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Analysis of passive-sampler monitored atmospheric ammonia at 74 sites across southern Ontario, Canada

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Abstract

Weekly/biweekly concentrations of atmospheric NH_3 were collected using passive samplers at 74 sites across southern Ontario, Canada during the period from June 2006 to March 2007 with tens of sites running as early as March 2006. The annual average of NH_3 (AAN) at all the sites across southwestern Ontario was over $1 \mu\text{g m}^{-3}$, a value that was recently proposed as the new critical level for protecting vegetation. High ANN values ($3.6\text{--}6.1 \mu\text{g m}^{-3}$) were observed at eight sites located inside the intensive livestock production zones. The AAN values at the sites across southeastern Ontario were generally less than $1 \mu\text{g m}^{-3}$ and the values were less than $0.4 \mu\text{g m}^{-3}$ at non-agricultural sites. Regional transport from the southwest region to the southeast region was identified to be the main contributor to the observed NH_3 at the southeastern non-agricultural sites. However, different transport mechanisms were proposed in different seasons. The transport of NH_3 produced through bi-directional air-surface exchange along air mass trajectories was believed to be the main mechanism in the hot seasons while the transport of NH_4NO_3 produced at source locations followed by its evaporation at receptor sites was thought to be dominant in the cold seasons. A sharp increase in NH_3 concentration was surprisingly observed at 20 out of the 74 sites during the coldest two weeks when ambient temperature was lower than -7°C , and cannot be explained by known sources or with existing knowledge. Recently developed NH_3 emission inventory for southern Ontario was also evaluated with the measurement data and emissions within two small zones were identified to be potentially underestimated.

1 Introduction

Atmospheric ammonia (NH_3) is an important reactive nitrogen compound in the geosphere and biosphere of the earth. NH_3 gas has been found to cause direct adverse effects on plant community composition even at low concentration levels and the value

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can best be verified using high spatial resolution concentration measurements over reasonably long term periods.

Besides land use, ambient conditions such as temperature (T), relative humidity (RH), rainfall, snowfall, and concentration of acidic gases can also affect the concentration of NH_3 gas (Ianniello et al., 2010, 2011; Sutton et al., 2009). To assess the NH_3 emission inventory in southern Ontario, Environment Canada established a high spatial-resolution monitoring network comprising 74 sites (Fig. 1) and measured weekly/biweekly concentrations of NH_3 during the period from June 2006 to March 2007. The measurements of NH_3 at tens of these sites were made as early as March 2006. The dataset not only allows an evaluation and improvement of the Canadian NH_3 emission inventory for the region of southern Ontario, but also allows a better understanding NH_3 -related sciences through in-depth data analysis and data-model comparison (e.g., Wen et al., 2013).

In this study, we first analyzed geographical distributions of NH_3 across southern Ontario (Sect. 3.1) in order to improve the understanding of NH_3 sources. We then analyzed the seasonal variations of NH_3 in different concentration level zones (Sects. 3.2–3.4) in terms of impacts of agricultural activity, ambient T , and regional transport. To understand the phenomena identified in Sect. 3, various explanations/hypotheses were developed (Sects. 4.1–4.3). Finally, a brief evaluation of Environment Canada's most recent NH_3 emission inventory was conducted (Sect. 4.4) using knowledge obtained in Sects. 3 and 4.

2 Experiments

Funded by the National Agri-Environmental Standards Initiative (NAESI), a project known as the Southern Ontario Ammonia Passive Sampler Survey (SOAPSS) was launched in March 2006 to monitor atmospheric NH_3 in southern Ontario, Canada (Lil-lyman et al., 2009). A total of 74 sites were selected across southern Ontario with distances between the sites of approximately 20 km. Passive diffusion samplers were

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used for monitoring NH_3 . The samplers are available commercially and can be considered an inexpensive and simple method for measuring NH_3 over periods of days and weeks. Comparability of passive samplers to complex methods has been well established in the literature (Cape et al., 2004; Puchalski et al., 2011). The acceptable maximum uncertainty of passive sampler is $\pm 20\%$ for NH_3 (Sutton et al., 2001). From March to May 2006, only tens of sites started running for consistency check and sampler evaluation. All the 74 sites measured ambient concentration of NH_3 starting June 2006. Thus, only approximately 20% of sites had the NH_3 data between March and May 2006 despite the fact strongest NH_3 emissions occur in this region in the month of May (Lillyman et al., 2009). Note that weekly samples were collected before 5 December 2006 while biweekly samples were collected after this date in expectation of low concentration of NH_3 in the cold seasons. The project provided highly spatial-resolved atmospheric NH_3 concentration data although with relatively low temporal resolution.

3 Results

3.1 Spatial variations in NH_3 concentrations

According to recent publications, more than 80% of NH_3 emissions in southern Ontario are from agricultural activity while non-agricultural sources (e.g., industrial sources, vehicle emissions, open sources (except animals), non-industrial fuel combustion, miscellaneous and incineration) contribute to the remaining < 20% (Lillyman et al., 2009). For the agricultural generated emissions, livestock production accounts for approximately 80%, with the remaining 20% being associated with fertilizer and pesticide application. However, two potential sources are not included in the emission inventory of NH_3 in Canada (Lillyman et al., 2009). One is biogenic N fixation in soil followed by soil N cycling processes that release NH_3 from soil and/or via plants to the atmosphere. The other is atmospheric deposition of NO_y to soil followed by soil N cycling processes

that release NH_3 to the atmosphere. These emissions can be considered as natural emission or reemission of predeposited N that is converted to NH_3 .

The geographical distribution of annual average NH_3 concentration (ANN – calculated using nine to 12 month data depending on data availability for individual sites) was generally consistent with that of NH_3 emissions across southern Ontario (Fig. 2a, b). Low AAN ($< 1 \mu\text{g m}^{-3}$) was observed at rural and remote non-agricultural zone sites (highlighted in black in Fig. 2a) because of low emissions of NH_3 . The AAN in agricultural zones across southern Ontario was generally larger than $1 \mu\text{g m}^{-3}$. However, there were seven sites (Galbraith (GAL), Holland (HOL), Lyndhurst (LYH), Merrickville (MER), Montebello (MON), Maynard (MYN) and Westport CAPMON (WPT)) in south-eastern Ontario (Fig. 2a) with AAN only in the range of 0.4–0.7 $\mu\text{g m}^{-3}$. The low values were likely associated with low intensity of agricultural activity. On the other hand, there were eight sites (Arkona (ARK), Lynden (LYD), Mildmay (MLM), Milverton (MVT), New Dundee (NDD), St. Marys (SMY), Sweaburg (SWB) and Teviotdale (TEV)) with AAN as high as 3.6 to 6.1 $\mu\text{g m}^{-3}$. These high AAN values were approximately 2–5 times larger than those at most of sites in the agricultural zones and were likely associated with high emissions of NH_3 from livestock production (Zbieranowski and Aherne, 2012, 2013).

