



# Is vehicular emission a significant contributor to ammonia in the urban atmosphere?



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## HIGHLIGHTS

- NH<sub>3</sub> emission factors from on-road vehicles were <0.5–0.9 ppb NH<sub>3</sub> per 50 ppb NO.
- Vehicle-derived NH<sub>3</sub> contributes <10% to urban atmospheric ammonia.
- Soil could emit much more NH<sub>3</sub> than on-road vehicles in urban atmosphere.

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## ABSTRACT

To investigate emissions of NH<sub>3</sub> from on-road vehicles and their contribution to atmospheric NH<sub>3</sub>, we analyzed a suite of measurements including NH<sub>3</sub>, NO, SO<sub>2</sub>, black carbon (BC), NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub>, etc., collected in summer 2007 at a site near a highway with the highest traffic density in Canada. From 26 to 28 August 2007, large variations of NO mixing ratio (from <1 ppb to >110 ppb) and BC concentration (from <0.5 to >6 µg m<sup>-3</sup>) were simultaneously observed and were found to be associated with varying contributions of air pollutants emitted by vehicles on the highway. Using NO as a tracer of vehicular plumes, the estimated emission factor of NH<sub>3</sub> relative to NO from on-road vehicles was less than 0.5–0.9 ppb NH<sub>3</sub> per 50 ppb NO. The average mixing ratios of NH<sub>3</sub> and NO during the three days were 4.0 ± 2.4 ppb and 23 ± 33 ppb, respectively. The NH<sub>3</sub> derived from on-road vehicular emissions was estimated to be less than 0.4 ppb on average during the measurement period, accounting for ~10% of the mixing ratio of NH<sub>3</sub> measured at the sampling site. Several spikes of NH<sub>3</sub> were observed on these days with the maximum mixing ratio of NH<sub>3</sub> reaching 16.9 ppb. The observed spikes of NH<sub>3</sub> were probably ascribed to non-traffic emissions of NH<sub>3</sub> near the sampling site. We conclude that emissions of NH<sub>3</sub> from on-road vehicles only accounted for a much small fraction of urban atmospheric ammonia, and more important sources are yet to be identified. However, it is still unknown whether negligible emissions of NH<sub>3</sub> from vehicles in Toronto are just the result of its local traffic composition or they are generally true world wide. In addition, the negligible emissions could also be due to unknown loss in the GP-IC, although it is not found so far.

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## 1. Introduction

Ammonia plays an important role in atmospheric chemical processes because it is the major alkali gas in the atmosphere (Sutton et al., 2009; Ellis et al., 2011). In the urban atmosphere, on-

road vehicular emissions have been proposed as the largest or one of the largest contributors to ammonia (Sutton et al., 2000; Dore et al., 2005; Li et al., 2006; Whitehead et al., 2007; Ianniello et al., 2010; Saylor et al., 2010; Meng et al., 2011). The introduction of three-way catalytic converters is commonly believed to be the cause of the increased NH<sub>3</sub> in vehicular plumes (Fraser and Cass, 1998; Huai et al., 2003; Cape et al., 2004; Heeb et al., 2012). However, vehicular emission factors of NH<sub>3</sub> have been reported to be highly variable (Kean et al., 2009; Bishop et al., 2012) and the contribution from traffic emissions to ammonia in the urban

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atmosphere is also controversial (Nowak et al., 2012; Reche et al., 2012). Thus, more studies are needed to examine emissions of  $\text{NH}_3$  from on-road vehicles and their contribution to urban atmospheric ammonia.

If on-road vehicular emission is indeed a significant contributor to ammonia in the urban atmosphere, as proposed in the literature, a roadside site near a high-traffic-density highway should be an ideal place to examine the assumption. 401 Highway had the highest traffic density, estimated to be  $4.0 \times 10^5$  vehicles/day in Toronto, in Canada in 2007 (Bhuie et al., 2005). As estimated in this study, 60–70% of the traffic on 401 Highway consisted of light-duty vehicles. The air mass near the highway either had significantly high concentrations of air pollutants (e.g., NO and black carbon (BC)) emitted by on-road vehicles or contained much lower amounts of these pollutants, as presented later, depending on wind direction. This large difference makes it possible to estimate the emission factor of  $\text{NH}_3$  relative to NO (or BC) emitted by on-road vehicles.

An intensive campaign was undertaken between 17 and 28 August, 2007 to measure gas and particle concentrations at a site near 401 Highway in an urban area of Toronto, Canada (Fig. 1) (Yao et al., 2011). The collected data include one-minute resolution NO,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_3$  and BC and 15-min  $\text{NH}_3$  gas and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$ . Using the dataset, we attempt to estimate the emission factor of  $\text{NH}_3$  from on-road vehicles and to quantify the contribution of vehicular emissions to urban atmospheric ammonia.

