AGU100 ADVANCING EARTH AND SPACE SCIENCE

JGR Atmospheres

RESEARCH ARTICLE
10.1029/2019JD030380

Ambient Ammonia Concentrations Across New York State

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Abstract Ammonia (NH_3) was monitored at four locations (two urban and two rural) across New York State from April 2016 to October 2017 using active and passive systems. The two rural sites were Pinnacle State Park (PIN) and the Village of Potsdam, and the two urban sites were the City of Rochester and Queens College in New York City. Active and passive concentrations were well correlated across all sites ($r^2 = 0.866$), but the active systems measured 6.2% higher NH_3 concentrations. The mean (±SD) NH_3 concentrations measured using active systems in Queens College, City of Rochester, Village of Potsdam, and PIN were 3.22 ± 2.23, 2.84 ± 1.91, 1.29 ± 1.12, and 0.82 ± 0.64 ppb, respectively. Ambient NH_3 concentrations varied with diel vehicular and seasonal agricultural activities. NH_3 concentrations at the urban sites had lower seasonal variability than the rural sites. NH_3 concentrations were generally related to regional and in-state NH_3 emissions although less regional influence was observed at the urban sites. Local NH_3 source directions were identified using conditional bivariate probability function. The urban sites were affected by local NH_3 sources such as vehicular emissions and urban population centers. Likely distant NH_3 source locations affecting the four sites were identified using simplified quantitative transport bias analysis model. Rural sites were more highly affected by transported NH_3. Midwestern and Atlantic were major NH_3 source areas. NH_3 emissions from the south of PIN were probably due to the use of diesel trucks and other diesel engines in the hydraulic fracturing industry in Pennsylvania near the New York State border.

Key Points:

- Hourly ambient NH3 has been measured at 2 urban and 2 rural sites in NYS for 18 months showing urban concentrations are higher than rural.
- Diel variations at the rural sites are driven by temperature while urban values are related to high traffic periods
- There appear to be errors in the national emission inventory with overestimates for natural gas combustion and underestimation for vehicles.

Supporting Information:

- Supporting Information S1

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Citation:
Zhou, C., Zhou, H., Holsen, T. M., Hopke, P. K., Edgerton, E. S., & Schwab, J. J. (2019). Ambient ammonia concentrations across New York State. *Journal of Geophysical Research: Atmospheres*, *124*, 8287–8302. https://doi.org/10.1029/2019JD030380

Received 27 JAN 2019
Accepted 6 JUL 2019
Accepted article online 16 JUL 2019
Published online 30 JUL 2019

Author Contributions:
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Data curation: Hao Zhou, Philip K. Hopke
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Funding acquisition: Thomas M. Holsen
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(continued)

1. Introduction

Ammonia (NH_3) is the most dominant volatile base in the atmosphere and results in the formation of secondary inorganic aerosol through reactions with sulfuric and nitric acids. NH_3 now has a reduced impact on human health since it only makes a limited contribution of $PM_{2.5}$ (Gu et al., 2014) due to the substantial reductions in secondary inorganic aerosol and it precursor gas concentrations (Rich et al., 2019; Squizzato et al., 2018a). NH_3 has other potential adverse environmental effects. For example, long-range transported NH_3 can reduce the biodiversity of remote ecosystems (Bittman et al., 2017; Ellis et al., 2013). Deposited NH_3 and ammonium (NH_4^+) formed by reacting with acid gases in the atmosphere can cause aquatic eutrophication (Tang et al., 2017). NH_3 can also affect the climate since it is a strong greenhouse gas (Wang et al., 2017). However, more recently, the importance of the role of NH_3 as an air pollutant was recognized as NH_3 was found to be a critical factor in the nucleation process of new particle formation (Yue et al., 2010; Zheng et al., 2012). Both lab and field observations have suggested that NH_3 can increase nucleation rates 100- to 1,000-fold even at ppt levels (Meng et al., 2017; Seinfeld & Pandis, 2016). Therefore, NH_3 can significantly affect ambient air quality as the key precursor of the formation of secondary sulfate and nitrate particles (major components of $PM_{2.5}$; Liu et al., 2015; Seinfeld & Pandis, 2016; Sun et al., 2017). In addition, the importance of NH_3 in terms of its global impacts has increased because of the substantial reductions of SO_2 and NO_x emissions (Emami et al., 2018; Squizzato et al., 2018a) while there have been only limited reductions of NH_3 emissions (Tang et al., 2017; Xu et al., 2017).

On a global scale and in the United States, NH_3 emissions from agricultural activities including the decay of domestic livestock waste, volatilization losses from fertilizers, emissions from soils, and biomass burning (Bray et al., 2018) have been considered to be the major NH_3 sources (>80%; Bittman et al., 2017; Zhang

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et al., 2018). These agricultural emissions can impact urban air pollution through atmospheric transport (Gu et al., 2014; Reche et al., 2012). In urban areas, major NH_3 emissions are due to nitrogen oxide (NO_x) emission control equipment, such as three-way catalysts (TWC) on light-duty vehicles (Nevalainen et al., 2018; Thiruvengadam et al., 2016) and selective catalytic reduction (SCR) systems on both stationary sources (Forzatti, 2001) and new heavy-duty diesel engines (Thiruvengadam et al., 2016). In a TWC, NH_3 is formed as a byproduct of incomplete reduction and emitted by both gasoline and natural gas vehicles (Sun et al., 2017). In electricity generating unit SCR systems, industrial heaters, and cogeneration plants, NH_3 is injected as a reductant causing major NH_3 emissions or "slip" (Forzatti, 2001). Thiruvengadam et al. (2016) reported that SCR-equipped heavy-duty diesel tractors can emit NH_3 particularly as they age. In addition, NH_3 emitted from urban wastes such as garbage and sewage can be important in high population communities (Galan Madruga et al., 2018).

NH_3 transported from agricultural sources was also considered to be important for urban atmospheres given they were thought to dominate the emissions (Gu et al., 2014). Agricultural NH_3 emissions were reported to have high seasonal variability and usually peaked in spring or summer due to the increased fertilizer use and/or manure spreading activities and temperature (Sigurdarson et al., 2018). Urban NH_3 emissions, that is, from TWC and SCRs, as well as residential natural gas combustion were considered to be more important to urban areas in winter time (Forzatti, 2001; Shelef & Gandhi, 1974). However, the extent of agricultural NH_3 emission impacts on urban areas has been uncertain (Pan et al., 2016) because (1) uncertainties exist in agricultural NH_3 emissions estimates as these processes depend on detailed spatial and temporal information on local agricultural practices and environmental conditions (Paulot et al., 2014; Zhang et al., 2018); (2) the lifetime of NH_3 can vary depending on the physicochemical properties of the atmosphere (Aneja et al., 2000; Kruit et al., 2012; Vieno et al., 2014); and (3) the importance of urban NH_3 emissions has increased with the shift of fuels from coal to natural gas in power plants over the past decade (especially in the United States) and changing vehicular control system. Since new natural gas generators are new sources, they would be required to be equipped with SCRs. There has also been an increased penetration of SCR-equipped heavy-duty diesel vehicles into the on-road truck fleet since their introduction in 2010. There have also been changes in light duty vehicles to reduce their emission of NO_x. Their NH_3 emissions are generally unregulated (Thiruvengadam et al., 2016).

Although there have been efforts to reduce agricultural NH_3 emissions at local to international scales (Bittman et al., 2017; Tang et al., 2017; Wang et al., 2017), Bittman et al. (2017) suggested that atmospheric NH_3 concentrations are not declining in Canada and the United States because the reductions in acid gas concentrations tend to increase its residence time and resulting NH_3 concentrations (Meng et al., 2017; Pinder et al., 2011).

