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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 seven to eleven years were investigated at fourteen 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/agriculture 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/agriculture and at four remote U.S. 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 2008-2015) and four remote sites (0.3-0.5 ppb, 100-200% increase from 2008-2015). Increased ambient temperature was identified to be a cause for the increasing trends in NH_3 mixing ratio at four out of the seven U.S. sites, but what caused the increasing trends at other U.S. sites needs further investigation.

Keywords: Gas-particle partitioning, reduced nitrogen, Ensemble Empirical Mode

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23 Decomposition, climate impact.

24

25 **1. Introduction**

26 Atmospheric ammonia (NH_3) plays an important role in formation of ammonium
27 sulfate/nitrate aerosols in the size range of nanometer to supermicron (Kulmala et al.,
28 2004; Ianniello et al., 2011; Yao and Zhang, 2012; Schiferl et al., 2014; Paulot and
29 Jacob, 2014). The sum of sulfate, nitrate and ammonium ions (NH_4^+) usually consist
30 of the major portion of $PM_{2.5}$ across Canada and the U.S. (Dabek-Zlotorzynskaet al.,
31 2011; Hand et al., 2012). With significant decreases in acidic gas emissions in the last
32 decades across North America, e.g., emissions of SO_2 and NO_x in Canada decreased
33 from $2.28x10^6$ and $2.72x10^6$ tones/year in 2003 to $1.23x10^6$ and $2.06x10^6$ tones/year
34 in 2013, respectively,
35 (http://www.ec.gc.ca/inrp-npri/donnees-data/ap/index.cfm?lang=En), more attentions
36 are paid to the relationship between NH_3 and NH_4^+ aerosols (Zhang et al., 2010; Day
37 et al., 2012; Nowak et al., 2012; Yao and Zhang, 2012; Schiferl et al., 2014; Zhu et al.,
38 2013; Markovic et al., 2014; Paulot and Jacob, 2014).

39

40 NH_3 mixing ratios are affected by several factors such as NH_3 emissions, NH_3/NH_4^+
41 partitioning, and meteorological conditions (Sutton et al., 2009; Yao and Zhang, 2013;
42 Hu et al., 2014). In Europe, previous studies showed that the long-term trend in
43 atmospheric NH_3 observed in some countries didn't show a decrease with a dramatic
44 decrease in NH_3 emissions and the phenomena was referred as "Ammonia Gap"

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(Sutton et al., 2009; Ferm and Hellsten, 2012). Long-term trends in atmospheric NH_3 across North America are poorly understood (Zbieranowski and Aherne, 2011; Hu et al., 2104; Van Damme et al., 2014). Such knowledge is important for accurate prediction of ammonium sulfate/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-agriculture emissions such as those from local traffics, waste containers and soil/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 percentages of the total NH_3 emissions in Canada and the U.S. 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 the traffic-derived NH_3 was a negligible contributor to atmospheric NH_3 in Toronto. However, under climate warming, soil/vegetation NH_3 emissions are expected to increase accordingly, e.g., NH_3 volatilization potential nearly doubles under every 5˚ C increase (Pinder et al., 2012; Sutton et al., 2013).

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Atmospheric NH_3 and ammonium sulfate/nitrate aerosols can be transported downwind and eventually deposited to natural ecosystems to enhance carbon fixation. Excessive NH_3 deposition may cause adverse effects such as reduced biodiversity and eutrophication (Krupa et al., 2003; Erisman et al., 2007; Beem et al., 2010; Bobbinket al., 2010; Pinderet al., 2012). Recent evidence shows changes in species composition for sensitive vegetation types at the annual average concentration of 1 μg m^{-3} NH_3 (Cape et al., 2009). Climate warming may increase the vulnerability of ecosystems towards exposure to NH_3. Thus, trend analysis of atmospheric NH_3 at remote sites will help to better understand its potential impacts on sensitive natural eco-systems.

In this paper, interannual variabilities in atmospheric NH_3 at fourteen sites across Canada and the U.S. were investigated, with particular attention paid to its long-term trends and causes. The fourteen sites include four urban sites, four remote sites and six rural/agriculture sites distributing 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 et al., 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

In this study, mixing ratios of atmospheric NH_3 generated at monthly interval were

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compiled from three data sources, i.e., the National Air Pollution Surveillance (NAPS, http://www.ec.gc.ca/rnspa-naps/) network, the Canadian Air and Precipitation Monitoring Network (CAPMoN), and the Passive Ammonia Monitoring Network (AMoN, http://nadp.sws.uiuc.edu/nh3Net). Missing data is a common problem during long-term observations. The sites chosen in this study were based on data availabilities as detailed below.

