Supplement of

Quantifying the Importance of Vehicle Ammonia Emissions in an Urban Area of the Northeastern US Utilizing Nitrogen Isotopes

Walters et al.

Correspondence to: Wendell W. Walters (wendell_walters@brown.edu)

Table of Contents:

Figure S1. Correlogram of measured parameters..... S1

Figure S2. Spatiotemporal ground-based NH_3 and pNH_4^+ Observations..... S2

Figure S3. Potassium Ion Correlation with NH_3 and pNH_4^+..... S3

Text S1. Rationale of $\delta^{15}N(NH_3)$ source values S4-S5

References..... S6

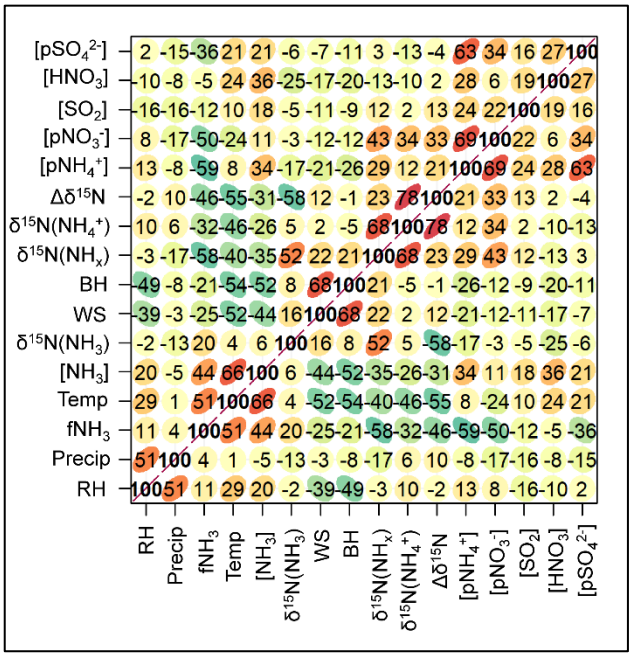

Figure S1. Correlogram of the various meteorological parameters (i.e., Temperature (Temp), relative humidity (RH), wind direction (WD), and precipitation (Precip), boundary height (BH)), gas, particle, and nitrogen isotope data at Providence, RI.