Hierarchical cluster analysis was used to investigate the geographical distribution of NH_3 across southern Ontario and the results are shown in Fig. 3a, b. In the analysis, sites with similar temporal variations of NH_3 concentration were grouped together and the groups were then placed into different Classes based on the extent of the differences in the temporal variations of NH_3 concentrations. Class 1 consists of only one site (TEV), as does Class 2 (LYD). Class 3 has two sites (MVT and SWB), and Class 4 has 4 sites (MLM, SMY, ARK and NDD). At seven of the eight sites (Classes 1–4), a few concentration spikes $> 10 \mu\text{g m}^{-3}$ (as shown later) made the temporal trends of NH_3 different from those at the other 66 sites.

Class 5 consists of six sites (Inwood (INW), Mildmay (MIL), Eberts (EBT), West Lorne (WLO), Hudson (HUD), Brigden (BGD)). Four of the six sites in Class 5 were located

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near the strong NO_x emissions (Fig. S1). NO_2 can be oxidized to HNO_3 which can then possibly form NH_4NO_3 in the atmosphere, thereby leading to depletion of atmospheric NH_3 . Conversely, higher atmospheric deposition of NO_y in high NO_x emission areas can add N to soils which could be a potential emission source of NH_3 . In Class 6, 12 sites in southwestern Ontario and one site ~ 500 km northeast were grouped together. Of these, 12 sites were scattered over ~ 200 km range and encircling sites in Classes 1 to 5 (Fig. 3b). Similar land use and simultaneous agricultural activity at the 12 sites probably led to their consistent temporal variations of NH_3 concentrations, leading to them being grouped together.

The remaining 47 sites were defined as Class 7, of which 43 sites were situated in southeastern Ontario and 4 sites were located near Lake Erie. The dominant wind direction in southwestern Ontario was from the west and southwest (Fig. 2a and Bein et al., 2008). Under the dominant wind condition, most of the sites in Class 7 are located downwind of those zones with higher concentrations of NH_3 . Long-range transport of semi-volatile ammonium salts followed by evaporation or regional transport of NH_3 via Hypothesis-A could contribute to the NH_3 observed at most of sites in Class 7 as discussed later, leading to temporal variations of ambient NH_3 concentration in Class 7 being different from those in Class 6.

Based on an $1 \mu\text{g m}^{-3}$ critical level of ammonia for the protection of vegetation (Cape et al., 2009), the 74 monitoring sites were classified into three concentration categories for interpreting the seasonal variations of ambient NH_3 concentration, i.e, Category 1 for $\text{AAN} > 3 \mu\text{g m}^{-3}$ (Classes 1–4), Category 2 for AAN in the range of $1\text{--}3 \mu\text{g m}^{-3}$ (Classes 5–6 and 17 out of 47 sites in Class 7), and Category 3 for $\text{AAN} < 1 \mu\text{g m}^{-3}$ (30 out of 47 sites in Class 7). These are discussed in Sects. 3.2 to 3.4 below.

3.2 Seasonal variations of NH_3 in high concentration zones

The AAN was greater than $3 \mu\text{g m}^{-3}$ at the eight sites belonging to Classes 1–4 which were distributed within intensive livestock zones (Fig. 2a). A few weekly spikes of $> 10 \mu\text{g m}^{-3}$ were observed at seven of the eight sites and two spikes of $7.7\text{--}8.3 \mu\text{g m}^{-3}$

NH₃ (Misselbrook et al., 2001; Sutton et al., 2009). Moreover, the lower ambient *T* could favor formation of NH₄NO₃ in the atmosphere, which has been observed at a few places of southern Ontario (Zhang et al., 2008; Yao et al., 2011), and thus led the depletion of NH₃ gas.

However, a biweekly peak of NH₃ concentration was observed in the early of February 2007 at MVT (8.8 ppb), ARK (6.4 ppb) and SWB (6.2 ppb) when the lowest ambient *T* occurred. The peak concentration of NH₃ at each site was 1–2 times higher than the site's average value during the period from December 2006 to March 2007. This phenomenon was not detected at the other five sites. The peaks in the coldest weeks were also observed at some sites belonging to Classes 5–7 as presented later. These peaks will be discussed later.

3.3 Seasonal variations of NH₃ in medium concentration zones

Category 2 includes sites with an AAN ranging from 1 to 3 μg m⁻³ and has a total of 36 sites. Category 2 was further classified into two sub-Categories, i.e., Category 2A for sites having no peaks occurred under the lowest *T* (< -7°C) and Category 2B for sites having peaks under the lowest *T*.

Category 2A includes 22 sites (Fig. 5a). The concentration of NH₃ in each weekly/biweekly sample was averaged over 22 sites and the time series of the spatially averaged value was obtained for analysis. The simple approach can make the common trends among sites more obvious. The disadvantage of this approach is that it smoothes the distinctive trends associated with specific sites. The spatially averaged value of NH₃ over the 22 sites in each weekly/biweekly sample fluctuated at 1.8 ± 0.9 μg m⁻³ (mean ± standard deviation, Fig. 5a) during the period from 1 June to 7 November 2006. The spatially averaged value decreased by approximately 20% and fluctuated at 1.4 ± 0.7 μg m⁻³ during the period from 7 November to 19 December 2006. The spatially averaged value sharply decreased down to 0.8 ± 0.4 μg m⁻³ at mid-December 2006 and then slowly increased and reached 1.3 ± 0.7 μg m⁻³ at the end of March 2007. Similar to those in the high concentration zones, the elevated concen-

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No significant correlations existed between the concentration of NH_3 and RH or T during the six-week period with high NH_3 levels (Fig. 7a, b). Regional transport of NH_3 from the high concentration zones may have led to the higher concentration of NH_3 in the low concentration zones. However, the broad peak of NH_3 in the Category 3 had a few weeks delay when compared to the peaks observed at the sites in high concentration zones in southwestern Ontario (Figs. 4–6), the latter cases being consistent with seasonal variations of NH_3 emissions associated with agricultural activities. For example, as reported by Lillyman et al. (2009), the agricultural emissions of NH_3 in June or in July across southern Ontario were only approximately one third of those in May. Zbieranowski and Aherne (2012, 2013) also pointed out that the highest concentration of NH_3 across agricultural zones of southern Ontario occurred in May. As presented above, a few peaks of NH_3 in the high concentration zones indeed occurred before or during early June 2006.

However, the enhanced emissions of NH_3 from agricultural and non-agricultural activity before or during early June cannot explain the broad peak during the period from 13 June to 1 August 2006 in Category 3 (Fig. 7a). The lifetime of atmospheric ammonia is relatively short (a few days, Wen et al., 2013). It was unlikely to take such a long time (more than a week) to transport NH_3 from higher concentration zones to these low concentration sites with known wind conditions, despite the dominant wind was from the west and the southwest (Fig. 2a). As discussed later, negative correlations were obtained for NH_3 concentration measured at tens of sites between southeastern Ontario and southwestern Ontario. Thus, the regional transport of NH_3 likely happened in a way described in Hypothesis-A, which will be detailed in Sect. 4.1.