The NAPS network is to provide accurate and long-term air quality data across Canada. At each site, a $PM_{2.5}$ sampler equipped with 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 operates for a 24-hr duration on every third day. 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/agriculture 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 was only ~70% months when 8-10 sets of 24-hr data were available to calculate the monthly average value. In a few months, there were only 1-3 sets of 24-hr data available to do so. 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.

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111 The site is located at a rural/agriculture area. The data was also averaged monthly for
112 the trend analysis. The six Canadian sites were referred as Sites 1-6 on basis of their
113 annual average mixing ratios of atmospheric NH_3 in decreasing order.
114
115 The AMoN within the National Atmospheric Deposition Program in the U.S. started
116 operation in fall 2007. An important objective of AMoN is to assess long-term trends
117 in NH_3 concentrations and its deposition. AMoN included only sixteen sites in 2007
118 and dozens of sites are now available. The Radiello® passive samplers are deployed
119 every two weeks at each site according to the standard operating procedure for
120 monitoring atmospheric NH_3. Puchalski et al. (2015) recently compared the bi-weekly
121 passive measurements with those measured by annular denuder systems (ADS) at
122 several AMoN sites and found that the mean relative percentage difference between
123 the ADS and AMoN sampler was -9%. In this study, mixing ratios of atmospheric
124 NH_3 at eight AMoN's sites were selected for the trend analysis on basis of two criteria
125 (Fig 1): 1) the length of the valid data should be at least seven years according to
126 Walker et al., (2000); and 2) there were no monthly average data missing in each year.
127 The eight sites were refereed as Site 7-14 (Fig 1), four of which were located at rural
128 areas and another four at remote areas. Consistent with the six sites across Canada, the
129 monthly averages at the eight sites were used for data analysis if not specified.
130 Moreover, all ambient temperature (T) data were obtained from on-site records or
131 nearby meteorological stations.
132

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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 the data flaws aforementioned were indeed presented in our selected datasets to different extents, the M-K analysis is thereby used to resolve the time series of the annual average of NH_3 in this study. The M-K method yields qualitative trend results such as "increasing/decreasing", "probable increasing/decreasing", "stable" and "no trend", depending on the calculated "S" statistic, confidence factor and coefficient of variation (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 et al., 2009). The EEMD built on Empirical Mode Decomposition (EMD) and was updated by Wu et al. (2009) to overcome the problem of mode mixing in the EMD. The method has since been applied widely (e.g., Erturk et al., 2103; 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 affected 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,

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155 respectively. In the EMD, any dataset is assumed to consist of different simple
156 intrinsic modes of oscillations. Each of these intrinsic oscillatory modes is represented
157 by an intrinsic mode function (IMF). In the EEMD, white noise is added to the single
158 data set, X(t), and the ensemble mean is used to improve accuracy of measurements.
159
160 **3. Results and discussion**
161 *3.1 Temporal variations of atmospheric NH_3 at the six Canadian sites*
162 Fig. 2 shows monthly variations of atmospheric NH_3 in mixing ratio at the six
163 Canadian sites. At Site 1, an urban site in downtown Toronto, the measured mixing
164 ratios were 2.6±1.2 ppb (average ± standard deviation) during the period from July
165 2003 to June 2014 (Fig 2a and Table 1). When compared with those reported in other
166 urban atmospheres, the long-term average value of 2.6 ppb ranked at a moderately
167 low concentration level (Whitehand et al., 2007; Saylor et al., 2010; Alebic-Juretic,
168 2008; Meng et al., 2011). Interannual variations were evident at Site 1 with the
169 coefficient of variation (CV) of 0.11, defined as the ratio of the standard deviation to
170 the average. It should be noted that the annual averages in 2004 and 2005 were
171 calculated from July 2003 to June 2004 and from July 2004 to June 2005, respectively,
172 instead of a calendar year, in order to obtain the longest time series of annual averages.
173 The similar calculations were used for other years and other sites. The M-K analysis
174 result suggested an increasing trend from 2004 to 2014 with a confidence level of
175 98%. When intra-annual variations were analyzed at Site 1, a distinctive seasonal
176 trend was obtained with the highest seasonal average value of 3.7±0.7 ppb in summer

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(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, e.g., the CV values calculated from annul 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 at a rural/agriculture area in Saint-Anicet of Quebec. The largest seasonal average value occurred in the fall during the measurement period of September 2003 - August 2014. 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-hr sample in October having a mixing ratio 1-2 orders of magnitude higher than other samples collected before or after (figure not shown). 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 in some years,

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but not in every year. The episodes further led to large interannual variations with the value of CV reached 0.19.

