Trends in atmospheric ammonia at urban, rural, and remote sites across North America

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Abstract. Interannual variabilities in atmospheric ammonia (NH\(_3\)) during the most recent 7–11 years were investigated at 14 sites across North America using the monitored data obtained from NAPS, CAPMoN and AMoN networks. The long-term average of atmospheric NH\(_3\) ranged from 0.8 to 2.6 ppb, depending on location, at four urban and two rural/agricultural sites in Canada. The annual average at these sites did not show any deceasing trend with largely decreasing anthropogenic NH\(_3\) emission. An increasing trend was actually identified from 2003 to 2014 at the downtown Toronto site using either the Mann–Kendall or the ensemble empirical mode decomposition method, but “no” or “stable” trends were identified at other sites. The ∼20% increase during the 11-year period at the site was likely caused by changes in NH\(_4^+\)–NH\(_3\) partitioning and/or air–surface exchange process as a result of the decreased sulfur emission and increased ambient temperature. The long-term average from 2008 to 2015 was 1.6–4.9 ppb and 0.3–0.5 ppb at four rural/agricultural and at four remote US sites, respectively. A stable trend in NH\(_3\) mixing ratio was identified at one rural/agricultural site while increasing trends were identified at three rural/agricultural (0.6–2.6 ppb, 20–50% increase from 2008 to 2015) and four remote sites (0.3–0.5 ppb, 100–200% increase from 2008 to 2015). Increased ambient temperature was identified to be a cause for the increasing trends in NH\(_3\) mixing ratio at four out of the seven US sites, but what caused the increasing trends at other US sites needs further investigation.

1 Introduction

Atmospheric ammonia (NH\(_3\)) plays an important role in formation of ammonium sulfate and nitrate aerosols in the size range of nanometer to supermicron (Yao et al., 2007; Kulmala et al., 2004; Ianniello et al., 2011; Yao and Zhang, 2012; Schiferl et al., 2014; Paulot and Jacob, 2014). The sum of sulfate, nitrate, and ammonium ions (NH\(_4^+\)) usually consists of the major portion of PM\(_{2.5}\) across Canada and the United States (Dabek-Zlotorzynska et al., 2011; Hand et al., 2012). With significant decreases in acidic gas emissions in the last decades across North America (e.g., emissions of SO\(_2\) and NO\(_x\) in Canada decreased from 2.28 × 10\(^6\) and 2.72 × 10\(^6\) t year\(^{-1}\) in 2003 to 1.23 × 10\(^6\) and 2.06 × 10\(^6\) t year\(^{-1}\) in 2013, respectively (http://www.ec.gc.ca/inrp-npri/donnees-data/ap/index.cfm?lang=En)), more attention is being paid to the relationship between NH\(_3\) and NH\(_4^+\) aerosols (Zhang et al., 2010; Day et al., 2012; Nowak et al., 2012; Yao and Zhang, 2012; Schiferl et al., 2014; Paulot and Jacob, 2014). NH\(_3\) mixing ratios are affected by several factors such as NH\(_3\) emissions, NH\(_3\)–NH\(_4^+\) partitioning, and meteorological conditions (Sutton et al., 2009; Yao and Zhang, 2013; Hu et al., 2014). In Europe, previous studies showed that the long-term trend in atmospheric NH\(_3\) observed in some countries did not reflect the dramatic decrease in NH\(_3\) emissions and the phenomenon was referred to as “ammonia gap” (Sutton et al., 2009; Ferm and Hellsten, 2012; Sintermann et al., 2012). Long-term trends in atmospheric NH\(_3\) across North America are poorly understood (Zbieranowski and Aherne, 2011; Hu et al., 2014; Van Damme et al., 2014).
Such knowledge is important for accurate prediction of ammonium sulfate and nitrate aerosol levels in the future (Pye et al., 2009; Walker et al., 2012). In North America, established anthropogenic NH$_3$ emission inventories showed that agricultural emissions accounted for over 80% of the total anthropogenic NH$_3$ emissions (Lillyman et al., 2009; Behera et al., 2013; Xing et al., 2013). However, agricultural emission sources only affect mixing ratios of atmospheric NH$_3$ at short downwind distances (Theobald et al., 2012; Yao and Zhang, 2013). Non-agricultural emissions such as those from local traffic, waste containers, and soil and vegetation were reported to be important contributors to NH$_3$ in urban atmospheres (Whitehead et al., 2007; Ellis et al., 2011; Reche et al., 2012; Sutton et al., 2013; Yao et al., 2013; Hu et al., 2014), although these sources only accounted for a few percentage of the total NH$_3$ emissions in Canada and the United States. Due to new technology adopted, traffic-derived NH$_3$ decreased gradually (Bishop et al., 2010; http://www.ec.gc.ca/inrp-npri/donnees-data/ap/index.cfm?lang=En). Yao et al. (2013) and Hu et al. (2014) recently reported that traffic-derived NH$_3$ was a negligible contributor to atmospheric NH$_3$ in Toronto. However, under climate warming, soil and vegetation NH$_3$ emissions are expected to increase accordingly. For example, NH$_3$ volatilization potential nearly doubles under every 5°C increase (Pinder et al., 2012; Sutton et al., 2013; Fowler et al., 2015).