Atmospheric NH_3 has been monitored by the Ammonia Monitoring Network (AMoN) since 2007 (officially since 2010) as a part of the National Atmospheric Deposition Program (NADP). In New York State (NYS), seven monitoring sites were established and are currently active. The AMoN sites measure NH_3 concentrations on a biweekly basis with passive diffusion gas samplers. However, few active sampling, temporally resolved NH_3 monitoring sites (or networks) have been established that can provide real-time information on NH_3 concentration patterns, source types, and likely source locations (Saylor et al., 2010).

According to the recent emissions inventory (USEPA, 2016), agricultural activities (contributing 64%), including direct livestock emissions, manure decomposition, and fertilizer, dominate the total NH_3 emissions in NYS. However, they were significantly lower in NYS compared to other agricultural regions in the United States, such as the Midwest and Southeast (contribute around 80%; Paulot et al., 2014; USEPA). NH_3 emissions from urban sources were found to be comparable with agricultural emissions for the two urban counties included in this study (Monroe and Queens; USEPA, 2016). Therefore, it is important to determine whether the transported NH_3 from agricultural regions (in-state and out-state) is a major contributor to atmospheric NH_3 in NYS.

In this study, ambient NH_3 concentrations (5-min values aggregated to 60-min averages) were measured with active sampling systems at four NYS sites: Queens College (QUE), Rochester (ROC), Pinnacle State Park (PIN), and Potsdam (PTD). The diel, weekly, and monthly patterns of NH_3 concentrations at these NYS urban and rural sites were characterized. The ambient NH_3 concentrations were also investigated by examining ambient meteorological conditions, such as temperature, relative humidity (RH), wind speed, and direction. The contributions of transported agricultural NH_3 were determined with multiple statistical approaches: (1) correlations between NH_3 concentrations and state or regional NH_3 emissions were established, (2) the importance and directionality of local NH_3 sources were investigated using conditional bivariate probability function (CBPF), and (3) likely source locations for the long-distance transported NH_3 were identified based on a trajectory ensemble receptor model, simplified quantitative transport bias (SQTBA).

2. Ambient Ammonia Measurement

2.1. Methods

2.1.1. Monitoring Sites

The four monitoring sites are shown in Figure 1. QUE (40.73614, −73.82153) was located in New York City (Queens County), ROC was located in southeastern Rochester (43.14618, −77.54822, Monroe County), PIN was located in Pinnacle State Park (42.09142, −77.20978, Steuben County), and PTD (44.662118, −75.001016) was located at Clarkson University, Potsdam (St. Lawrence County). The sampling periods were from April 2016 to October 2017 except QUE (from June 2016 to October 2017). QUE and ROC were urban sites located in populated regions that can be directly affected by urban emissions, such as vehicle emissions, nonpoint human activities, and wastewater treatment facilities. PIN and PTD were rural sites since agricultural NH_3 emission, such as livestock and fertilizer application, dominated these sites. However, vehicular and other diesel emissions may also be important at PIN as there were increasing heavy-duty vehicles servicing the fracking activities in northern Pennsylvania (Squizzato et al., 2018b).

Meteorological data including hourly ambient air temperature, RH, and wind speed and direction were recorded at the monitoring site or at nearby meteorological stations. The meteorological data used for analysis in PIN, QUE, and ROC were obtained from Elmira Corning Regional Airport, LaGuardia Airport, and Rochester International Airport, respectively. The meteorology data used for analysis in PTD were recorded -on-site.

2.1.2. Ammonia Measurements

NH_3 was measured using active (continuous) and passive (biweekly) systems. The active system used a denuder difference technique through a dual-channel nitric oxide-ozone (NO-O_3) chemiluminescence detector system with 5-min time resolution for data reporting and analysis as described in detail by Saylor et al. (2010). As shown in supporting information Figure S1, ambient air is drawn through Na_2CO_3-coated annular denuders (URG, Inc., Chapel Hill, NC) at a flow rate of 1.25 L/min to remove HNO_3 and other reactive NO_y compounds in both channels. The air flow was continuously maintained through each set of converters and diverted sequentially to the chemiluminescence detector. The flow in Channel 1 was directed through a 600 °C Pt mesh converter to oxidize the reduced nitrogen species (primarily NH_3 and particulate NH_4^+) to NO_y followed by a 350 °C Mo converter to reduce the NO_y to NO. The flow in Channel 2 was directed to a citric acid-coated annular denuder to remove all NH_3 before being directed to the Pt and Mo converters. The NH_3 concentrations were defined as the differences between the nitrogenous species measured in the two channels. The NO monitor is zero checked daily and span checked every other day. The denuders were replaced monthly or when there was a disparity between the concentrations measured in the two channels suggesting breakthrough had occurred such as negative values. The detection limit for the difference signal is 200–300 ppt and is driven largely by day-to-day variability in zero checks used for the baseline adjustments. The expanded instrumental uncertainties for the instrument measuring ammonia in a clean background gas based on the uncertainties in the calibration standard, instrument response, conversion efficiency, and flow with a coverage factor of 2 were 10%. The overall expanded uncertainty in the active NH_3 measurement was estimated to be ±15% to 20% based on the variations in the comparisons with the integrated concentrations measured as the ammonia captured in the citric acid denuder (Edgerton et al., 2007; Saylor et al., 2010).

The collocated passive system diffusion samplers have no moving parts (Radiello, Sigma-Aldrich) and were obtained from the AMoN operated by the NADP. Ammonia monitoring was added to NADP in 2010 after pilot testing beginning in 2007 (http://nadp.slh.wisc.edu/amon/). The radiello samplers are described in detail in radiello manual available from https://www.restek.com/pdfs/radiello-manual.pdf. The NH_3 samplers are prepared in a central laboratory (now at the University of Wisconsin-Madison) and, after being

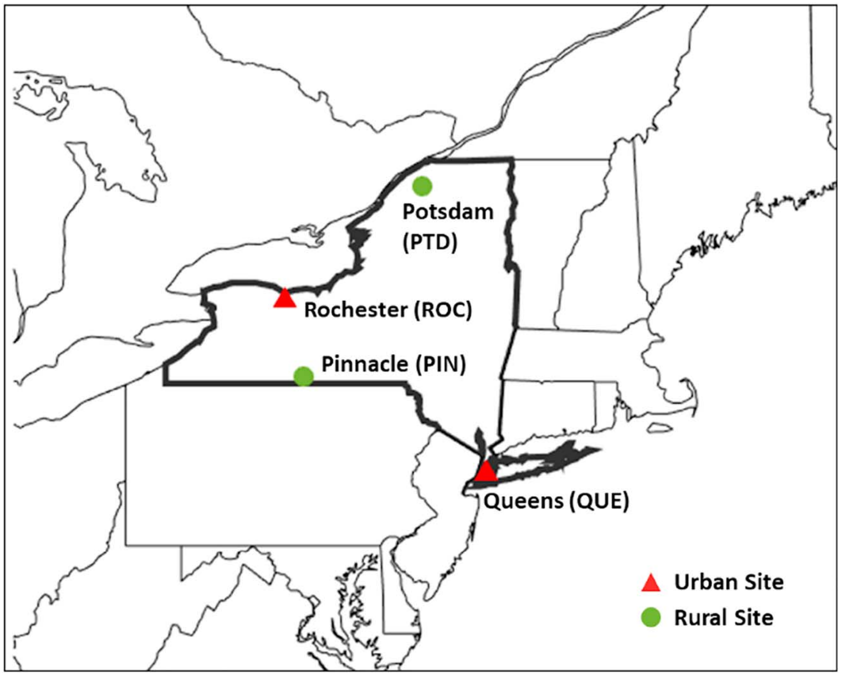

Figure 1. Map of the four NH_3 monitoring sites.

returned to the lab, are analyzed using flow injection analysis by reaction with phenate as described in the AMoN operations manual (http://nadp.slh.wisc.edu/lib/manuals/AMON_Operations_Manual_v_1-3.pdf) and the NADP QA/QC plan (http://nadp.slh.wisc.edu/lib/qaplans/NADP_Network_Quality_Assurance_Plan.pdf). They were installed at each site in accordance to the AMoN standard operating procedures. Each sampler was exposed for a 2-week period and then returned to the central laboratory for analysis and reporting of the resulting concentrations. Calculations are based on the values provided in the radiello manual. AMoN/NADP provided the quality control as described by Puchalski et al. (2011). Puchalski et al. (2011) report that the coefficient of variation between duplicate, collocated samplers was about 10%. The measurement error was not reported but is very likely to be larger than 10%.

