitive terrestrial, aquatic, and marine ecosystems (Davidson et al., 2012; Fowler et al., 1998; Walker et al., 2000). In the U.S., NH4+ concentrations in precipitation have increased at 90% of monitoring sites (National Trends Network, National Atmospheric Deposition Program (NADP)) from 1985 to 2002 wherein increases exceeding 50% occurred in a large area of the central U.S. (Lehmann et al., 2005). Given that NOx (NOx = NO + NO2) emissions have decreased 36% since the implementation of the U.S. Clean Air Act, and NH3 are generally
unregulated in the U.S., NH₃ is predicted to constitute 60% of nitrogen deposition by 2020 (Davidson et al., 2012). As a result NH₃ transport and deposition have become of increasing concern to air quality managers, modelers, epidemiologists and ecosystem scientists.

Global NH₃ emission sources are dominated by agricultural activities and in a review of NH₃ inventories reported for China, European Union, and U.S, livestock waste and fertilizer were determined to contribute between 80 and 93% of total NH₃ emissions (Reis et al., 2009). As opposed to NOₓ emissions that are predominantly fossil fuel-based, agriculturally-based NH₃ emissions occur in rural settings and can be deposited in nitrogen (N) sensitive ecosystems. Excess N loading to these sensitive ecosystems can lead to eutrophication of surface waters, decreased biodiversity, and increased soil acidity (Galloway et al., 2004).

Although the primary sources of NH₃ are agricultural, vehicles equipped with three-way catalytic converters can be a significant NH₃ source in urban areas (Cape et al., 2004; Kirchner et al., 2005). NH₃ is also emitted as ‘fuel NH₃’ from electrical generating units (EGUs) and as ‘NH₃ slip’ from EGUs equipped with selective catalytic reduction and selective non-catalytic NOₓ reduction technologies. These fossil fuel-based NH₃ emissions are significant in urban areas where NOₓ and SO₂ can react with NH₃ to form fine particulate matter. Elevated particulate matter concentrations degrade visibility and are associated with adverse human health effects (i.e. respiratory and cardiovascular disease (Pope and Dockery, 2006)); both of these adverse health effects can be exacerbated in densely populated urban areas.

Agricultural and fossil fuel emissions are usually associated with rural and urban areas, respectively. However, NH₃ has an atmospheric lifetime of a few hours to 5 days and can also react with acidic gases to form NH₄ aerosols with longer lifetimes (1–15 days) and thus allow transport over large distances (Anjea et al., 2001). Investigating emission transport from individual NH₃ sources is necessary to understand the impact of agricultural emissions to urban areas and how emissions from fossil fuel combustion can potentially impact rural areas.

NH₃ emissions associated with agricultural and fossil fuel activities are reported to have distinctly different nitrogen isotopic compositions (δ¹⁵N–NH₃) which can be used to characterize the transport of the varying NH₃ source emissions. Volatilized livestock waste NH₃ emissions from dairy operations, poultry operations, and other animal feeding operations are reported to have low δ¹⁵N–NH₃ values (–56‰ to –9‰) (Felix et al., 2013; Freyer, 1978; Heaton, 1987; Hristov et al., 2009; Schulz et al., 2001; Skinner et al., 2006). Volatilized fertilizer NH₃ emissions also have low values (–48.0‰ to –36.3‰) (Felix et al., 2013). In comparison, reported δ¹⁵N–NH₃ values of NH₃ emitted from coal combustion (–7 to +2‰) (Freyer, 1978), ‘NH₃ slip’ from EGUs (–14.6 to –11.3‰) (Felix et al., 2013) and vehicles (–4.6 to –2.2‰) (Felix et al., 2013) are considerably higher than those from livestock and fertilizer emissions. Building on this knowledge of varying isotopic signatures among NH₃ sources, this study: 1) documents the utility of ambient NH₃ δ¹⁵N values to examine transport of NH₃ across landscapes characterized by various land-use types (dairy operation, conventionally managed cornfield, concentrated animal feeding operation (CAFO) (i.e. large beef cattle feedlot), and tallgrass prairie); 2) uses an isotope mixing model to predict first order approximations of NH₃ source contributions to ambient NH₃ concentrations [NH₃]; 3) relates modeled NH₃ deposition flux to measured δ¹⁵N–NH₃ values and; and 4) uses δ¹⁵N to investigate NH₃ sources in an urban region.