Site 2 is located at 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. Soil/vegetation NH_3 emissions should be negligible in such cold winters, however, industrial and/or non-industrial anthropogenic sources might be enhanced in winter, which could explain the small seasonal variations in NH_3 mixing ratio at this site. This hypothesis was supported by the much higher (2.0-4.0 times) mixing ratios of SO_2, HONO and HNO_3 in winter as compared to those in summer (figure not shown).

3.2 Temporal variations of atmospheric NH_3 at the eight American sites

For the eight AMoN's sites in the U.S., 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 was used (Fig. 3 and Table 1). Site 7 is located at an intensive agriculture activity zone in Randall of Taxes, and Sites 8-10 are located at rural areas in Dodge of Wisconsin, Wayne of Michigan, and Champaign of Illinois, respectively, with moderately intensive agriculture activities. Long-term average of NH_3 was as high as 4.9±1.2 ppb at Site 7 where the

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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 average 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 at the remote areas in Tompkins of New York, Lake of Minnesota, Charleston of South Carolina, and Rio Arriba of 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/vegetation emissions were the major contributors to atmospheric NH_3, its mixing ratio usually exhibited as 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 fourteen 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

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dry soil was much small (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. S1a). 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. S1c). 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. S1f). The two parameters in the regression equation $[NH_3]$=0.24*exp(0.094*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 one 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 condition 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 a higher NH_3 emission from grassland under freezing condition, but the corresponding mechanism is still not clear.

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At Site 2, the exponential correlation was poor even with two outlier samples being excluded (Fig. S1b), implying that local soil/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. S1e). NH_3 in urban atmospheres were 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 S2a). Considered the high mixing ratios observed at the rural/agriculture site, it can be confirmed that local agriculture emissions were the major contributor to atmospheric NH_3 and the agriculture emissions appeared to be independent on ambient T. R^2 of 0.64, 0.69 and 0.45 at Sites 8-10, respectively, (Fig. S2b-d) suggested that local soil/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. S2e). R^2 was 0.25, 0.2 and 0.15 at remote Sites 12-14 (Fig S2f-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/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

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14 with R^2 still below 0.2 in different calendar years, suggesting that local soil/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/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/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. Fig S3a 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 agriculture, 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/vegetation NH_3 emissions but also affects NH_3/pNH_4^+ partitioning, 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 and

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increased NH_3 mixing ratios. 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^{o}C, the mixing ratio of atmospheric NH_3 was increased by ~1 ppb according to the regression equation.

Fig. S4 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 time scales. The EEMD-extracted long-term trend in atmospheric NH_3 was generally increased by ~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. S5). Correlation between the two EEMD-extracted long-term trends resulted in a regression equation of $[NH_3] = -1.41*[pNH_4^+] + 4.3$, with R^2=0.93 and P value <0.01 (Figure 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^+

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331 partitioning. The increasing T further enhanced this trend. When the EEMD-extracted
332 long-term trend in ambient T was correlated to that of atmospheric NH_3, we obtained
333 $[NH_3] = 0.13*T+1.5$, $R^2=0.47$ and P value <0.01 (Fig 4b). The EEMD-extracted
334 results suggest that the changes in NH_3/NH_4^+partitioning is one of the dominant
335 factors influencing the long-term NH_3 trend at Site 1. The relative importance
336 between (1) changes in NH_3/NH_4^+partitioning and (2) increased biogenic NH_3
337 emission due to increasing T is yet to be investigated.
338
339 At Site 2, the EEMD-extracted residual of atmospheric NH_3 varied within a very
340 small range (~10%, Fig. 5), which was consistent with stable trend generated from the
341 M-K analysis. Little correlation was found between the annual average NH_3 and T
342 ($R^2<0.05$) or pNH_4^+ ($R^2<0.01$). Thus, the NH_3 trend identified at Site 2 was seemingly
343 unaffected by changes in NH_3/NH_4^+partitioning and T-dependent biogenic NH_3
344 emission, or additional local factors cancelled out the impact from the two factors.
345
346 Site 3 is a rural/agriculture site and annual agriculture NH_3 emissions in Quebec were
347 stable from 2003 to 2009 with CV of 0.02 (Fig S3b). During the same period, mobile,
348 industrial and non-industrial emissions were decreased by 40% in Quebec. While the
349 M-K analysis result showed no consistent long-term trend in atmospheric NH_3, the
350 EEMD-extracted a bell-shaped pattern (Fig. 5), i.e., NH_3 increased from 1.7 ppb in
351 2003 to 2.5 ppb in 2009 and then decreased down to 1.3 ppb in 2014. The
352 anthropogenic NH_3 emission data from 2003 to 2009 didn't support the increasing

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353 trend in atmospheric NH_3 at this site during this period.