Atmospheric NH$_3$ and ammonium sulfate and nitrate aerosols can be transported downwind and eventually deposited to natural ecosystems to enhance carbon fixation (Krupa, 2003; Beem et al., 2010; Walker et al., 2012). Excessive NH$_3$ deposition may cause adverse effects such as reduced biodiversity and eutrophication (Krupa, 2003; Erisman et al., 2007; Beem et al., 2010; Bobbink et al., 2010; Pinder et al., 2012). Recent evidence shows changes in species composition for sensitive vegetation types at the annual average concentration of 1µg m$^{-3}$ NH$_3$ (Cape et al., 2009). Climate warming may increase the vulnerability of ecosystems towards exposure to NH$_3$ (Pinder et al., 2012). Thus, trend analysis of atmospheric NH$_3$ at remote sites will help to better understand its potential impacts on sensitive natural ecosystems.

In this paper, interannual variabilities in atmospheric NH$_3$ at 14 sites across Canada and the United States were investigated, with particular attention paid to its long-term trends and causes. The 14 sites include 4 urban sites, 4 remote sites and 6 rural/agricultural sites distributed at different latitudes. Two trend analysis tools, i.e., the Mann–Kendall (M–K) analysis (Gilbert, 1987) and the ensemble empirical mode decomposition (EEMD, Wu and Huang, 2009), were used to resolve the time series of atmospheric NH$_3$ in mixing ratio at these sites. The analysis results provided new light on the long-term trends in atmospheric NH$_3$ at various sites across North America.

2 Methodology

2.1 Data sources of atmospheric NH$_3$

In this study, mixing ratios of atmospheric NH$_3$ generated at monthly interval were compiled from three data sources, i.e., the Canadian National Air Pollution Surveillance (NAPS, http://www.ec.gc.ca/rnspa-naps/) network, the Canadian Air and Precipitation Monitoring Network (CAPMoN; http://www.ec.gc.ca/natchem/default.asp?lang=En&n=90EDB4BC-1), and the US Passive Ammonia Monitoring Network (AMoN, http://nadp.sws.uiuc.edu/AMoN). Missing data are a common problem during long-term observations. The sites chosen in this study were based on data availabilities as detailed below.

The NAPS network provides accurate and long-term air quality data across Canada. At each site, a Partisol Model 2300 sequential speciation sampler (Thermo Scientific) equipped with dry denuders is used to measure concentrations of NH$_3$ and acidic gases and particulate chemical components such as pNH$_4^+$ and pNO$_3^-$ in PM$_{2.5}$. The sampler maintains a constant flow rate of 10 L min$^{-1}$ and operates for a 24 h duration on every third day. The 24 h integrated denuder and filter samples were carried back to the lab where they were extracted and analyzed by ion chromatography (Dabek-Zlotorynska et al., 2011). At a few sites, technical problems resulted in NH$_3$ and pNH$_4^+$ concentration data missing for several months. At four urban sampling sites and one rural/agricultural site (Fig. 1), the measurements allowed obtaining continuous time series of monthly averaged concentrations of atmospheric NH$_3$ and pNH$_4^+$ and were thereby used for trend analysis. However, these sites also suffer from the problem of missing data. For example, there were only 70–90% months when 8–10 sets of 24 h data were available to calculate the monthly average value (Fig. S1 in the Supplement). This may cause uncertainty on the calculated trends in atmospheric NH$_3$ and pNH$_4^+$. Moreover, one site at Egbert in the southern Ontario (Fig. 1), the part of CAPMoN, also had the long-term measurement concentrations of atmospheric NH$_3$ and pNH$_4^+$ using the identical sampler as used in the NAPS network. The site is located in a rural/agricultural area. The data were also averaged monthly for the trend analysis. The six Canadian sites were referred to as Sites 1–6 on the basis of their annual average mixing ratios of atmospheric NH$_3$ in decreasing order.