## 2. Experimental

During the period from 17 to 28 August, 2007, two mobile laboratories were parked side-by-side, 5 m apart, in a parking lot (with a cement ground surface) and were approximately 190 m from 401 Highway in the Greater Toronto Area (Fig. 1). When the wind direction was from the northwest, north and northeast, 401 Highway was situated upwind of the labs. A complementary suite of gas and particle analyzers was deployed, including a gas particle ion chromatograph (GP-IC, Dionex Corporation) for measuring gas and particle components, and a multi-angle absorption photometer for measuring black carbon (MAAP, Thermo

5012),  $\text{NO}_x$  (TECO 42C),  $\text{SO}_2$  (TECO 43CTL) and  $\text{O}_3$  (TECO 49C). The MAAP and gas analyzers yielded concentrations of BC and mixing ratios of NO,  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{O}_3$  at 1-min resolution. The  $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{O}_3$  analyzers had a regular calibration following the standard protocol (US EPA, Quality Assurance Guidance Document 2.3).

The Dionex GP-IC builds on the technique developed by Dasgupta's group (Al-Horr et al., 2003; Ullah et al., 2006) and yields a 15-min interval time-series of gas and particulate species concentrations. The GP-IC has two channels. In the gas channel of the GP-IC, air sampled at 5 LPM flowed through a diffusion wet denuder 45 cm in length was used to collect HCl,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{SO}_2$  and  $\text{NH}_3$  gases. The long denuder provided high efficiency for removing  $\text{SO}_2$  and the measured mixing ratio of  $\text{SO}_2$  agreed well with that measured by an  $\text{SO}_2$  analyzer (Yao et al., 2009, 2011). Even higher collection efficiency was expected for  $\text{NH}_3$  because Henry's constant for  $\text{NH}_3$  is larger than that for  $\text{SO}_2$ . The denuder effluent was then sequentially passed through cation and anion concentrator columns. All anions were absorbed by the anion concentrators while the  $\text{NH}_4^+$  was absorbed by the cation concentrators. During the 15-min analysis period, 15 mM NaOH was used to elute anions captured by the anion concentrator column, and the anions were analyzed directly online using a Dionex ICS-2000 system. 15 mM NaOH was used to elute the  $\text{NH}_4^+$  from the cation concentrator and  $\text{NH}_4^+$  was passed across a carbonate removal device (CRD-200). In the CRD-200, the ammonia diffused through the membrane into a deionized water stream where it hydrolyzed back to  $\text{NH}_4^+$  and was then detected by a CD25A conductivity detector. The  $(\text{NH}_4)_2\text{SO}_4$  solution was quantitatively injected into the system and it made a standard curve for calibration of  $\text{NH}_3$ . The analytical error for  $\text{NH}_3$  gas was  $\pm 10\%$  when the mixing ratio of  $\text{NH}_3$  ranged from 3 to 20 ppb. The instrument detection limit for  $\text{NH}_3$  was 0.6 ppb. A weekly calibration and maintenance program was conducted to minimize the analytical error for  $\text{NH}_3$  and  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$ . In the particle channel of the GP-IC, air sampled at 5 LPM flowed through a cyclone with a 2.5 micron cut-point to remove particles  $>2.5 \mu\text{m}$  and a diffusion wet denuder. A continuous particle collector was used to collect and