354

355 A good correlation was found between the EEMD-extracted long-term trends in NH_3
356 and T with a linear regression relationship of $[NH_3] = 0.39*T - 0.30$, with $R^2=0.80$
357 and P value <0.01. The slope of 0.39 was consistent with that reported by Sutton et al
358 (2013), i.e., NH_3 volatilization potential nearly doubles every 5ºC. On the contrary,
359 little correlation was found between the EEMD-extracted residuals for atmospheric
360 NH_3 and pNH_4^+ ($R^2<0.1$), suggesting that the NH_3/pNH_4^+ partitioning likely played a
361 negligible role on the long-term trend in atmospheric NH_3 at this site. The increasing
362 trend in NH_3 should mainly be caused by increased biogenic NH_3 emission due to the
363 increased T.

364

365 A similar conclusion could also be generated for Site 4 to that for Site 3. The M-K
366 analysis results showed a stable trend in atmospheric NH_3 and a slightly decreasing
367 trend in pNH_4^+ with a confidence level of >99%. The EEMD-extracted long-term
368 trend showed that NH_3 decreased by ~5% from 2007 to 2008 and then increased by
369 ~50% afterwards. Although the correlation between the annual averages NH_3 and T
370 was not very good ($R^2=0.39$, P=0.13), correlation between the EEMD-extracted
371 long-term trends in NH_3 and T was almost perfect ($R^2= 0.90$, P<0.01). No correlation
372 was found between the annual average NH_3 and $[pNH_4^+]$ ($R^2<0.01$), and a relatively
373 low correlation was found between the EEMD-extracted long-term trends in
374 atmospheric NH_3 and pNH_4^+ ($R^2=0.39$, P value <0.01). These results suggested that

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375 the long-term change in ambient T possibly dominated the long-term trend in
376 atmospheric NH_3 at the site.
377
378 Site 5 is an urban site located in British Columba, Canada. Anthropogenic NH_3
379 emissions were decreased from 2003 to 2013 in this province (Fig S3c). The M-K
380 analysis result showed no trend in atmospheric NH_3 at Site 5 from 2003 to 2014 and
381 the EEMD-extracted long-term trend was almost constant. Based on the correlation
382 analysis of the EEMD-extracted results (not shown), the long-term changes in
383 ambient T and pNH_4^+ cannot explain the EEMD-extracted trend in atmospheric NH_3
384 at this site.
385
386 At Site 6, the EEMD-extracted trend in atmospheric NH_3 showed an increase of ~10%
387 from 2003 to 2006 and then a decrease of ~40% afterwards (Fig. 5). Poor correlations
388 were found between annual average NH_3 and T or between NH_3 and NH_4^+ with P
389 values >0.05. Meaningless correlations between the EEMD-extracted trends in NH_3
390 and T or between the EEMD-extracted trends in NH_3 and NH_4^+ were obtained. The
391 trend in T and NH_3/NH_4^+ partitioning cannot explain the long-term variations of
392 atmospheric NH_3.
393
394 *3.5 Cause analysis of trends in atmospheric NH_3 at the U.S. sites*
395 At the eight U.S. sites, R^2 between annual average NH_3 and T were all below 0.2 with
396 P values all larger than 0.1. The simple correlation analysis did not provide direct

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evidence that T was the dominant 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 Site 7, 8, 9 and 13, respectively, and with P values small than 0.01. Thus, the increasing T should be one of the main 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. 6a), from 2.4 ppb in August of 2008 to 3.0 ppb in July of 2015 at Site 8 (Fig. 6b), from 1.8 ppb in August of 2008 to 2.8 ppb in July of 2015 at Site 9 (Fig. 6c), a complex varying pattern during the period from August 2008 to July 2015 at Site 10 (Fig. 6d), and an increasing trend (by 0.3-0.5 ppb, or 100-200% in percentages) at Sites 11-14 (Fig. 6e-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/agriculture 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 along is not enough to explain the ~50% increase in NH_3 from 2008 to 2015 at Site 7 which is located in Taxes. The

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increased T is believed to be 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 Site 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, urban, and rural/agriculture sites, respectively, across the North America. 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 dominant factors causing the long-term trends in atmospheric NH_3 at these sites.

