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# Spatial and temporal patterns of nitrogen isotopic composition of ammonia at U.S. ammonia monitoring network sites

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## HIGHLIGHTS

- Monthly $\delta^{15}$N-$NH_3$ values are reported for 9 AMoN sites over a year.
- $\delta^{15}$N-$NH_3$ values ranged from −42.4 to +7.1‰ with an average of −15.1 ± 9.7‰.
- US agricultural regions have low and seasonally variable $\delta^{15}$N-$NH_3$ values.
- Rural nonagricultural areas have higher and seasonally consistent $\delta^{15}$N-$NH_3$ values.
- US spring agricultural activity peak is accompanied by a decrease in $\delta^{15}$N-$NH_3$ values.

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## ABSTRACT

Ammonia ($NH_3$) emissions and ammonium ($NH_4^+$) deposition can have harmful effects on the environment and human health but remain generally unregulated in the U.S. $PM_{2.5}$ regulations require that an area not exceed an annual average $PM_{2.5}$ value of 12 μg/m$^3$ (averaged over three years), and since $NH_3$ is a significant precursor to $PM_{2.5}$ formation these are the closest indirect regulations of $NH_3$ emissions in the U.S. If the U.S. elects to adopt $NH_3$ emission regulations similar to those applied by the European Union, it will be imperative to first adequately quantify $NH_3$ emission sources and transport, and also understand the factors causing varying emissions from each source. To further investigate $NH_3$ emission sources and transport at a regional scale, $NH_3$ was sampled monthly at a subset of nine Ammonia Monitoring Network (AMoN) sites and analyzed for nitrogen isotopic composition of $NH_3$ ($\delta^{15}$N-$NH_3$). The observed $\delta^{15}$N-$NH_3$ values ranged from −42.4 to +7.1‰ with an average of −15.1 ± 9.7. The observed $\delta^{15}$N-$NH_3$ values reported here provide insight into the spatial and temporal trends of the $NH_3$ sources that contribute to ambient [$NH_3$] in the U.S. In regions where agriculture is prevalent (i.e., U.S. Midwest), low and seasonally variable $\delta^{15}$N-$NH_3$ values are observed and are associated with varying agricultural sources. In comparison, rural nonagricultural areas have higher and more seasonally consistent $\delta^{15}$N-$NH_3$ values associated with a constant "natural" (e.g. soil, vegetation, bi-directional flux, ocean) $NH_3$ source. With regards to temporal variation, the peak in U.S. spring agricultural activity (e.g. fertilizer application, livestock waste volatilization) is accompanied by a decrease in $\delta^{15}$N-$NH_3$ values at a majority of the sites, whereas higher $\delta^{15}$N-$NH_3$ values in other seasons could be due to shifting sources (e.g. coal-fired power plants) and/or fractionation scenarios. Fractionation processes that may mask $NH_3$ source signatures are discussed and require further investigation to optimize the utility of the nitrogen isotopic composition to determine $NH_3$ sources and dynamics.

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## 1. Introduction

Ammonium ($NH_4^+$) in wet deposition in the U.S. has increased over 49% during the past three decades and currently accounts for 60% of the total dissolved inorganic nitrogen (DIN) in wet deposition (Du et al., 2014). This relative contribution is expected to

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increase given that ammonia ($NH_3$) emissions are generally unregulated in the U.S. whereas air quality regulations have led to dramatic decreases in $NO_x$ emissions, a precursor to the other primary DIN component in wet deposition, nitrate ($NO_3^-$). $NH_3$ and subsequent wet and dry $NH_x$ deposition products are substantial sources of nitrogen (N) to sensitive ecosystems and contribute to soil acidification, water body eutrophication, and decreases in biodiversity (Davidson et al., 2012; Fowler et al., 1998; Galloway et al., 2004). $NH_x$ deposition to ecosystems, coupled with other forms of N input, have caused 20% of U.S. natural vegetation to receive N in excess of a critical load (1000 mg (N) $m^{-2}$ $yr^{-1}$) as defined by Dentener et al., 2006. Prior to $NH_x$ deposition to various ecosystems, $NH_3$ emissions can react with acidic species (e.g. $H_2SO_4$ and $HNO_3$) to form particulate aerosols. Fine particulate matter (PM) decreases visibility, is linked to human health impacts (respiratory and cardiovascular disease) (Pope and Dockery, 2006) and can affect climate through changing radiative forcing caused by particulate aerosols that scatter or absorb solar radiation (Zhu et al., 2015). $PM_{2.5}$ is regulated by a U.S. EPA National Ambient Air Quality Standard that requires an area not to exceed an average $PM_{2.5}$ concentration of 12 $\mu g/m^3$ (EPA, 2013). This $PM_{2.5}$ regulation is the closest indirect regulation of $NH_3$ emissions in the U.S. because modeled results indicate that $PM_{2.5}$ attainment goals can be reached via decreasing $NH_3$ emissions (Banzhaf et al., 2013; Bessagnet et al., 2015; Gu et al., 2014; Pinder and Adams, 2007; Zhu et al., 2015). However, reduction of $NH_3$ may prove more difficult than previous air quality goals. Unlike other pollutants that are released consistently and predictably through industrial or mechanical processes (e.g. $NO_x$ or $SO_x$ emissions from vehicles or power plants) and are readily quantifiable, $NH_3$ emissions from area sources (e.g. livestock waste and fertilizer) are a function of both chemical and biological process that often depend on climate and environmental conditions. Therefore, these sources are often highly variable over space and time and can lead to large uncertainties in total $NH_3$ emission inventories for the U.S and the globe (2.8–3.2 and 44–83 Tg $NH_3$-N $yr^{-1}$, respectively) (Paulot et al., 2014). To produce effective policies or regulations, it is critical to quantify emissions of $NH_3$ from key sources including fertilizer application, livestock waste, vehicles, coal-fired power plants. It is equally important to understand $NH_3$ transport and factors that affect $NH_3$ emissions fluxes including climate, agricultural techniques, waste mitigation techniques, soil and vegetation characteristics (USDA, 2014).