2.1.3. CBPF

Local NH_3 source directions were estimated using CBPF analysis that provides a conditional probability field for high concentrations dependent on wind speed and direction (Masiol et al., 2017; Uria-Tellaetxe & Carslaw, 2014). It is defined as

$$\mathrm{CBPF}_{\Delta\theta,\Delta u} = \frac{\mathrm{m}_{\Delta\theta,\Delta u}|c \geq x}{\mathrm{n}_{\Delta\theta,\Delta u}}, \tag{1}$$

where $\mathrm{m}_{\Delta\theta,\Delta u}$ is the number of samples in the wind sector $\Delta\theta$ with wind speed interval Δu having concentration C greater than a threshold value x, $\mathrm{n}_{\Delta\theta,\Delta u}$ is the total number of samples in that wind direction-speed interval. For these analyses, the threshold values were set as the top 25% concentrations of each site.

The wind direction-speed intervals with higher CBPF values indicate that the contaminant concentrations have high probability to be associated with the corresponding wind speed and direction. Local source directions can be determined when high CPBF regions are observed.

2.1.4. SQTBA

Likely NH_3 source locations that contribute to long-distance transport events were evaluated using SQTBA, a trajectory ensemble receptor model that can be applied to data collected at multiple sites (Brook et al., 2004; Hopke, 2016; Zhou et al., 2004). SQTBA was performed using the TraPSA software (Zhou et al., 2016), which is a specialized software developed for potential source apportionment based on trajectory ensemble models, combined with the NOAA/ARL HYSPLIT4 model (Stein et al., 2015; H. Zhou et al., 2018; Hao Zhou et al., 2017). The NCEP/NCAR Reanalysis database was used for generating back trajectories.

The lifetime of NH_3 in the atmosphere ranges from 1–5 days since it can react with acid gases or be dissolved in liquid water (Tang et al., 2017; Wang et al., 2017). However, NH_3 will convert to NH_4^+ by reacting with gaseous sulfuric or nitric acid during transport, and the resulting NH_4^+ particles can have atmospheric lifetimes of the order of 1–15 days (Aneja et al., 2000; Kruit et al., 2012; Vieno et al., 2014). In addition, NH_3 can remain longer in the atmosphere when the particulate form changes from $(NH_4)_2SO_4$ to NH_4NO_3, since NH_4NO_3 is in equilibrium with gaseous nitric acid and ammonia and can release NH_3 at higher temperatures (Tang et al., 2017). Therefore, the back trajectories were calculated for 72 hr (3 days) with a starting height of 500 m above ground level.

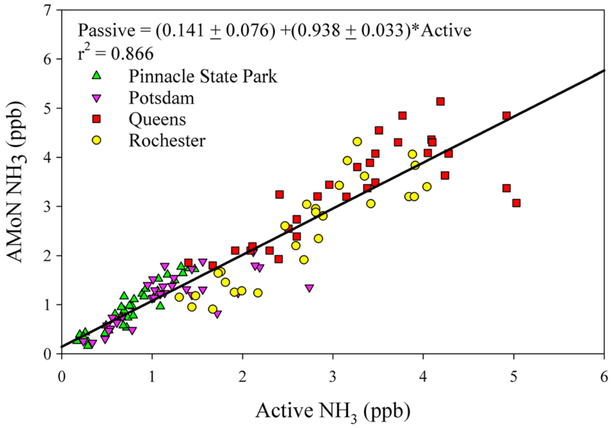

Figure 2. NH_3 concentration measured by active (biweekly average) and passive systems.

3. Results

3.1. Active Sampler Versus Passive Sampler

As shown in Figure 2, biweekly average concentrations from the active NH_3 systems were compared with NH_3 concentrations measured using the AMoN passive system after blank correction. One obvious outlier was observed; an AMoN value from QUE was anomalously low (below the reported detection limit) and was excluded from the comparison. The correlation between the remaining active and passive systems data was strong (r^2 = 0.866). However, the active system measured higher average NH_3 concentrations (6.2% higher on average) that is within the uncertainties for both measurement systems. There were no apparent differences in the fits across all four sites suggesting that these results were not dependent on the specific active measurement system, operator, or site characteristics. It is not possible to know which of the two systems provides the more accurate estimate of the ambient ammonia concentration since both approaches involve assumptions and measurement uncertainties but were subjected to routine calibrations and quality assurance procedures.

3.2. Hourly Ammonia Concentrations

The average NH_3 concentrations measured at the QUE, ROC, PTD, and PIN were 3.22 ± 2.23, 2.84 ± 1.91, 1.29 ± 1.12, and 0.82 ± 0.64 ppb, respectively. The temporal variations in the ammonia concentrations for each of the four sites are presented in Figures 3 and 4. The lines provide mean values while the shaded area describes the 5% and 95% limits to the distributions. These variations for the four sites separated by season are shown in Figures S2 to S5 for PIN, PTD, QUE, and ROC, respectively. NH_3 concentrations at the urban sites (QUE and ROC) were significantly higher (Kruskal–Wallis test, $p < 0.01$) than that at the rural sites (PTD and PIN). The enhanced NH_3 concentrations in urban areas can pose more serious environmental concerns due to the denser populations and poorer dispersion (Galan Madruga et al., 2018). To evaluate the potential influence of in-state agricultural emissions to urban areas, the daily average NH_3 concentrations were compared between urban and rural sites day to day by plotting the differences in the daily values among the sites (Figure S6). It can be seen that the urban sites had higher daily NH_3 average concentrations (higher by 2.37 ppb on average) for the most days (96%). Therefore, it is unlikely that the enhanced NH_3 concentrations found at the urban sites were mainly responding to the in-state agricultural emissions even though the total NH_3 emissions in NYS were dominated by this source type.

3.3. Diel Patterns

The diel patterns of NH_3 concentration on weekdays and weekends at the four sites are shown in Figures 3 and 4. NH_3 concentrations peaked at 7 A.M. (high peak) and 8 P.M. (low peak) at the urban sites. The peaks at the urban sites corresponded to morning-evening rush hours when the NH_3 concentrations can be enhanced by increased emissions from high traffic volume with stop-and-go conditions (Sun et al., 2017; Wang et al., 2016). The evening peaks at the urban site corresponded to the NH_3 residual from the afternoon rush hour given the poorer dispersion conditions due to the lower mixed layer heights and lower wind speeds. Figure S7 shows diel patterns of the distributions for temperature and wind speed at the four monitoring sites with larger day/night variations at the rural sites than the urban sites. This difference is likely