At the four Canadian sites, no decreasing trends in atmospheric NH_3 were found despite significant decreases in anthropogenic NH_3 emissions from main sectors in the last decade. The decreased NH_3 anthropogenic emission was compensated or overwhelmed by the increased biogenic emission and/or changes in NH_3/NH_4^+

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441 partitioning. This was supported by pNH_4^+ data which exhibited a decreasing trend,
442 likely caused by a combination of reduced SO_2 and NO_x emission and increased
443 temperature. No decreasing trends in atmospheric NH_3 were found at other two
444 Canadian sites, but it was unknown what caused this.
445
446 The M-K analysis showed an increasing trend in atmospheric NH_3 at seven out of the
447 eight U.S. sites, which was also supported by the EEMD-extracted results. NH_3
448 increased by 20-50% from 2008 to 2015 at the three rural/agriculture sites and by
449 100%-200% at the four remote sites. If the same increasing trend continues in the next
450 5-7 years, the annual average NH_3 at two remote sites will exceed 1 μg m^{-3}, a level
451 below which has been proposed to protect sensitive eco-systems at the remote sites.
452
453 In most cases, the two statistical approaches used in the present study yield consistent
454 trends in atmospheric NH_3 measured at different sites. The EEMD method appeared
455 to have more powerful interpretation ability for resolving trends because 1) it is less
456 affected by extremely high concentration points, and 2) it yields a continuous and
457 quantitative trend result. However, this method occasionally suffers from "the end
458 effect" and leads to physically meaningless results. Using the combined (or more than
459 one statistical methods) can better resolve and interpret long-term trends in
460 atmospheric NH_3.
461
462 **Acknowledgement**

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650 Table 1. The mixing ratios of atmospheric NH_3 at fourteen sites (NH_3 unit in ppb, T unit in ^0C, Sites 1-14 were defined in the text)

Site	Sampling Period	Annual	Spring		Summer		Fall		Winter	
		NH_3	NH_3	T	NH_3	T	NH_3	T	NH_3	T
1	July. 2003-June. 2014	2.6±1.2	2.8±1.2	8.0±6.0	3.7±0.7	21.6±1.5	2.8±0.7	11.8±5.7	1.3±0.6	-2.5±3.1
2	May. 2006-Apr. 2014	2.4±0.6	2.3±0.6	3.7±7.4	2.4±0.4	16.7±1.9	2.6±0.6	4.2±7.7	2.3±0.9	-19.8±4.5
3	Sep. 2003-Aug. 2014	2.1±2.0	1.6±0.8	6.1±6.7	3.0±1.5	19.5±2.2	3.2±2.8	9.1±5.6	0.5±0.3	-6.8±2.9
4	Nov. 2007-Oct. 2014	1.9±0.8	1.7±0.7	8.3±6.9	2.7±0.5	21.5±2.1	2.1±0.4	9.4±6.3	1.0±0.2	-6.1±2.6
5	Sep. 2003-Aug. 2014	1.6±0.5	1.5±0.4	10.1±2.9	1.9±0.4	17.8±1.9	1.7±0.5	10.6±4.1	1.4±0.4	4.2±1.5
6	Aug. 2003-July 2011	0.8±0.6	1.0±0.7	6.7±5.8	1.2±0.4	19.4±2.2	0.7±0.3	9.7±5.3	0.2±0.2	-5.6±2.8
7	Aug. 2008-July. 2015	4.9±1.2	4.6±1.2	14.2±4.2	5.5±0.8	25.5±1.7	4.7±1.5	14.7±5.3	4.6±1.4	3.0±1.8
8	Aug. 2008-July. 2015	2.6±1.4	3.2±1.2	7.4±6.5	3.8±0.9	20.7±1.8	2.5±0.6	9.3±5.9	1.0±0.5	-7.4±3.8
9	Aug. 2008-July. 2015	2.2±1.0	2.6±1.0	10±6.1	3.2±0.7	22.4±1.7	2.1±0.7	11.5±5.5	1.1±0.3	-3.2±3.3
10	Aug. 2008-July. 2015	1.6±1.0	2.3±1.0	11.3±5.7	1.9±0.4	22.1±1.5	1.8±0.8	11.2±5.6	0.4±0.4	-3.3±3.3
11	Aug. 2008-July. 2015	0.5±0.4	0.7±0.4	6.6±6.5	0.8±0.3	18.4±1.5	0.3±0.2	9.2±5.0	0.1±0.1	-4.9±3.4
12	Sep. 2008-Aug. 2015	0.3±0.3	0.3±0.2	3.4±6.1	0.5±0.3	17.5±2.6	0.3±0.3	5.5±6.7	0.1±0.1	-13±4.5
13	Aug. 2008-July. 2015	0.3±0.4	0.2±0.2	11±3.6	0.7±0.5	23.8±1.5	0.2±0.2	12.5±6.0	0.2±0.1	0.2±2.3
14	Aug. 2008-July. 2015	0.3±0.3	0.4±0.2	18.6±4.2	0.5±0.3	27.8±1.0	0.2±0.2	19.7±4.8	0.2±0.2	10.3±3.2

