

1 **Spatial and temporal patterns of nitrogen isotopic composition of ammonia at U.S.**

2 **ammonia monitoring network sites**

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42 **Abstract**

43
44 Ammonia (NH₃) emissions and ammonium (NH₄⁺) deposition can have harmful effects
45 on the environment and human health but remain generally unregulated in the U.S. PM_{2.5}
46 regulations require that an area not exceed an annual average PM_{2.5} value of 12μg/m³ (averaged
47 over three years), and since NH₃ is a significant precursor to PM_{2.5} formation these are the
48 closest indirect regulations of NH₃ emissions in the U.S. If the U.S. elects to adopt NH₃ emission
49 regulations similar to those applied by the European Union, it will be imperative to first
50 adequately quantify NH₃ emission sources and transport, and also understand the factors causing
51 varying emissions from each source. To further investigate NH₃ emission sources and transport
52 at a regional scale, NH₃ was sampled monthly at a subset of nine Ammonia Monitoring Network
53 (AMoN) sites and analyzed for nitrogen isotopic composition of NH₃ (δ¹⁵N-NH₃). The observed
54 δ¹⁵N-NH₃ values ranged from -42.4 to +7.1‰ with an average of -15.1 ± 9.7. The observed
55 δ¹⁵N-NH₃ values reported here provide insight into the spatial and temporal trends of the NH₃
56 sources that contribute to ambient [NH₃] in the U.S. In regions where agriculture is prevalent
57 (i.e., U.S. Midwest), low and seasonally variable δ¹⁵N-NH₃ values are observed and are
58 associated with varying agricultural sources. In comparison, rural nonagricultural areas have
59 higher and more seasonally consistent δ¹⁵N-NH₃ values associated with a constant “natural” (e.g.
60 soil, vegetation, bi-directional flux, ocean) NH₃ source. With regards to temporal variation, the
61 peak in U.S. spring agricultural activity (e.g. fertilizer application, livestock waste volatilization)
62 is accompanied by a decrease in δ¹⁵N-NH₃ values at a majority of the sites, whereas higher δ¹⁵N-
63 NH₃ values in other seasons could be due to shifting sources (e.g. coal-fired power plants) and/or
64 fractionation scenarios. Fractionation processes that may mask NH₃ source signatures are

65 discussed and require further investigation to optimize the utility of the nitrogen isotopic
66 composition to determine NH₃ sources and dynamics.

67
68 **1. Introduction:**

69
70 Ammonium (NH₄⁺) in wet deposition in the U.S. has increased over 49% during the past
71 three decades and currently accounts for 60% of the total dissolved inorganic nitrogen (DIN) in
72 wet deposition (Du et al., 2014). This relative contribution is expected to increase given that
73 ammonia (NH₃) emissions are generally unregulated in the U.S. whereas air quality regulations
74 have led to dramatic decreases in NO_x emissions, a precursor to the other primary DIN
75 component in wet deposition, nitrate (NO₃⁻). NH₃ and subsequent wet and dry NH_x deposition
76 products are substantial sources of nitrogen (N) to sensitive ecosystems and contribute to soil
77 acidification, water body eutrophication, and decreases in biodiversity (Davidson et al., 2012;
78 Fowler et al., 1998; Galloway et al., 2004). NH_x deposition to ecosystems, coupled with other
79 forms of N input, have caused 20% of U.S. natural vegetation to receive N in excess of a critical
80 load (1000 mg (N) m⁻² yr⁻¹) as defined by Dentener et al., 2006. Prior to NH_x deposition to
81 various ecosystems, NH₃ emissions can react with acidic species (e.g. H₂SO₄ and HNO₃) to form
82 particulate aerosols. Fine particulate matter (PM) decreases visibility, is linked to human health
83 impacts (respiratory and cardiovascular disease) (Pope and Dockery, 2006) and can affect
84 climate through changing radiative forcing caused by particulate aerosols that scatter or absorb
85 solar radiation (Zhu et al., 2015). PM_{2.5} is regulated by a U.S. EPA National Ambient Air
86 Quality Standard that requires an area not to exceed an average PM_{2.5} concentration of 12µg/m³
87 (EPA, 2013). This PM_{2.5} regulation is the closest indirect regulation of NH₃ emissions in the
88 U.S. because modeled results indicate that PM_{2.5} attainment goals can be reached via decreasing
89 NH₃ emissions (Banzhaf et al., 2013; Bessagnet et al., 2015; Gu et al., 2014; Pinder and Adams,

90 2007; Zhu et al., 2015). However, reduction of NH₃ may prove more difficult than previous air
91 quality goals. Unlike other pollutants that are released consistently and predictably through
92 industrial or mechanical processes (e.g. NO_x or SO_x emissions from vehicles or power plants)
93 and are readily quantifiable, NH₃ emissions from area sources (e.g. livestock waste and fertilizer)
94 are a function of both chemical and biological process that often depend on climate and
95 environmental conditions. Therefore, these sources are often highly variable over space and time
96 and can lead to large uncertainties in total NH₃ emission inventories for the U.S and the globe
97 (2.8-3.2 and 44-83 Tg NH₃-N yr⁻¹, respectively) (Paulot et al., 2014). To produce effective
98 policies or regulations, it is critical to quantify emissions of NH₃ from key sources including
99 fertilizer application, livestock waste, vehicles, coal-fired power plants. It is equally important to
100 understand NH₃ transport and factors that affect NH₃ emissions fluxes including climate,
101 agricultural techniques, waste mitigation techniques, soil and vegetation characteristics (USDA,
102 2014)

103 As a consequence of recent increases in NH_x deposition fluxes, there is heightened
104 interest in improving our understanding of NH₃ emission sources, the processes controlling the
105 formation and decomposition of NH₄⁺ aerosols subject to long-range transport, and ultimately
106 the deposition and bi-directional flux of NH₃ products in wet and dry deposition. As a result of
107 this growing concern, U.S. monitoring networks for wet and dry deposition chemistry, the
108 National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends
109 Network (CASTNET), respectively, have established a monitoring network, the “Ammonia
110 Monitoring Network (AMoN).” The network began with trials in fall 2007, became an official
111 NADP network in October 2010, and has rapidly expanded to include more than 90 sites with an
112 ultimate goal of NH₃ monitoring sites adequately covering North America (NADP, 2015). The