Again, at three sites (RBY, Vansickle (VAL) and GAL), a peak of NH_3 was observed in January–February 2007 when T was as low as -10°C (Fig. 7c). The peak concentration of NH_3 observed at each site was 2–3 times higher than the site's average value during the period from December 2006 to March 2007.

4 Discussion

4.1 Regional transport of NH₃ to low concentration zones at $T > 0\text{ }^{\circ}\text{C}$

To examine the contribution of direct atmospheric transport of NH₃ from higher emission sites to lower emission sites, the relationship between the site TEV, which had the highest AAN (6.1 $\mu\text{g m}^{-3}$) among all of the 74 sites, and the site DDK, which was 30 km downwind of TEV (noting that the dominant wind was from the west and the southwest) and had an AAN of 1.7 $\mu\text{g m}^{-3}$, was investigated as an example. A moderately good correlation, i.e., $[\text{NH}_3]_{\text{DDK}} = 0.36 \cdot [\text{NH}_3]_{\text{TEV}} + 0.13$ with $R^2 = 0.58$ ($P < 0.01$), was obtained for NH₃ concentration between the two sites when six NH₃ spikes $> 9\text{ }\mu\text{g m}^{-3}$ at TEV were excluded (Fig. 8). The correlation should at least partially due to regional transport and/or similar meteorological conditions. As discussed above, the concentrations of NH₃ at most of the agriculture sites were higher than 1 $\mu\text{g m}^{-3}$. It is thus reasonable to assume that the local emission of NH₃ at DDK contributed 1 $\mu\text{g m}^{-3}$ to the total of 1.7 $\mu\text{g m}^{-3}$ (AAN). This suggests that NH₃ from atmospheric transport only contributed 0.7 $\mu\text{g m}^{-3}$ to the ANN at DDK, which was only one tenth of the ANN at TEV. Moreover, in five out of the six spikes at TEV, the weekly concentrations of NH₃ at TEV were approximately one order of magnitude higher than those at DDK during the same period. It can be expected that the direct transport to further locations (e.g., a few hundred kilometers away) from agricultural zones would be much smaller. A similar conclusion was also found in a previous study (Theobald et al., 2012).

However, when the concentrations of NH₃ in each pair of 74 sites were correlated to each other, a few negative correlations were obtained between southwestern sites and southeastern sites. Table 1 and Fig. S4 showed these pairs in which negative correlations were obtained with $R^2 > 0.4$ and $P < 0.01$.

The dominant wind from the west and the southwest likely played an important role on regional transport of NH₃ from southwestern Ontario to southeastern Ontario (Wen et al., 2013). In addition, land-lake breeze (land wind is from the south in daytime while

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lake wind is from the north at night) might have influenced the regional transport of NH_3 to the southeastern sites adjacent to Lake Ontario. Regional transport signal of NH_3 at the southeastern sites adjacent to Lake Ontario could be different from that at sites dozens or hundreds kilometers north of Lake Ontario. To explore the role of regional transport in the negative correlations of NH_3 identified between southwestern and southeastern sites, NH_3 concentration at four selected sites in southeastern Ontario were analyzed in detail. The four selected sites, Whitney (WTY) → Hartsmere (HTS) → Fernleigh (FNL) → Crow Lake (CWL), follow a northwest to southeast transect, and are all located in non-agricultural zones.

At WTY, NH_3 concentrations were negatively correlated to those at Tobermory (TOB) and at EGC (Table 1 and Fig. 9a). NH_3 at TOB fluctuated and increased during the period from 6 June to 29 August 2006 and then fluctuated and decreased till the end of December 2006. The temporal trend matched that of T well ($R^2 = 0.44$ with $P < 0.01$). Higher ambient T usually disfavors formation of ammonium nitrate which is the sink of NH_3 gas (Seinfeld and Pandis, 1998). In contrast, higher soil T favors decomposition of organics, but inhibits the nitrification process (Grunditz and Dalhammar, 2001; Pagans et al., 2006). Thus, higher soil T usually results in higher emissions of NH_3 (Lillyman et al., 2009). The temporal variation of NH_3 at EGC was generally similar to that at TOB. However, during the period from 6 June to 29 August 2006, NH_3 at WTY fluctuated and decreased and reached a minimum of $0.2 \mu\text{g m}^{-3}$ in August, which probably represented the maximum contribution from local emissions at this site because T was the highest during this period. Higher concentrations of NH_3 at WTY in early June were probably from external transport of NH_3 associated with enhanced agricultural emissions in May. With the external transport signal decreasing from June to August, the concentrations of NH_3 at WTY decreased accordingly. From the end of September to the end of October, NH_3 at WTY fluctuated and increased while T decreased. The increase of NH_3 in concentration probably reflected the enhancement of new external transport signal.

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At HTS, concentrations of NH_3 were negatively correlated with that at AYL. The concentration of NH_3 at HTS increased from $< 0.1 \mu\text{g m}^{-3}$ in early June to the maximum value of $0.6 \mu\text{g m}^{-3}$ in the end of June (Fig. 9b). From early July to the end of July, the concentration of NH_3 at HTS decreased to $\sim 0.1 \mu\text{g m}^{-3}$ and remained at 0.1 – $0.2 \mu\text{g m}^{-3}$ in August and September. The $0.2 \mu\text{g m}^{-3}$ should represent the maximum contribution from local emissions at this site because T was the highest in the early of August. The increase of NH_3 at HTS in June 2006 was probably due to transport of NH_3 from the southwestern agriculture zones with higher emissions of NH_3 . The maximum value at HTS had more than two weeks delay when compared to the spikes of NH_3 observed in the southwestern Ontario (Figs. 4–6). Thus, the Hypothesis-A was likely a reasonable mechanism to explain the regional transport of NH_3 to HTS in the June. The decrease of NH_3 at HTS from early July 2006 was probably due to decreased external transport signal. In early October, NH_3 rapidly increased and then fluctuated at a higher value, which should attributed to new external transport signal arrived at HTS.

At FNL, NH_3 concentrations were negatively correlated with those at Kincardine (KIN) and Zurich (ZUR) (Table 1 and Fig. 9c). A broad peak of NH_3 at FNL occurred during the period from the mid-June to the end of July. NH_3 rapidly decreased to $\sim 0.2 \mu\text{g m}^{-3}$ in early August and stayed low through the rest of August. Similar to discussions for the above two sites, $0.2 \mu\text{g m}^{-3}$ was proposed to be the maximum contribution from local emissions at FNL. The broad peak between June and July was also likely related to regional transport and can be explained by Hypothesis-A. NH_3 gradually increased from early September to mid-October, suggesting a new transport signal appeared. After mid-October, NH_3 fluctuated at higher concentration levels. The reverse temporal trend was generally observed at KIN and ZUR, leading to their concentrations of NH_3 being negatively correlated to that at FNL.