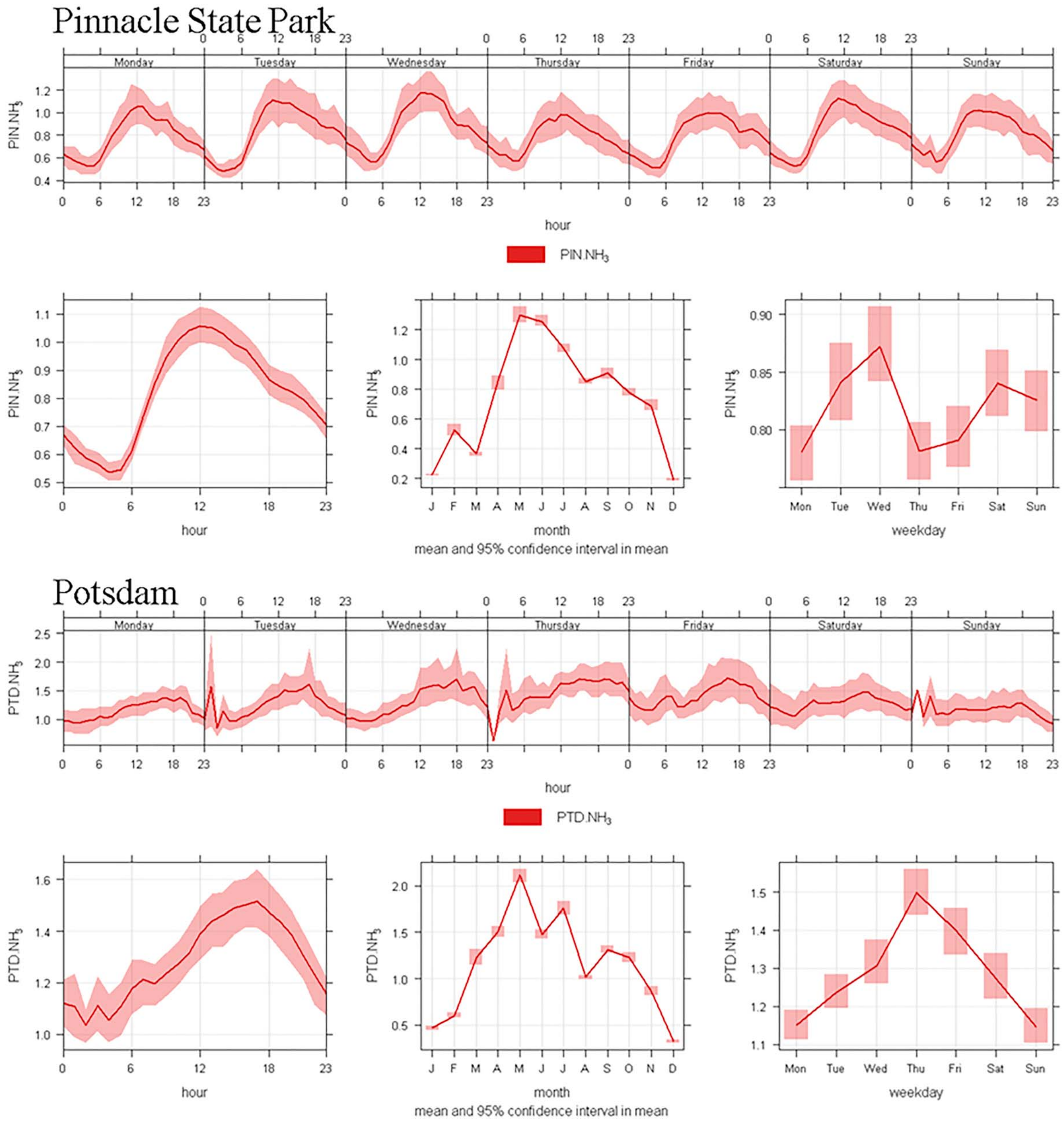

Figure 3. Temporal variations in the NH$_3$ hourly concentrations at the rural sites (Pinnacle State Park and Village of Potsdam). The lines represent mean values and the shaded areas are the 95% confidence intervals.

the result of the urban heat island effect where urban materials retain heat more than rural soils. The diel NH$_3$ patterns were found to be different between weekdays and weekends at the urban sites (Figure 4). On the weekend days, hourly and peak (rush hour) NH$_3$ concentrations were lower than on weekdays in the urban sites, which can be related with reduced NH$_3$ emission from smaller peak traffic volumes on the weekend (McDonald et al., 2014; Wang et al., 2018; Zhu et al., 2015).

NH$_3$ concentrations peaked in mid/late afternoon at the rural sites as shown in Figure 3 due to the increased temperatures in the afternoon. Hourly NH$_3$ concentrations at the rural sites were found to be strongly correlated with the temperature. However, there were no such correlations found for the urban sites. These results suggest that the NH$_3$ concentrations at the rural sites are largely controlled by temperature variations. However, other NH$_3$ sources that are independent of temperature, such as vehicular TWCs and mobile and stationary SCRs, are important at the urban sites.

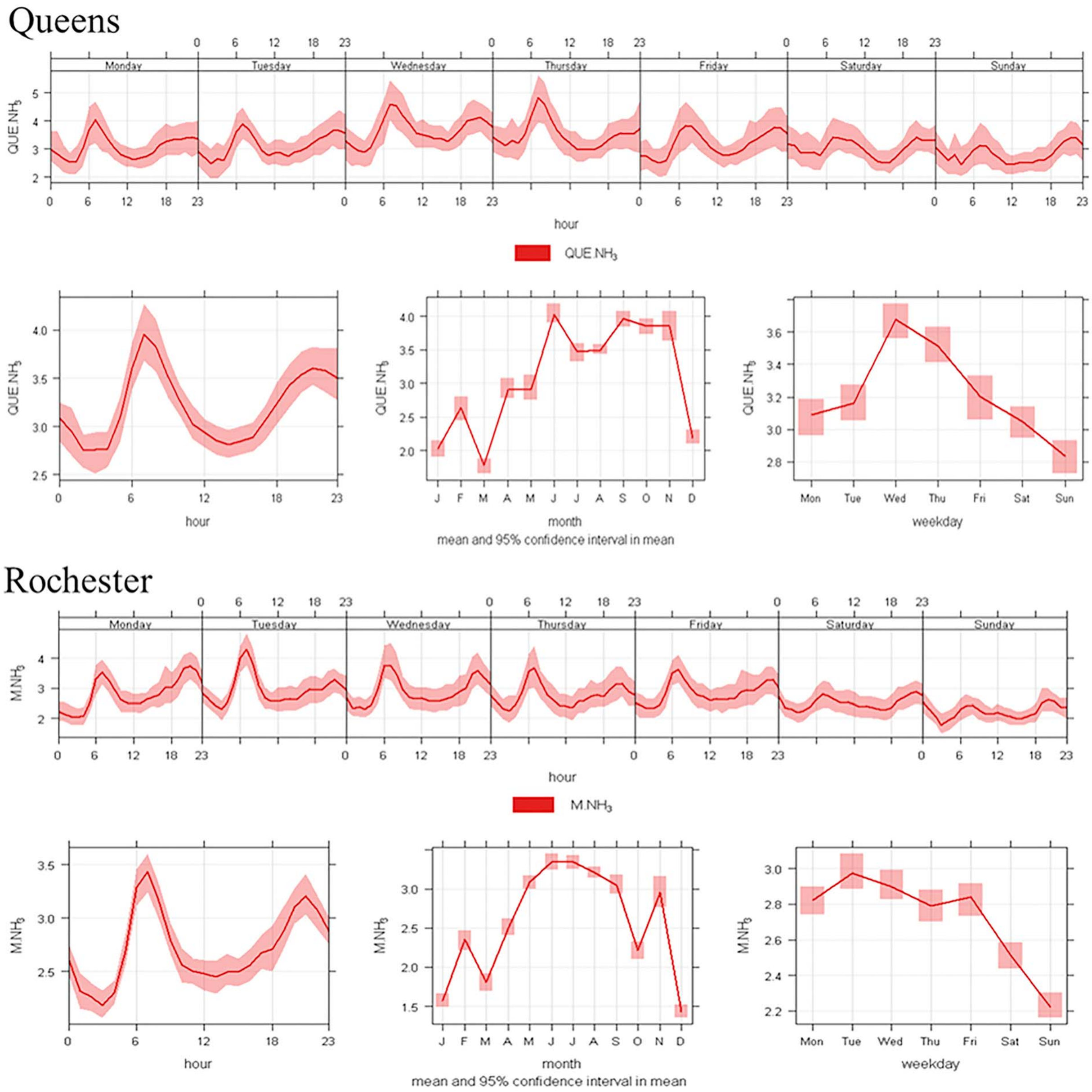

Figure 4. Temporal variations in the NH_3 hourly concentrations at the urban sites (Queens College and City of Rochester). The lines represent mean values and the shaded areas are the 95% confidence intervals.