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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-259, 2016
Manuscript under review for journal Atmos. Chem. Phys.
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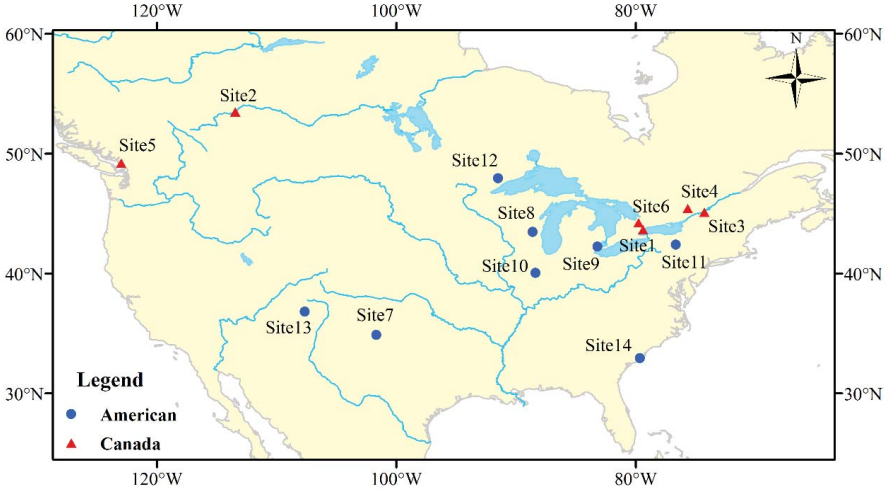
668 Fig 1



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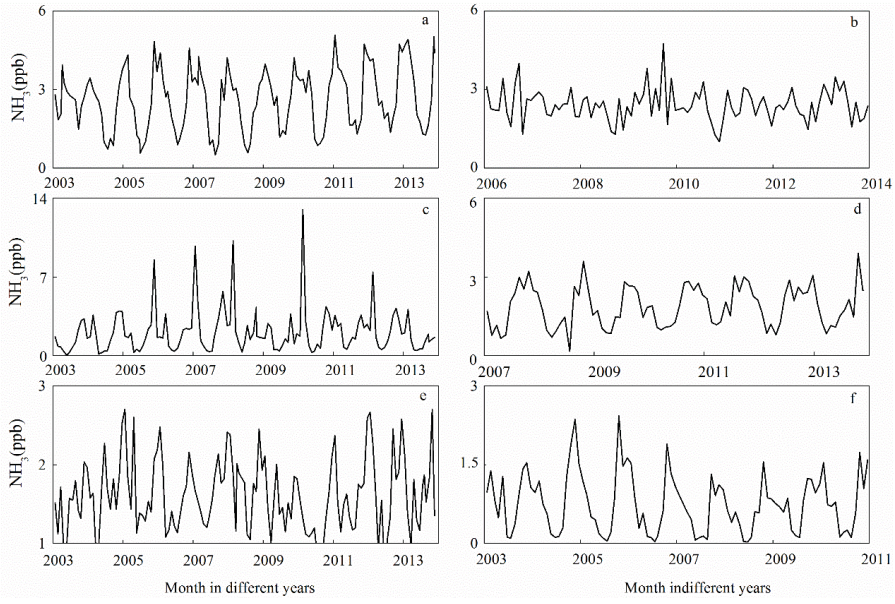
683 Fig 2