At CWL, NH_3 concentrations were negatively correlated with those at COM and WLO (Fig. 9d). The concentrations of NH_3 at CWL increased from $0.2 \mu\text{g m}^{-3}$ in early June to the maximum concentration of $1.4 \mu\text{g m}^{-3}$ during 11–18 July and then decreased. The reverse trend was observed at COM and WLO. The concentration peak of NH_3

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at CWL in mid-July was also likely associated with regional transport of NH_3 and can be explained by Hypothesis-A. This is because the peak has over one month delay, compared to high agricultural emissions of NH_3 in May and the early of June at sites of southwestern Ontario. The concentrations of NH_3 at CWL reached a lower value ($\sim 0.2 \mu\text{g m}^{-3}$) in September and then fluctuated between September and November. $0.2 \mu\text{g m}^{-3}$ could also represent the maximum contribution from local sources to the observed NH_3 concentration. The concentrations of NH_3 at CWL gradually increased after the end of November, suggesting the arrival of a new transport signal.

4.2 Regional transport of NH_3 to low concentration zones at $T < 0^\circ\text{C}$

As shown in Figs. 7a–c and 9a–d, no decreases of NH_3 concentrations were observed at these low concentration sites during the period from December 2006 through March 2007. At a few sites, the concentrations of NH_3 in the winter even increased to some extent and were higher than their respective concentrations in June and July 2006. For example, NH_3 at WTY and FNL gradually increased from the lowest concentration in the end of August to a higher value in mid-October and then fluctuated at the higher value through the winter. The average value of NH_3 ($0.5 \pm 0.2 \mu\text{g m}^{-3}$) at WTY during the period from the mid-October 2006 through March 2007 was significantly higher than the average ($0.4 \pm 0.1 \mu\text{g m}^{-3}$) during the period from June through July 2006 with 95 % confidence. The same phenomenon was also observed at FNL.

The maximum contribution from local emissions to NH_3 measured at WTY and FNL was likely $\leq 0.2 \mu\text{g m}^{-3}$ as discussed in Sect. 4.1. The Hypothesis-A should also apply in the cold season, which might have increased NH_3 at WTY and FNL. However, the magnitude of NH_3 increase in the cold seasons via this mechanism should be much smaller than that in the hot seasons due to the very low T and thus low natural and reemissions of NH_3 along the transport paths. Thus, the higher NH_3 levels in the cold seasons compared to the hot seasons at these sites were likely caused by different mechanisms. One likely candidate is the regional transport of NH_4NO_3 formed at pol-

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luted areas to less polluted areas followed by its evaporation that produces NH_3 gas. In the cold seasons, NH_4NO_3 can be formed in the polluted environments of the southern Ontario (Yao et al., 2011; Yao and Zhang, 2012). The chemically formed NH_4NO_3 in the atmosphere was mainly present in the particles $< 2.5 \mu\text{m}$ (Zhang et al., 2008; Yao and Zhang, 2012) and can be transported over dozens to hundreds of kilometers, depending on ambient conditions. When the NH_4NO_3 arrived at receptor sites with low concentrations of NH_3 , the product of $[\text{HNO}_3] \cdot [\text{NH}_3]$ was probably less than the equilibrium constant of NH_4NO_3 and resulted in the release of NH_3 gas from the particle phase. In the warm seasons from June to August, the chemically formed NH_4NO_3 in the atmosphere was often thermodynamically disfavored in southern Ontario (Zhang et al., 2008) and ammonium was mainly associated with sulfate in atmospheric particles. Thus, this mechanism might be more important in winter than in summer for producing NH_3 at remote locations downwind of polluted areas.

4.3 Analysis of elevated NH_3 concentration at $T < -7^\circ\text{C}$

As mentioned early, the elevated concentrations were observed at 20 out of the 74 total sites when the biweekly averaged ambient T sharply decreased to below -7°C . In southwestern Ontario, these sites were situated either at Algonquin Arch or evenly distributed at the two sides of the Arch (Fig. 10a). Note that Algonquin Arch was formed in Paleozoic time (Johnson, 1992). However, the sites in southeastern Ontario were located on a much narrow line, which almost overlapped the demarcation line between non-agriculture and agriculture zones in this region.

Among these sites, a good correlation existed between the elevated concentration and associated AAN; so was the case between the elevated concentration and the net increase of NH_3 (calculated as the difference between the elevated concentration and the minimum concentration in January and February) (Fig. 10b). At the southwestern sites, the good correlation implies that the elevated NH_3 concentration were mainly due to local emissions. However, agricultural activity was limited in January and February. Emissions from accident outdoor agricultural activity at the lowest ambient T were

unlikely. Indoor agricultural activity should neither be the main cause for the elevated concentration. This is because indoor activity occurred throughout the whole winter and should not cause elevated concentration only in the coldest two weeks and only at specific sites. In southeastern Ontario, the elevated NH_3 supposed to be related to regional transport of NH_3 . However, regional transport should cause an increase of NH_3 in a broad band zone downwind of source zones instead of only on a narrow line along ~ 300 km length in the middle of agricultural and non-agricultural areas. Thus, the elevated NH_3 under extremely low T at sites in both agricultural and non-agricultural regions cannot be explained by existing knowledge.

Satellite data during that period showed that the percentage of snow-covered soil across the southern Ontario was approximately 100 %, except over lakes, rivers and traffic roads, etc. (Fig. S2). The emission of NH_3 from snow-covered soil under harsh low-temperature conditions were traditionally considered to be very low (Sommer and Hutchings, 2001; Sutton et al., 2009; Sheppard et al., 2010). However, a few studies had demonstrated that microbial processes continued in snow-covered soils, and a significant portion of decomposition and production of microbially derived trace gases can occur in snow-covered soils (Groffman et al., 2001; Nemergut et al., 2005; Edwards et al., 2006). This is because snow can insulate soil and protect the microbial community from freezing ambient conditions (Nemergut et al., 2005). These previous studies and observations in this study suggested that emissions of NH_3 from snow-covered soil need to be re-examined.

4.4 Missing emission sources of NH_3 in two agricultural zones

When the geographical distribution of NH_3 concentration was compared with that of NH_3 emission inventory recently developed by Environment Canada, inconsistency was found at two zones (B and D) as circled in Fig. 2a, b. Two sites (TOB and WIA) between Lake Huron and Georgian Bay (circled B zone in Fig. 2a) were approximately 100–150 km distance from the high NH_3 emission zone (circled A zone in Fig. 2a). NH_3 at the two sites was $1.1 \mu\text{g m}^{-3}$, which was approximately a quarter of those in A

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zone. However, NH_3 emission from B zone was approximately one order of magnitude smaller than that from A zone. Direct regional transport of NH_3 from A zone to B zone was likely unimportant because of the 100–150 km distance between the two zones. In fact, AAN at MOO, a site between A zone and B zone and approximately 30 km from A zone, was only $1.0 \mu\text{g m}^{-3}$. NH_3 transported from A zone to B zone should be diluted to a much higher extent than that from A zone to the site of MOO due to further distance to B zone. Thus, NH_3 emission from B zone was thought to be underestimated by a factor of 2 to 3.