The AMoN within the National Atmospheric Deposition Program in the United States started operation in fall 2007. An important objective of AMoN is to assess long-term trends in NH$_3$ concentrations and its deposition. AMoN included only 16 sites in 2007, and dozens of sites are now available. The Radiello® passive samplers are deployed every 2 weeks at each site according to the standard operating procedure for monitoring atmospheric NH$_3$. Puchalski et al. (2015) recently compared the bi-weekly passive measurements with those measured by annular denuder systems.
(ADSs) at several AMoN sites and found that the mean relative percentage difference between the ADS and AMoN sampler was ~9%. In this study, mixing ratios of atmospheric NH$_3$ at eight AMoN sites were selected for the trend analysis on the basis of two criteria (Fig. 1): (1) the length of the valid data should be at least 7 years according to Walker et al. (2000), and (2) there were no monthly average data missing each year. The eight sites were referred to as Sites 7–14 (Fig. 1), four of which were located in rural areas and another four in remote areas. Consistent with the six sites across Canada, the monthly averages at the eight sites were used for data analysis if not specified. Moreover, all ambient temperature ($T$) data were obtained from on-site records or nearby meteorological stations.

### 2.2 Statistical methods

The M–K analysis is a non-parametric statistical procedure which can be used to analyze trends in data sets including irregular sampling intervals, data below the detection limit, and trace or missing data (Kampata et al., 2008). Considering that the data flaws aforementioned were indeed present in our selected data sets to a certain extent, the M–K analysis is thereby used to resolve the time series of the annual average of NH$_3$ in this study. According to the analysis, the time series of $n$ data points and $T_i$ and $T_j$ as two subsets of data where $i = 1, 2, 3, \ldots n−1$ and $j = i+1, i+2, i+3, \ldots n$ are considered. The series of data is used to calculate $S''$ statistic, confidence factor and coefficient of variation. The calculated values were further used to test the null hypothesis $H_0$ assuming that there is no trend and the alternative hypothesis $H_1$ assuming that there is a trend, yielding qualitative trend results such as “increasing/decreasing”, “probable increasing/decreasing”, “stable”, and “no trend” (Gilbert, 1987). Moreover, the EEMD is a recently developed statistical tool to determine the trend of a time series of a variable in various fields such as economics, health, environment, and climate (Wu and Huang, 2009). The EEMD built on Empirical Mode Decomposition (EMD) and was updated by Wu and Huang (2009) to overcome the problem of mode mixing in the EMD. The method has since been applied widely (e.g., Erturk et al., 2013; Ren et al., 2014) because it is most suitable for resolving non-stationary and non-linear signals. The mixing ratio of atmospheric NH$_3$ was affected not only by its emissions, atmospheric transport, dilution, and deposition but also by non-stationary and non-linear chemical reactions (Ianniello et al., 2011; Hu et al., 2014). Thus, the EEMD is also used in this study and is briefly introduced here.

In general, all data are amalgamations of signal and noise as shown below:

$$X(t) = S(t) + N(t),$$

where $X(t)$ is the record data, and $S(t)$ and $N(t)$ are the true signal and noise, respectively. In the EMD, any data set is assumed to consist of different simple intrinsic modes of oscillations. Each of these intrinsic oscillatory modes is represented by an intrinsic mode function (IMF). In the EEMD, white noise is added to the single data set, $X(t)$, and the ensemble mean is used to improve accuracy of measurements.

### 3 Results and discussion

#### 3.1 Temporal variations of atmospheric NH$_3$ at the six Canadian sites

Figure 2 shows monthly variations of atmospheric NH$_3$ in mixing ratio at the six Canadian sites. At Site 1, an urban site in downtown Toronto, the measured mixing ratios were 2.6 ± 1.2 ppb (average ± standard deviation) during the period from July 2003 to June 2014 (Fig. 2a and Table 1). When compared with those reported in other urban atmospheres, the long-term average value of 2.6 ppb ranked at a moderately low concentration level (Whitehead et al., 2007; Saylor et al., 2010; Alebic-Juretic, 2008; Meng et al., 2011). Inter-annual variations were evident at Site 1 with the coefficient of variation (CV) of 0.11, defined as the ratio of the standard deviation to the average. It should be noted that the annual averages in 2004 and 2005 were calculated from July 2003 to June 2004 and from July 2004 to June 2005, respectively, instead of a calendar year, in order to obtain the longest time series of annual averages. The similar calculations were used for other years and other sites. The M–K analysis result suggested an increasing trend from 2004 to 2014 with a confidence level of 98%. When intra-annual variations were analyzed at Site 1, a distinctive seasonal trend was obtained with the highest seasonal average value of 3.7 ± 0.7 ppb in summer (June to August) and the lowest of 1.3 ± 0.6 in winter (December to the next February).

