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

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HIGHLIGHTS

- We document the utility of $\delta^{15}N-NH_3$ values for examining NH_3 transport.
- We use an isotope mixing model to make approximations of NH_3 source contributions.
- We relate modeled NH_3 deposition flux to measured $\delta^{15}N-NH_3$ values.

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ABSTRACT

The proportion of reactive nitrogen in wet deposition attributable to ammonium (NH_4^+) has increased over the last three decades in the U.S. due to steadily increasing NH_3 emissions and concomitant reductions in NO_x emissions. The importance of examining NH_3 emission sources and transport is amplified as the fraction of NH_3 contributing to reactive nitrogen budget increases. Presented here is a study illustrating how the nitrogen stable isotopic composition of NH_3 ($\delta^{15}N-NH_3$) can be used to characterize the transport of NH_3 emissions at the landscape-scale. To accomplish this, ambient NH_3 was sampled across varying land use types (e.g. conventionally managed cornfield, tallgrass prairie, concentrated animal feeding operation (CAFO), dairy operation, urban setting) and analyzed for $\delta^{15}N-NH_3$ values. Ambient $\delta^{15}N-NH_3$ values at a conventionally managed cornfield were used in an isotope mixing model to make first order approximations of NH_3 source contributions to ambient air over the cornfield. Results suggest that while volatilized fertilizer is a primary contributor to ambient NH_3 after fertilizer application, during periods of low or no fertilization, vehicle NH_3 emissions can be a substantial contributor to ambient NH_3 over cornfields that are adjacent to roadways. These source approximations can aid in evaluating NH_3 emission abatement techniques to local landscapes. Modeled NH_3 deposition flux at a CAFO was found to contribute a considerable amount of nitrogen to the landscape and $\delta^{15}N-NH_3$ values were used to trace the livestock source contributing to this flux. Ambient NH_3 concentrations and $\delta^{15}N-NH_3$ values were measured across an urban region and $\delta^{15}N-NH_3$ values indicated primarily fossil fuel-based emissions and large spatial variations in NH_3 concentrations.

1. Introduction

Ammonia (NH_3) emissions lead to wet and dry atmospheric deposition of NH_3 and ammonium (NH_4^+) 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., NH_4^+ 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 NO_x ($NO_x = NO + NO_2$) emissions have decreased 36% since the implementation of the U.S. Clean Air Act, and NH_3 are generally

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unregulated in the U.S., NH_3 is predicted to constitute 60% of nitrogen deposition by 2020 (Davidson et al., 2012). As a result NH_3 transport and deposition have become of increasing concern to air quality managers, modelers, epidemiologists and ecosystem scientists.

Global NH_3 emission sources are dominated by agricultural activities and in a review of NH_3 inventories reported for China, European Union, and U.S, livestock waste and fertilizer were determined to contribute between 80 and 93% of total NH_3 emissions (Reis et al., 2009). As opposed to NO_x emissions that are predominantly fossil fuel-based, agriculturally-based NH_3 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 NH_3 are agricultural, vehicles equipped with three-way catalytic converters can be a significant NH_3 source in urban areas (Cape et al., 2004; Kirchner et al., 2005). NH_3 is also emitted as 'fuel NH_3' from electrical generating units (EGUs) and as 'NH_3 slip' from EGUs equipped with selective catalytic reduction and selective non-catalytic NO_x reduction technologies. These fossil fuel-based NH_3 emissions are significant in urban areas where NO_x and SO_2 can react with NH_3 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, NH_3 has an atmospheric lifetime of a few hours to 5 days and can also react with acidic gases to form NH_4^+ aerosols with longer lifetimes (1–15 days) and thus allow transport over large distances (Aneja et al., 2001). Investigating emission transport from individual NH_3 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.

NH_3 emissions associated with agricultural and fossil fuel activities are reported to have distinctly different nitrogen isotopic compositions ($\delta^{15}N-NH_3$) which can be used to characterize the transport of the varying NH_3 source emissions. Volatilized livestock waste NH_3 emissions from dairy operations, poultry operations, and other animal feeding operations are reported to have low $\delta^{15}N-NH_3$ 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 NH_3 emissions also have low values (−48.0‰ to −36.3‰) (Felix et al., 2013). In comparison, reported $\delta^{15}N-NH_3$ values of NH_3 emitted from coal combustion (−7 to +2‰) (Freyer, 1978), 'NH_3 slip' from EGU's (−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 NH_3 sources, this study: 1) documents the utility of ambient NH_3 $\delta^{15}N$ values to examine transport of NH_3 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 NH_3 source contributions to ambient NH_3 concentrations [NH_3]; 3) relates modeled NH_3 deposition flux to measured $\delta^{15}N-NH_3$ values and; and 4) uses $\delta^{15}N$ to investigate NH_3 sources in an urban region.

2. Methods

2.1. NH_3 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 NH_3 emissions and monitor [NH_3] (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 NH_3 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 NH_3 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 [NH_3] so the 'blank concentration' could be subtracted from concentration of deployed samplers.

2.2. NH_3 concentration analysis method

After collection on the passive sampler filters, NH_3 was eluted with Milli-Q water and analyzed as NH_4^+ using the phenolate method (Eaton et al., 2005) and a Thermo Evolution 60S UV–vis. NH_3 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 NH_3 samples

After NH_3 collected on a filter is eluted, NH_4^+ in the eluant is analyzed for nitrogen isotopic composition according to Felix et al. (2013). Briefly, this approach for $\delta^{15}N-NH_4$ 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 NH_4^+ (diluted to 10 μM NH_4^+) in the sample to nitrite (NO_2^-). Conversion of NH_4^+ to NO_2^- is quantitative. After oxidation, sample pH is adjusted to between 3 and 9 using 6N HCl. 20 nmoles of sample NO_2^- is then converted to N_2O using the bacterial denitrifier *Pseudomonas aureofaciens* 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 $\delta^{15}N$ 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 N_2 as follows:

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

International reference standards USGS34, USGS32, USGS25, and USGS26 were used for data correction according to Felix et al., 2013.