3.4. Seasonality

Monthly average NH_3 concentrations were positively correlated with temperature for the all sites. These results suggest that the NH_3 concentrations can be enhanced at both in urban and rural sites by higher temperatures that can increase the partitioning of NH_3 from aqueous (or particulate) phase into the gas phase as well as increasing the formation of NH_3 and emission from anaerobic processes in animal manure, soil, and vegetation (Sutton et al., 1993; Zhu et al., 2015). Monthly variations at each site were estimated using a criteria value defined as (maximum month average − minimum month average)/annual average. Criteria values for the four sites are PIN = 1.47, PTD = 1.57, ROC = 0.76, and QUE = 0.72. As previously reported (Felix et al., 2017; Paulot et al., 2014), larger monthly variations were found at the rural sites. At the rural sites, NH_3 emissions were mainly from agricultural activities such as manure spreading, soil emissions, and vegetation that can be impacted by the changing meteorological conditions including temperature, RH, wind speed, and atmospheric dispersion conditions (Asman et al., 1998; Sutton et al., 1993). Thus, the low rural concentrations in winter are NH_3 emissions in urban areas had less seasonality, which can be important to urban PM concentrations in the cold season (Huang et al., 2012; Paulot et al., 2014; Sun et al., 2017). However, there are also decreases in urban ammonia concentrations during the winter months (Figure 4). These decreases are attributed to the formation of particulate ammonium nitrate during the colder months. The ammonium nitrate particles would pass through the citric acid denuder, add to the NO measured in both channels, and, therefore, be subtracted out. There may also be some additional loss of ammonia to precipitation scattering during the winter months.

4. Factors Affecting the Ammonia Concentrations

4.1. Temperature

Higher NH_3 concentrations occurring at higher temperatures have been reported at both urban and rural locations (Bray et al., 2018; Wang et al., 2018). Increased temperature can shift NH_3 from the aqueous (or particulate) phase to the gas phase, and increase NH_3 emissions from animal manure, soil, and vegetation, and thereby increase the ambient NH_3 concentrations (McDonald et al., 2014; Zhu et al., 2015). In addition, biological activity associated with anaerobic digestion that occurs in manure piles or lagoons can also be enhanced by higher temperatures. Consistent results were also found in this project as daily NH_3 concentrations increased exponentially with increasing temperature as shown in Figure 5. Large variations were found at the urban sites for a given temperature. However, the lowest correlation was obtained at PTD likely as a result of the outliers of high NH_3 concentrations in the spring and summer. It is likely that known instances of manure spreading on local farms resulted in some of these elevated values.

4.2. Emissions

4.2.1. In-State Emissions

The NH_3 emissions and emission density in NYS were evaluated for each county based on NEI 2014 (Figure S8) and the in-county emissions for the four monitoring sites are presented in Table 1. A more detailed delineation of the emission sources is provided in Table S1. The ambient NH_3 concentrations in the atmosphere were generally correlated with nearby NH_3 emissions (Tang et al., 2017; Van Zanten et al., 2017). The QUE site that had the highest measured NH_3 concentrations is located in the New York City metropolitan area (Queens County), had the highest population density (Masiol et al., 2017), and had the highest in-county emissions and emission density. Residential heating with natural gas was reported to be the largest source in this county (55.7%) with on-road light duty motor vehicles second (21.2%) and natural gas combustion for electricity generation (12.2%; Table S1; USEPA, 2016). Rochester (Monroe County) is one of the most populated cities in the western NY. The largest source was again reported to be the residential natural gas heating (36.0%) followed by on-road light duty vehicles (21.3%) representing most of the nonagricultural sources (Table S1). However, the attribution of such a high fraction of the local ammonia emissions from residential natural gas combustion emissions is not compatible with either the seasonal or seasonal diel patterns (Figures S4 and S5). There are substantial drops in ammonia concentrations during the winter months. The traffic rush hour pattern remains for QUE and ROC. There is certainly no seasonal rise or increase overnight when residential heating would peak in the winter. Thus, it appears that residential natural gas combustion emissions may be overestimated. The emission factors for residential natural gas combustion were first developed in the 1950s and 1960s.

Using them and a 1976 study (Muzio & Arand, 1976), Cass et al. (1982) developed the emission factor reported by Battye et al. (1994) that was then incorporated in USEPA AP-42 emissions factors (USEPA, 1996) and used in the 2014 NEI analysis (USEPA, 2016). Since the 1970s, natural gas combustion appliances have become much more efficient with current units having efficiencies greater than 98%. Thus, the chemistry of those emissions and the potential for ammonia formation have likely changed significantly. The results presented here do not appear to be consistent with residential combustion of natural gas as the largest source of urban ammonia emissions.

The temporal patterns are more consistent with motor vehicles being the largest source. The QUE site is within 2 km of the Long Island Expressway and the Van Wyck Expressway, two heavily trafficked highways (Venkatachari et al., 2006). The ROC site is located near two interstate and one state highways within 1 km of the site and was affected by NH_3 emissions from the vehicles on these roads as well as the diesel trains that

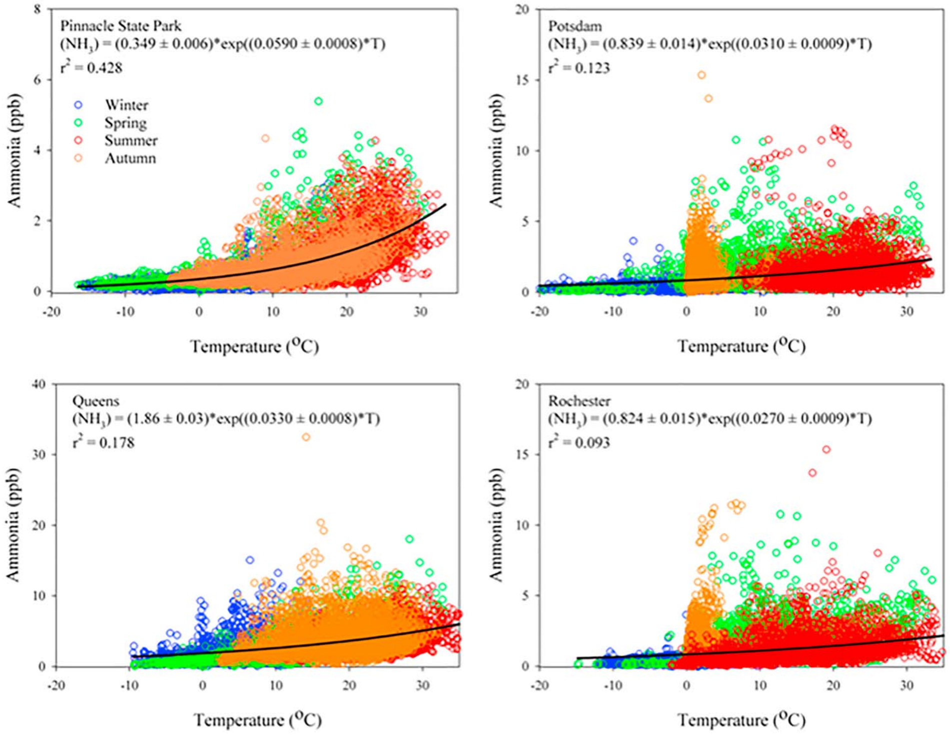

Figure 5. Daily average temperature compared with hourly NH_3 concentrations measured at each of the four sites.

run within 50 m of the monitor (Emami et al., 2018; Zhou et al., 2018). Monroe County had the lowest emission rate of the four counties but had the second highest average ammonia concentrations. These results suggest that the NH_3 concentrations at the ROC site were driven largely by local urban NH_3 sources particularly vehicular traffic. At ROC, traffic appears to dominate even though nonagricultural emissions only contributed 58% of the total reported in-county NH_3 emissions.