The M–K analysis results showed either “no” or “stable” trends in atmospheric NH$_3$ at the other Canadian sites with long-term average of 2.4 ± 0.6 ppb at Site 2, 2.1 ± 1.2 ppb at Site 3, 1.9 ± 0.8 ppb at Site 4, 1.6 ± 0.5 ppb at Site 5, and...
0.8 ± 0.6 ppb at Site 6 (Fig. 2b–f). However, interannual variations at these sites were evident. For example, the CV values calculated from annual averages varied from 0.07 to 0.19, depending on location (Table 1). Atmospheric NH$_3$ at Sites 3, 4, and 6 exhibited a distinctive seasonal variation, but this was not the case at Sites 2 and 5. The largest seasonal variation occurred at Site 3 while the smallest occurred at Site 2. The two sites were selected as examples for further discussion below.

Site 3 is situated in a rural/agricultural area in Saint-Anicet of Québec. The largest seasonal average value occurred in the fall during the measurement period of September 2003–August 2014. Fertilizer application in the late fall (mid- to late October) is very common in Canada (Lillyman et al., 2009). Fertilizer is applied at the time when the turf has stopped growing but is still green. Such a practice can ensure early growing in the following spring. With the late-fall fertilizer application, spring fertilization can be postponed until late May to early June. The fertilizer application usually leads to a sharp increase in atmospheric NH$_3$ mixing ratio (Lillyman et al., 2009; Yao and Zhang, 2013), and this was indeed observed at Site 3. For example, there was usually one 24 h sample in October having a mixing ratio 1–2 orders of magnitude higher than other samples collected before or after. The on-site sampling was performed every third day, and strong NH$_3$ emissions associated with fertilization application generally occurred within the initial 3–5 days (Lillyman et al., 2009). Thus, extremely high mixing ratios could be observed on one day in October some years but not every year. The episodes further led to large interannual variations with the value of CV reached 0.19.

Site 2 is located in an urban area in Edmonton. Mixing ratios of atmospheric NH$_3$ were 2.4 ± 0.6 ppb, and the differences between seasonal average values were only 0.1–0.3 ppb during the period of May 2006–April 2014. However, the seasonal average temperature of 16.7 ± 1.9 °C in summer was much higher than that of −19.8 ± 4.5 °C in winter. The small seasonal variations in NH$_3$ mixing ratio at this site were caused by two contrasting factors in winter season. On the one hand, extremely low temperature limited soil and vegetation NH$_3$ emissions to a level close to negligible (Zhang et al., 2010), as was also seen at Site 1 at ambient temperature less than −9 °C (Hu et al., 2014). On the other hand, NH$_3$ emissions from industrial and/or non-industrial anthropogenic sources seemed to be enhanced in winter (Lillyman et al., 2009; Behera et al., 2013), as was supported by the 2–4 times higher mixing ratios of SO$_2$, HONO, and HNO$_3$ in winter than in summer.

### 3.2 Temporal variations of atmospheric NH$_3$ at the eight American sites

For the eight AMoN sites in the United States, the data measured from August 2008 to July 2015 were used for analysis at all the sites except at Site 12 for which the data measured during the period of September 2008–August 2015 were used (Fig. 3 and Table 1). Site 7 is located at an intensive agricultural activity zone in Randall, Texas, and Sites 8–10 are located in rural areas in Dodge, Wisconsin; Wayne, Michigan;
and Champaign, Illinois; respectively, with moderately intensive agricultural activities. Long-term average of NH$_3$ was as high as 4.9 ± 1.2 ppb at Site 7 where the seasonal average in summer was approximately 20% higher than those in the other seasons. The M–K analysis result showed an increasing trend at this site with a confidence level of 99.9%. Long-term averages of NH$_3$ at Sites 8–10 were 2.6 ± 1.4, 2.2 ± 1.0, and 1.6 ± 1.0 ppb, respectively, and distinctive seasonal variations were seen at the three sites with the lowest values in winter. The M–K analysis results showed an increasing trend at Sites 9–10 with a confidence level of >98% and no trend at Site 8.

Sites 11–14 are located in the remote areas in Tompkins, New York; Minnesota Lake, Minnesota; Charleston, South Carolina; and Rio Arriba, New Mexico, respectively. The long-term average NH$_3$ was only 0.3–0.5 ppb at these four remote sites but with distinctive seasonal variations with the highest in summer and the lowest in winter (Table 1). The M–K analysis results showed an increasing trend at the four sites with a confidence level of >95%.