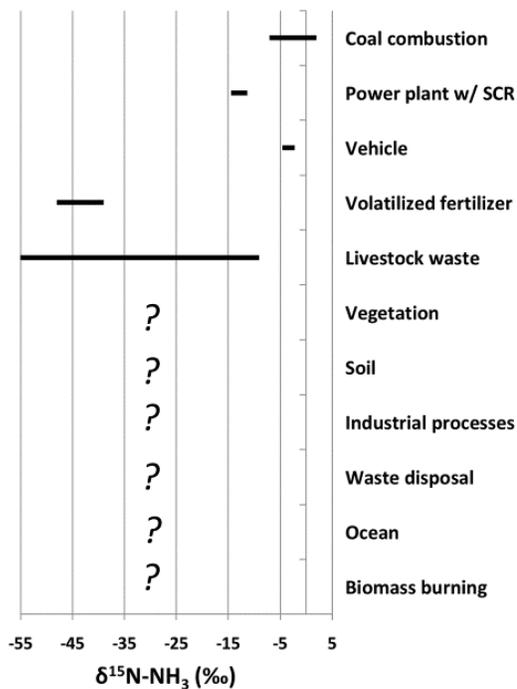
113 network deploys Radiello passive samplers to obtain NH₃ concentrations and aims to provide
114 spatially dense long term ambient NH₃ concentration [NH₃] data that aids air quality modelers,
115 ecologists and policy-makers in validating atmospheric models, estimating N deposition, and
116 assessing PM_{2.5} compliance (NADP, 2015). Preliminary results from the AMoN network along
117 with other more localized NH₃ studies have helped quantify spatial and temporal trends in
118 ambient [NH₃] (Butler et al., 2015; Chen et al., 2014; Mukerjee et al., 2012; NADP, 2015; Yao
119 and Zhang, 2013). Most of these studies report high [NH₃] in spring and summer due to peak
120 agricultural activity and volatilization, with lower concentrations in winter due to lack of
121 agricultural activity and limited volatility and condensation (Bari et al., 2003; Felix et al., 2014;
122 Mukerjee et al., 2012; Reche et al., 2015).

123 Air mass back trajectories, emission dispersion models and knowledge of seasonal
124 variation in emission source activity allow researchers to infer probable emission sources that
125 contribute to ambient [NH₃]. However, these generalizations can lead to errors in source
126 attribution and cannot explain seasonal [NH₃] anomalies that have been reported (Butler et al.,
127 2015; Chen et al., 2014; Yao and Zhang, 2013). For instance, Chen et al., 2014 report relatively
128 high [NH₃] at agricultural sites when NH₃ volatilization should be minimal and Yao and Zhang,
129 2013 observed [NH₃] increases at some sites when ambient temperature was < -7°C. Also, while
130 much of the NH₃ emissions in the U.S. are attributed to agricultural activity, [NH₃] in urban
131 areas are often higher than in rural areas where most agricultural activity takes place (Edgerton et
132 al., 2007; Felix et al., 2014). NH₃ in cities may result from transport from rural agricultural
133 sources but urban sources (e.g. vehicles, wastewater, sewage, and industry) may also be the
134 primary contributors. Urban studies report large ranges in [NH₃] within an urban region which

135 makes it difficult to qualify sources contributing to ambient [NH₃] (Bari et al., 2003; Felix et al.,
136 2014; Mukerjee et al., 2012; Reche et al., 2015).

137 An approach to aid in identifying NH₃ emission source contribution to ambient
138 concentrations is to exploit the difference between the $\delta^{15}\text{N-NH}_3$ values associated with different
139 NH₃ emission sources (Figure 1). For instance, the primary sources of NH₃, volatilized livestock
140 waste and fertilizer, are generally reported to have low $\delta^{15}\text{N-NH}_3$ values, -56‰ to -9‰ and -
141 48‰ to -36‰, respectively (Felix et al., 2013; Freyer and Republic, 1978; Heaton, 1987; Hristov
142 et al., 2009). In contrast, $\delta^{15}\text{N-NH}_3$ values of NH₃ emitted from coal combustion (-7 to +2‰)
143 (Freyer and Republic, 1978; Heaton, 1986), ‘NH₃ slip’ (unreacted NH₃ used for NO_x reduction in
144 selective catalytic reduction systems) from coal-fired power plants (-14.6 to -11.3‰) (Felix et
145 al., 2013) and vehicles (-4.6 to -2.2‰) (Felix et al., 2013) are higher relative to those from
146 livestock waste and fertilizer emissions. A recent urban NH₃ study in Pittsburgh, PA, USA,
147 used the distinct isotopic compositions of these NH₃ sources to explain potential sources of
148 ambient NH₃ and concluded that in this urban region most NH₃ can be attributed to vehicle and
149 industrial sources (Felix et al., 2014).

150 To investigate application of this isotope approach to infer NH₃ sources on a regional
151 scale and to supplement the national AMoN [NH₃] data, NH₃ was sampled at a subset of nine
152 AMoN sites and analyzed for isotopic composition of NH₃ ($\delta^{15}\text{N-NH}_3$). This work couples NH₃
153 source $\delta^{15}\text{N}$ measurements with observed $\delta^{15}\text{N-NH}_3$ values at nine AMoN sites over a year
154 period and aims to: 1) investigate the spatial and temporal trends of $\delta^{15}\text{N-NH}_3$ across the U.S.;
155 and 2) explore whether $\delta^{15}\text{N-NH}_3$ observations in disparate regions across the U.S. are a function
156 of variable ammonia sources and/or potential fractionation processes and transport mechanisms.
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158

159 Figure 1: $\delta^{15}\text{N-NH}_3$ values of emissions sources and a list of source that have not been
 160 characterized (Felix et al., 2013; Freyer and Republic, 1978; Heaton, 1987; Hristov et al., 2009
 161 Heaton, 1986).

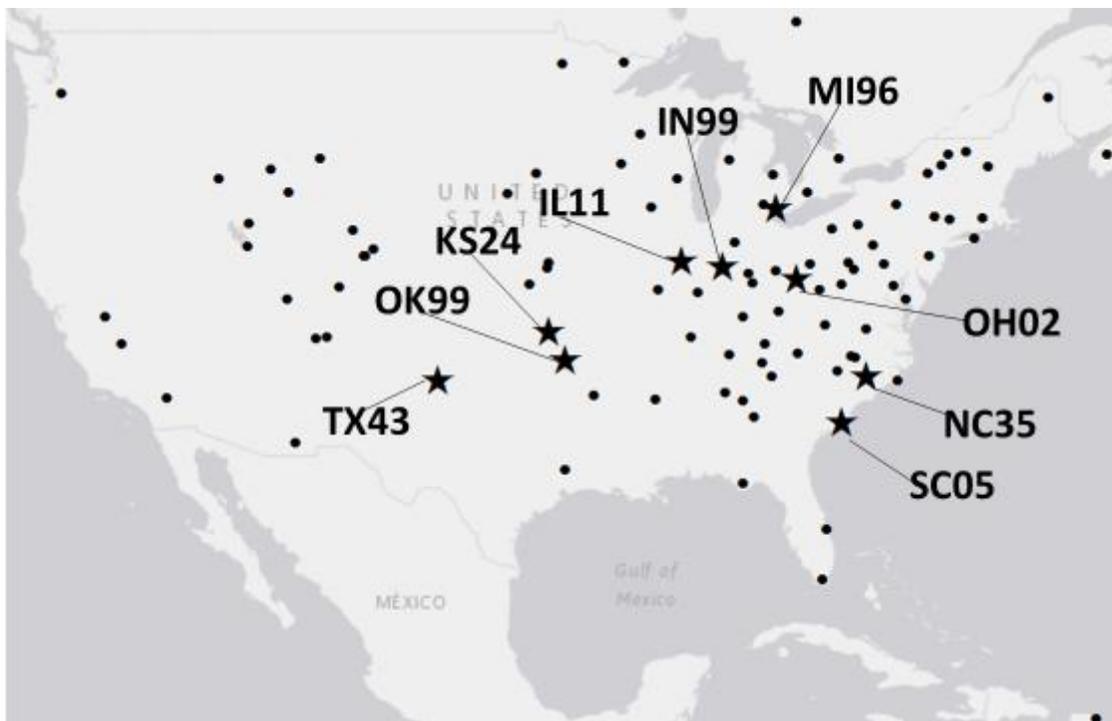
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163 2. Methods

