Quantifying the importance of vehicle ammonia emissions in an urban area of northeastern USA utilizing nitrogen isotopes

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Abstract. Atmospheric ammonia (NH₃) is a critical component of our atmosphere that contributes to air quality degradation and reactive nitrogen deposition; however, our knowledge of NH₃ in urban environments remains limited. Year-long ambient NH₃ and related species were measured for concentrations and the nitrogen isotopic compositions (δ¹⁵N) of NH₃ and particulate ammonium (pNH₄⁺) were measured to understand the temporal sources and chemistry of NH₃ in a northeastern US urban environment. We found that urban NH₃ and pNH₄⁺ concentrations were elevated compared to regional rural background monitoring stations, with seasonally significant variations. Local and transported sources of NH₃ (NH₃ + pNH₄⁺) were identified using polar bivariate and statistical back trajectory analysis, which suggested the importance of vehicles, volatilization, industry, and stationary fuel combustion emissions. Utilizing a uniquely positive δ¹⁵N(NH₃) emission source signature from vehicles, a Bayesian stable isotope mixing model (SIMMR) indicates that vehicles contribute 46.8 ± 3.5 % (mean ± 1σ) to the annual background level of urban NH₃, with a strong seasonal pattern with higher relative contribution during winter (56.4 ± 7.6 %) compared to summer (34.1 ± 5.5 %). The decrease in the relative importance of vehicle emissions during the summer was suggested to be driven by temperature-dependent NH₃ emissions from volatilization sources, seasonal fuel-combustion emissions related to energy generation, and change in seasonal transport patterns based on wind direction, back trajectory, and NH₃ emission inventory analysis. This work highlights that reducing vehicle NH₃ emissions should be considered to improve wintertime air quality in this region.

1 Introduction

Ammonia (NH₃) is a critical component of the atmosphere and the global nitrogen cycle (Behera et al., 2013; Galloway et al., 2004). As the primary alkaline atmospheric molecule, NH₃ plays an important role in neutralizing atmospheric acids, leading to fine particulate matter (PM₂.₅), including particulate ammonium (pNH₄⁺), which have important implications for air quality, human health, visibility, and climate change (Behera and Sharma, 2010; Updyke et al., 2012; Wang et al., 2015). Agricultural activities, including fertilizer application and livestock waste, dominate the emission of NH₃, accounting for over 60 % of the global inventory (Bouwman et al., 1997); however, there are significant NH₃ spatiotemporal variabilities due to its short atmospheric life-
time, typically a few hours to a day, and numerous emission sources (Van Damme et al., 2018). Urban regions have been shown to have elevated levels of NH₃ and nitrogen deposition (Plautz, 2018; Joyce et al., 2020; Hu et al., 2014; Decina et al., 2020, 2017), indicating the potential for important non-agricultural emission sources that may disproportionately impact human and environmental health. In recent years, quantifying surface-level NH₃ and its deposition products in the US has been a focus of several national monitoring networks, including the Ammonia Monitoring Network (AMoN), the Interagency Monitoring of Protected Visual Environments (IMPROVE), the National Atmospheric Deposition Program (NADP), and the Clean Air Status and Trends Network (CASTNET). However, these measurements are typically conducted in rural locations. Long-term records of NH₃ and its deposition products in urban regions are exceedingly scarce, which often leads to models evaluated to observations primarily conducted in rural locations (Paulot et al., 2014).

The NH₃ sources contributing to the urban budget remain contested. Several studies have identified vehicle emissions as a major urban NH₃ emission source (Sun et al., 2017, 2014; Suarez-Bertoa et al., 2014, 2017). In contrast, other studies have suggested that vehicle emissions are relatively unimportant for urban regions and instead have found evidence for significant local and transported emissions due to temperature-dependent volatilization sources (Hu et al., 2014; Yao et al., 2013; Nowak et al., 2006). Recent satellite observations, taking advantage of the COVID-19 lockdown period, have for the first time confirmed vehicle emissions as a significant localized source of NH₃ in an urban region (Cao et al., 2021). However, quantifying the contribution of local urban NH₃ emissions to the urban background is complex as it is coupled to meteorological parameters that influence NH₃ and particulate ammonium (pNH₄⁺) partitioning, mixing/dispersion of local emissions, and contributions via long-range transport from agricultural regions (Meng et al., 2011; Walker et al., 2004).

The nitrogen stable isotopic composition (δ¹⁵N(‰)) = [(¹⁵N/¹⁴N)sample/(¹⁵N/¹⁴N)reference − 1]×1000, where ¹⁵N is the ratio of ¹⁵N/¹⁴N, and air is the N isotopic reference) may be a useful chemical fingerprinting tool to track source contributions and validate model apportionments of urban NH₃ (Felix et al., 2017, 2013). Indeed, numerous studies have utilized δ¹⁵N of NH₃ and pNH₄⁺ for source apportionment (e.g., Felix et al., 2017; Pan et al., 2016; Berner and Felix, 2020; Liu et al., 2018; Pan et al., 2018; Wu et al., 2019; Bhattarai et al., 2020; Xiao et al., 2020; Zhang et al., 2021), taking advantage of the suggested lower δ¹⁵N signatures of agricultural NH₃ emissions relative to fossil fuel combustion (Felix et al., 2013; Chang et al., 2016). In this study, we have characterized the seasonal ambient NH₃ (NH₃ + pNH₄⁺) source contributions using concentration and isotope measurements at an urban site in Providence, RI, US, using laboratory-verified and field-tested collection techniques shown to quantitatively collect NH₃ for accurate and precise δ¹⁵N characterizations (Walters and Hastings, 2018; Walters et al., 2019). The study site is a mid-sized coastal city located within the northeastern US megalopolis. This is an important region to monitor because the northeastern US wintertime air quality has not improved as much as expected, despite aggressive reductions of precursor emissions in recent decades (Shah et al., 2018). We have recently characterized the δ¹⁵N(NH₃) from urban vehicle plumes, which has indicated this source to have a unique positive δ¹⁵N signature of 6.6 ± 2.1 ‰ compared to other NH₃ sources that tend to have negative δ¹⁵N values (Walters et al., 2020). Here we aim to quantify the importance of vehicle NH₃ emissions at our urban site. Our study contributes to the first δ¹⁵N measurements of speciated NH₃ in New England and contributes to our understanding of seasonal urban NH₃ source apportionment in an environment where particulate nitrate (pNO₃⁻) formation is commonly NH₃-limited (Park et al., 2004).