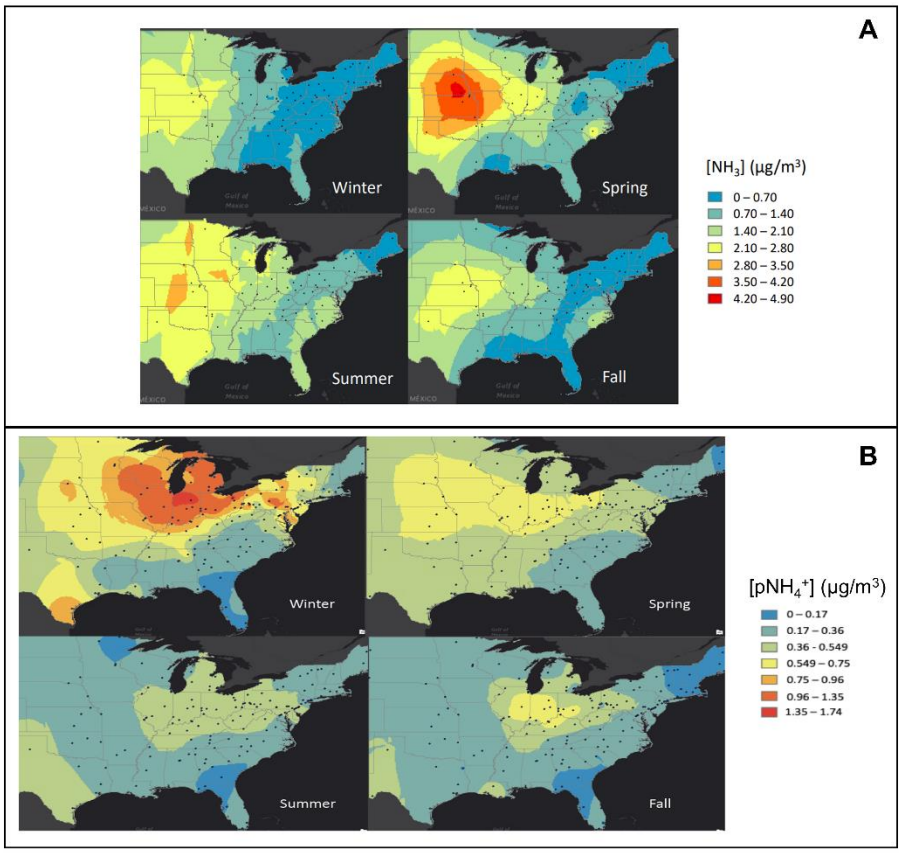

Figure S2. Spatiotemporal overview of (A) [NH_3] and (B) [pNH_4^+] across the eastern half of the contiguous US for winter (DJF), spring (MAM), summer (JJA), and fall (SON) for 2018. The data points correspond to Ammonia Monitoring Network (AMoN; n= 103) for [NH_3] and either Chemical Speciation Network (CSN; n =104) or Clean Air Status and Trends Network (CASTNET; n=66) for [pNH_4^+]. The seasonal means were respectively interpolated utilizing the Kriging method, converted to raster output, and cropped to the confines of the United States to improve the data visualization.

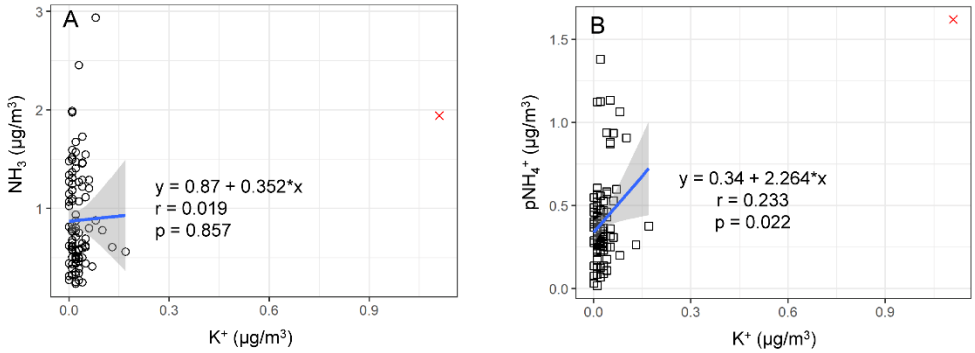

Figure S3. Correlation plots of potassium ion (K^+) with (A) [NH_3] and (B) [pNH_4^+]. The K^+ data was from the Chemical Speciation Network in East Providence, RI. An outlier associated with July 4th, a period of significant firework activity in the US, was shown as an "X" and was not considered in the regression analysis.

Text S1: $\delta^{15}N(NH_3)$ Emission Source Values:

The collection technique, either passive or active, has been shown to influence $\delta^{15}N(NH_3)$ quantification. Recently, passive sampling techniques have resulted in a bias of ~-15.5‰ relative to active sampling techniques near emission sources and background ambient air studies due to a hypothesized diffusion isotope effect associated with passive collection of NH_3 (Walters et al., 2020; Pan et al., 2020). We note that the bias associated with passive $\delta^{15}N(NH_3)$ characterization may be able to be accounted for in the future. However, we still do not know if the observed ~-15.5‰ bias is consistent across all sampling conditions (e.g., temperature, relative humidity, NH_3 collection amounts). Thus, while the vast majority of NH_3 source characterization studies have utilized passive collection techniques, we have selected $\delta^{15}N(NH_3)$ source values obtained using active sampling techniques since these values should be more accurate than the value obtained using passive sampling. Below we discuss our reasoning behind the choice of these values.