164 2.1 NH_3 collection and Ammonia Monitoring Network sites

165 NH_3 was collected at nine AMoN sites (Figure 2) from 7/2009 to 6/2010 using Adaptive
 166 Low-Cost High Absorption Passive samplers (ALPHA). Site descriptions and potential NH_3
 167 sources near each site are reported in SI Table1. The ALPHA sampler is a circular polyethylene
 168 vial (26 mm height, 27 mm diameter) with one open end. The vial contains a position for a
 169 25mm filter coated with a 2% (m/v) phosphorous acid in methanol solution and a position for a
 170 PTFE membrane for gaseous NH_3 diffusion (Tang et al., 2009). When compared to active NH_3
 171 concentrations collected using an annular denuder (the reference NH_3 collection method), the
 172 ALPHA is slightly biased low (-2.4 %)(Puchalski et al., 2011). Precision is reported as $\pm 7\%$ in
 173 a study of among duplicates (n =1081) (Puchalski et al., 2011). The UK national ammonia

174 monitoring network uses the ALPHA sampler at their monitoring sites and reports a monthly
175 sampling detection limit of $0.02 \mu\text{g}/\text{m}^3$ (DEFRA, 2015). For isotopic analyses, ALPHA
176 samplers were chosen due to their lower detection limits, greater accuracy, and the advantage of
177 a larger surface area that allows for a greater amount of NH_3 collection relative to other filter-
178 based samplers (Felix et al., 2013; 2014; Puchalski et al., 2011). The larger collection capacity is
179 important to ensure adequate sample mass for isotopic analysis. ALPHA samplers were sealed
180 in glass jars containing ammonia-absorbing packets (API Ammo-Chips) to lower possible
181 contamination from any ambient ammonia the samplers may come into contact with during
182 travel. Samplers were shipped overnight in coolers with ice packs to AMoN sites for
183 deployment. A ‘travel blank’ sampler was treated in the same manner as the field samplers
184 except the travel blanks were never taken out of the mason jars and deployed. After a month
185 deployment samplers were collected, re-sealed in mason jars, put in coolers with ice-packs and
186 shipped overnight to the University of Pittsburgh, Pittsburgh, PA, USA for processing and
187 chemical analysis. Note: Radiello ammonia passive samplers are deployed at AMoN sites and
188 were used for comparison to the ALPHA sampler concentration data obtained in this study.



189

190 **Figure 2:** Current ammonia monitoring network sites are marked with circles and stars. Stars
 191 are used to denote sites employed in this study.

192

193 **2.2 NH_3 concentration method**

194 After collection on the passive sampler filters, NH_3 concentrations were determined by
 195 eluting NH_4^+ with 5 mL of 18.2 M Ω .cm water (Milli-Q System) and analyzed as NH_4^+ using the
 196 phenol method (Eaton et al., 2005) and a Thermo Evolution 60S UV-Visible spectrophotometer.
 197 NH_3 air concentrations were calculated according to the ALPHA sampler protocol (Tang et al.,
 198 2009). Lab blanks were negligible but travel blanks (mean 13% of sample) had detectable
 199 amounts of NH_3 and were used to correct the $[NH_3]$ according to ALPHA sampler protocol
 200 (Tang 2009). Although travel blanks were detectable, they generally did not have sufficient
 201 $[NH_3]$ present to measure isotopic composition and thus precluded an isotopic blank correction.
 202 As a result, the isotopic blank interference was assumed negligible but should be noted as a

203 possible interference. Samples (n = 8) with concentrations $\leq 0.2 \mu\text{g}/\text{m}^3$ were not analyzed for
204 isotopic composition due lack of adequate N mass for isotope analysis.

205 **2.3 NH_3 isotopic analysis**

206 The isotopic composition of NH_3 was determined using a coupled bromate oxidation-
207 denitrifier method (Felix et al., 2013). In brief, a hypobromite oxidation solution was used to
208 oxidize the NH_4^+ in the sample to nitrite (NO_2^-) (Zhang et al., 2007). After oxidation, the sample
209 pH is adjusted to between 3 and 9 using 6N HCl. Twenty nmoles of sample NO_2^- is then
210 converted to N_2O using the bacterial denitrifier *Pseudomonas aureofaciens* and introduced to an
211 isotope ratio mass spectrometry (IRMS) instrument. Samples were analyzed for nitrogen
212 isotopic composition using an Isoprime Trace Gas and Gilson GX-271 autosampler coupled with
213 an Isoprime Continuous Flow-IRMS at the *Regional Stable Isotope Laboratory for Earth and*
214 *Environmental Science Research* at University of Pittsburgh. Values are reported in parts per
215 thousand relative to atmospheric N_2 as follows:

$$216 \quad \delta^{15}\text{N} (\text{‰}) = \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{standard}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} \times 1000 \quad (1).$$

217 International reference standards USGS34, USGS32, USGS25, and USGS26 were used for data
218 correction.

219 **2.4 $\delta^{15}\text{N}$ - NH_3 and NH_3 correlations**

220 Four of the nine AMoN sites were co-located with NADP National Trends Network
221 (NTN) sites that measure multiple analyte concentrations (Ca^+ , Mg^{2+} , K^+ , Na^+ , NH_4^+ , NO_3^- , Cl^- ,
222 SO_4^{2-} , H^+ , conductivity) in wet deposition. When corresponding data was available (n=36),
223 $\delta^{15}\text{N}$ - NH_3 and $[\text{NH}_3]$ were compared to monthly NTN analyte precipitation weighted mean
224 concentration data to investigate potential correlations. Results of this correlation analysis is

225 reported in SI Table 2. All [NH₃] and δ¹⁵N-NH₃ data was compared to average monthly site
226 temperature to investigate potential correlations.

227 **3. Results**

228 **3.1. Summary NH₃ concentration and δ¹⁵N-NH₃ results**

229 Mean [NH₃] for all sites was 1.8 µg/m³ with a range of 0.0 (or nondetect) to 13.0 µg/m³
230 (n = 94) (Table 1) (Figure 3). These NH₃ concentrations collected from passive samplers used in
231 this study are strongly correlated with NH₃ concentrations reported for the same sites by the
232 AMoN network (R= 0.83, p <0.00001, slope = 1.07) (SI Figure 1). Concentration differences
233 likely result from different deployment time periods (i.e., one month for this study, biweekly for
234 AMoN). NH₃ concentrations were strongly correlated with monthly average site temperature
235 (R= 0.35; p = 0.0005).