2 Materials, methods, and datasets

2.1 Collection of NH₃ and associated gases and particles

Simultaneous collections of reactive gases and PM₂.₅ were conducted using a series of coated glass honeycomb denuders and a downstream filter pack housed in a ChemComb Speciation Cartridge. This sampling system has been extensively evaluated for its ability to speciate between inorganic gases and particulate matter for offline concentration determination (Koutrakis et al., 1993, 1988). Additionally, this system is a suitable technique for the characterization of δ¹⁵N(NH₃) and δ¹⁵N(pNH₄⁺) with a precision of ±0.8 ‰ and ±0.9 ‰ (1σ), respectively (Walters and Hastings, 2018; Walters et al., 2019). Briefly, the sampler consisted of a PTFE-coated inlet to minimize reactive gas loss, a PM₂.₅ impactor plate, a basic-coated honeycomb denuder (2 % carbonate (w/v) + 1 % glycerol (w/v) in 80 : 20 water–methanol (v/v) solution) to collect acidic gases including nitric acid (HNO₃) and sulfur dioxide (SO₂), an acid-coated denuder (2 % citric acid (w/v) + 1 % glycerol (w/v) in 20 : 80 water–methanol (v/v) solution) to collect NH₃, and a filter pack consisting of a nylon filter and 5 % (w/v) citric acid-coated cellulose filter for the collection of pNH₄⁺. All denuder and filter preparation, handling, and extraction techniques have been previously described (Walters and Hastings, 2018; Walters et al., 2019). The samplers were held vertically to limit the potential for gravitational settling of particles on the denuder surfaces and were housed in a custom-built weather-protected container. Ambient air was sampled at a flow rate of 10 L min⁻¹. Collections were conducted for 24 h (15:00 to 15:00 eastern time (ET) the following day) approximately twice per week in Providence, RI, USA (41.83° N, 71.40° W) on the rooftop of a building from 6 February 2018 to 1 February 2019 (Fig. 1). The study loca-
2.2 Concentration and $\delta^{15}$N(NH$_4$)$_4$ isotopic analysis

The concentrations of the denuder and filter extraction solutions were analyzed using colorimetry and ion chromatography analytical techniques. The colorimetric analysis included measurements of NH$_4^+$ using the indophenol blue method (i.e., US EPA Method 350.1) and NO$_2^-$ via diazotization with sulfanilamide dihydrochloride (i.e., US EPA Method 353.2) that was automated by a discrete UV-Vis spectrophotometer (Westco SmartChem). Anion concentrations that included Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ were analyzed using ion chromatography (Dionex DX500). The limit of detection (LOD) was approximately 0.5 µmol L$^{-1}$ for NH$_4^+$ and NO$_2^-$ and 2 µmol L$^{-1}$ for Cl$^-$, NO$_3^-$, and SO$_4^{2-}$. The relative standard deviations for all quantified ions were less than 5%. Laboratory blanks of denuder and filter samples were periodically taken, representing approximately 10% of the collected samples. The blanks were below our LOD, except for Cl$^-$ that had a large and variable blank for both the carbonate denuder and nylon filter, such that these data were not reported in this work.

The determination of $\delta^{15}$N of the NH$_4^+$ in the denuder and filter extracts was conducted using a chemical technique that converts NH$_4^+$ to NO$_2^-$ using an alkaline hypobromite solution and reducing the generated NO$_2^-$ to N$_2$O using sodium azide in an acetic acid buffer solution (Zhang et al., 2007). The generated N$_2$O was purified and concentrated using an automated extraction system coupled to a continuous-flow isotope ratio mass spectrometer for $\delta^{15}$N determination as previously described (Walters and Hastings, 2018). In each sample batch, unknowns were calibrated to two internationally recognized NH$_4^+$ isotopic reference materials, IAEA-N2 and USGS25, with $\delta^{15}$N values of 20.3 ‰ and −30.3 ‰ (Böhlke et al., 1993; Böhlke and Coplen, 1993), respectively. An in-house NH$_4^+$ quality control ($\delta^{15}$N = −1.5 ‰) and an NO$_2^-$ reference material with a known isotope composition (RSIL-N10219; $\delta^{15}$N = 2.8 ‰) (Böhlke et al., 2007) were also run intermittently as quality control to monitor the conversion of NO$_2^-$ to N$_2$O and system stability across runs. Corrections to determine $\delta^{15}$N(NH$_4^+$) were performed by accounting for isobaric influences, blank effects, and calibrating the unknowns to the internationally...
recognized $\delta^{15}N(\text{NH}_4^+)$ standards. The correction scheme resulted in an average slope between the measured $\delta^{15}N(\text{N}_2\text{O})$ and the standard $\delta^{15}N(\text{NH}_4^+)$ values of $0.501 \pm 0.024$ near the theoretical line of 0.500 for the azide/acetate acid reduction method (Zhang et al., 2007; McIlvin and Altabet, 2005). The pooled standard deviations of the isotopic reference materials were $\pm 0.6\%$ ($n = 62$), $\pm 0.7\%$ ($n = 62$), $\pm 0.5\%$ ($n = 14$), and $\pm 1.3\%$ ($n = 18$), for IAEA-N2, USGS25, in-house NH$_4^+$, and RSIL-N10219, respectively. Due to the numerous steps and potential interferences associated with the employed chemical conversion technique, we established the following quality assurance criteria for our sample unknowns: (1) NH$_4^+$ greater than 5 µmol L$^{-1}$ to combat the significant alkaline hypobromite reagent blank, (2) NO$_3^-$ / NH$_4^+$ ratio less than 5 % since NO$_3^-$ is an interferent, and (3) quantitative yield of NH$_4^+$ to NO$_3^-$ conversion (i.e., incomplete conversion would lead to undesirable $\delta^{15}N$ fractionation). These criteria were met for 90 out of 97 NH$_3$ samples and 60 out of 97 $p$NH$_4^+$ samples. The 7 rejected NH$_3$ samples were because of criterion 3, while the rejected NH$_4^+$ samples included 18 from criterion 1, 8 from criterion 2, and 11 from criterion 3. The presence of significant amounts of NO$_3^-$ was found exclusively on the nylon filters, which likely reflect fractionation. Replicate measurements of sample unknowns across batch analyses were conducted for approximately 10% of samples and had an average deviation of $\pm 1.4\%$.