## 2. Methods

### 2.1. NH₃ emission collection methods for concentration and isotope analysis

Passive samplers, either Ogawa or Adapted Low-Cost Passive High Absorption (ALPHA), have been used in previous studies to collect NH₃ emissions and monitor [NH₃] (Cape et al., 2004; Rogers et al., 2009; Sather et al., 2008; Siefert et al., 2004; Skinner et al., 2004, 2006; Tang et al., 2001; Felix et al., 2013). The Ogawa is a double-sided passive diffuse 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 PTFE membrane for gaseous NH₃ diffusion (Tang et al., 2009). In this study the Ogawa passive sampler was only used at the small dairy operation field site because the sampling surface was smaller than that of the ALPHA sampler, thus minimizing the amount of NH₃ collected for subsequent isotope analysis. During this study, ALPHA blanks in a sealed mason jar traveled with the deployed ALPHA samplers and were later analyzed for [NH₃] so the ‘blank concentration’ could be subtracted from concentration of deployed samplers.

### 2.2. NH₃ concentration analysis method

After collection on the passive sampler filters, NH₃ was eluted with Milli-Q water and analyzed as NH₄ using the phenolate method (Eaton et al., 2005) and a Thermo Evolution 60S UV–vis. NH₃ air concentrations were calculated according to Ogawa or ALPHA sampler protocol (Ogawa and Co, USA, 2006; Tang et al., 2009).

### 2.3. Nitrogen isotopic analysis of NH₃ samples

After NH₃ collected on a filter is eluted, NH₄ in the eluant is analyzed for nitrogen isotopic composition according to Felix et al. (2013). Briefly, this approach for δ¹⁵N–NH₄ isotopic analysis combines two existing methods (Sigman et al., 2001; L. Zhang et al., 2007). An oxidation method (Zhang et al., 2007) employing a hypobromite oxidation solution was used to oxidize the NH₄ (diluted to 10 μM NH₄) in the sample to nitrite (NO₂). Conversion of NH₄ to NO₂ is quantitative. After oxidation, sample pH is adjusted to between 3 and 9 using 6N HCl. 20 nmoles of sample NO₂ is then converted to N₂O using the bacterial denitrifier Pseudomonas aeruginosa and introduced to an Isotope Ratio Mass Spectrometer (IRMS) (Sigman et al., 2001). 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 an Isoprime Trace Gas and Gilson GX-271 autosampler coupled with an Isoprime Continuous Flow IRMS at the University of Pittsburgh, Regional Stable Isotope Laboratory for Earth and Environmental Research. Values are reported in parts per thousand relative to atmospheric N₂ as follows:

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

International reference standards USGS34, USGS32, USGS25, and USGS26 were used for data correction according to Felix et al., 2013.
2.4. Calculating NH3 deposition flux from concentrations

To investigate quantities of NH3 deposition to a landscape surrounding a concentrated animal feeding operation (CAFO), deposition flux was modeled using a simplified approach according to European Environment Agency Guidance on modeling the concentration and deposition of ammonia emitted from intensive farming (European Environment Agency, 2010). Deposition flux is calculated as:

\[ F = V_d \ast C \]  \hspace{1cm} (2)

where \( C \) is [NH3] at each transect sampling site (\( \mu g \) m\(^{-3}\)), \( V_d \) is NH3 dry deposition velocity (m/s), and \( F \) is deposition flux (\( \mu g \) NH3 m\(^{-2}\) s\(^{-1}\)). Flux is calculated using deposition velocities that vary with [NH3] as NH3 deposition velocity decreases with increasing concentrations. ([20–30] = 0.01 m/s, [30–80] = 0.005 m/s, [80–135] = 0.003 m/s). [NH3] indicates \( \mu g \) m\(^{-3}\).

2.5. Description of sites for NH3 source sampling and transects

2.5.1. Small dairy barn transect

A pilot study was conducted in summer 2009 to assess the effectiveness of passive samplers for collection of NH3 for subsequent isotopic analysis. A transect was established radiating from a small, 150-head dairy barn in Western Pennsylvania downwind to the edge of a forest. Ogawa passive samplers were placed at the upwind opening of the dairy barn, 10 m outside the barn directly near ventilation fans, 50 m, and 200 m downwind from the dairy barn. The passive samplers were deployed for one month (6/28/09 to 7/28/09). It should be noted that while some of the sampling transects presented in this paper have an upwind site to represent a site less impacted by emission source, it has been reported that upwind sites can also be significantly impacted by NH3 source emissions (Jones et al., 2013).