### 3.3 Exponential correlations between NH$_3$ and $T$

When local soil and vegetation emissions were the major contributors to atmospheric NH$_3$, its mixing ratio usually exhibited an exponential function of ambient $T$ (Sutton et al., 2009; Flechard et al., 2013; Hu et al., 2014). Thus, the exponential correlation relationship was examined at the 14 sites to identify potential major contributors to atmospheric NH$_3$. Note that a perfect exponential correlation with $R^2$ > 0.9 would occur only when the soil–air mass transfer of NH$_3$ was not the limitation factor (Flechard et al., 2013; Hu et al., 2014), and soil–air mass transfer rate associated with dry soil was much smaller (Su et al., 2011).

A moderately good exponential correlation was obtained at Site 1 with $R^2 = 0.74$ and $P$ value < 0.01 (Fig. S2a). NH$_3$ emissions from green space surrounding this site likely played a major role in the observed NH$_3$ level (Hu et al., 2014). Similar results were obtained at Sites 3, 4, and 6 when a few exterior data points were excluded. For example, five data points at Site 3 severely deviate from the regression curve because of fertilizer application (Fig. S2c). When these five data points were excluded, $R^2$ reached 0.60 and $P$ value < 0.01. In addition, $R^2$ was 0.75 at the rural Site 6 when one outlier data point was excluded (Fig. S2f). The two parameters in the regression equation [NH$_3$] = 0.24 × exp(0.994 × $T$) were largely different from those obtained at the two downtown sites, i.e., [NH$_3$] = 1.48 × exp(0.048 × $T$) at Site 1 and [NH$_3$] = 1.29 × exp(0.036 × $T$) at Site 4, noting that the parameters were close between the two downtown sites. Under the condition of $T$ below or close to 0°C, the mixing ratios of atmospheric NH$_3$ at the rural Site 6 were almost 1 order of magnitude smaller than those at the downtown sites, leading to the large difference for parameters in regression equations between the rural and urban sites. The
higher mixing ratio under freezing conditions at the Toronto downtown site was proposed to be likely associated with NH$_3$ emissions from green space (Hu et al., 2014). Flechard et al. (2013) also reported higher NH$_3$ mixing ratios over a grassland under freezing conditions, which could be due to slower dry deposition process and/or shallow boundary layer.

At Site 2, the exponential correlation was poor even with two outlier samples being excluded (Fig. S2b), implying that local soil and vegetation emissions were less likely the major contributors to atmospheric NH$_3$. Like Site 2, $R^2$ was only 0.39 at Site 5 even with two exterior data points being excluded (Fig. S2e). NH$_3$ in urban atmospheres was reported to come from various sources (Whitehead et al., 2007; Ianniello et al., 2010; Saylor et al., 2010; Meng et al., 2011; Reche et al., 2012), some of which were less dependent on ambient $T$.

$R^2$ between atmospheric NH$_3$ and ambient $T$ was below 0.1 at Site 7 (Fig. S3a). Considering the high mixing ratios observed at the rural/agricultural site, it can be confirmed that local agricultural emissions were the major contributor to atmospheric NH$_3$ and the agricultural emissions appeared to be independent on ambient $T$. $R^2$ of 0.64, 0.69, and 0.45 at Sites 8–10, respectively (Fig. S3b–d), suggested that local soil and vegetation emissions should be among the major contributors to atmospheric NH$_3$. The same can be said for the remote Site 11 with $R^2$ of 0.63 (Fig. S3e). $R^2$ was 0.25, 0.2, and 0.15 at remote Sites 12–14 (Fig. S3f–i), respectively. When the data measured in calendar year 2011, 2012, 2013, and 2014 at Site 13 were used for correlation analysis, respectively, the values of $R^2$ were 0.47 in 2011, 0.58 in 2012, 0.69 in 2013, and 0.74 in 2014. Local soil and vegetation emissions might be among the major contributors to atmospheric NH$_3$ at the site while the low $R^2$ values in 2011–2012 could be due to analytical errors. In fact, the mixing ratios at the site in 2011–2012 were generally close to the detection limit. A similar calculation was conducted at Site 14 with $R^2$ still below 0.2 in different calendar years, suggesting that local soil and vegetation emissions were unlikely the major contributors to atmospheric NH$_3$. Yao and Zhang (2013) proposed that long-range transport could be an important contributor to atmospheric NH$_3$ at remote sites in North America. When a similar calculation was conducted at Site 12, $R^2$ was 0.57 in 2012, 0.81 in 2013, and 0.39 in 2014. Local soil and vegetation emissions were possibly among the major contributors to atmospheric NH$_3$ at the site in 2012 and 2013, but the long-range transport together with local soil and vegetation emissions might be important contributors to atmospheric NH$_3$ in 2014.