Comparisons between B zone and C zone also support the above conclusion (Fig. 2b). The AANs at B zone were close to or even higher than most of sites at C zone. However, the emission of NH_3 from B zone was significantly lower than that from C zone (Fig. 2b), suggesting the potential underestimation of NH_3 emission from B zone. Another zone which NH_3 emission was also potentially underestimated was D zone. AANs inside D zone were approximately half of those inside A zone, but the emission from D zone was approximately one-third of that from A zone. NH_3 emission from D zone seemed to be underestimated by several ten percent (30–50 %).

Ammonia in soils can be constantly formed from biological degradation of organic compounds (Sommer, 2001; Beusen et al., 2008). In agricultural zones, external N input to soil mainly includes manure and N fertilizer application, atmospheric deposition of NO_y and biogenic N fixation. Atmospheric deposition of NO_y and biogenic N fixation could release NH_3 gas through soil N cycling processes, but were not considered in the emission inventory of NH_3 . Atmospheric deposition of NO_y might be a negligible source to N budget in soil at B zone because of low NO_2 concentration (Fig. S1). Globally, the estimated N fixed biologically in agricultural systems was 50–70 Tg N per year. Soybean was the dominant crop legume and fixed 16.4 Tg N globally and 5.7 Tg N in the US (Galloway et al., 2008; Herridge et al., 2008). Biogenic N fixation in agriculture systems followed by soil N cycling in B agriculture zones should be investigated in the future in order to identify missing sources.

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C zone is located immediately downwind of the zone with intensive anthropogenic emission of NO_x (Fig. S1). High atmospheric deposition of NO_y was expected at C zone. The deposited NO_y can infiltrate to sub-surface soil and convert into NH_3 through soil N cycling processes. Atmospheric deposition of NO_y could be one of the important sources for local emissions of NH_3 at C zone and might have contributed to the underestimation of NH_3 emissions. Moreover, N fixed biologically by agriculture systems could also be a potential source at C zone.

5 Conclusions

A comprehensive analysis was conducted on the high spatial-resolution weekly/biweekly ambient NH_3 concentration data measured mainly from June 2006 to March 2007 at 74 sites across southern Ontario. In the remote and rural non-agricultural zones, the AAN was less than $1 \mu\text{g m}^{-3}$ and the same was true for a few sites in low intensity agricultural zones. Approximately 50 % of the sites had an AAN in the range of $1\text{--}3 \mu\text{g m}^{-3}$ and exceeded the new critical level value. There were eight sites situated inside the intensive livestock production zones having an AAN in the range of 3.0 to $6.1 \mu\text{g m}^{-3}$. These high NH_3 concentration levels could have a potential damage to vegetation.

At non-agricultural sites with low NH_3 concentrations, local emissions contributed a maximum of $0.2 \mu\text{g m}^{-3}$ to the overall measured concentration, the rest was from regional transport which was the dominant contributor during most of the time. The transport of NH_3 to these sites in the warm seasons from June through August 2006 can be explained by a proposed mechanism combining bi-directional air/soil and air/plant exchanges of NH_3 and transport of air masses containing the so-produced NH_3 along the trajectories. Such a process generally took a few weeks transporting NH_3 from emission sources in southwestern Ontario to receptor sites in southeastern Ontario, consistent with the time-lag in peak concentrations between the two regions. However, in the cold seasons from the end of October 2006 to March 2007, the transport of NH_3

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was likely associated with regional transport of NH_4NO_3 followed by the release of NH_3 from NH_4NO_3 at receptor sites. One unexplained phenomenon was the increase of ambient NH_3 level observed in the coldest two weeks at 20 out of 74 sites. The 20 sites were distributed along a banana-sharp curve in ~ 600 km length extending from southwestern to southeastern Ontario. The mechanisms causing the high NH_3 at these sites are not clear and require further studies.

In two agriculture zones, the observed high concentrations of NH_3 were contradictory to the low emissions in the recently developed emission inventory. Emissions of NH_3 at the two zones were likely underestimated. N fixed biologically in agricultural systems and/or atmospheric deposition of NO_y followed by soil N cycling processes should be considered in future development of NH_3 emission inventory to explain the missing sources.

Supplementary material related to this article is available online at:

<http://www.biogeosciences-discuss.net/10/12773/2013/>

[bgd-10-12773-2013-supplement.pdf](#).

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Table 1. Negative correlation between each pair of the sites.

Southwestern site	Southeastern site	R^2 ($P < 0.01$)
FNL	EGC	0.49
	KIN	0.47
	MIL	0.43
	MLM	0.49
	SMY	0.43
	WLO	0.52
	ZUR	0.47
MON	MOO	0.40
	TEV	0.41
	ZUR	0.51
AYL	HTS	0.42
	MYN	0.48
CWL	COM	0.42
CWL	WLO	0.40
WTY	TOB	0.54
WTY	EGC	0.44
GAL	MOO	0.43

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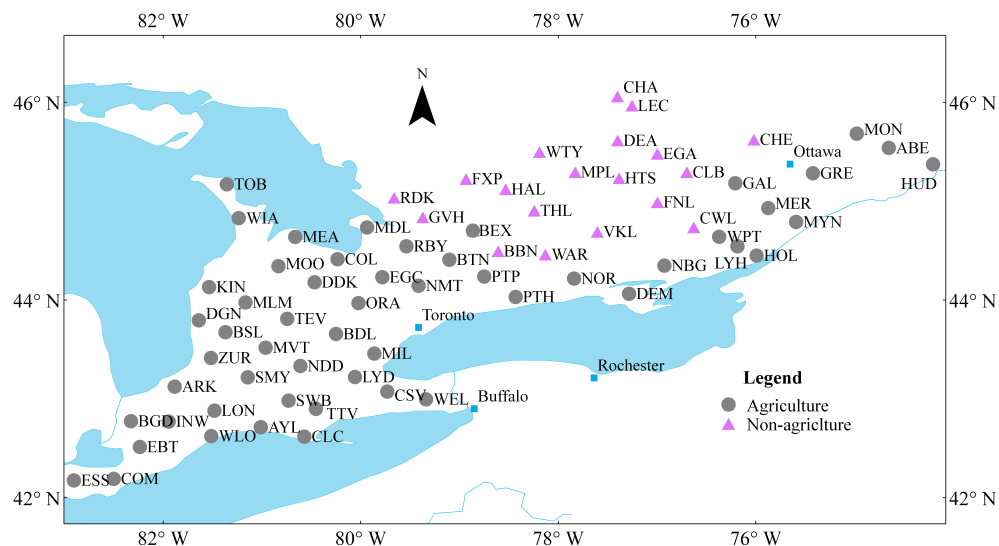


Fig. 1. Locations of the 74 sampling sites across southern Ontario.