2.5.2. Conventionally managed cornfield transect

The Optimizing Production Inputs for Economic and Environmental Enhancement (OPE3) site at the USDA ARS facility (Beltsville Agricultural Research Center (BARC)) in Beltsville Maryland (USA) consists of four adjacent watersheds that are managed with different crop management systems. Field B at OPE-3 was chosen as a sampling transect site because it represents traditional farming practices common in Midwestern states, mainly corn row crops with a uniform application of urea—ammonia—nitrate industrial fertilizer applied with planting (40 kg N/ha) and later as side-dressing (135 kg N/ha) (USDA, 2013). The sampling transect began at the midpoint of Field B and ended in a downwind riparian area (Fig. 1). A site upwind of the transect was also sampled directly adjacent to the cornfield and near a commuter road. The transect at Field B was sampled a total of four times over a two-year period (Table 1). Although this transect was established to sample NH3 volatilization from fertilizers, it was adjacent to a commuter road and within 500 m of the Baltimore–Washington parkway (a heavily trafficked road with ~91,000 vehicles/day) (MDOT, 2012).

2.5.3. Confined animal feeding operation transect and livestock waste

A concentrated animal feeding operation (CAFO) containing 30,000 head of beef cattle over 59 ha was sampled in central Kansas. A transect was established radiating from the CAFO edge (0 m) to 9 downwind sites (30, 130, 230, 330 m, and 1.6 km from the CAFO edge). The average wind direction during the summer at the CAFO site is from the south and southeast (Bonifacio, 2009). The CAFO passive sampling was conducted from 8/6/10 to 8/21/10.

2.5.4. Native tallgrass prairie

Konza Prairie Biological Station (KPBS) is a 3487 ha native tallgrass prairie preserve located in the Flint Hills of Kansas and home of the Konza Long-term Ecological Research (Konza, 2013). Konza is divided into sections subjected to management treatments including grazing, non-grazing, burning, and non-burning. We established a transect (5 sites ~50 m apart and varying in elevation) across Section K2A, an ungrazed plot subject to a two year burn cycle (Konza) to characterize ambient NH3 background concentrations. Konza passive sampling was conducted from 8/5/10 to 8/21/10.

2.5.5. Pittsburgh, PA urban region sampling

ALPHA passive samplers were deployed in summer 2012 (7/5/12 to 7/19/12). Ten sites were selected from a suite of 36 previously-characterized sites located across the Pittsburgh metropolitan area. Sites were chosen to capture variability in traffic density, industrial emissions, and elevation; these are key predictors of spatial variance in combustion-related air pollution in this region (Shnool et al., 2014). Samplers were placed randomly on ten telephone poles at a height of 10 ft throughout the city of Pittsburgh, PA (population 307,000) to capture urban NH3 emissions.

3. Results and discussion

3.1. NH3 collection for isotope analysis

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 thus limited the amount of NH3 collected for isotopic analysis. The \( ^{15}N – NH_3 \) 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 NH3 concentrations. ALPHA samplers were used throughout the

| Table 1 Description of conventionally managed cornfield sampling sessions. |
|-------------------------------|-----------------|-----------------|
| Sampling session | Date | Fertilizer application |
| 1 | 5/22/10 to 6/3/10 | 40 kg N/ha |
| 2 | 6/19/10 to 7/22/10 | 135 kg N/ha |
| 3 | 6/2/11 to 6/19/11 | 40 kg N/ha |
| 4 | 6/23/11 to 7/22/11 | 135 kg N/ha |

* Urea Ammonia Nitrate (UAN) was the fertilizer applied. The fertilizer is “side-dressed” meaning that the nitrogen is applied to the soil subsurface within the root zone.
remaining study sites and the average standard deviation for triplicate ALPHA samplers is ±2.6‰ and ranged from 1.5 to 4.5‰. Triplicate samplers were deployed on a single post and thus collected NH3 at slightly varying heights and from wind varying directions. Thus, physical differences in deployment among the triplicate samplers may be partially responsible for the range in standard deviations observed herein. ALPHA samplers results for NH3 collection and subsequent isotopic analysis are described further in Felix et al. (2013).