Significant NH_3 Emission Sources. Based on a combination of local wind analysis, air mass back trajectory analysis, and National Emission Inventory data, we found evidence for significant NH_3 emission contributions from vehicles, NH_3 volatilization, industry, and fuel combustion. We acknowledge that additional miscellaneous NH_3 sources exist in an urban environment, including pets, household products, humans, and wood combustion; however, we assumed these sources were negligible compared to the three main identified emission sources. Thus, we conduct isotope mixing analysis using vehicles, NH_3 volatilization, industry, and fuel combustion as major contributing emission sources as an *a priori*.

Vehicles. The vehicle $\delta^{15}N(NH_3)$ signature was defined as 6.6±2.1‰, deriving from an extensive study of near-highway stationary measurements in Providence, RI, mobile on-road measurements in the Northeastern US, and stationary monitoring measurements in Shenyang China (Walters et al., 2020). While there was evidence for significant spatiotemporal $\delta^{15}N(NH_3)$ variabilities due to differences in fuel type (i.e., gasoline vs. diesel), the chosen emission signature of 6.6±2.1‰ was representative of vehicle plumes with a fleet composition typical of urban regions that are dominated by gasoline vehicles. This value is also near a recent study of vehicle plume measurements utilizing an active sampling filter-based collection system in Shenyang, China of 6.3±1.6‰ (Song et al., 2021). Overall, the vehicle $\delta^{15}N(NH_3)$ emission signature is well-constrained and will enable tracking of urban vehicle NH_3 emission contributions.

NH_3 Volatilization. The volatilization of NH_3 from livestock waste and fertilizer application has been the subject of numerous studies (Heaton, 1987; Freyer, 1978; Felix et al., 2013; Hristov et al., 2011; Frank et al., 2004; Chang et al., 2016), which has demonstrated a large range of $\delta^{15}N(NH_3)$ values reflecting a process-driven $\delta^{15}N$ effect as NH_3 volatilization tends to result in a gradual increase in $\delta^{15}N$. For example, $\delta^{15}N(NH_3)$ from dairy manure was reported to range from -31 to -15‰ over a period of ~2 weeks that increased with N loss (Hristov et al., 2011). This effect occurs due to the kinetic isotopic fractionation favoring the initial release of $^{14}NH_3$, leading to low $\delta^{15}N(NH_3)$ values. As NH_3 is lost, the nitrogen content of volatilized material (urea or NH_4^+) is enriched in ^{15}N, increasing the emitted $\delta^{15}N(NH_3)$ value. The process-driven $\delta^{15}N$ effect is associated with NH_3 volatilization and the large reported range of $\delta^{15}N(NH_3)$ values. Here we define the $\delta^{15}N(NH_3)$ emission signature as -19.2±8.3‰, which represents an average of field measurements in cow and shed sheds, reflecting an integrated measurement of NH_3 volatilization, and process-driven $\delta^{15}N(NH_3)$ from volatilization studies (Frank et al., 2004; Hristov et al., 2011).