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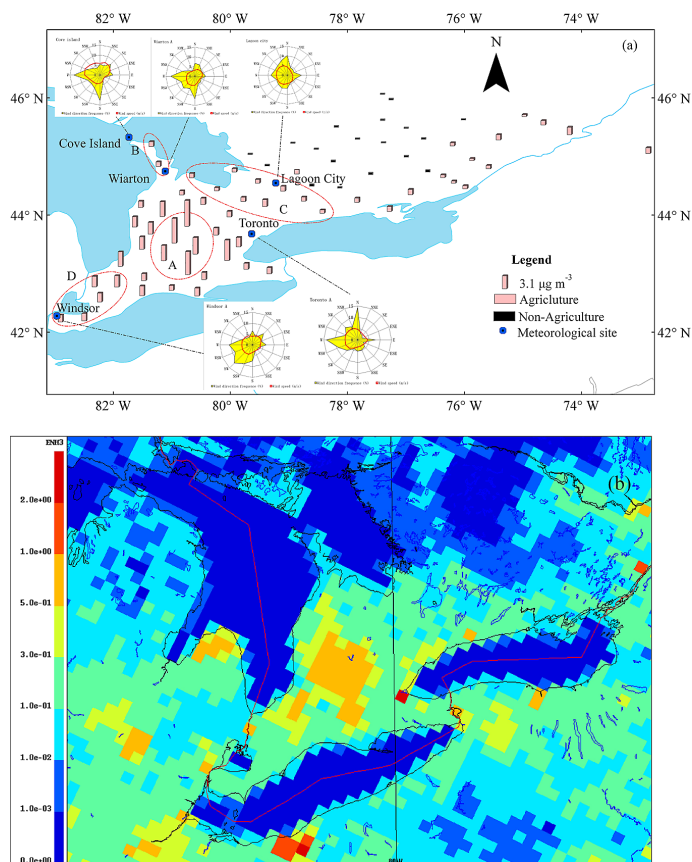


Fig. 2. (a) Geographical distribution of annual average ambient NH_3 concentration with superimposed wind roses at five meteorological stations; and (b) 2011 NAESI NH_3 emission inventory in the unit of $\text{ktonnes yr}^{-1} \text{grid}^{-1}$ ($15\text{km} \times 15\text{km}$).

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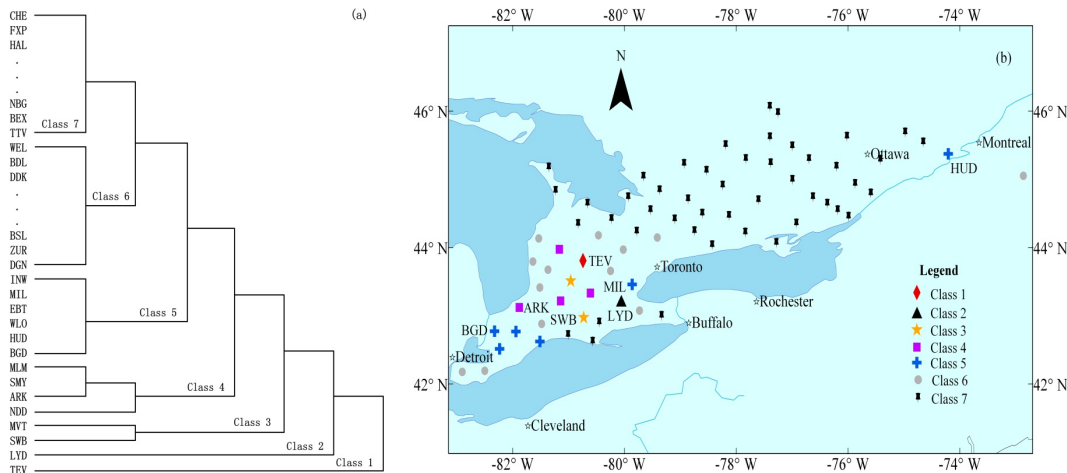


Fig. 3. Dendrogram of cluster tree for NH_3 at 74 sites (a) and their geographical distribution across southern Ontario (b).

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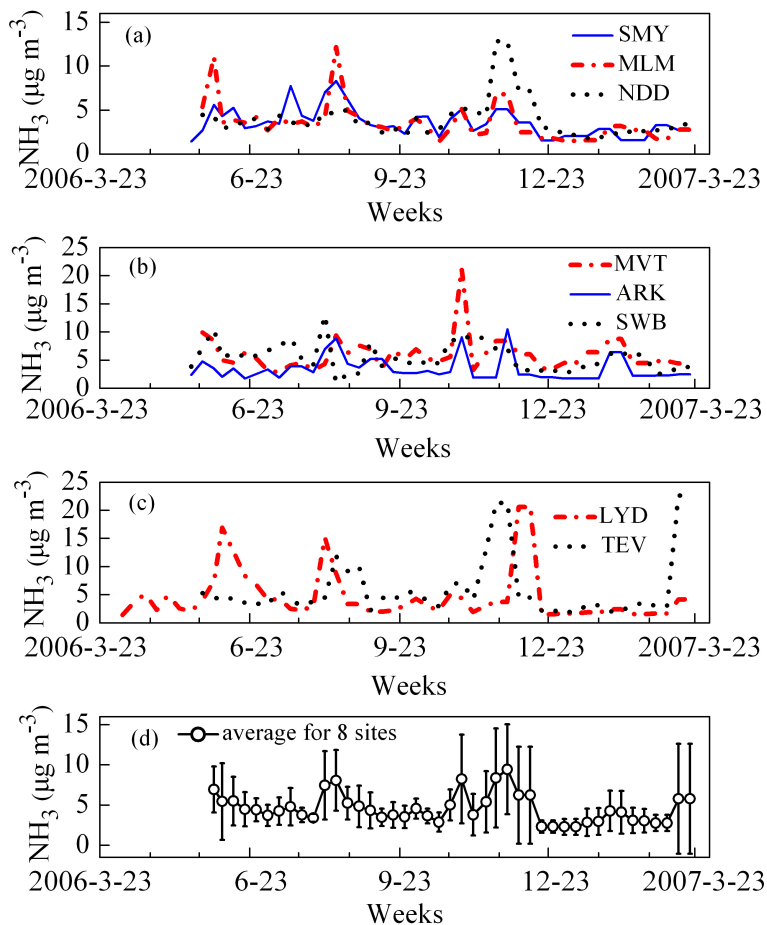


Fig. 4. Temporal variations of NH_3 in 2006–2007 at high concentration zone sites: **(a)** three sites having no spike in winter, **(b)** three sites having a spike in winter, **(c)** two sites having data before June, and **(d)** the spatially averaged value over eight sites.