3.2. Dairy barn transect

The pilot study results from the small dairy barn operation demonstrate that passive samplers collect sufficient NH3 for isotopic analysis, and further that the δ15N–NH3 values follow a systematic pattern with distance from the facility (Fig. 2). δ15N–NH3 values increased toward the ambient, background value, with decreasing [NH3] downwind of the barn. In a similar study performed at intensive animal units, Skinner et al. (2006) suggest that along with mixing with background air, fractionation occurring during the conversion of NH3 to NH4 may be the cause of higher δ15N–NH3 values further from the animal waste source. The kinetically driven reaction of NH3 to NH4 would favor the reaction of the NH3 containing the lighter 14N isotope producing NH3 enriched in the 15N isotope (Freyer, 1978). These pilot study results provided proof of concept that it would be viable to more intensively sample at future larger transect locations using collection devices with a larger surface area.

3.3. Konza tallgrass prairie transect

δ15N–NH3 values at each site of the Konza tallgrass prairie transect fell within the standard deviation of the δ15N–NH3 value at each other transect site (Fig. 2B). The consistent δ15N–NH3 values were expected since there is no immediate NH3 point source near the transect. The samplers were collecting ambient NH3 over the prairie and this demonstrated that no δ15N–NH3 gradient was seen across landscapes without immediate NH3 sources. Mean δ15N–NH3 value (−7.0 ± 1.6‰) may represent the NH3 emitted from natural prairie soils but there also may be mixing with other NH3 source emissions transported to the prairie (e.g. livestock waste or biomass burning).

3.4. Conventionally managed cornfield transect

3.4.1. NH3 concentration, δ15N–NH3

Table 2 summarizes [NH3] and δ15N–NH3 data at the conventionally managed cornfield. [NH3] aren’t significantly different at sites over the cornfield following the 40 kg N/ha fertilizer application (t-test: p = 0.62). [NH3] are higher at sampling sites over the cornfield and decrease significantly away from the field into the riparian area after the 135 kg N/ha fertilizer application (t-test: p = 0.0002) (Fig. 3). [NH3] at sites over the cornfield (1–4), were 3–14 times higher after the 135 kg N/ha fertilizer application than after the initial 40 kg N/ha fertilizer application (Fig. 3). Volatilization of the applied fertilizer produces the higher [NH3] at sites over the cornfield. A decreasing fertilizer source and possible ‘scrubbing out’ or uptake by the trees is likely responsible for the decreasing [NH3] observed as the sampled sites move into the riparian area. The hypothesis of decreasing NH3 source in the riparian area holds true except for one outlier point at site 6 after the 2011 40 kg N/ha fertilizer application in which the [NH3] at site 6 increases. It is possible this increase is due to an increased localized NH3 source such as animal waste directly adjacent to the passive sampler.

δ15N–NH3 values are higher on average at the upwind site than the sites over the field (−15.9‰ and −27.5‰, respectively) due to vehicle exhaust NH3 contribution (Fig. 4). δ15N–NH3 values were lower at the sites over the cornfield indicating contribution from

Fig. 2. A.) [NH3] and δ15N–NH3 at the small dairy barn transect. Standard deviation is not reported because one filter was used for concentration and the duplicate was used for isotope analysis. B.) δ15N–NH3 values at Konza tallgrass prairie transect. C.) δ15N–NH3 values and [NH3] at the CAFO. For all [NH3] is represented by blue triangles and δ15N–NH3 values are represented by orange squares. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Fertilizer δ15N values range from 0 ± 2‰ (Bateman and Kelly, 2007), this indicates an average fractionation factor between NH4 fertilizer and NH3 (g) of −40.7‰ which may vary from site to site as NH3 volatilization depends on varying environmental conditions (e.g. temperature, wind speed, pH) (Hristov et al., 2011). This fractionation factor falls within the literature range of 30–60‰ (Frank et al., 2004) reported for NH3 volatilization. Fractionation over the cornfield can also occur during air-surface (soil and vegetation) exchange of NH3 or uptake by vegetation. Plants can grow exclusively on atmospheric NH3 as their nitrogen source but bi-directional exchange between air and plant may take place depending on environmental conditions (Erisman et al., 2007; Walker et al., 2006). For instance, NH3 exchange between the plant and atmosphere can cause plants to be an NH3 source or sink and this exchange can vary as the NH3 compensation point varies. The NH3 compensation point is when net uptake of NH3 is zero or when the NH3 partial pressure in the atmosphere is equal to that of the plant (Farquhar et al., 1980). Multiple factors influence this compensation point including temperature, vegetation type, vegetation growth, and nitrogen status (Wu et al., 2009 and ref therein). All of these factors can change the rate of uptake or emissions and with each change different degrees of fractionation may be taking place leading to varying δ15N–NH3 values across the field site. For example, in a high N supply agricultural environment, such as the cornfield in this study, plants tend to emit NH3 rather than absorb it from the atmosphere (Husted et al., 2000). It is possible that lower δ15N values over the cornfield in this study could be a result of the process of NH3 emission from plants favoring the lighter 14NH3 molecule. Continual quantification of how these bi-directional fluxes may be altering δ15N–NH3 values is an important step to using δ15N values to quantify NH3 sources and should prove to be a valuable area of study.