2.3 Ancillary datasets

Annual emission data of NH$_3$ at the county level were accessed from the US EPA National Emission Inventory 2014 (NEI-14), and chemically speciated gridded hourly NH$_3$ emission data were generated using the Sparse Matrix Operator Kerner Emissions (SMOKE) model (Baek and Seppanen, 2021). The SMOKE processor was initialized using the NEI-2014 emissions modeling platform (EMP) version 7.1, as this was the most recently available NEI at the time of the analysis. The model output was binned by month. Ancillary meteorological parameters were accessed from the Rhode Island Department of Health air monitoring and Chemical Specification Network (CSN) monitoring station at East Providence, RI (41.73°N, 71.43°W) using the North American Mesoscale (NAM) 12 km meteorology initiated at the end of each sampling period. Atmospheric NH$_3$ has a lifetime typically on the order of 2.1 d (Paulot et al., 2016), such that the chosen trajectory time should account for the potential of long-range transport of NH$_3$ to the sampling site. A new back trajectory was calculated every 3 h for a maximum of 8 trajectories encompassing the 24 h sampling period at 100 m above ground level.

2.4 Statistical analyses

Geospatial statistical analysis that included bivariate wind direction and wind speed polar plots and back-trajectory clustering was conducted using the “open-air” program package using R (Carslaw and Ropkins, 2012). Local NH$_3$ source identification was estimated using the conditional bivariate probability function (CBPF) analysis that provides a conditional probability field for high concentrations dependent on wind speed and direction (Uria-Tellae and Carslaw, 2014). It is defined as the following (Eq. 1):

$$\text{CBPF}_{\Delta \theta, \Delta u} = \frac{m_{\Delta \theta, \Delta u}|C \geq x}{n_{\Delta \theta, \Delta u}},$$

(1)

where $m_{\Delta \theta, \Delta u}$ is the number of samples in the wind sector $\Delta \theta$ with wind speed interval $\Delta u$ having concentration $C$ greater than a threshold value $x$, $n_{\Delta \theta, \Delta u}$ is the total number of samples in that wind direction–speed interval. The threshold values were set as the top 25% concentration for these analyses. These bivariate polar plots show how a concentration of species varies with wind speed and direction in polar coordinates and are useful in characterizing emission sources (Carslaw and Ropkins, 2012; Carslaw et al., 2006; Tomlin et al., 2009; Zhou et al., 2019). Additionally, source locations that contribute to long-range NH$_3$ transport were evaluated using the potential source contribution function (PSCF). This analysis combines atmospheric concentrations with air mass trajectories and uses residence time information to identify air parcels that contribute to high concentrations at a receptor site (Fleming et al., 2012; Pekney et al., 2006; Begum et al., 2005). The PSCF calculation indicates the probability that a source is located at latitude $i$ and longitude $j$ and is calculated as the following (Eq. 2):

$$\text{PSCF} = \frac{m_{ij}}{n_{ij}},$$

(2)

where $n_{ij}$ is the number of times that the trajectories pass through the cell $(i, j)$ and $m_{ij}$ is the number of times that a source concentration was high when the trajectories passed through the cell $(i, j)$, and the criterion for determining $m_{ij}$ was defined as the 90th percentile (Carslaw and Ropkins, 2012).
Figure 2. Time-series plots of the measured NH$_3$ data including (a) NH$_3$, (b) pNH$_4^+$, and (c) fNH$_3$ and the reported meteorology data including (c) temperature (Temp), relative humidity (RH), and wind speed (WS) from February 2018 to February 2019 in Providence, RI, USA. The light data points refer to the 24 h integrated samples (a, b, c) or 24 h averaged meteorology data (d, e, f), and the dark lines represent approximate 2-week moving averages.

3 Results and discussion

3.1 Urban NH$_3$ and pNH$_4^+$ temporal concentrations

The urban NH$_3$ and pNH$_4^+$ were monitored under a range of meteorological conditions (Fig. 2). The annual NH$_3$ ranged from 0.234 to 2.94 µg m$^{-3}$ with a mean of 0.890 ± 0.517 µg m$^{-3}$ ($n = 97$), and pNH$_4^+$ ranged from 0.019 to 1.62 µg m$^{-3}$ with a mean of 0.412 ± 0.287 µg m$^{-3}$ ($n = 97$). The NH$_x$ partitioning between gas and particle phase was quantified as fNH$_3$ ($f$NH$_3 = \text{NH}_3_{\text{mol}}/(\text{NH}_3_{\text{mol}} + p\text{NH}_4^{+}_{\text{mol}})$) and ranged from 0.307 to 0.972 with an average of 0.688 ± 0.141 ($n = 97$). A strong seasonal pattern was observed for both NH$_3$ and fNH$_3$, with the highest values observed during warmer periods. No significant seasonal pattern was observed for pNH$_4^+$ that remained relatively consistent throughout each season and characterized by frequent spike events in cold and warm months, including near 4 July, corresponding to a period of significant firework activity.