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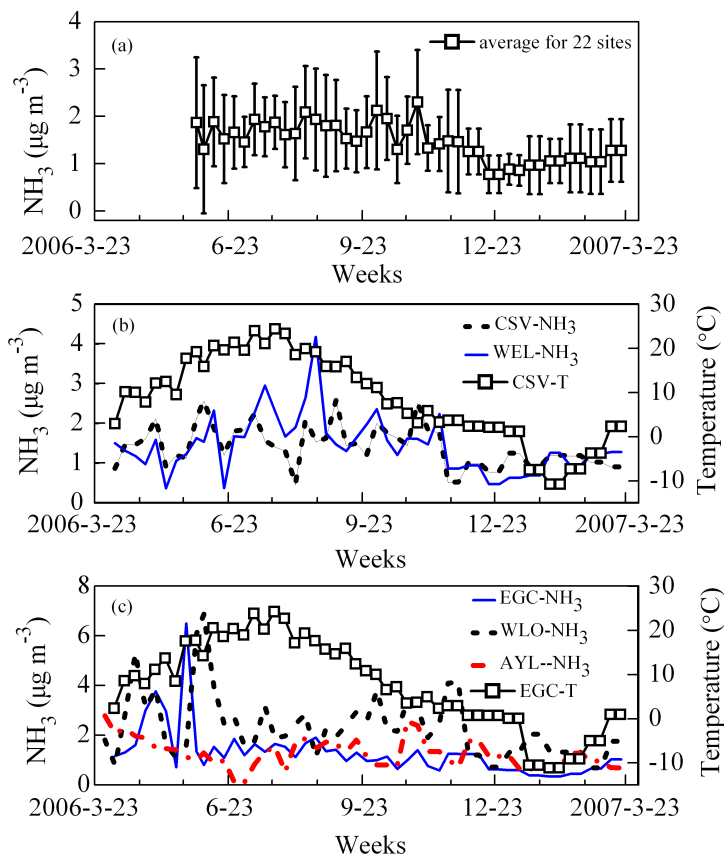


Fig. 5. Temporal variations of NH_3 in 2006–2007 at sites located in the medium concentration zones but absent of spikes during the coldest temperature periods: **(a)** the spatially averaged value over 22 sites, **(b)** two sites having no spikes before the early of June, and **(c)** three sites having spikes before the early of June.

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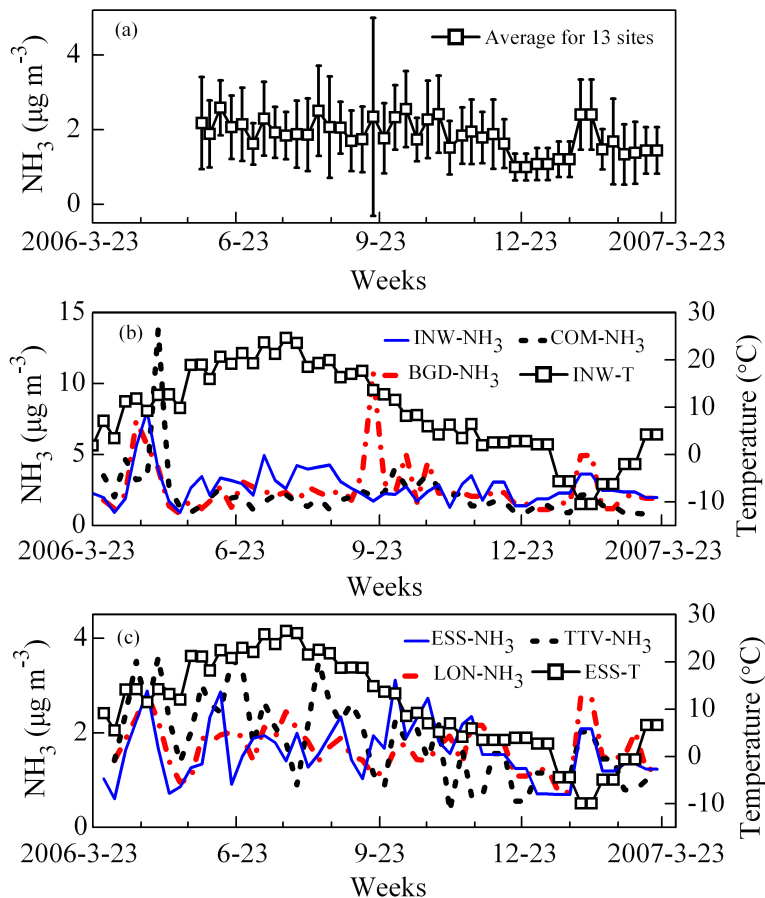


Fig. 6. Temporal variations of NH_3 in 2006–2007 at sites located in the medium concentration zones sites but with spikes during the coldest temperature periods: **(a)** the spatially averaged value over 13 sites, **(b)** three sites having spikes before the early of June, and **(c)** three sites having no spikes before the early of June.

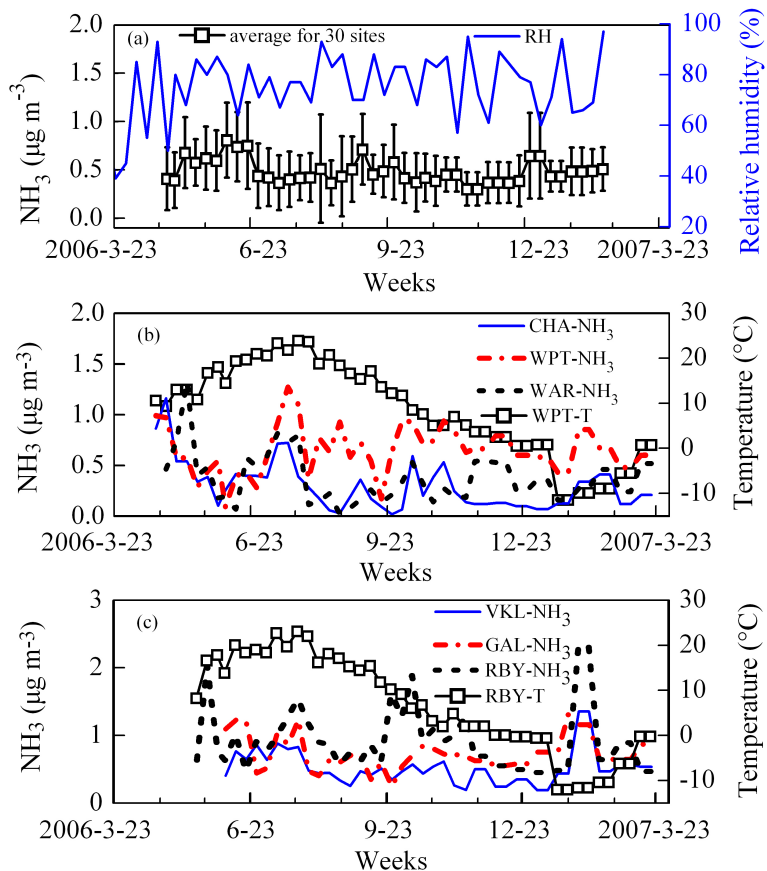


Fig. 7. Temporal variations of NH_3 in 2006–2007 at sites located in the low concentration zones: **(a)** the spatially averaged value over 30 sites, **(b)** three sites having data before June, and **(c)** three sites having no data before June.