3.4.2. Predicting % NH3 source contribution at a conventionally managed cornfield

An isotope mixing equation was used to predict % NH3 source contribution to the air [NH3] at a conventionally managed cornfield assuming the two main contributors to [NH3] at the field site are vehicle exhaust and volatilized fertilizer (Equation (3)).

\[
\delta^{15}N-\text{NH}_3\text{obs} = f_{\text{vehicle}} \left( \delta^{15}N-\text{NH}_3\text{vehicle} \right) + (1 - f_{\text{vehicle}}) \left( \delta^{15}N-\text{NH}_3\text{fertilizer} \right)
\]

where \(\delta^{15}N-\text{NH}_3\text{obs}\) is the observed δ15N value at each cornfield site, \(f_{\text{vehicle}}\) is the fraction vehicle NH3, \(\delta^{15}N-\text{NH}_3\text{vehicle}\) is the vehicle δ15N endmember, (1 – \(f_{\text{vehicle}}\)) is the fraction fertilizer NH3, \(\delta^{15}N-\text{NH}_3\text{fertilizer}\) is the volatilized fertilizer δ15N endmember. For this analysis, δ15N–NH3 values for vehicle NH3 range from −4.6 to −2.2‰ and are based on δ15N–NH3 values collected using passive samplers at a moderately trafficked tunnel (Felix et al., 2013). δ15N–NH3 values for volatilized fertilizer range from −48.0 to −36.3‰ and are the δ15N–NH3 values from observed at Sites 2 through 4 at the cornfield after both 135 kg N/ha fertilizer applications (Felix et al., 2013). The relative contribution from each

<table>
<thead>
<tr>
<th>Site</th>
<th>Session 1 40 kg N/ha</th>
<th>Session 2 135 kg N/ha</th>
<th>Session 3 40 kg N/ha</th>
<th>Session 4 135 kg N/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NH3] (μg/m³)</td>
<td>δ15N–NH3 (%d)</td>
<td>[NH3] (μg/m³)</td>
<td>δ15N–NH3 (%d)</td>
<td>[NH3] (μg/m³)</td>
</tr>
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<td>21.3</td>
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<td>−13.1</td>
<td>20.7</td>
<td>−39.4</td>
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<tr>
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<td>3.0</td>
<td>−7.8</td>
<td>19.8</td>
<td>−41.4</td>
</tr>
<tr>
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<td>1.9</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>1.4</td>
<td>−5.1</td>
<td>12.5</td>
<td>−27.9</td>
</tr>
<tr>
<td>UW</td>
<td>3.6</td>
<td>−1.3</td>
<td>9.2</td>
<td>−30.4</td>
</tr>
</tbody>
</table>

Fig. 3. [NH3] for each BARC cornfield sampling session. The ‘UW’ is the upwind site and is ~200 m upwind of site 1.