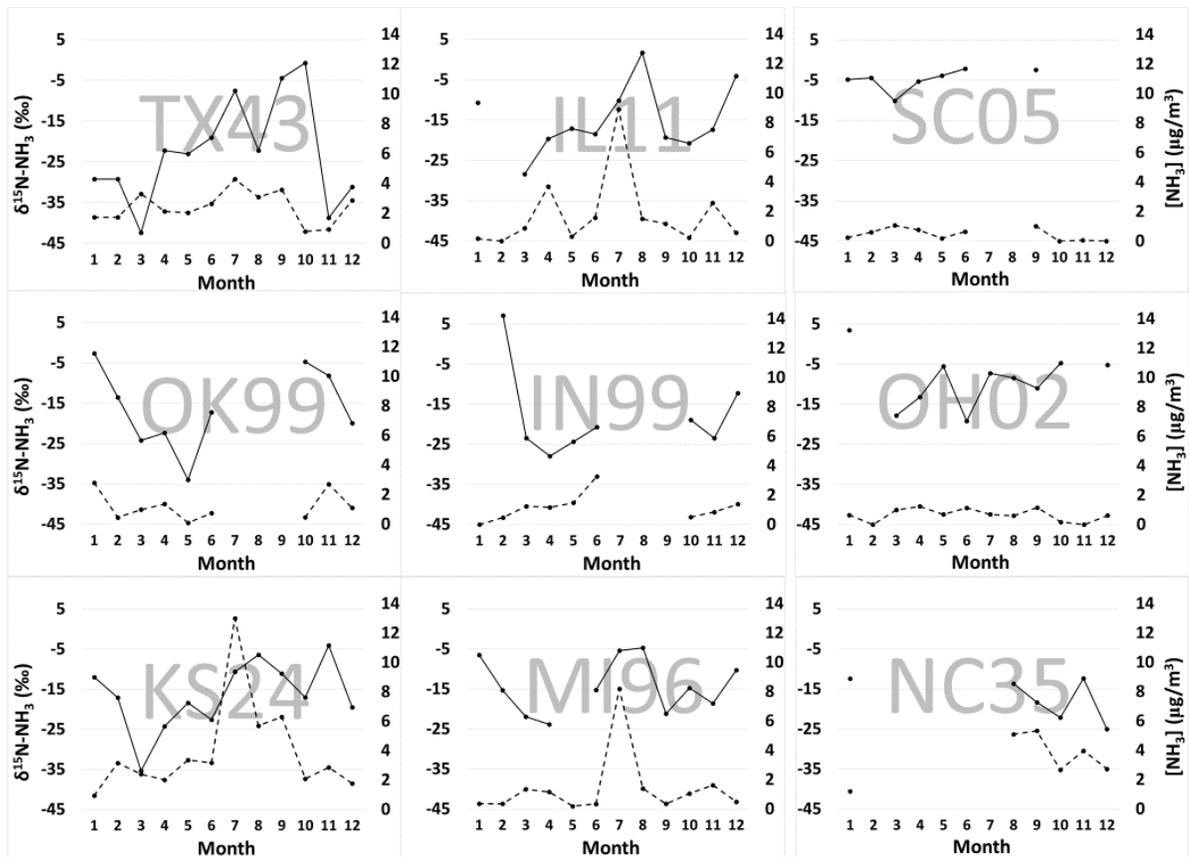
236 Mean and concentration-weighted mean δ¹⁵N-NH₃ values for all sites were -15.2‰ and -
237 15.1‰, respectively, with a range of -42.4 to +7.1‰ (n = 86) (Table 1) (Figure 3). The isotopic
238 variation in seven quadruplicate samples (4 separate co-located samplers) and one duplicate
239 sample (two separate co-located samplers) was explored (n = 30). These samples were chosen
240 from six of the nine sites and had a concentration range of 0.8 to 5.3 µg/m³ to ensure sample
241 diversity. Co-located sampler δ¹⁵N-NH₃ standard deviation ranged from 0.1 to 6.6‰ with an
242 average of 3.3‰. This high standard deviation generally resulted from a single outlier for six of
243 the seven quadruplicate deployments. When each single outlier is excluded, standard deviation
244 ranges from 0.1 to 2.5‰ with an average of 1.7‰. There was no significant correlation between
245 δ¹⁵N-NH₃ and [NH₃] (R = 0.002, p = 0.99) for the entire data set.

246 Combined mean and concentration-weighted mean δ¹⁵N-NH₃ values of all sites were
247 calculated for each season (winter = Dec, Jan, Feb; spring = Mar, Apr, May; summer = Jun, Jul,

248 Aug; fall = Sep, Oct, Nov) to investigate temporal $\delta^{15}\text{N-NH}_3$ trends (Table 1). Mean and
 249 concentration-weighted mean $\delta^{15}\text{N-NH}_3$ values are lowest during spring and are significantly
 250 different from the other seasons (ANOVA: $p < 0.05$). Winter, summer and fall did not
 251 significantly differ from each other. $\delta^{15}\text{N-NH}_3$ was not correlated with monthly average site
 252 temperature whether the data set is investigated as a whole ($R = 0.04$; $p = 0.71$) or by individual
 253 site (for all sites $p > 0.05$). To investigate spatial trends $\delta^{15}\text{N-NH}_3$, annual mean and
 254 concentration-weighted mean $\delta^{15}\text{N-NH}_3$ values of all sites were calculated (Table 1).

255 **Table 1:** Average and weighted average $[\text{NH}_3]$ ($\mu\text{g}/\text{m}^3$) and $\delta^{15}\text{N-NH}_3$ values for each AMoN
 256 site annually and by season. Weighted average $\delta^{15}\text{N-NH}_3 = \Sigma [[\text{NH}_3] * \delta^{15}\text{N-NH}_3 / \Sigma[\text{NH}_3]]$
 257

Site	Analyte	n	Year		Wint		Spr		n	Sum	Fall					
			Ave	Wt ave	Ave	Wt ave	Ave	Wt ave			Ave	Wt ave				
MI96	$\delta^{15}\text{NH}_3$	11	-14.3	-10.8	2	-10.7	-10.6	2	-22.9	-22.8	3	-8.4	-5.6	3	-18.2	-17.6
	$[\text{NH}_3]$	12	1.4		3	0.4		3	0.9		3	3.3		3	1.0	
IL11	$\delta^{15}\text{NH}_3$	11	-14.9	-13.7	2	-7.4	-5.6	3	-21.7	-21.0	3	-8.9	-9.7	3	-19.1	-18.1
	$[\text{NH}_3]$	12	1.8		3	0.2		3	1.6		3	4.0		3	1.3	
IN99	$\delta^{15}\text{NH}_3$	8	-18.0	-20.0	2	-2.5	-7.2	3	-25.2	-25.1	1	-20.7	-20.7	2	-21.2	-21.7
	$[\text{NH}_3]$	9	1.2		3	0.6		3	1.3		1	3.3		2	0.7	
KS24	$\delta^{15}\text{NH}_3$	12	-16.5	-14.1	3	-16.2	-17.0	3	-26.0	-25.1	3	-13.2	-11.2	3	-10.7	-10.4
	$[\text{NH}_3]$	12	3.9		3	2.0		3	2.6		3	7.3		3	3.8	
OH02	$\delta^{15}\text{NH}_3$	10	-8.9	-10.6	2	-0.9	-0.7	3	-12.2	-12.9	3	-11.6	-13.1	2	-7.8	-10.1
	$[\text{NH}_3]$	12	0.7		3	0.4		3	1.0		3	0.8		3	0.3	
OK99	$\delta^{15}\text{NH}_3$	9	-16.3	-12.1	3	-12.0	-8.1	3	-26.8	-23.5	1	-17.2	-17.2	2	-6.4	-7.6
	$[\text{NH}_3]$	9	1.2		3	1.5		3	0.8		1	0.8		2	1.6	
NC35	$\delta^{15}\text{NH}_3$	6	-17.3	-17.1	2	-18.7	-21.1	3	na	na	1	-13.6	-13.6	3	-17.6	-17.2
	$[\text{NH}_3]$	6	3.5		2	2.0		3	na	na	1	5.1		3	4.0	
TX43	$\delta^{15}\text{NH}_3$	12	-22.5	-21.6	3	-29.9	-30.1	3	-29.2	-31.3	3	-16.2	-15.1	3	-14.6	-9.9
	$[\text{NH}_3]$	12	2.4		3	2.1		3	2.5		3	3.4		3	1.8	
SC05	$\delta^{15}\text{NH}_3$	7	-4.7	-5.1	2	-4.6	-1.4	3	-6.4	-7.7	1	-2.2	-2.2	1	-2.4	-2.4
	$[\text{NH}_3]$	9	0.5		3	0.3		3	0.7		1	0.6		3	0.4	
All	$\delta^{15}\text{NH}_3$	86	-15.2	-15.1	22	-12.1	-15.4	23	-21.2	-23.5	19	-12.0	-11.4	22	-14.3	-13.5
	$[\text{NH}_3]$	94	1.8		24	1.0		18	1.4		26	3.4		26	1.7	