Lower NH_3 concentrations were found at the rural sites (PIN and PTD) and can be related to the lower in-county emission densities from the widely dispersed agricultural activities although the total emissions were relatively large (Figure S8). In addition, long-distance transported air parcels with high NH_3 concentrations from out-state NH_3 emission source can enhance the measured NH_3 concentrations for both rural and urban sites as will be discussed below.

4.2.2. Out-of-State Emissions

NH_3 has a relatively short lifetime in the atmosphere (1–5 days or less), although it can remain in the air longer in warm weather as NH_3 can be released from semivolatile NH_4NO_3 particles that have longer lifetimes (1–15 days; Aneja et al., 2000; Kruit et al., 2012; Tang et al., 2017; Vieno et al., 2014). Therefore, only central and eastern U.S. regions were considered as potential sources of out-of-state NH_3 emissions although significant NH_3 was emitted from areas further west (Paulot et al., 2014; USEPA, 2016). Annual NH_3

Table 1
Local NH_3 Emissions and Emissions Densities (County-Based) for the Four Sites Based on NEI 2014

Monitoring site	Counties	Total NH_3 emission (ton/year)	Total NH_3 emission density (ton/year/km^2)	Nonagricultural emission (%)
NYS total		33,337	0.24	63
QUE	Queens	1,101	2.38	99
ROC	Monroe	748	0.21	58
PTD	St. Lawrence	1,027	0.14	1
PIN	Steuben	960	0.26	1

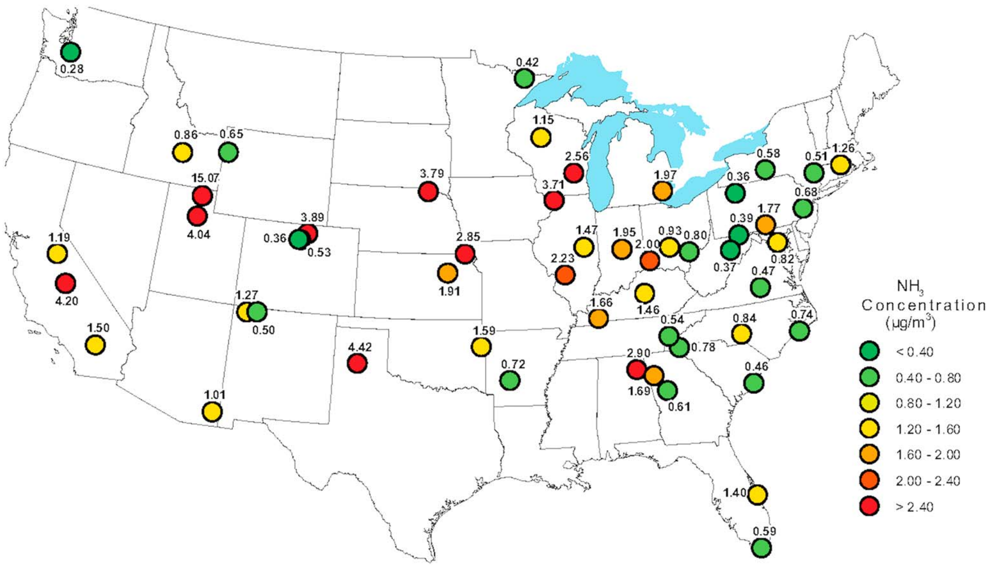

Figure 6. Annual NH_3 emissions in the central and eastern U.S. (divided into five regions with different border color) and AMoN site (presented as circles) concentrations.

emission amounts in the central and eastern United States are presented in Figure 6 along with average NH_3 concentrations from 2016 to 2017 obtained from AMoN. NYS had lower in-state NH_3 emissions compared to the states with major livestock industries such as Iowa and North Carolina. The AMoN sites with high NH_3 concentrations (>2.0 ppb) were all located outside of NYS. Therefore, long-distance transported NH_3 from these states can potentially affect NH_3 concentrations in NYS given the prevailing southwest to northwest wind directions.

4.2.3. Emissions Seasonality

Ambient NH_3 concentrations can be affected by the seasonality of the NH_3 emissions. In particular, agricultural NH_3 emissions are reported to have high seasonal variability and usually peak in spring or summer due to increased fertilizer application and/or manure handling activities (Sigurdarson et al., 2018). Monthly NH_3 emissions were estimated for five regions of central and eastern United States using the annual NH_3 emissions amount (NEI 2014) and monthly variations estimated for the five regions based on a previous study (Krupa & Moncrief, 2002; Paulot et al., 2014). The divisions of the five regions are shown in Figure 6: upper Midwest (Michigan, Minnesota, and Wisconsin), Midwest (Iowa, Illinois, Indiana, Kentucky, Missouri, Ohio, and West Virginia), Southeast (Alabama, Arkansas, Georgia, Mississippi, and Tennessee), Northeast (Connecticut, Maine, Massachusetts, New Hampshire, and Vermont), Atlantic (Delaware, Maryland, New Jersey, Pennsylvania, North Carolina, South Carolina, and Virginia), and local (New York). The monthly NH_3 emissions at the national and regional scales for different types of NH_3 source are shown in Figure S9. Livestock contributes most of the NH_3 emissions nationally and in the Northeast region. Emissions are low in winter, peaked in May, and remained at relatively high levels in summer and autumn due to manure processing (Paulot et al., 2014). NH_3 emissions from fertilizer application also peaked in May. However, emissions rapidly decreased in summer and autumn. The NH_3 emissions from livestock and fertilizer had high seasonal variations whereas low seasonal variations were reported for other NH_3 emission types, such as fuel combustion and vehicle emissions.

To evaluate the contributions of regional/local NH_3 emissions to NYS ambient NH_3 concentrations, nonnegative multivariable regressions were calculated for the monthly NH_3 emissions and the monthly average NH_3 concentrations. This equation can be written as

$$\text{Conc.}(\text{NH}_3) = \text{a} + \sum b_i (\,Regional\ \ Emission)_i \tag{2}$$

where a is the contribution coefficient of local emissions, such as vehicles and stationery SCR, and b_i is the contribution coefficient of emissions from region i, with a and b_i forced to be nonnegative since negative

Table 2
Nonnegative Regression Results for the NH_3 Concentrations at the Four Sites

Site	Midwest	Upper Midwest	Northeast	Atlantic	Southeast	Local	r^2
PIN	0.000331	0.0138	0.291	0.00	0.00	0.00	0.76
PTD	0.00	0.0196	0.00	0.0296	0.00	0.00	0.60
ROC	0.00	0.00	0.837	0.00	0.00	1.31	0.42
QUE	0.00	0.00	0.703	0.00	0.00	2.00	0.30

contributions are not physically possible. The contribution coefficient cannot be estimated when the emissions were not positively correlated to the NH_3 concentrations.

The regression results presented in Table 2 indicate that NH_3 emissions from the Northeast region were important (contribution coefficients >0) to all four sites indicating significant impacts from in-state emission to NH_3 concentrations at the four monitoring sites. The contribution coefficients of local emissions (a) were only found to be important at the urban sites (ROC and QUE). These values were much larger than contribution coefficients of the Northeast region suggesting that local emissions dominated the ambient urban NH_3 concentrations. The out-of-state NH_3 emissions from the Upper Midwest and Atlantic were also found to be important for the rural sites (PIN and PTD) implying the long-distance transported NH_3 can be more important to the rural sites as they had lower NH_3 concentrations. Note that more analyses are needed to confirm the contributions of out-state emissions to rural sites as the increasing similarity (correlation) of agricultural activities between NYS and other states can also increase these contribution coefficients. Therefore, the likely source locations from out-state emissions should be identified using SQTBA and will be discussed below.