The NH$_3$ and fNH$_3$ were positively correlated with temperature ($r = 0.66; p < 0.01$ & $r = 0.51; p < 0.01$; Fig. S1). This relationship was consistent with previous observations in rural and urban locations that suggested NH$_3$ to be influenced by temperature-dependent volatilization (e.g., agriculture, vegetation, sewage, and waste) and evaporation from semi-volatile NH$_4$NO$_3$ particles (Wang et al., 2015; Hu et
was higher in Providence, RI than the two most remote regional CASTNET sites, including Ashland, ME and Woodstock, NH (p < 0.05), but not significantly different from the Abington, CT or Underhill, VT sites. It is important to note that methodology differences in the collection of \( p\text{NH}_4^+ \) could have significantly influenced the \( p\text{NH}_4^+ \) annual differences and seasonal patterns. Our collection method (nylon filter + acid-coated filter) should lead to the quantitative collection of \( p\text{NH}_4^+ \) (Walters et al., 2019; Yu et al., 2006). In contrast, \( p\text{NH}_4^+ \) collections at the CASTNET sites utilize PTFE filters which could be biased low due to the potential for significant loss of semi-volatile \( \text{NH}_4\text{NO}_3 \) (Ashbaugh and Eldred, 2004; Yu et al., 2005). The potential for \( \text{NH}_4\text{NO}_3 \) volatilization should be more significant for warmer temperatures (Ashbaugh and Eldred, 2004; Yu et al., 2005). However, we did not observe a significant difference in summer \( p\text{NH}_4^+ \) between the Providence, RI and regional CASTNET sites. Thus, the influence of sampling methodologies on the spatiotemporal \( p\text{NH}_4^+ \) patterns remains difficult to quantify.

Localized \( \text{NH}_3 \) emissions likely play an important role in contributing to the observed elevated urban \( \text{NH}_3 \) and the spatiotemporal patterns across New England (Fig. 4). The NEI-14 emission profiles at the AMoN sites indicated that agricultural activities drive the seasonal \( \text{NH}_3 \) emissions, while non-agricultural sources, including stationary fuel combustion (electricity generating units and residential heating) and vehicles, were important during winter but their relative contributions significantly decreased during warmer periods. In contrast, the annual \( \text{NH}_3 \) emission in Providence, RI were dominated by fuel-combustion emissions. The total \( \text{NH}_3 \) emission density in Providence, RI had less seasonal variability than the regional AMoN/CASTNET locations despite a potential seasonal change in emissions with relatively high contributions from residential heating (i.e., oil, gas, wood combustion) during winter compared to summer. We note that natural gas and oil stationary fuel combustion, which is predicted to be the main \( \text{NH}_3 \) emission source at our urban study site as well as in other major urban areas in regions with a large heating demand (Zhou et al., 2019), has a highly uncertain \( \text{NH}_3 \) emission factor established from limited studies conducted before 1982 (Muzio and Arand, 1976; Cass et al., 1982). Additionally, it has recently been pointed out that vehicle \( \text{NH}_3 \) emission, another major source of urban \( \text{NH}_3 \), might be underpredicted by at least a factor of 2 in the NEI (Sun et al., 2017; Fenn et al., 2018).

### 3.3 Urban \( \delta^{15}\text{N} \) of urban \( \text{NH}_3 \)

Measurements of \( \delta^{15}\text{N} \) at the Providence, RI monitoring site were utilized to enhance understanding of source contributions to urban \( \text{NH}_3 \). The measured \( \delta^{15}\text{N}(\text{NH}_3) \) ranged from \(-21.4\%e\) to \(-2.0\%e\) with an average of \(-11.9\pm5.0\%e \) (\( n = 90 \)), and \( \delta^{15}\text{N}(p\text{NH}_4^+) \) ranged from \(-7.4\%e\) to \(17.5\%e\) with a mean of \(4.9\pm6.2\%e \) (\( n = 60 \)) (Fig. 5). The measured \( \delta^{15}\text{N} \) data were binned by season that included winter...
Figure 3. Box and whiskers plots that summarize the annual and seasonal (a) NH$_3$ and (b) pNH$_4^+$ distributions (lower extreme, lower quartile, median, upper quartile, and upper extreme) with the mean (open triangle) and outlier (black asterisk) at the Providence, RI (PVD) site and the New England AMoN/CASTNET sites including Abington, CT (CT), Underhill, VT (VT), Woodstock, NH (NH), and Ashland, ME (ME). Similar lowercase letters in the box and whiskers plots represent categories with statistically similar values.

Figure 4. Monthly-based NH$_3$ emission densities speciated between agricultural, fuel combustion, mobile, other, waste, and wood combustion computed by the SMOKE model for the NH$_3$ monitoring sites in the counties of New England.

(December, January, February), spring (March, April, May), summer (June, July, August), and autumn (September, October, November). The $\delta^{15}$N(NH$_3$) was statistically higher during spring ($-7.6 \pm 3.5\%e$, $n = 21$ ($\bar{x} \pm 1\sigma$)) compared to the other seasons (summer = $-13.9 \pm 4.1\%e$, $n = 21$; autumn = $-13.1 \pm 5.1\%e$, $n = 21$; winter = $-13.4 \pm 5.2\%e$, $n = 18$, $p < 0.05$). The $\delta^{15}$N(pNH$_4^+$) also indicated significant seasonality with lower values during summer ($0.4 \pm 4.9\%e$, $n = 18$) compared to autumn ($7.4 \pm 4.8\%e$, $n = 15$) and winter ($9.0 \pm 5.8\%e$, $n = 14$) ($p < 0.05$). However, springtime $\delta^{15}$N(pNH$_4^+$) ($4.1 \pm 5.2\%e$, $n = 13$) was not statistically different from any season.