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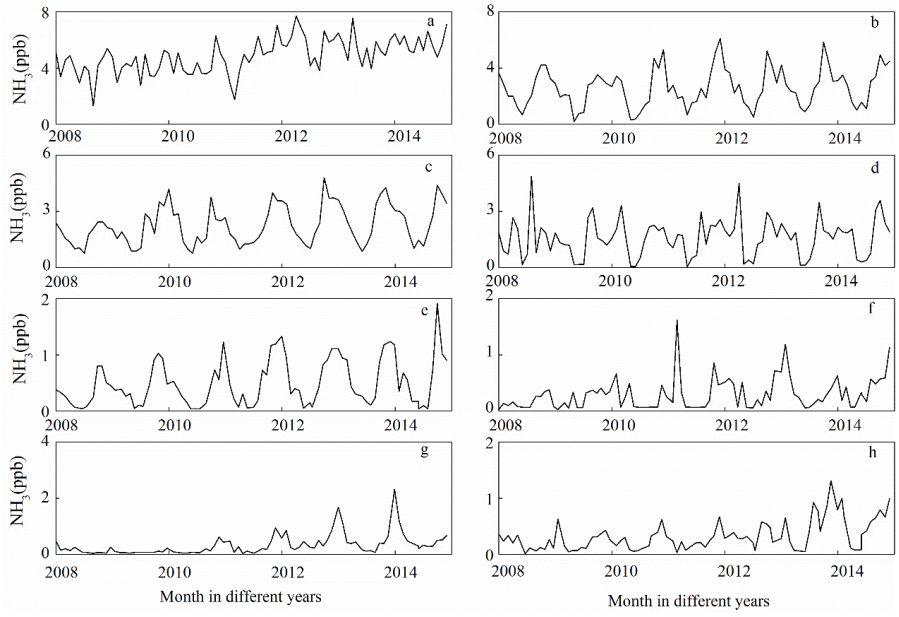
698 Fig 3



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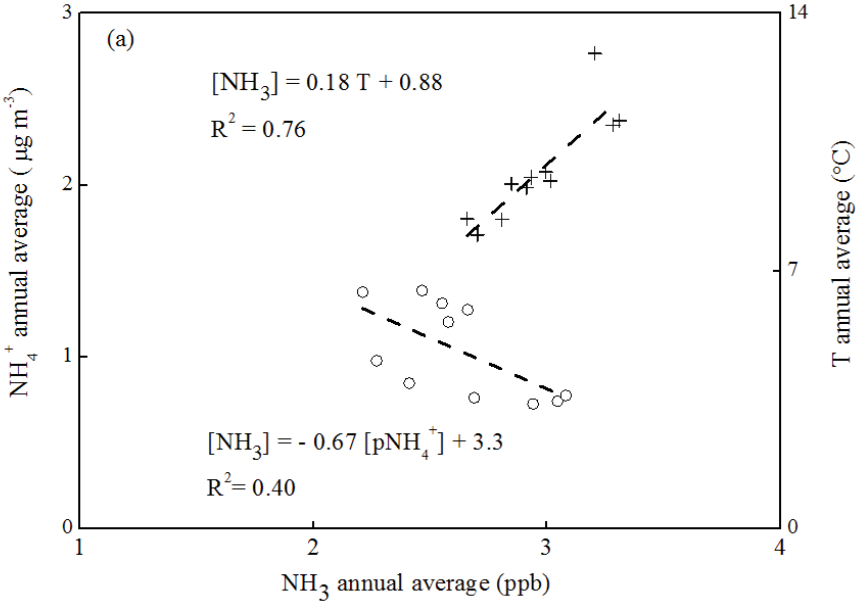
712 Fig 4



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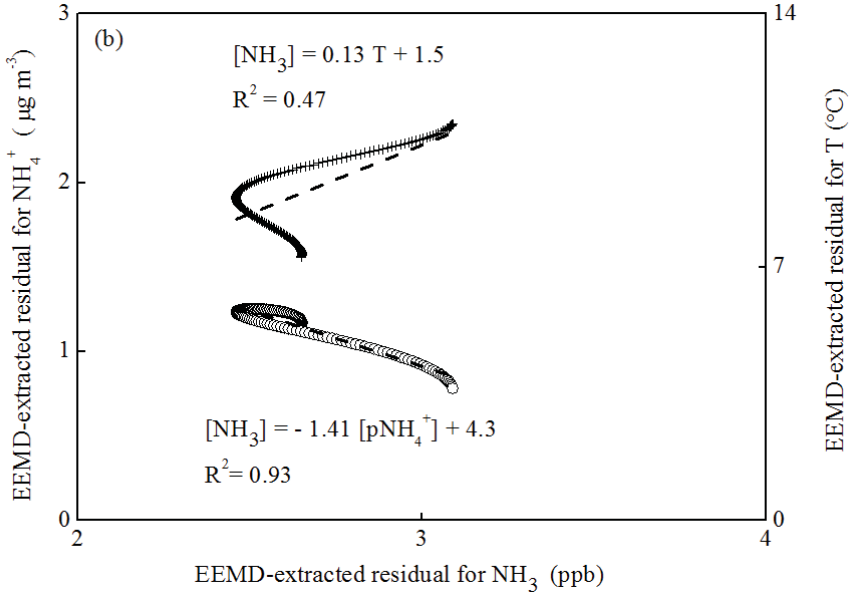