Fig. 4. δ15N–NH3 values for each BARC cornfield sampling session. The ‘UW’ is the upwind site and is ~200 m upwind of site 1.
source to sites across the transect are predicted using Monte Carlo simulation and assumed uniform distribution for each source \( \delta^{15}N-NH_3 \) values among each source range. Percent vehicle and volatilized fertilizer contributions to each cornfield transect sampling were similar for consecutive years (Fig. 5). The maximum likelihood estimation (MLE) results indicate that 28% and 97% of ambient \( NH_3 \) over the cornfield (sites 1–4) is contributed from volatilized fertilizer during the sampling periods following the 40 kg N/ha and 135 kg N/ha fertilization, respectively. These results suggest vehicle \( NH_3 \) emissions can be a substantial contributor to ambient \( NH_3 \) over a cornfield adjacent to commuter and/or highly trafficked roadway during periods of low or no fertilization. However, during large fertilizer application, volatilized fertilizer \( NH_3 \) emissions over the field dominate that of vehicles. Infeasible solutions included those where modeled source contributions exceed 100% or are less than 0% and could result from the contributions of additional sources to ambient \( NH_3 \) not accounted for here, potential variability of \( NH_3 \) in August at the closest Ammonia Monitoring Network site (Konza prairie, KS, 1.5 g/m³, ~225 km away) (NADP, 2013). \( NH_3 \) concentrations decrease within the first 100 m of the CAFO (109.3 µg/m³), stay constant over the next ~350 m (~50 µg/m³) (Fig. 2C) and decline at 1600 m downwind of the CAFO (26.9 µg/m³). [\( NH_3 \)] are greatly elevated near the CAFO compared to the [\( NH_3 \)] in August at the closest Ammonia Monitoring Network (AMoN) site (Konza prairie, KS, 1.5 µg/m³, ~225 km away) (NADP, 2013).

\( NH_3 \) deposition flux at sites downwind of the CAFO was calculated to investigate the amount of \( NH_3 \) being contributed to the landscape from livestock waste emissions. The modeled deposition flux predicts that the landscape 0–1600 km downwind from the CAFO can receive 5.1 to 4.0 kg N/ha during the month of August. For comparison, the conventionally managed cornfield site discussed earlier receives two fertilizer applications during the growing season totaling 175 kg N/ha/yr. This modeled \( NH_3 \) soil deposition flux suggests CAFO emissions can provide considerable amounts of fertilization from atmospheric \( NH_3 \) to a crop field and suggest that crops downwind of CAFOs may require lower rates of fertilizer N application. N loading due to dry \( NH_3 \) deposition flux may be more significant in a nutrient sensitive ecosystem downwind of a CAFO since the deposition velocity is concentration dependent with lower concentrations having a higher deposition velocity.

The contributions of \( NH_3 \) deposition to land surrounding the CAFO underscores the importance of tracing the transport and deposition of \( NH_3 \) sources. \( \delta^{15}N-NH_3 \) values at the CAFO increase with decreasing [\( NH_3 \)] and with distance from the CAFO. This indicates a decreasing contribution from livestock waste and mixing with background air. As with the small dairy barn transect, higher \( \delta^{15}N-NH_3 \) values at further distances from the animal waste may also result from fractionations that occur during the conversion of \( NH_3 \) to \( NH_4^+ \) (Skinner et al., 2006). The changing \( \delta^{15}N-NH_3 \) values can be used to infer contributions of livestock waste emissions to \( NH_3 \) deposition flux to the landscape.

3.5. CAFO

3.5.1. CAFO [\( NH_3 \)] and \( \delta^{15}N-NH_3 \)

\( NH_3 \) concentrations decrease within the first 100 m of the CAFO (109.3 µg/m³), stay constant over the next ~350 m (~50 µg/m³) (Fig. 2C) and decline at 1600 m downwind of the CAFO (26.9 µg/m³). [\( NH_3 \)] are greatly elevated near the CAFO compared to the [\( NH_3 \)] in August at the closest Ammonia Monitoring Network (AMoN) site (Konza prairie, KS, 1.5 µg/m³, ~225 km away) (NADP, 2013).

\( NH_3 \) deposition flux at sites downwind of the CAFO was calculated to investigate the amount of \( NH_3 \) being contributed to the landscape from livestock waste emissions. The modeled deposition flux predicts that the landscape 0–1600 km downwind from the CAFO can receive 5.1 to 4.0 kg N/ha during the month of August. For comparison, the conventionally managed cornfield

**Fig. 5.** Percent \( NH_3 \) contribution from vehicle exhaust and volatilized fertilizer after each fertilizer application. Contribution maximum likelihood estimations were obtained using Monte Carlo simulations. The ‘UW’ is the upwind site and is ~200 m upwind of site 1. Sites 1 through 4 are over the cornfield and sites 5 and 6 are in the riparian area.