4.3. Ammonia Source Locations

4.3.1. Local Source Directions

The local NH_3 seasonal patterns for the four monitoring sites were characterized using CBPF as shown in Figures 7 for PTD and 8 for ROC. The plots for PIN and QUE are presented in Figures S10 and S11. The corresponding seasonal wind roses for these sites are also presented in these figures. At the rural sites (PIN and PTD), high CBPF regions were mainly associated with higher wind speeds (Figures 7 and S10). These results suggest that advection from source areas increased the ambient NH_3 concentrations. The PTD site (Figure 7) was likely to have been affected by the NH_3 emitted from dairy farms surrounding the site. The PTD patterns appear to be largely driven by the prevailing wind directions. There is an enhancement of the northeasterly probabilities in the summer compared to the spring values, but the reasons for the shift in direction are not known. The concentrations diminish in autumn with the decreasing temperatures and become very small during the cold winters.

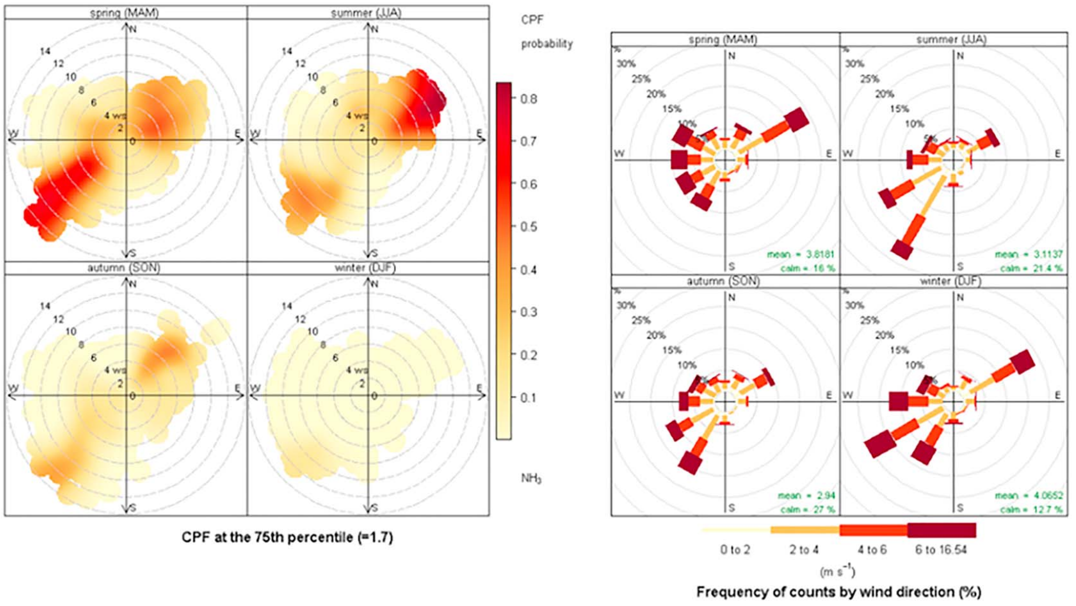

Figure 7. Seasonal conditional bivariate probability function results for Potsdam.

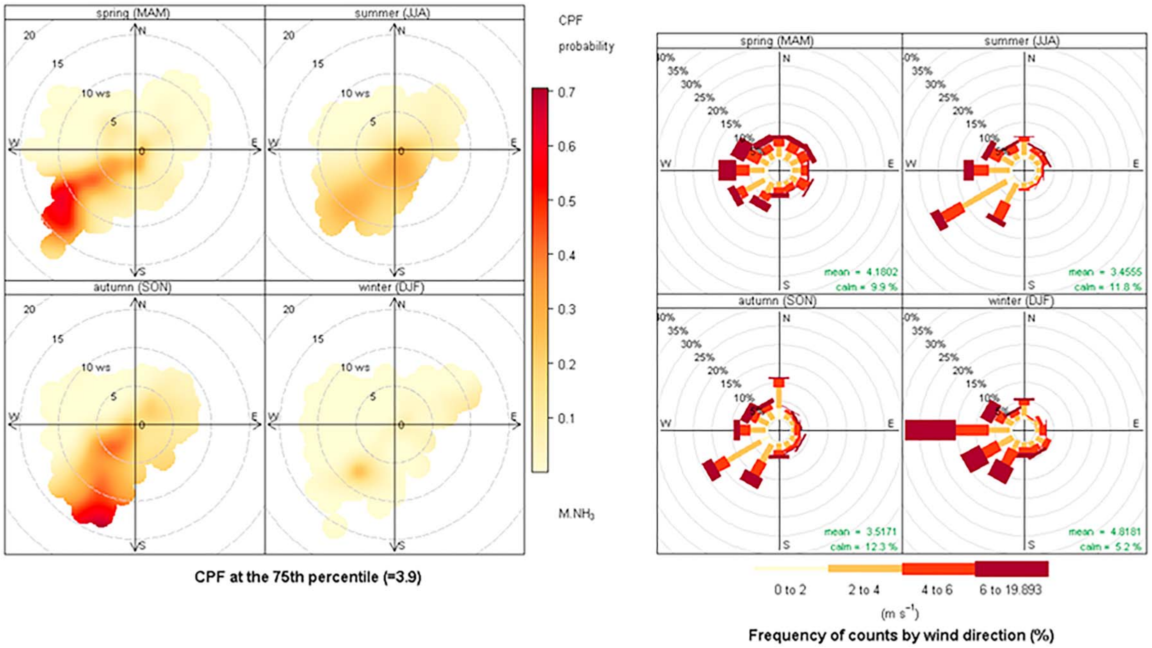

Figure 8. Seasonal conditional bivariate probability function results for Rochester.

The PIN site in the summer when temperatures are highest and agricultural activity peaks also had CBPF values driven by the prevailing winds from the southwest. However, in spring, autumn, and winter, the highest probabilities were toward the south and southeast even though these wind directions had low frequencies (Figure S10). This site was likely impacted by the NH_3 emitted from the trucking related with the hydraulic fracturing industry in Pennsylvania. Squizzato et al. (2018b) reported an anomalously high contribution of diesel PM in the same directions as the Pinnacle site in their analysis of composition data. The locations of the fracking sites can be seen in Figure S65 in the supplementary material for Squizzato et al. (2018b). Thus, areas further east of the PIN site could be expected to have enhanced concentrations arising from the fracking area emissions.

At the urban sites (ROC and QUE), high CBPF regions were mainly observed at low to moderate wind speeds suggesting the dominance of local NH_3 sources (Figures 8 and S10). The ROC site had a high CBPF zone to the southwest of the site probably due to the vehicular emissions from interstate and state highways combined with the prevailing wind directions. The QSC site is very close to the Long Island Expressway and at low wind, vehicular emission likely had a high impact. There is a high summer CBPF area to the west of the site that may be related with NH_3 emission from the Ravenswood generating station (largest point NH_3 emission source in Queens [Table S1] and located to the west of the site). This station is used mainly for meeting peak electricity demands in the summer.

4.3.2. Source Locations of Transported NH_3

The likely distant NH_3 source locations were identified with SQTBA for the four sites for the four seasons as shown in Figures 9 (rural sites) and S11 (urban sites). The areas with higher SQTBA values (presented as red) on the maps indicate higher potential as likely NH_3 source locations. The AMoN sites with relatively high NH_3 concentrations (>2.9 ppb) in the corresponding periods (April 2016 to November 2017) were also marked on the maps (circles). As shown in the figures, the AMoN sites in the likely NH_3 source locations identified by SQTBA had relatively high NH_3 concentrations suggesting that SQTBA model results represent these emissions and it is reasonable to accept the identified likely NH_3 source locations.