The $\delta^{15}$N of atmospheric NH$_3$ and pNH$_4^+$ reflects a combination of source effects from different NH$_3$ emission sources and isotopic equilibrium between NH$_3$ and pNH$_4^+$ that has been shown to have a large influence on setting the N isotopic distribution between these molecules (Walters et al., 2018; Savard et al., 2017; Kawashima and Ono, 2018).
2019). Indeed, the annual $\delta^{15}\text{N}(p\text{NH}_4^+)$ was statistically higher than $\delta^{15}\text{N}$(NH$_3$) ($p < 0.01$), reflecting the contributions from the nitrogen isotope exchange reactions between NH$_3$ and NH$_4^+$, which tends to elevate the $\delta^{15}\text{N}(p\text{NH}_4^+)$ relative to $\delta^{15}\text{N}$(NH$_3$) (Walters et al., 2018; Kawashima and Ono, 2019; Urey, 1947). The isotopic difference or isotope enrichment factor ($15\varepsilon_{p\text{NH}_4^+/\text{NH}_3}$) between $\delta^{15}\text{N}(p\text{NH}_4^+)$ and $\delta^{15}\text{N}$(NH$_3$) was calculated as the following (Eq. 3):

$$\Delta\delta^{15}\text{N} \approx 15\varepsilon_{p\text{NH}_4^+/\text{NH}_3} = \delta^{15}\text{N}(p\text{NH}_4^+) - \delta^{15}\text{N}$(NH$_3$). (3)

The $\Delta\delta^{15}\text{N}$ ranged from $-0.1\%e$ to $34.1\%e$ and averaged $17.6 \pm 7.8\%e$ ($n = 56$) (Fig. 6). There was a strong seasonal $\Delta\delta^{15}\text{N}$ pattern with higher values during colder periods, and $\Delta\delta^{15}\text{N}$ was weakly correlated with temperature ($r = -0.55$, $p < 0.01$; Fig. S1) suggesting that these values were difficult to predict. The observed $\Delta\delta^{15}\text{N}$ was significantly lower than the expected temperature-dependent theoretical isotopic equilibrium values between NH$_3$ and NH$_4^+$ of 35 ± 3% at 25°C (Walters et al., 2018) and previous field $\Delta\delta^{15}\text{N}$ observations (Savard et al., 2017), indicating that incomplete isotopic equilibrium between NH$_3$ and pNH$_4^+$ was achieved at the study site. This result has important implications for previous $\delta^{15}\text{N}$ source apportionment studies of NH$_3$ and pNH$_4^+$, which commonly utilize an assumed and theoretically calculated phase-dependent fractionation (e.g., Zhang et al., 2021; Pan et al., 2016; Gu et al., 2022a, b; Berner and Felix, 2020). A potential explanation for the observed incomplete isotopic equilibrium would be that localized NH$_3$ emissions perturbed the isotopic equilibrium between NH$_3$ and pNH$_4^+$, which may take tens of minutes to several hours to be achieved (Kim et al., 1993). Indeed, previous laboratory dynamic flow chamber experiments have demonstrated that fresh NH$_3$ emissions tend to result in $\Delta\delta^{15}\text{N}$ values below the theoretically predicted value (Kawashima and Ono, 2019). Additionally, there may be other contributing isotope effects between NH$_3$ and pNH$_4^+$, such as the hypothesized kinetic isotope effect associated with NH$_3$ diffusion to an aerosol surface leading to a lower $\delta^{15}\text{N}(p\text{NH}_4^+)$ value compared to $\delta^{15}\text{N}$(NH$_3$) (Pan et al., 2016). The observed $\Delta\delta^{15}\text{N}$ seasonality remains difficult to explain. Still, we speculate that it may be related to higher localized emissions of NH$_3$ during warmer periods that perturb the NH$_3$ / pNH$_4^+$ isotopic equilibrium and/or seasonal changes in PM chemical compositions (Pan et al., 2016), such as higher NH$_3$NO$_3$ during colder months.

To account for the complex phase-dependence on $\delta^{15}\text{N}$ variability, we calculated $\delta^{15}\text{N}$(NH$_4^+$) according to the following (Eq. 4):

$$\delta^{15}\text{N}$(NH$_4^+$) = $f$NH$_3$ × $\delta^{15}\text{N}$(NH$_3$) + $(1 - f$NH$_3$) × $\delta^{15}\text{N}(p\text{NH}_4^+)\quad$ (4)

The annual $\delta^{15}\text{N}$(NH$_4^+$) ranged from $-17.4\%e$ to $6.3\%e$ and averaged $-6.0 \pm 4.9\%e$ ($n = 56$) (Fig. 5). There was significant seasonality with lower values during summer ($-9.0 \pm 4.2\%e$, $n = 18$) compared to winter ($-3.4 \pm 5.3\%e$, $n = 13$) and spring ($-3.8 \pm 3.3\%e$, $n = 10$). The annual $\delta^{15}\text{N}$(NH$_3$) ($-6.2 \pm 4.1\%e$, $n = 15$) was not significantly different from any season. The $\delta^{15}\text{N}$(NH$_3$) is independent of the phase $\delta^{15}\text{N}$ fractionation, such that it should be a robust tracer reflecting the integrated source contributions and physical processing from locally emitted and transported NH$_3$ and pNH$_4^+$.

3.4 Identifying urban local sources of NH$_x$

Wind data and bivariate plot statistical analysis were utilized to investigate local and transported sources of urban NH$_x$. The local wind data indicated a clear shift in wind direction and speed from generally faster winds from the west/northwest during winter to slower winds from the south/southeast and northeast during summer (Fig. 7). Wind direction and wind speed polar bivariate CBPF plots of NH$_3$ and pNH$_4^+$
Figure 5. Measured $\delta^{15}\text{N}$ data of NH$_3$, $p\text{NH}_4^+$, and NH$_x$ collected in Providence, RI, including (a) time series and (b) seasonal box and whisker plots summarizing the distributions (lower extreme, lower quartile, median, upper quartile, and upper extreme) with the mean (open triangle) and outlier (black asterisk). Similar lowercase letters in the box and whisker plots represent categories with statistically similar values.