Fuel Combustion/Industry. Most point emission sources in Providence, RI derive from stationary fuel combustion (i.e., electricity generation at power plants or institutions (i.e., school, hospital, prison)) or industrial emissions. However, our knowledge of $\delta^{15}N(NH_3)$ emission signatures from direct fuel combustion and industrial emissions is limited. Previous NH_3 capture from direct flue emissions from coal-fired power plant emissions equipped with selective catalytic reduction (SCR) technology reported $\delta^{15}N(NH_3)$ values of -11.3‰ and -14.6‰ (Felix et al., 2013). This value is suspected to reflect the strong contribution of NH_3 slip from the SCR technology as the measured values were much lower than previous reports of NH_3 emitted from the combustion of brown and hard coal with values of -6.9‰, -4.3‰, and -7.2‰ (Freyer, 1978), in which NH_3 derives mainly from the nitrogen contained within the coal. New England fossil-fuel combustion mainly derives from oil and natural gas, such that the previously reported SCR $\delta^{15}N(NH_3)$ values may more closely represent the emission signature of stationary fuel combustion of this region. Direct NH_3 emissions from industrial activities have only been reported from a steel factory with a $\delta^{15}N(NH_3)$ value of -20.1‰ (Heaton, 1987). Still, it remains unclear whether this value is representative of all industry-related NH_3 emissions. A sector-based sampling of ambient NH_3 downwind from chemical and metal industries in Canada have reported an average of -15.1‰ (Savard et al., 2017), which supports that industrial emissions tend to have a low $\delta^{15}N(NH_3)$ value consistent with the one available direct industrial emission $\delta^{15}N(NH_3)$ signature. Overall, due to some of the uncertainties and overlap with the available data for stationary fuel combustion and industrial emissions, we chose a $\delta^{15}N(NH_3)$ signature for this combination of emission sectors to be -15.3±3.6‰, which represents the average of the available direct measurements of power plants with SCR technology and industrial emissions (Heaton, 1987; Felix et al., 2013).

References

Chang, Y., Liu, X., Deng, C., Dore, A. J., and Zhuang, G.: Source apportionment of atmospheric ammonia before, during, and after the 2014 APEC summit in Beijing using stable nitrogen isotope signatures, Atmospheric Chem. Phys., 16, 11635–11647, 2016.

Felix, D. J., Elliott, E. M., Gish, T. J., McConnell, L. L., and Shaw, S. L.: Characterizing the isotopic composition of atmospheric ammonia emission sources using passive samplers and a combined oxidation-bacterial denitrifier approach, Rapid Commun. Mass Spectrom., 27, 2239–2246, 2013.

Frank, D. A., Evans, R. D., and Tracy, B. F.: The role of ammonia volatilization in controlling the natural ^{15}N abundance of a grazed grassland, Biogeochemistry, 68, 169–178, 2004.

Freyer, H. D.: Seasonal trends of NH_4^+ and NO_3^- nitrogen isotope composition in rain collected at Jülich, Germany, Tellus, 30, 83–92, 1978.

Heaton, T. H. E.: $^{15}N/^{14}N$ ratios of nitrate and ammonium in rain at Pretoria, South Africa, Atmospheric Environ. 1967, 21, 843–852, 1987.

Hristov, A. N., Hanigan, M., Cole, A., Todd, R., McAllister, T. A., Ndegwa, P. M., and Rotz, A.: Ammonia emissions from dairy farms and beef feedlots, Can. J. Anim. Sci., 91, 1–35, 2011.

Pan, Y., Gu, M., Song, L., Tian, S., Wu, D., Walters, W. W., Yu, X., Lü, X., Ni, X., and Wang, Y.: Systematic low bias of passive samplers in characterizing nitrogen isotopic composition of atmospheric ammonia, Atmospheric Res., 105018, 2020.

Savard, M. M., Cole, A., Smirnoff, A., and Vet, R.: $\delta^{15}N$ values of atmospheric N species simultaneously collected using sector-based samplers distant from sources – Isotopic inheritance and fractionation, Atmos. Environ., 162, 11–22, 2017.

Song, L., Walters, W. W., Pan, Y., Li, Z., Gu, M., Duan, Y., Lü, X., and Fang, Y.: ^{15}N natural abundance of vehicular exhaust ammonia, quantified by active sampling techniques, Atmos. Environ., 255, 118430, 2021.

Walters, W. W., Song, L., Chai, J., Fang, Y., Colombi, N., and Hastings, M. G.: Characterizing the spatiotemporal nitrogen stable isotopic composition of ammonia in vehicle plumes, Atmospheric Chem. Phys., 20, 11551–11567, 2020.