3.4 Cause analysis of trends in atmospheric NH$_3$ at Canadian sites

Site 1 is located in Downtown Toronto, Ontario. Figure S4a shows the annual anthropogenic NH$_3$ emissions from 2003 to 2013 in Ontario, Canada. Not only the total NH$_3$ emissions, but also emissions from the four major sectors including agricultural, mobile, industrial, and non-industrial generally decreased. However, an increasing trend in annual average NH$_3$ was found at Site 1, which was identified to be caused by (1) the increased $T$ and (2) the decreased SO$_2$ emission. Increasing $T$ not only increases soil and vegeta-
tion NH$_3$ emissions but also favors more NH$_3$ partitioning in the gas phase (Pinder et al., 2012; Sutton et al., 2013); both processes would increase NH$_3$ mixing ratios. The decreased SO$_2$ emissions due to the tightened emission control policies since 2008 by the city and provincial governments led to significant declines in SO$_2$ oxidation products (Hu et al., 2014; Pugliese et al., 2014), which in turn also affected NH$_3$–pNH$_4^+$ partitioning, the surface resistance for NH$_3$, and increased NH$_3$ mixing ratios (Yao et al., 2007; Fowler et al., 2015). These hypotheses were supported by the trends in $T$ and pNH$_4^+$ and their correlations with that in NH$_3$, as detailed below.

A moderately good correlation ($R^2 = 0.76$, $P$ value $< 0.01$) was obtained between the annual average NH$_3$ and the annual average $T$, while a negative correlation ($R^2 = 0.40$ and $P$ value $< 0.05$) was obtained between the annual average NH$_3$ and pNH$_4^+$ (Fig. 4a). Note that a decreasing trend in annual average pNH$_4^+$ was found with a confidence level of $> 99\%$ based on M–K analysis. When ambient $T$ was increased by 5 °C, the mixing ratio of atmospheric NH$_3$ was increased by $\sim 1$ ppb according to the regression equation. The annual average $T$ shown in Fig. 4 was calculated from the daily averaged values of $T$ on the sampling days when valid NH$_3$ data were available, not every day of the year, and thus might be different from the actual annual average $T$. The moderately good correlation between the annual average values of NH$_3$ and ambient temperature might be coincident. This is also supported by the decreasing correlation when the EEMD-extracted results were used for calculation as presented below.

Figure S5 shows the intrinsic mode functions (IMFs) and residuals solved by the EEMD at Site 1. The extracted residuals represented the long-term trend in atmospheric NH$_3$, and the IMFs represented other fluctuations in different timescales. The EEMD-extracted long-term trend in atmospheric NH$_3$ was generally increased by $\sim 20\%$ from 2003 to 2014. The EEMD was also used to extract the long-term trend in pNH$_4^+$ in PM$_{2.5}$ from 2003 to 2014 (Fig. S6). Correlation between the two EEMD-extracted long-term trends resulted in a regression equation of $[\text{NH}_3] = -1.41 \times [\text{pNH}_4^+] + 4.3$, with $R^2 = 0.93$ and $P$ value $< 0.01$ (Fig. 4b). The unit of NH$_3$ is in ppb while the unit of pNH$_4^+$ is in µg m$^{-3}$. The absolute value of the regression slope was almost the same as the unit conversion coefficient. Thus, the EEMD-extracted long-term trend in atmospheric NH$_3$ seemed to be mainly determined by the change in NH$_3$–pNH$_4^+$ partitioning. The increasing $T$ further enhanced this trend. When the EEMD-extracted long-term trend in ambient $T$ was correlated to that of atmospheric NH$_3$, we obtained $[\text{NH}_3] = 0.13 \times T + 1.5$, $R^2 = 0.47$ and $P$ value $< 0.01$ (Fig. 4b). The EEMD-extracted results suggest that the change in NH$_3$–NH$_4^+$ partitioning is one of the dominant factors influencing the long-term NH$_3$ trend at Site 1. The relative importance between (1) changes in NH$_3$–NH$_4^+$ partitioning and (2) increased biogenic NH$_3$ emission due to increasing $T$ is yet to be investigated.

At Site 2, the EEMD-extracted residual of atmospheric NH$_3$ varied within a very small range ($\sim 10\%$, Fig. 2), which was consistent with stable trend generated from the M–K analysis. Little correlation was found between the annual average NH$_3$ and $T$ ($R^2 < 0.05$) or pNH$_4^+$ ($R^2 < 0.01$). Thus, the NH$_3$ trend identified at Site 2 was seemingly unaffected by changes in NH$_3$–NH$_4^+$ partitioning and $T$-dependent biogenic NH$_3$ emission, or additional local factors canceled out the impact from the two factors.