Figure 6. Seasonal $\Delta\delta^{15}\text{N}$ data at the monitoring site in Providence, RI. In panel (a), the light data points and lines represent the observations, and the thick lines are four-point (~2 weeks) moving averages. Panel (b) shows a box and whisker plot summarizing the seasonal distributions (lower extreme, lower quartile, median, upper quartile, and upper extreme) with the mean (open triangle) and outlier (black asterisk).

indicated relatively high probability under conditions of low wind speeds (i.e., $<2\text{ m s}^{-1}$) for all seasons, suggesting the importance of local emitted NH$_3$ sources and $p\text{NH}_4^+$ formation. These elevated CBPF probabilities were also associated with winds from the southeast to west, the direction of I-195 and I-95, major interstate highways, and industrial sources (Fig. 1). The highest $\delta^{15}\text{N}(\text{NH}_3)$ values within each season were observed with winds from these directions, implicating the importance of vehicle emissions, which have an elevated $\delta^{15}\text{N}(\text{NH}_3)$ signature of $6.6\pm 2.1\%$ compared to other NH$_3$ sources that tend to have $\delta^{15}\text{N}(\text{NH}_3)$ values below $0\%$, including available industrial $\delta^{15}\text{N}(\text{NH}_3)$ emissions (Walters et al., 2020).

Additionally, high conditional probability function (CPF) probabilities for both NH$_3$ and $p\text{NH}_4^+$ were observed during the warmer seasons of summer and autumn from moderate winds ($2-4\text{ m s}^{-1}$) from the northeast and west. This result may implicate local temperature-dependent NH$_3$ emission sources such as sewage lines, trash cans, soil emissions from green spaces, and regional transport (Hu et al., 2014; Sutton et al., 2000; Pandolfi et al., 2012; Reche et al., 2012; Meng et al., 2011; Galán Madruga et al., 2018; Zhou et al., 2019). These winds were associated with a relatively low $\delta^{15}\text{N}(\text{NH}_3)$, consistent with volatilization contributions with a low $\delta^{15}\text{N}(\text{NH}_3)$ emission signature between $-56.1\%$ to $-10.3\%$ based on livestock waste and fertilizer studies (Heaton, 1987; Freyer, 1978; Felix et al., 2013; Chang et al.,...
Figure 7. Overview of (a) wind rose plots and polar bivariate (wind direction and wind speed) plots of the conditional bivariate probability function (CBPF) for (b) NH$_3$ and (c) $p$NH$_4^+$, and (d) mean $\delta^{15}$N(NH$_3$) in Providence, RI, sorted by season.
Low CPF probabilities for both NH$_3$ and $\rho$NH$_4^+$ were generally associated with high wind speeds (i.e., $> 4$ m s$^{-1}$), reflecting the dilution of these pollutants and strong background mixing. An exception to this trend was observed for $\rho$NH$_4^+$ during the winter, with elevated CPF probabilities with high wind speeds indicating the importance of long-range transport. Interestingly, there was a seasonal difference in $\delta^{15}$N(NH$_3$) from this wind profile, with high values during the cold seasons and low values during summer, suggesting that the background NH$_3$ had larger contributions from vehicle emissions and volatilization during the cold and warm seasons, respectively.

3.5 Role of long-range transport as a source of urban NH$_x$

Air mass back trajectories and PSCF analysis were utilized to identify source locations of transported NH$_3$ and $\rho$NH$_4^+$ to Providence, RI. The clustered seasonal air mass back trajectories indicated a shift in the seasonal air mass origin, with winds originating from the north and west during winter with higher contributions of air masses derived from the south and along the coast during summer (Fig. 8). During summer and autumn, potentially significant NH$_3$ and $\rho$NH$_4^+$ source regions originated over the Mid-Atlantic, Midwestern USA (the Midwest), Atlantic coast, Southeastern USA, Southeastern Ontario, and Southeastern Quebec. These regions have significant agricultural-related NH$_3$ emissions, such as fertilizer application, livestock waste, and significant urban and industrial activities. Transport from these regions tended to have relatively low mean $\delta^{15}$N(NH$_3$) values (i.e., $-15\%e$ to $-5\%e$), consistent with transport of volatilized agricultural NH$_3$ emissions that favor the release of isotopically light $^{14}$NH$_3$ (Heaton, 1987; Freyer, 1978; Felix et al., 2013; Chang et al., 2016) and available industrial emissions with a reported low $\delta^{15}$N(NH$_3$) value of $-20.1\%e$ from a steel factory (Heaton, 1987). We also note that NH$_3$ deposition and re-volatilization during transport of any NH$_3$ emission source may also lead to significant isotope fractionation as NH$_3$ is transported downwind. Because NH$_3$ volatilization has been shown to lead to the initial release of NH$_3$ depleted in $^{15}$N, it is reasonable to assume that this long-range transported NH$_3$ would contribute low $\delta^{15}$N(NH$_3$) (Frank et al., 2004; Hristov et al., 2009). Thus, low $\delta^{15}$N(NH$_3$) values from the identified important contribution regions during the warmer seasons may also reflect the bidirectional exchange of NH$_3$ as it is long-range transported downwind from agricultural, urbanized, and industrialized regions. Available ground-based monitoring data indicate that the identified source regions tend to have elevated ambient NH$_3$ and $\rho$NH$_4^+$, consistent with these regions as potential NH$_3$ and $\rho$NH$_4^+$ source contributors to Providence, RI (Fig. S2). Additionally, the Atlantic coast may represent contributions from ocean NH$_3$ flux expected to increase during warmer periods (Paulot et al., 2015), which has been suggested to have low $\delta^{15}$N values (Jickells et al., 2003).