258

259 **Figure 3:** The $\delta^{15}\text{N-NH}_3$ (solid line) values and $[\text{NH}_3]$ (dashed line) are reported for each site.

260 Left y-axis is $\delta^{15}\text{N-NH}_3$ (‰), right y-axis is $[\text{NH}_3]$ $\mu\text{g}/\text{m}^3$ and the x-axis is deployment month (1

261 = Jan, 2 = Feb, 3 = Mar...).

262

263 4. Discussion

264 4.1. NH_3 concentration and $\delta^{15}\text{N-NH}_3$

265 In this section, we explore whether NH_3 and $\delta^{15}\text{N-NH}_3$ observations in disparate regions

266 across the U.S. may be a function of variable ammonia sources, fractionations, or transport.

267 4.1.1 Regional ammonia emission sources

268 $\delta^{15}\text{N-NH}_3$ values were compared to the relative proportions of county level NH_3

269 emissions at each site as reported by the U.S. EPA 2011 National Emissions Inventory (Figure 4)

270 (SI Table 3). Sites with the highest mean $\delta^{15}\text{N-NH}_3$ values were OH02 (-8.9‰) and SC05 (-
271 4.7‰). The OH02 site is located in the Ohio River Valley region where there is a high density of
272 emissions from coal-fired power plants (Elliott et al., 2007) that are characterized by relatively
273 higher $\delta^{15}\text{N-NH}_3$ values (-14.6 to +2‰) (Felix et al., 2013; Freyer and Republic, 1978; Heaton,
274 1986). Despite the concentration of power plant emissions near OH02, this site has consistently
275 low $[\text{NH}_3]$ ($0.7 \mu\text{g}/\text{m}^3$) and suggests the site's NH_3 concentration may not be significantly
276 impacted by power plant NH_3 emissions but the higher $\delta^{15}\text{N-NH}_3$ values suggest possible
277 influence of power plant NH_3 mixing with natural NH_3 sources. Of the nine sites, the OH02 had
278 the lowest county-level NH_3 emissions ($0.14 \text{ Tons NH}_3/\text{km}^2$) (US EPA NEI 2011); this also
279 suggests that this site could be influenced by natural processes. The SC05 site is located at a
280 relatively remote, pristine barrier island and among the sites is located in a county with the
281 second lowest total estimated NH_3 source emission density ($0.18 \text{ Tons NH}_3/\text{km}^2$) (US EPA NEI
282 2011). A low mean $[\text{NH}_3]$ ($0.5 \mu\text{g}/\text{m}^3$) and high mean $\delta^{15}\text{N-NH}_3$ value (-4.7‰) indicated a
283 natural processes or ocean NH_3 source. For instance, NH_3 collected at a prairie in KS, USA had
284 a 'background' $\delta^{15}\text{N-NH}_3$ value of $(-7.0 \pm 1.6\text{‰})$ that could be indicative of a natural soil source
285 and/or a mixture of natural processes (e.g. bi-directional flux) (Felix et al., 2014). Jickells, 2003
286 report a $\delta^{15}\text{N-NH}_4^+$ value of -8 to -5‰ from ocean aerosols and Altieri et al., 2014 report $\delta^{15}\text{N-NH}_4^+$
287 NH_4^+ values of $-4.1 \pm 2.6\text{‰}$ in rain events with marine air mass histories. SC05 also has the least
288 variable $\delta^{15}\text{N-NH}_3$ values during the study period so the site is likely influenced by a consistent
289 natural and/or marine NH_3 source.

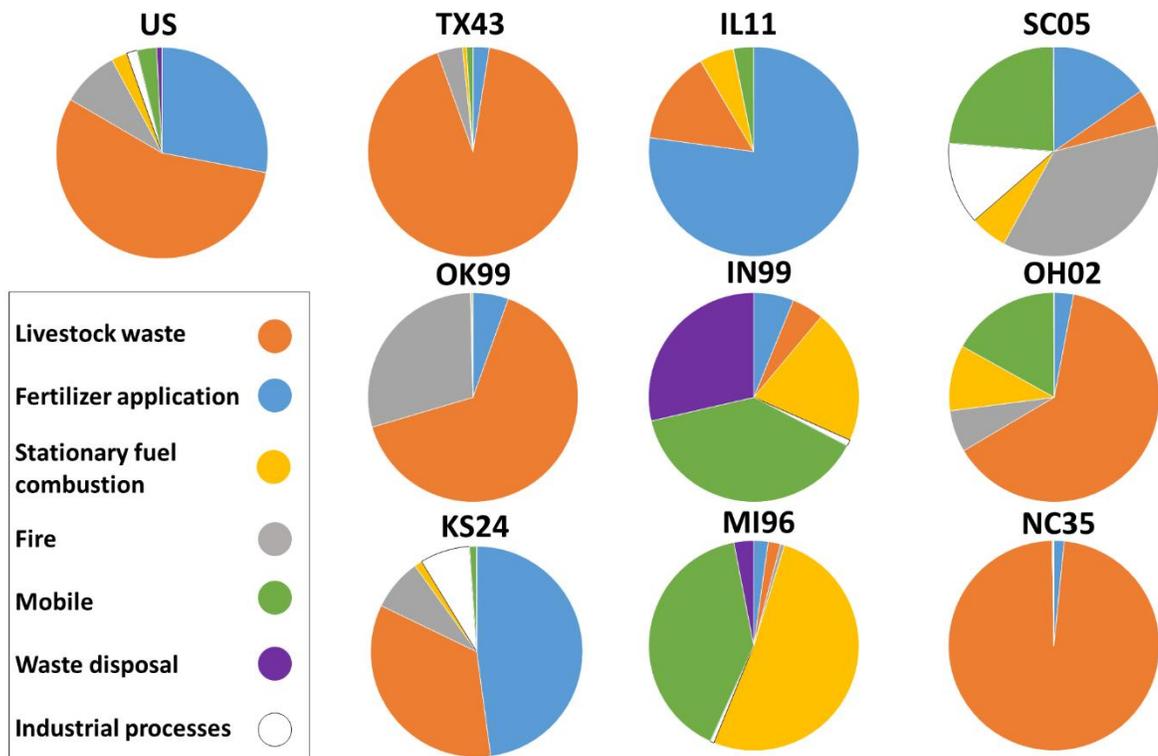
290 In contrast, TX43 has the lowest mean $\delta^{15}\text{N-NH}_3$ values (-22.5‰). Sources in the
291 vicinity include volatilized fertilizer from cropland and volatilized waste from grazing cattle,
292 both of which have low $\delta^{15}\text{N-NH}_3$ values. NC35 represents a site centered in a dense hog