Site 3 is a rural/agricultural site and annual agricultural NH$_3$ emissions in Québec were stable from 2003 to 2009 with a CV of 0.02 (Fig. S4c). During the same period, mobile, industrial, and non-industrial emissions were decreased by 40% in Québec. While the M–K analysis result showed no consistent long-term trend in atmospheric NH$_3$, the EEMD-extracted a bell-shaped pattern (Fig. 2). That is, NH$_3$ increased from 1.7 ppb in 2003 to 2.5 ppb in 2009 and then decreased down to 1.3 ppb in 2014. The anthropogenic NH$_3$ emission data from 2003 to 2009 did not support the
increasing trend in atmospheric NH$_3$ at this site during this period. However, Sintermann et al. (2012) reported that NH$_3$ emission factors highly depend on meteorology and efficiencies of technical controls on NH$_3$ emission processes. NH$_3$ emission factors adopted in NH$_3$ emission inventories may suffer from uncertainties to some extent, which in turn may transfer to the estimated NH$_3$ emission and affect its relationship with the observed atmospheric NH$_3$.

A good correlation was found between the EEMD-extracted long-term trends in NH$_3$ and $T$ with a linear regression relationship of \[ [\text{NH}_3] = 0.39 \times T - 0.30, \] with $R^2 = 0.80$ and $P$ value < 0.01. The slope of 0.39 was consistent with that reported by Sutton et al. (2013). That is, NH$_3$ volatilization potential nearly doubles every 5°C. On the contrary, little correlation was found between the EEMD-extracted residuals for atmospheric NH$_3$ and pNH$_3^+$ ($R^2 < 0.1$), suggesting that the NH$_3$–pNH$_3^+$ partitioning likely played a negligible role on the long-term trend in atmospheric NH$_3$ at this site.

A similar conclusion could also be generated for Site 4 to that for Site 3. The M–K analysis results showed a stable trend in atmospheric NH$_3$ and a slightly decreasing trend in pNH$_3^+$ with a confidence level of > 99%. The EEMD-extracted long-term trend showed that NH$_3$ decreased by ~5% from 2007 to 2008 and then increased by ~50% afterwards. Although the correlation between the annual averages NH$_3$ and $T$ was not very good ($R^2 = 0.39$, $P = 0.13$), correlation between the EEMD-extracted long-term trends in NH$_3$ and $T$ was almost perfect ($R^2 = 0.90$, $P < 0.01$). No correlation was found between the annual average NH$_3$ and [pNH$_3^+$] ($R^2 < 0.01$), and a relatively low correlation was found between the EEMD-extracted long-term trends in atmospheric NH$_3$ and pNH$_3^+$ ($R^2 = 0.39$, $P$ value < 0.01). These results suggested that the long-term change in ambient $T$ possibly affected the long-term trend in atmospheric NH$_3$ at the site. However, longer measurements are still needed to confirm the trends in atmospheric NH$_3$ and ambient $T$ as well as their relationship at the site because of the inherent weaknesses in this data set, such as only 7 years and only one 24 h sample every 3 days available data, and some missing data during this period.

Site 5 is an urban site located in British Columbia, Canada. Anthropogenic NH$_3$ emissions were decreased from 2003 to 2013 in this province (Fig. S4c). The M–K analysis result showed no trend in atmospheric NH$_3$ at Site 5 from 2003 to 2014, and the EEMD-extracted long-term trend was almost constant. We conducted the correlation analysis of the EEMD-extracted results and found that the long-term changes in ambient $T$ and pNH$_3^+$ cannot explain the EEMD-extracted trend in atmospheric NH$_3$ at this site.

At Site 6, the EEMD-extracted trend in atmospheric NH$_3$ showed an increase of ~10% from 2003 to 2006 and then a decrease of ~40% afterwards (Fig. 2). Poor correlations were found between annual average NH$_3$ and $T$ or between NH$_3$ and pNH$_3^+$ with $P$ values > 0.05. Meaningless correlations between the EEMD-extracted trends in NH$_3$ and $T$ or between the EEMD-extracted trends in NH$_3$ and pNH$_3^+$ were obtained. The trend in $T$ and NH$_3$–pNH$_3^+$ partitioning cannot explain the long-term variations of atmospheric NH$_3$.

### 3.5 Cause analysis of trends in atmospheric NH$_3$ at the US sites

At the eight US sites, $R^2$ values between annual average NH$_3$ and $T$ were all below 0.2 with $P$ values all larger than 0.1. The simple correlation analysis did not provide direct evidence that $T$ was the significant factor affecting the NH$_3$ trend. However, the EEMD-extracted trends in NH$_3$ and $T$ had a much better correlation at some sites, e.g., with $R^2 = 0.85$, 0.99, 0.54, and 0.99 at Sites 7, 8, 9, and 13, respectively, and with $P$ values smaller than 0.01. Thus, the increasing $T$ was likely one of important factors causing the long-term trend in NH$_3$ at these four sites. Note that no reasonable relationship was identified between trends in NH$_3$ and $T$ at the other four sites using the EEMD method.