Elevated PSCF probabilities were identified for $\rho$NH$_4^+$ during the winter from the Mid-Atlantic and the Midwest, which is consistent with available $\rho$NH$_4^+$ ground-based observations that tend to peak during this period due to ambient conditions that favor the formation of NH$_3$NO$_3$ (Fig. S2). This transport region tended to have relatively high mean $\delta^{15}$N(NH$_3$) values (e.g., $-5\%e$ to $0\%e$) from the Mid-Atlantic and relatively low mean from the Mid-Atlantic ($\sim -10\%e$). Across USA, NH$_3$ was lowest during winter due to decreased agricultural activities (Fig. S2). Indeed, the NEI-14 indicates that the relative importance of non-agricultural NH$_3$ sources increases during winter (Fig. 4), such that the higher $\delta^{15}$N(NH$_3$) values deriving from the Midwest may reflect the regional importance of sources with an elevated $\delta^{15}$N(NH$_3$) value such as vehicles and/or fuel combustion. Lower mean $\delta^{15}$N(NH$_3$) values derived from the Mid-Atlantic may suggest that agricultural emissions such as animal housing remain an important wintertime NH$_3$ source contributor to Providence, RI. Additionally, there could be contributions from stationary fuel combustion that have a reported $\delta^{15}$N(NH$_3$) signature of $-14.6\%e$ to $-11.3\%e$ (Felix et al., 2013), and contributions from upwind volatilized NH$_3$ emissions from Canada.

3.6 Urban NH$_x$ source apportionment

The NH$_x$ source contributions at Providence, RI, including local and transported emissions, were quantified using a stable isotope mixing model (SIMMR; Parnell et al., 2010). The model was initiated using the measured $\delta^{15}$N(NH$_3$) values and assuming that vehicles, volatilization, stationary fuel combustion (i.e., residential fuel combustion, industrial fuel combustion, energy generating units), and industry were the main sources, as evidenced by the local wind direction and back trajectory analysis and the NEI-14 predictions. Biomass burning, while a significant global source of NH$_3$ (Behera et al., 2013), was not considered in the mixing model since there was insufficient evidence from the local wind direction and long-range transport analysis that it was a major contributing source to our study location. Further, the NEI-14 predicted residential wood combustion represented less than 5% of the annual emission of NH$_3$ in the Providence County, with seasonal variation, including higher relative emissions during the colder months (Fig. 4). Still, potassium (K$^+$), a common biomass burning tracer, from PM$_{2.5}$ samples collected from the nearby CSN site in East Providence, RI, was not significantly correlated with NH$_3$ ($r = 0.019$; $p = 0.857$) and weakly correlated with $\rho$NH$_4^+$ ($r = 0.233$; $p = 0.022$), excluding an outlier on 4 July (Fig. S3). We acknowledge that there are additional miscellaneous NH$_3$ sources in an urban environment, including pets, household products, and humans (Ampollini et al., 2019; Sutton et al., 2000; Li et al., 2020); however, we assumed that these sources were negli-
Figure 8. Influence of long-range transport including (a) clustered seasonal air mass back trajectories, (b) seasonal NH$_3$ potential source contribution function (PSCF) probability, (c) seasonal NH$_3$ PSCF probability, and (d) seasonal air mass back trajectory $\delta^{15}$N(NH$_3$) mean values.

Gible compared to the main identified emission sources. Excluding biomass burning and other miscellaneous sources of NH$_3$ was not expected to impact the goal of the mixing model calculations, which was to estimate the relative amounts of the main identified NH$_3$ emission sources and their temporal variation at the study site in Providence, RI.

The source apportionment results are sensitive to the number of considered sources, their designated $\delta^{15}$N(NH$_3$) emission signatures, and uncertainty. The input $\delta^{15}$N(NH$_3$) emission source signatures were deliberately chosen from sampling methodologies that have utilized active sampling approaches, as it has been well-documented from several stud-
ies that passive samplers result in a $\delta^{15}$N(NH$_3$) bias and could be unreliable (Pan et al., 2020; Kawashima et al., 2021; Walters et al., 2020). Fertilization application is a significant source of NH$_3$ emissions globally and within USA. However, fertilizer application represents a small component of the overall agricultural emissions at our site ($\sim$ 1.8%) and within our region (7.1%; US EPA Region 1) based on the NEI-14. Further, fertilization-related NH$_3$ emissions tend to peak during spring; however, we neither identified any significant NH$_3$ long-range transport region nor observed a relative decrease in $\delta^{15}$N(NH$_3$) during spring, which would be consistent with a suspected low fertilizer volatilization $\delta^{15}$N(NH$_3$) emission signature. Thus, fertilizer application was not directly considered in our source apportionment model but lumped into the considered volatilization category.

The input source values for vehicles, stationary fuel combustion/industry, and volatilization were fixed at 6.6±2.1% (Walters et al., 2020), −15.3±3.6% (Heaton, 1987; Freyer, 1978), and −19.2±8.3% (Freyer, 1978; Heaton, 1987; Hristov et al., 2009; Frank et al., 2004). Stationary fuel combustion and industry $\delta^{15}$N(NH$_3$) emission signatures were grouped due to their similar values (Sect. S1 in the Supplement). The volatilization $\delta^{15}$N(NH$_3$) emission signature represents integrated volatilization measurements conducted in animal sheds (Freyer, 1978; Heaton, 1987), and measurements that include monitoring volatilization as a function of time, which indicate significant $\delta^{15}$N(NH$_3$) variability (Hristov et al., 2009; Frank et al., 2004). The volatilization category represented waste volatilization from agricultural activities and urban sources (i.e., sewer, trash, green spaces) and transported NH$_3$ that has re-volatilized to the atmosphere because of NH$_3$ bidirectional exchange. Further details on our rationale for the chosen source $\delta^{15}$N values are provided in the “Supporting information” section (Sect. S1).