As a consequence of recent increases in $NH_x$ deposition fluxes, there is heightened interest in improving our understanding of $NH_3$ emission sources, the processes controlling the formation and decomposition of $NH_4^+$ aerosols subject to long-range transport, and ultimately the deposition and bi-directional flux of $NH_3$ products in wet and dry deposition. As a result of this growing concern, U.S. monitoring networks for wet and dry deposition chemistry, the National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNET), respectively, have established a monitoring network, the "Ammonia Monitoring Network (AMoN)." The network began with trials in fall 2007, became an official NADP network in October 2010, and has rapidly expanded to include more than 90 sites with an ultimate goal of $NH_3$ monitoring sites adequately covering North America (NADP, 2015). The network deploys Radiello passive samplers to obtain $NH_3$ concentrations and aims to provide spatially dense long term ambient $NH_3$ concentration [$NH_3$] data that aids air quality modelers, ecologists and policy-makers in validating atmospheric models, estimating N deposition, and assessing $PM_{2.5}$ compliance (NADP, 2015). Preliminary results from the AMoN network along with other more localized $NH_3$ studies have helped quantify spatial and temporal trends in ambient [$NH_3$] (Butler et al., 2015; Chen et al., 2014; Mukerjee et al., 2012; NADP, 2015; Yao and Zhang, 2013). Most of these studies report high [$NH_3$] in spring and summer due to peak agricultural activity and volatilization, with lower concentrations in winter due to lack of agricultural activity and limited volatility and condensation (Bari et al., 2003; Felix et al., 2014; Mukerjee et al., 2012; Reche et al., 2015).

Air mass back trajectories, emission dispersion models and knowledge of seasonal variation in emission source activity allow researchers to infer probable emission sources that contribute to ambient [$NH_3$]. However, these generalizations can lead to errors in source attribution and cannot explain seasonal [$NH_3$] anomalies that have been reported (Butler et al., 2015; Chen et al., 2014; Yao and Zhang, 2013). For instance, Chen et al., 2014 report relatively high [$NH_3$] at agricultural sites when $NH_3$ volatilization should be minimal and Yao and Zhang, 2013 observed [$NH_3$] increases at some sites when ambient temperature was <−7 °C. Also, while much of the $NH_3$ emissions in the U.S. are attributed to agricultural activity, [$NH_3$] in urban areas are often higher than in rural areas where most agricultural activity takes place (Edgerton et al., 2007; Felix et al., 2014). $NH_3$ in cities may result from transport from rural agricultural sources but urban sources (e.g. vehicles, wastewater, sewage, and industry) may also be the primary contributors. Urban studies report large ranges in [$NH_3$] within an urban region which makes it difficult to qualify sources contributing to ambient [$NH_3$] (Bari et al., 2003; Felix et al., 2014; Mukerjee et al., 2012; Reche et al., 2015).

An approach to aid in identifying $NH_3$ emission source contribution to ambient concentrations is to exploit the difference between the $\delta^{15}N$-$NH_3$ values associated with different $NH_3$ emission sources (Fig. 1). For instance, the primary sources of $NH_3$, volatilized livestock waste and fertilizer, are generally reported to have low $\delta^{15}N$-$NH_3$ values, −56‰ to −9‰ and −48‰ to −36‰, respectively

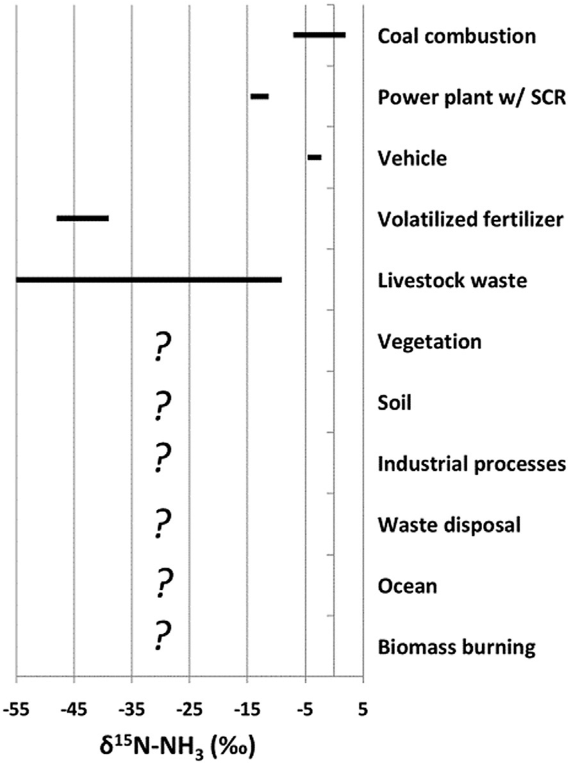

**Fig. 1.** : $\delta^{15}N$-$NH_3$ values of emissions sources and a list of source that have not been characterized (Felix et al., 2013; Freyer and Republic, 1978; Heaton, 1987; Hristov et al., 2009; Heaton, 1986).

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