\( NH_3 \) concentrations in the Pittsburgh region range from 1.1 to 12.4 µg/m³ with a mean of 4.7 ± 3.7 µg/m³ (Fig. 6) revealing the spatially heterogeneous nature of \( NH_3 \) emissions in urban landscapes. \( \delta^{15}N-NH_3 \) values range from −22.9 to +0.7‰ with a mean of −8.5 ± 7.2‰ (Fig. 6). In general, \( \delta^{15}N-NH_3 \) values fall within the ranges reported for \( NH_3 \) from vehicle and power plant emission (8 of 10 sites). Two observed \( \delta^{15}N-NH_3 \) values fall between the vehicle/power plant and livestock/fertilizer \( \delta^{15}N-NH_3 \) source signatures. This could be due to mixing between fossil fuel sources and \( NH_3 \) transported from agricultural activity in surrounding rural areas, or contributions of other \( NH_3 \) sources such as volatilized \( NH_3 \) from sewer entrances or streams receiving excess waste inputs.
Fig. 6. [NH₃] at the Pittsburgh sampling sites are represented by proportional black circles and δ¹⁵N–NH₃ at the Pittsburgh sampling sites are represented by color graduated circles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Divers et al., 2013). Notably, the site with the lowest δ¹⁵N–NH₃ value (~22.9‰) is located on a road between two golf courses. Therefore, NH₃ collected at this site could reflect the contributions of volatilized fertilizer characterized by low δ¹⁵N values at these golf courses. In general, the relatively high δ¹⁵N–NH₃ values in this urban region reveal that while global emission inventories estimate agricultural NH₃ emissions are responsible for 80–93% of NH₃ emissions globally, in urban areas, sources associated with fossil fuel combustion can be a primary source of reactive NH₃. Moreover, these results highlight the highly spatial variability of NH₃ in an urban system and potential complexity of source attribution in a system with a mixture of sources.

4. Conclusion

NH₄ contribution to total N deposition in the U.S. is expected to continue to rise (Davidson et al., 2012) and its subsequent impacts on the environment have led to mounting concern. Quantifying NH₃ contributions from individual sources and understanding NH₃ emission transport are important for reducing adverse impacts attributed to NH₃ emissions.

This work demonstrates how the stable isotopic composition of NH₃ can be used to investigate the relative influence of individual NH₃ sources and their transport across landscapes. NH₃ concentrations at dairy barn and CAFO transects decreased with distance from the livestock waste NH₃ source. Concomitant decreases in δ¹⁵N–NH₃ values with distance indicate that isotopic ratios can be used as an additional tool for quantifying contributions to ambient [NH₃]. Modeled NH₃ deposition fluxes at the CAFO transect contribute considerable amounts of reactive nitrogen to the landscape. In this same setting, δ¹⁵N–NH₃ values were effectively used to trace the livestock waste source contributing to this flux. Fertilizer application to fields adjacent to livestock operations may be reduced if the amount of N deposition from the livestock waste source can be estimated. Future studies should aim to quantify how original δ¹⁵N source signatures can be altered through fractionating processes (e.g. bidirectional flux, kinetic reactions) and will be an important next step in using δ¹⁵N–NH₃ values to trace emissions.

At a conventionally managed cornfield, ambient δ¹⁵N–NH₃ values across a transect were used to predict first order approximations of fertilizer or vehicle NH₃ source contributions. Vehicle-derived NH₃ emissions were found to be substantial contributors to ambient [NH₃] over the cornfield during periods of low or no fertilizer application. This type of source contribution estimate can ultimately aid in evaluating NH₃ emission abatement techniques for local landscapes.

Lastly, ambient [NH₃] was measured across an urban region and varied greatly. The δ¹⁵N–NH₃ values at urban sites provide evidence that sources leading to wide isotopic and concentration variations are related to fossil fuel combustion whether directly from ‘fuel’ NH₃ or as a byproduct of emission reduction technologies. While livestock waste and fertilizer are the major contributors to global ambient [NH₃], δ¹⁵N–NH₃ values at the urban region and cornfield transect suggest fossil fuel combustion-related emissions can be substantial sources to local landscape.

Reducing uncertainties in nonagricultural NH₃ sources, especially those originating from fossil fuel combustion are important initial steps in closing the gaps in reactive nitrogen budgets (Reis et al., 2009). An accurate NH₃ inventory is necessary to precisely investigate the efficacy of NH₃ reduction techniques. When direct NH₃ emission point sources are not clearly observable, δ¹⁵N–NH₃ values can be an effective additional tool for examining source contributions to ambient [NH₃] and can aid in constraining NH₃ inventories. While this study indicates that ambient δ¹⁵N–NH₃ values can be utilized to estimate contributions from various NH₃ emission sources, additional characterization of source values and subsequent fractionations are needed to use isotopic information with increasing confidence.

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