For the rural sites (Figure 9), the northeastern and midwestern regions of the United States were identified as likely NH_3 source locations for the spring and summer seasons likely as a result of fertilizer application, livestock, and active soil emissions. Pennsylvania was also determined as likely NH_3 source locations for the rural sites supporting the CBPF results. Likely source locations for the rural sites found in Quebec for the spring and summer periods suggest potential NH_3 emissions from boreal forest fires (Begum et al., 2005;

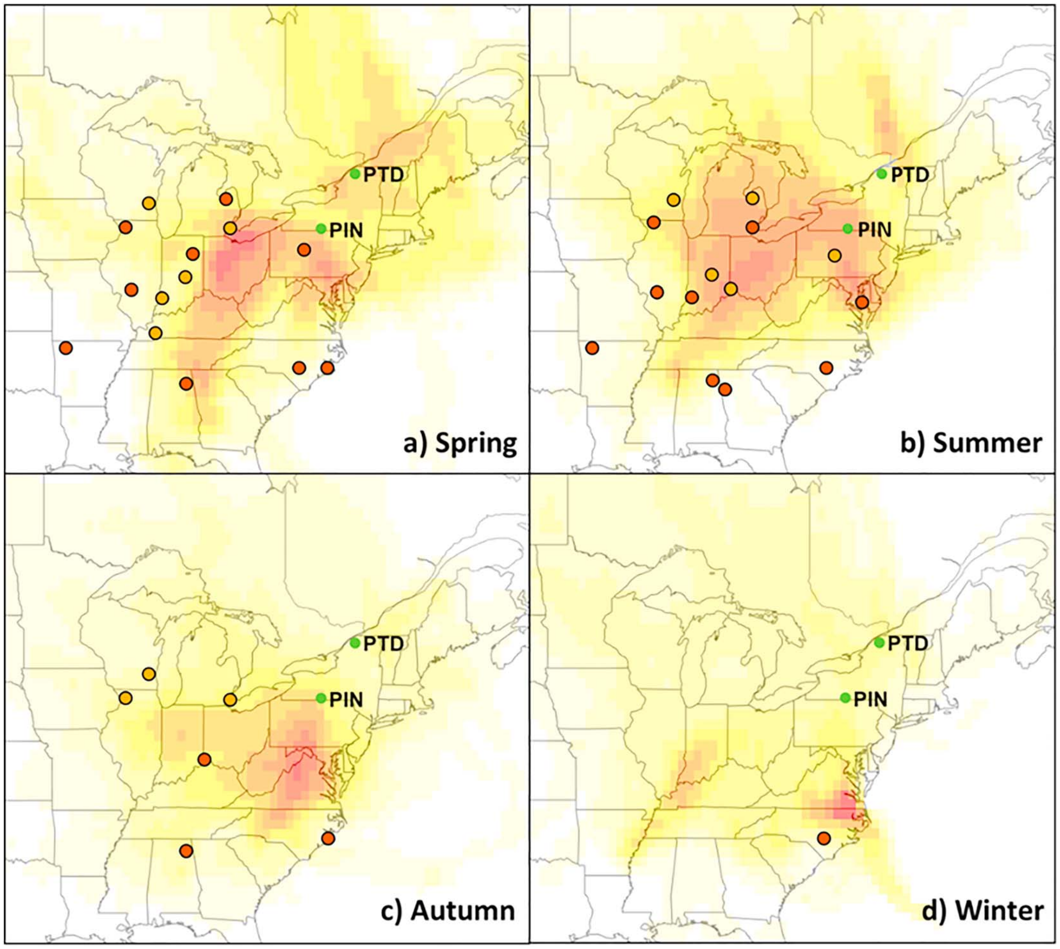

Figure 9. Simplified quantitative transport bias analysis results of different seasons for rural sites (PIN and PTD). The circles displayed on maps show the Ammonia Monitoring Network sites with relatively high NH_3 concentrations (>2.9 ppb) during the same periods. PIN = Pinnacle State Park; PTD = Village of Potsdam.

Wang et al., 2010). There could also be contributions from the agricultural activities in the St. Lawrence River Valley. The Mid-Atlantic coast region was identified as a likely source area throughout the year and appears more notable in autumn and winter. NH_3 can form in these estuarine areas in the coastal plain in anoxic sediments and soils. There are substantial concentrated animal feeding operations in the Delmarva peninsula and in North Carolina, but NH_3 emission from livestock in winter is relatively small (Wu, Hu, et al., 2008; Wu, Krishnan, et al., 2008), and transport to the rural sites from these concentrated animal feeding operation areas is relatively weak.

For the urban sites (Figure S12), the calculated SQTBA values were lower than rural sites (lighter color) suggested that the transported NH_3 was less important at the urban sites due to the significant local emissions, such as vehicle emissions, stationary source SCRs, and from domestic waste processing (Nevalainen et al., 2018; Thiruvengadam et al., 2016). The midwestern region of the United States was a likely NH_3 source area for spring, summer, and autumn, and eastern Pennsylvania and Maryland were important to the spring and summer values. These regions may represent emissions from the Chesapeake Bay estuarine areas. No significant distant source locations were determined for winter.

The SQTBA results for the combined four sites are displayed by season in Figure S13. These results are very similar to those obtained for the urban sites (Figure S12) since they represent all of the high NH_3 concentration values. However, it is clear that the high urban values are driven by local sources so that the trajectory ensemble methods are strongly biased by the significant differences in the concentration distributions between the two site types. Thus, Figure 9 better reflects the influence of transported ammonia for NYS.

5. Conclusions

Ambient NH_3 concentrations were measured at the four sites, PIN, PTD, ROC, and QUE, in NYS from April 2016 to November 2017 using both active and passive monitoring systems. The NH_3 concentrations measured using the active systems were found to be comparable with those measured using the passive system that were analyzed and quality controlled by the national AMoN program but the active system measured 6.2% higher NH_3 concentrations. The urban sites (QUE and ROC) had higher NH_3 concentrations than the rural sites emphasizing the importance of local sources such as traffic and population centers. There were distinctly different diel and somewhat different seasonal patterns between the urban and rural sites. Diel variations at the rural sites coincided with typical traffic patterns, while at the rural sites, concentrations tracked ambient temperature changes. Seasonal patterns were weaker at the urban sites and appeared to depend more on changes in the dispersion conditions.

These results suggest that the urban NH_3 emissions, mainly from vehicles and stationary SCRs, have impacts on urban NH_3 concentrations and resulting urban particulate air pollution even though agricultural NH_3 emissions dominated the total NYS NH_3 emissions. It appears that the ammonia emission factor for residential combustion of natural gas may overestimate those emissions given the changes in the efficiency of these heating appliances. Further efforts need to be made in reducing urban NH_3 emissions to further reduce the particulate air pollution at the urban areas. There were stronger seasonal patterns in the rural site concentrations driven by the agricultural activities in the region. However, an additional source of NH_3 at the Pinnacle site was likely the high level of hydraulic fracturing activity in neighboring Pennsylvania. The rural sites were also more strongly affected by regional transport of ammonia into NYS.

Data Availability

The data obtained in this study are available at http://pireds.asrc.cestm.albany.edu:3000/.

Acknowledgments
This study was supported by the New York State Energy Research and Development Authority (NYSERDA) under agreement Grant 59813. The work could not have been completed without the extensive assistance of URG, Inc., Chapel Hill, NC. We would like to thank David Chalupa of the Department of Environmental Medicine of the University of Rochester School of Medicine and Dentistry in maintaining the monitoring system in Rochester and the staff of the New York State Department of Environmental Conservation for the operation of the monitors at the QUE and ROC sites.

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