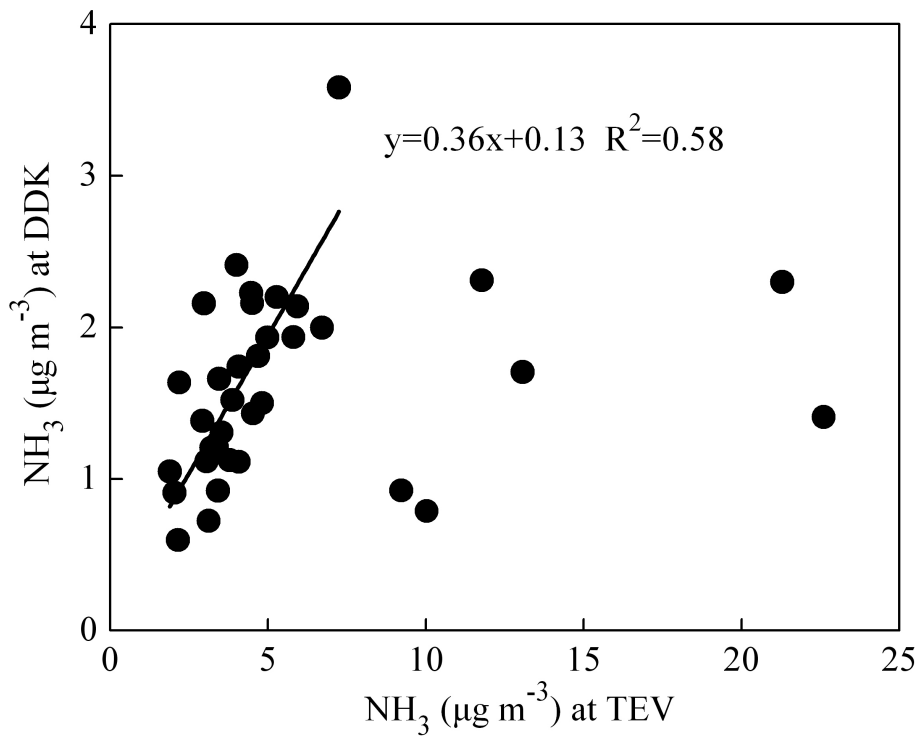


Fig. 8. Correlation of NH₃ between sites TEV and DDK.

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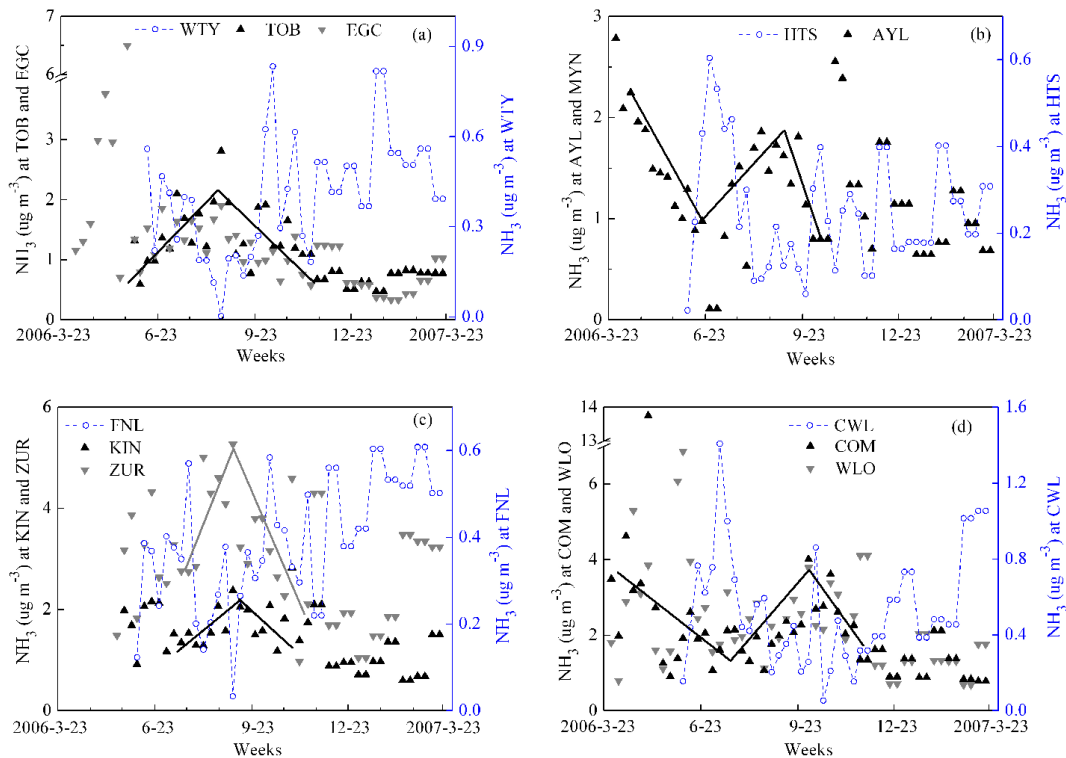


Fig. 9. Comparison of time series of NH_3 concentration between southwestern and southeastern sites (the straight lines are trend lines artificially drawn).

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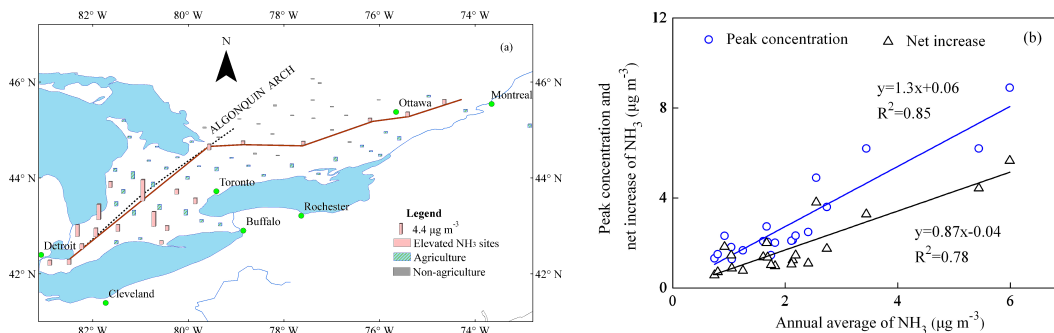


Fig. 10. (a) Distribution of sites with elevated NH_3 in the coldest weeks, and (b) correlations between peak (or net increase) concentrations and annual averages for these sites.

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