293 production corridor of the U.S. as well as substantial poultry production facilities. It has a
294 relatively low mean $\delta^{15}\text{N-NH}_3$ value (-17.3‰) and high $[\text{NH}_3]$ ($3.5 \mu\text{g}/\text{m}^3$) indicative of livestock
295 waste emissions. However, this site had limited data (the site was unavailable for sampling
296 during spring and early summer, a period of increased agricultural emissions). According to
297 proportional estimates of county-level NH_3 emissions, TX43 and NC35 had the highest %
298 contribution from agricultural sources, 94 and ~100%, respectively (US EPA NEI 2011).

299 The remaining five sites are generally located in the Midwestern U.S. (MI96, IL11,
300 KS24, OK99, IN99) region characterized as America's "breadbasket" and driven economically
301 by agriculture but also represented 39% of the nation's coal consumption in 2014 (EIA, 2016a).
302 As a whole, these sites have a high average $[\text{NH}_3]$ ($2.0 \mu\text{g}/\text{m}^3$) and low $\delta^{15}\text{N-NH}_3$ values (mean =
303 -15.9‰) that are not significantly different from each other (ANOVA: $p > 0.1$). The high $[\text{NH}_3]$
304 and relatively low $\delta^{15}\text{N-NH}_3$ values are indicative of the livestock waste and fertilizer sources
305 that accompany a significant economic sector of the Midwest, agriculture. However, the low
306 $\delta^{15}\text{N-NH}_3$ values are not as low as some of the agricultural $\delta^{15}\text{N-NH}_3$ emission source $\delta^{15}\text{N-NH}_3$
307 values which could be attributed to mixing with emissions related to the substantial coal
308 consumption in the region. Even though these Midwest sites represent a spatially large region of
309 the U.S., the similarity of $\delta^{15}\text{N-NH}_3$ values at the sites suggest an overall regional emission
310 source primarily related to agriculture but with mixing from emissions from the energy sector.
311 For instance, the estimated average % contribution from agriculture in the counties where these 5
312 sites are located is 51% but the average % contribution from combined fuel combustion and
313 mobile sources is 36%. It should be noted that this high percentage from fuel combustion and
314 mobile source are driven by sites MI96 and IN99 located in urban areas, Detroit and
315 Indianapolis, respectively. To further investigate the role of agricultural emissions significantly

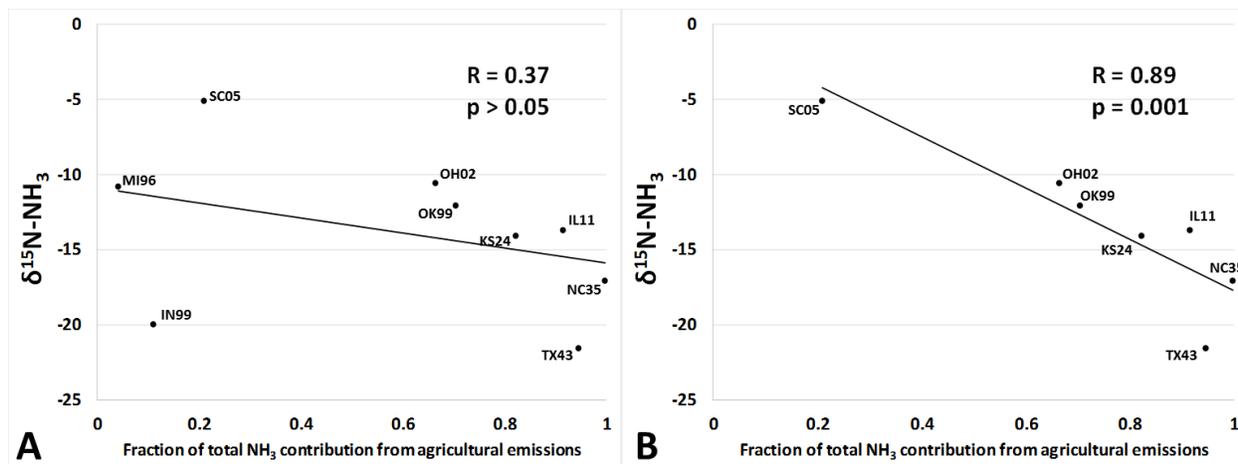
316 contributing to the $\delta^{15}\text{N-NH}_3$ value at the AMoN sites, Figure 5A and 5B correlate $\delta^{15}\text{N-NH}_3$ and
 317 % agriculture contribution at all sites. Results indicate that there is not a significant correlation
 318 ($p > 0.05$) between $\delta^{15}\text{N-NH}_3$ and % agriculture contribution but when the two urban sites, MI96
 319 and IN99, are removed there is strong negative correlation ($p = 0.001$). This suggests that
 320 although the large majority of NH_3 emissions in the U.S. are associated with agricultural sources,
 321 urban centers where a majority of the population lives are more significantly impacted by
 322 nonagricultural emissions.

323 Coupling the estimates of NH_3 emissions $\delta^{15}\text{N-NH}_3$ values at individual AMoN sites with
 324 estimates of NH_3 sources emissions illustrates how $\delta^{15}\text{N-NH}_3$ can aid in investigating the
 325 prominent local/regional NH_3 sources influencing ambient NH_3 concentrations. Additional
 326 factors including fractionation and transport dynamics should be studied further as they could
 327 potentially mask source signals. These factors are discussed further in the following section.



328

329 **Figure 4:** Pie charts representing the portion of NH₃ contributed to total NH₃ emissions in the
 330 county of each AMoN site and the US as a whole (EPA NEI 2011). It should be noted that while
 331 NEI estimates have agreed with observations on a national scale, large discrepancies have been
 332 reported at regional scales (Paulot et al., 2014 and refs within).
 333



334 **Figure 5:** A) Average values at each AMoN site vs the fraction of NH₃ emissions attributed to
 335 the agricultural sector. B) Average values at each AMoN site (excluding IN99 and MI96) vs the
 336 fraction of NH₃ emissions attributed to the agricultural sector (US EPA NEI 2011).
 337
 338

339 4.1.2 Ammonia emission source temporal trends

340 Mean $\delta^{15}\text{N-NH}_3$ values are lowest during the spring months (mean = -21.1‰; weighted
 341 mean = -23.5‰). Studies focusing on ambient atmospheric [NH₃] often report concentration
 342 increases in spring whereas studies focusing on $\delta^{15}\text{N-NH}_4^+$ in rainwater report lower $\delta^{15}\text{N}$ values
 343 in spring (Gao, 2002; Heaton, 1987; Occhipinti et al., 2008; Russell et al., 1998; Xie et al., 2008;
 344 Zhang et al., 2008; Zhao et al., 2009); both due to an increase in agricultural emissions. These
 345 agricultural emissions are primarily due to fertilizer application in spring and warming
 346 temperatures that cause livestock waste to more readily volatilize. Fertilizer application rates
 347 peak in March for the south-central U.S., and east and west coasts while April is the peak
 348 application period in the northern mid-west U.S. (Goebes et al., 2003). Both volatilized fertilizer
 349 and livestock waste have relatively low $\delta^{15}\text{N-NH}_3$ values compared to other NH₃ sources (Felix
 350 et al., 2013). The significantly lower springtime $\delta^{15}\text{N-NH}_3$ values observed in this study likely

351 result from an increase in NH_3 from these agricultural sources. Higher $\delta^{15}\text{N-NH}_3$ values reported
352 for the summer and winter months coincide with peaks in U.S. coal consumption suggesting that
353 coal-fired power plant emissions may play a role in the observed temporal $\delta^{15}\text{N}$ pattern (Figure
354 6A and 6B).