The EEMD-extracted long-term trend showed an increase in atmospheric NH$_3$ from 4.2 ppb in August 2008 to 6.8 ppb in July 2015 at Site 7 (Fig. 3a), from 2.4 ppb in August of 2008 to 3.0 ppb in July of 2015 at Site 8 (Fig. 3b), from 1.8 ppb in August of 2008 to 2.8 ppb in July of 2015 at Site 9 (Fig. 3c), a complex varying pattern during the period from August 2008 to July 2015 at Site 10 (Fig. 3d), and an increasing trend (by 0.3–0.5 ppb, or 100–200% in percentage) at Sites 11–14 (Fig. 3e–h). The percentage increases (100–200%) in NH$_3$ mixing ratio from 2008 to 2015 at the remote sites were substantially larger than those at the rural/agricultural sites (20–50%).

NH$_3$ emissions in the United States increased by 11% during the period from 1990 to 2010 due to the growth of livestock activities (Xing et al., 2013). This is particularly the case in North Carolina and Iowa. This increase alone is not enough to explain the ~50% increase in NH$_3$ from 2008 to 2015 at Site 7, which is located in Texas. The increased $T$ is possibly another important factor causing the increased NH$_3$ at this site, as mentioned above. It is also noted that the increasing trends in NH$_3$ at Sites 11–14 identified using the EEMD-extracted results were also consistent with the M–K analysis results.

The annual average NH$_3$ at the remote sites reached 0.4–0.6 ppb in 2015. Assuming the same increasing rate continues for another 7–10 years, the annual average will exceed the proposed critical level of 1 µg m$^{-3}$ at two sites for protecting sensitive ecosystems (Cape et al., 2009).

### 4 Conclusions

Long-term average of atmospheric NH$_3$ was in the range of 0.3–0.5, 1.6–2.6, and 0.8–4.9 ppb at the remote, ur-
urban, and rural/agricultural sites across North America, respectively. Moderate exponential correlations between atmospheric NH$_3$ and ambient $T$ were found at nine sites, implying that local biogenic emissions and/or NH$_3$–NH$_4^+$ partitioning were likely important factors causing the long-term trends in atmospheric NH$_3$ at these sites. However, the length of the used data covers only 7–11 years, and further examination is needed for the trend analysis when more data of atmospheric NH$_3$ are available.

No decreasing trends in atmospheric NH$_3$ were found at the four Canadian sites despite significant decreases in anthropogenic NH$_3$ emissions from main sectors in the last decade. The decreased NH$_3$ anthropogenic emission was compensated for or overwhelmed by the increased biogenic emission, changes in NH$_3$–NH$_4^+$ partitioning, and/or the increased surface resistance for NH$_3$ because of the less acidic surface associated with less SO$_2$ dry deposition. This was supported by pNH$_4^+$ data which exhibited a decreasing trend, likely caused by a combination of reduced SO$_2$ and NO$_x$ emission and increased temperature. No decreasing trends in atmospheric NH$_3$ were found at other two Canadian sites, but it was unknown what caused this phenomenon. Uncertainties in the NH$_3$ emission inventory are still a concern and may affect the trend analysis results of the relationship between atmospheric NH$_3$ and NH$_3$ emissions.

The M–K analysis showed an increasing trend in atmospheric NH$_3$ at seven out of the eight US sites, which was also supported by the EEMD-extracted results. NH$_3$ increased by 20–50% from 2008 to 2015 at the three rural/agricultural sites and by 100–200% at the four remote sites. If the same increasing trend continues in the next 5–7 years, the annual average NH$_3$ at two remote sites will exceed 1 µg m$^{-3}$, a level below which has been proposed to protect sensitive ecosystems at the remote sites.

In most cases, the two statistical approaches used in the present study yield consistent trends in atmospheric NH$_3$ measured at different sites. The EEMD method appeared to have more powerful interpretation ability for resolving trends because (1) it is less affected by extremely high concentration points, and (2) it yields a continuous and quantitative trend result. However, this method occasionally suffers from “the end effect” and leads to physically meaningless results. Using the combined approach (or more than one statistical methods) can better resolve and interpret long-term trends in atmospheric NH$_3$.

### 5 Data availability


The Supplement related to this article is available online at doi:10.5194/acp-16-11465-2016-supplement.

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