The mixing model predicts the relative fractional contributions of vehicles, volatilization, and stationary fuel combustion/industry emissions of (mean ±$\sigma$) 46.8±3.5%, 26.3±12.3%, and 26.9±14.4% to the annual NH$_3$ background in Providence, RI (Fig. 9a). The relative contribution of vehicle emissions had a strong seasonal profile with higher contributions during the colder seasons of winter (56.4±7.6%) and spring (55.4±5.8%) compared to the warmer seasons of summer (34.1±5.5%) and autumn (45.4±5.5%). The relative contribution for volatilization and stationary fuel combustion/industry was predicted to peak during summer with means of 31.7±15.4% and 34.2±18.2%, compared to winter with means of 20.9±10.3%, 22.6±12.1%, respectively. The annual and seasonal mass-weighted contributions of the considered sources were calculated utilizing the NH$_3$ concentrations (Fig. 9b). Overall, vehicles tended to be a consistent source of NH$_3$ with contributions of 35.2±2.6, 33.3±3.5, 32.8±5.3, 35.2±4.3, and 35.4±4.8 mmol m$^{-3}$ for the annual, spring, summer, autumn, and winter, respectively. The mass-weighted contributions for both volatilization and fuel combustion follow their relative fractional profiles with significant seasonal patterns that peaked during summer compared to winter, respectively. Based on the NEI-14, wind direction, and long-range transport analysis (Figs. 4, 7, and 8), we suspect the relative contribution of vehicle emissions diminished during summer due to the increased importance of temperature-dependent NH$_3$ volatilization emissions, increased energy consumption due to cooling demands, and/or change in transport over heavily industrialized regions such as highly urbanized Toronto and the East Coast shoreline. The exact NH$_3$ volatilization source remains unclear. However, there was evidence of significant contributions from local urban volatilization (i.e., sewage, waste, urban green spaces) and long-range transport from regional agricultural regions and over the ocean.

The source apportionment results were compared with the predicted NH$_3$ emissions from the NEI-14. We acknowledge that this comparison may not yield quantitative results because the NEI-14 was at a county-level resolution, and our single study site may not represent all the county-level NH$_3$ emission predictions; however, this comparison may yield a qualitative understanding in the uncertainties of urban NH$_3$. Overall, the seasonally consistent mass-weighted contribution of vehicle emissions from the mixing model source apportionment results was consistent with the NEI-14 that predicts nearly uniform vehicle emissions throughout the year (Fig. 4). However, the NEI-14 predicts a lower contribution of annual vehicle emissions in our study location of 31.9% compared to our mixing model results (46.8±3.5%). Our mixing model source apportionment results indicate a relatively low fractional and mass-weighted contribution for stationary fuel combustion for winter. Contrastingly, the NEI-14 indicated that residential fuel (natural gas and oil) combustion was the largest emission source of NH$_3$ at our study site, the rural CASTNET sites, and other cities during periods of significant heating demands (Zhou et al., 2019). While we acknowledge that the stationary fuel combustion $\delta^{15}$N(NH$_3$) emission signatures were uncertain, the mixing model and seasonal NH$_3$ results would suggest that residential NH$_3$ emissions were overpredicted in the NEI-14, while vehicle emissions may be underpredicted. Thus, vehicle and fuel-combustion emission factors may need to be revisited to more accurately model urban NH$_3$ and predict its human and ecological impacts.

4 Conclusions

Elevated urban NH$_3$ concentrations were observed in Providence, RI, relative to regional background monitoring stations in New England. Mixing model $\delta^{15}$N(NH$_3$) source apportionment results utilizing $\delta^{15}$N(NH$_3$) suggest that vehicles represent an important source of urban NH$_3$ with strong seasonal variability. The relative contribution of vehicle emissions was highest during winter/spring, which is significant because NH$_3$ emissions may contribute to the ele-
vated PM$_{2.5}$ observed during this time in the Eastern USA (Shah et al., 2018). Reductions in vehicle ammonia emissions may represent a promising way to mitigate the adverse impacts of elevated urban NH$_3$ concentrations and yield positive benefits for ecosystems and human health. However, vehicle NH$_3$ emissions result from the technology used to combat vehicle NO$_x$ and CO emissions. Decreasing vehicle NH$_3$ emissions may not be achievable until vehicle-fleet electrification. Expanding national observational networks to include urban measurements of NH$_3$ and $\delta^{15}$N(NH$_x$) are needed to monitor urban trends and design future regulatory NH$_3$ fossil-fuel-related emission reductions.

This work demonstrated that nitrogen isotopic analysis allows for further refinement of our understanding and quantification of urban NH$_x$ sources, laying the foundation for future source apportionment studies. Utilizing a laboratory-verified collection method suitable for NH$_x$ speciation and isotope analysis was critical for accurate source apportionment due to the observed complex phase-dependent $\delta^{15}$N isotope fractionation between NH$_3$ and $p$NH$_4^+$. Future studies should improve our understanding of the drivers behind NH$_3$ and $p$NH$_4^+$ phase $\delta^{15}$N fractionation, including controlled chamber studies and field observations, which may also provide important insights into controls on NH$_3$ / $p$NH$_4^+$ gas-to-particle-phase conversion. Still, this work highlights the need to improve our $\delta^{15}$N(NH$_3$) emission source values, particularly for our volatilization, industry, and fuel-combustion sources, to enhance the quality of the source apportionment results.

**Figure 9.** The calculated mean (a) fractional contribution and (b) mass-weighted contribution of the major identified emission sources (vehicle, volatilization, fuel combustion/industry) to NH$_3$ in Providence, RI, utilizing a stable isotope mixing model (SIMMR). The error bars represent the standard deviation of the model simulations.

**Data availability.** Data presented in this article are available on the Harvard Dataverse at https://doi.org/10.7910/DVN/JHMBRI (Walters, 2022) and in the Supplement.

**Supplement.** The supplement related to this article is available online at: https://doi.org/10.5194/acp-22-13431-2022-supplement.

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