355 Relatively low $\delta^{15}\text{N-NH}_3$ values were expected to persist from the spring into the summer
356 season due to continued agricultural activity and increased summer temperatures increasing
357 livestock waste volatilization. While this is generally true for the month of June (Figure 6A),
358 summer mean $\delta^{15}\text{N-NH}_3$ values are not significantly different from those in fall and winter and
359 while $[\text{NH}_3]$ was positively correlated with average monthly temperature ($R = 0.35$; $p = 0.0005$),
360 $\delta^{15}\text{N-NH}_3$ was not ($R = 0.04$; $p = 0.71$). This unexpected result could be due to 1) NH_3 *sources*
361 changing, 2) NH_3 *fractionation*, and 3) varying NH_3 *transport* mechanisms. Each of these
362 potential factors are discussed below.

363 *4.1.3. Source variations, fractionation, and transport mechanisms*

364 *1) Sources:* In general, peak fertilizer application is in the spring and is avoided during
365 warm summer months due to high volatilization rates (fertilizer losses) and during winter when
366 low infiltration rates associated with frozen soils decrease fertilization efficacy (Bouwman et al.,
367 1997; Goebes et al., 2003). The lack of residual fertilizer from spring applications and absence
368 of application in mid/late summer and throughout winter, lowers seasonal fluxes of volatilized
369 ammonia (with low $\delta^{15}\text{N}$ values) and may play a role in the higher $\delta^{15}\text{N}$ values observed during
370 these seasons. Additionally, power plant energy consumption peaks during the summer and
371 winter months (EIA, 2015) (Figure 6B) wherein fossil fuel combustion and ‘ NH_3 slip’ have
372 higher $\delta^{15}\text{N-NH}_3$ values than agricultural sources. Lastly, higher $\delta^{15}\text{N-NH}_3$ values during the
373 summer may also be attributed to more NH_3 from increased biomass burning and wild fires.

374 Studies have reported increases in ambient $[\text{NH}_3]$ due to biomass burning (Chen et al., 2014;
375 Saylor et al., 2015) and biomass burning NH_3 is expected to have $\delta^{15}\text{N-NH}_3$ values similar to
376 coal combustion NH_3 as it is produced during a similar high heat combustion process that is less
377 selective for the lighter ^{14}N than the volatilization processes that produce NH_3 with low $\delta^{15}\text{N-}$
378 NH_3 values (e.g. volatilization of fertilizer and livestock waste).

379 2) *Fractionation:* While rising temperatures in the summer would lead to increased
380 livestock waste volatilization, higher temperatures also result in smaller fractionation between
381 ammonium and aqueous ammonia (e.g. 45.4‰ at 23°C and 37.7‰ at 50°C) (Li et al., 2012).
382 This smaller degree of fractionation associated with increasing temperature could increase the
383 relative $\delta^{15}\text{N-NH}_3$ value of livestock waste emissions during the warmer summer months.

384 Another possible fractionation influence on ambient $\delta^{15}\text{N-NH}_3$, is the $\delta^{15}\text{N}$ of the NH_3
385 emission source changing. Throughout the warming season, the ‘pool’ of $\delta^{15}\text{N-NH}_4^+$ in livestock
386 waste storage units (e.g. lagoons) can increase up to 20‰ (Karr et al., 2003; Mariappan et al.,
387 2009) due to continued favorable volatilization of lighter $^{14}\text{NH}_3$. If the $\delta^{15}\text{N}$ of the NH_3 emission
388 source is increasing up to 20‰ and the $\text{NH}_4^+_{(\text{aq})}$ to $\text{NH}_3_{(\text{g})}$ fractionation stays relatively
389 consistent, the overall $\delta^{15}\text{N-NH}_3$ of emitted NH_3 can increase up to 20‰ over the course of a
390 summer season. If livestock waste is a large emission contributor in the summer and the $\delta^{15}\text{N-}$
391 NH_4^+ of this source pool continues to increase, the $\delta^{15}\text{N-NH}_3$ contributing to the ambient
392 atmospheric NH_3 will increase. However, it should be noted that if there is continual addition of
393 “new” manure to waste storage units, this mixing will decrease the observed isotopic effect of
394 fractionation due to volatilization.

395 Additional fractionation can take place during bi-directional exchange; once NH_3 is
396 emitted and subsequently deposited to landscapes, it can re-emit during bi-directional exchange.

397 For instance, vegetation can uptake NH_3 but can also emit NH_3 depending on the NH_3
398 compensation point (i.e. point when net uptake of NH_3 is zero or when the NH_3 partial pressure
399 in the atmosphere is equal to that of the plant (Farquhar et al., 1980)). This bi-directional flux or
400 uptake and re-emission can cause equilibrium and kinetic fractionation of the original $\delta^{15}\text{N-NH}_3$
401 value. The extent of the fractionation depends on the many factors controlling the
402 compensations point (e.g. $[\text{NH}_3]$, temperature, vegetation type, vegetation growth, and nitrogen
403 status ((Wu et al., 2009) and ref therein). The magnitude and significance of the fractionation
404 associated with bi-directional flux is unknown and continued quantification is an important step
405 to using $\delta^{15}\text{N}$ values to quantify NH_3 sources and should prove to be a valuable area of study.