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718 Fig 5

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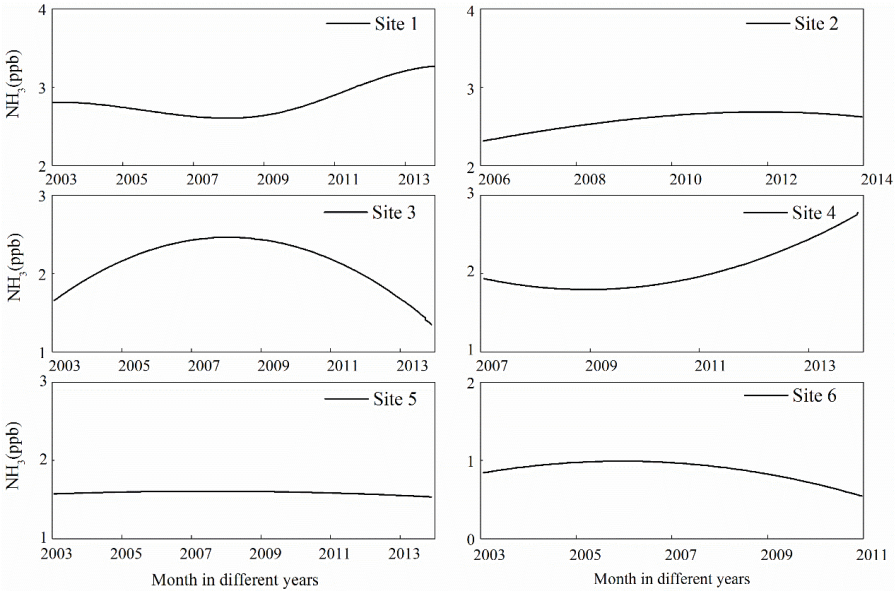

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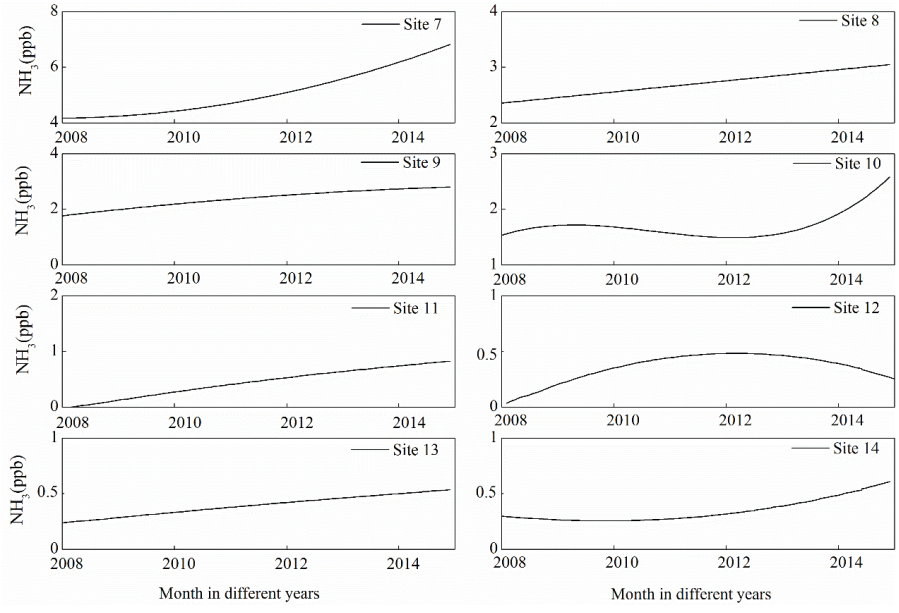
732 Fig 6



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