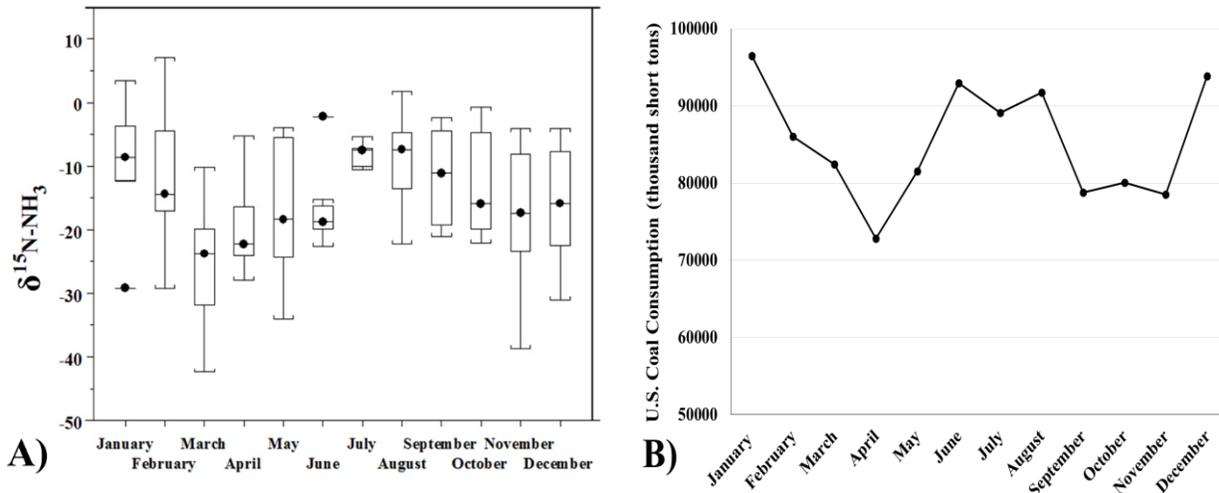
406 A fourth fractionation pathway can occur when NH_3 emissions react in the atmosphere
407 with acidic species (e.g. HNO_3 and H_2SO_4) to form particulate aerosols. When NH_3 condenses
408 into the acidic aerosol, the $\text{NH}_{3(\text{g})} \rightleftharpoons \text{NH}_{4^+(\text{aq})}$ exchange can occur at equilibrium. Fractionation
409 factors for this exchange reaction have been determined to be between +25 and +35‰ (Heaton et
410 al., 1997; Mariotti, 1984; York et al., 1947) with the $\text{NH}_{4^+(\text{aq})}$ being enriched in $\delta^{15}\text{N}$. If an
411 equilibrium hasn't been established, a unidirectional reaction ($\text{NH}_{3(\text{g})} \rightarrow \text{NH}_{4^+(\text{aq})}$) will cause
412 kinetic fractionation associated with a negative fractionation factor leaving the $\text{NH}_{4^+(\text{aq})}$ more
413 enriched in $\delta^{14}\text{N}$ (Freyer and Republic, 1978; Heaton et al., 1997). Therefore, NH_3 reactions
414 with acidic species can lead to fractionation that will increase or decrease the original $\delta^{15}\text{N-NH}_3$
415 value of the source emissions. As with other fractionation pathways, little is known about the
416 significance of this potential fractionation on the original emission source $\delta^{15}\text{N}$ signature and
417 thus is a rich area for future study.

418 3) *Transport*: NH_3 has a high deposition velocity, and once emitted, can deposit as dry
419 deposition close to the source. However, if NH_3 reacts with acidic species to form particulate

420 aerosols, it can be transported up to 100s km from the source (Asman et al., 1998; Zhang et al.,
421 2012). Consequently, $\delta^{15}\text{N-NH}_3$ values near the source are more likely to represent a source
422 signature whereas NH_3 collected further away is more likely to reflect NH_3 that has undergone
423 fractionation. For instance, when NH_3 reacts to form NH_4NO_3 , it increases its atmospheric
424 residence time and thus transportation potential and may decrease or increase its $\delta^{15}\text{N}$ value due
425 to kinetic or equilibrium fractionation. Once NH_4NO_3 is transported to another region it can
426 dissociate due to higher temperatures or lower atmospheric NH_3 that shifts the equilibrium
427 toward $\text{NH}_{3(g)}$ (Seinfeld and Pandis, 2006; Yao and Zhang, 2013). The ambient NH_3 would thus
428 have the altered $\delta^{15}\text{N}$ value obtained during reaction with the acidic species and the dissociation
429 itself may favor $^{14}\text{NH}_3$; leaving the dissociation $\text{NH}_{3(g)}$ product more enriched in ^{14}N . This
430 transport mechanism depends on the availability of different acidic species to react with NH_3 .
431 For instance, since the product of the NH_3 and H_2SO_4 reaction, $(\text{NH}_4)_2\text{SO}_4$, is relatively non-
432 volatile and the product of the NH_3 and HNO_3 reaction, NH_4NO_3 , readily dissociates, NH_3
433 reactions with HNO_3 lead to less potential for NH_3 transport (Fowler et al., 2015). Increased air
434 quality regulations have reduced SO_x and NO_x emissions at different rates thus decreasing their
435 availability to react with atmospheric NH_3 and also altering transport mechanisms. These
436 regulations will continue to modify atmospheric transport and understanding how this transport
437 mechanism fractionates source $\delta^{15}\text{N-NH}_3$ values will allow for insight to NH_3 transport distances
438 and dynamics. As with all fractionation scenarios, they are not easily qualified or quantified and
439 future work should focus on characterizing these fractionation scenarios in order to optimize the
440 use of stable isotopes for source apportionment.

441

442



443
 444 **Figure 6:** A) Box and whisker plot representing minimum, maximum, median, upper quartile,
 445 lower quartile, and outlier $\delta^{15}\text{N-NH}_3$ values observed each month from 07/2009 to 06/2010 at
 446 AMoN sites in this study. B) Monthly U.S coal consumption for the period of study (7/09 to
 447 6/10) (EIA, 2016b).

448
 449 **Conclusion:**

450
 451 Nitrogen is a necessary nutrient for all living things and with increasing global food
 452 demands, the introduction of ever increasing amounts of fixed nitrogen to the environment is
 453 unavoidable. To sustain a growing global population while maintaining a healthy environment,
 454 it is essential to understand nitrogen dynamics and learn how to appropriately mitigate nitrogen
 455 emissions. In working with the newly established Ammonia Monitoring Network, we report
 456 ambient $\delta^{15}\text{N-NH}_3$ values at nine locations across the U.S. The observed $\delta^{15}\text{N-NH}_3$ values
 457 reported here provide insight into the spatial and temporal trends of the NH_3 sources that
 458 contribute to ambient $[\text{NH}_3]$ in the U.S. In regions where agriculture is prevalent (i.e., U.S.
 459 Midwest), low and seasonally variable $\delta^{15}\text{N-NH}_3$ values are observed and are associated with
 460 varying agricultural sources. In comparison, rural nonagricultural areas (i.e., a barrier island

461 national wildlife refuge in South Carolina) have higher and more seasonally consistent $\delta^{15}\text{N-NH}_3$
462 values associated with a constant “background” NH_3 source. With regards to temporal variation,
463 the peak in U.S. spring agricultural activity (e.g. fertilizer application, livestock waste
464 volatilization) produces a decrease in $\delta^{15}\text{N-NH}_3$ values at a majority of the sites, whereas higher
465 $\delta^{15}\text{N-NH}_3$ values in other seasons could be due to shifting sources and/or fractionation scenarios.
466 To optimize the utility of the nitrogen isotopic composition to determine NH_3 sources and
467 dynamics, the fractionating processes that can mask NH_3 source signatures require further
468 investigation. In addition, future research should continue to constrain the isotopic signatures of
469 primary NH_3 sources (e.g. volatilized fertilizer and livestock waste, vehicles) and also focus on
470 characterizing the signatures of less significant NH_3 sources (e.g. biomass burning, industrial
471 processes, soil, vegetation). With a robust inventory of NH_3 source signatures and fuller
472 understanding of fractionating processes, the isotopic composition of NH_3 may prove to be
473 valuable additional tool for distinguishing potential emission source contributions to varying
474 regions in the U.S.

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482

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