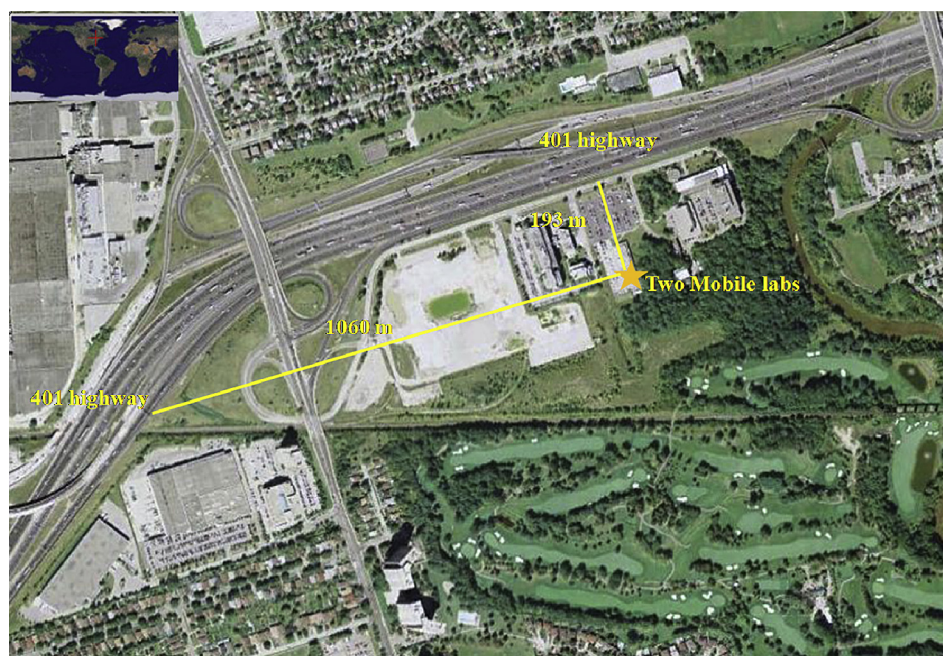
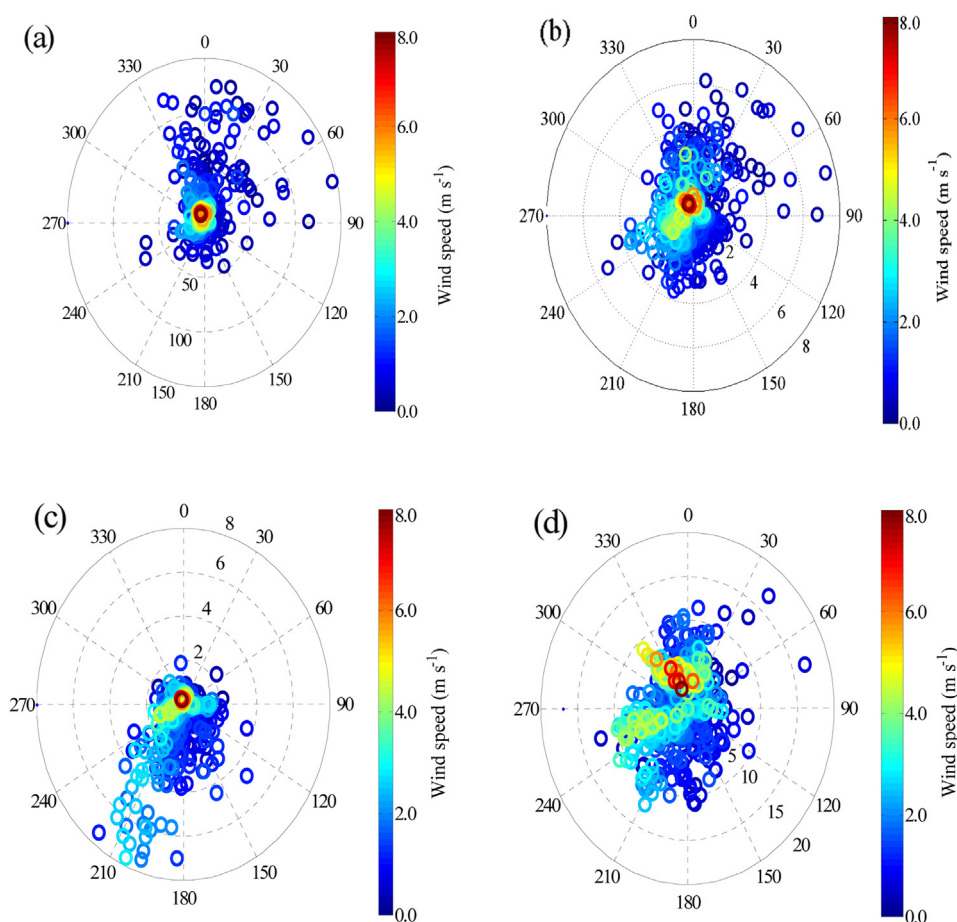


Fig. 1. Map of the sampling site near 401 Highway, Toronto, Canada.



**Fig. 2.** Polar plotting of mixing ratios or concentration of air pollutants in different wind directions and wind speeds (the radius represents the mixing ratio of pollutants in ppb or concentration in  $\mu\text{g m}^{-3}$ ; a: NO, b: BC, c:  $\text{SO}_2$ , d:  $\text{NH}_3$ ).

extract particles downstream of the denuder. The analytical methods were same as those in the gas phase.

The ambient air was drawn through a conductive silicone tube (Tsi, US) in  $\sim 2$  m length to the GP-IC. Temporal loss of  $\text{NH}_3$  due to adsorption on the inside surface of sampling lines has been reported to cause a delayed response for  $\text{NH}_3$  in field measurements and the time delay varied from dozens of seconds to tens of minutes (Yokelson et al., 2003; Schwab et al., 2007; Norman et al., 2009; von Bobritzki et al., 2010). However, the delay has a minor influence on the long-term averaged data, e.g., 30-min or even a longer time period which can completely cover the time delay. Norman et al. (2009) made a comparison between two  $\text{NH}_3$  gas measurements, in which one set of data was obtained from a GRAdient of AErosol and Gases Online Registrator (GRAEGOR) measurement with a sampling line in 30 cm length and one set of data was made by a Proton Transfer Reaction Mass Spectrometry (PTR-MS) with a much long sampling line in 17 m length. The two sets of data agreed well when 30-min average values (unit in ppb) were correlated with a regression equation of  $[\text{NH}_3]_{\text{PTR-MS}} = [\text{NH}_3]_{\text{GRAEGOR}} * 0.95 + 0.25$ ,  $R^2 = 0.83$  and  $N = 83$  samples. Our sampling line is only  $\sim 2$  m in length and between in 30 cm and 17 m used by Norman et al. (2009). The short-term delayed response for  $\text{NH}_3$  was not likely to affect our 15-min resolution  $\text{NH}_3$  measurements made by the GP-IC.

Meteorological data were obtained from the roof of a building about 100 m from two mobile labs. The data were in one-minute time resolution.

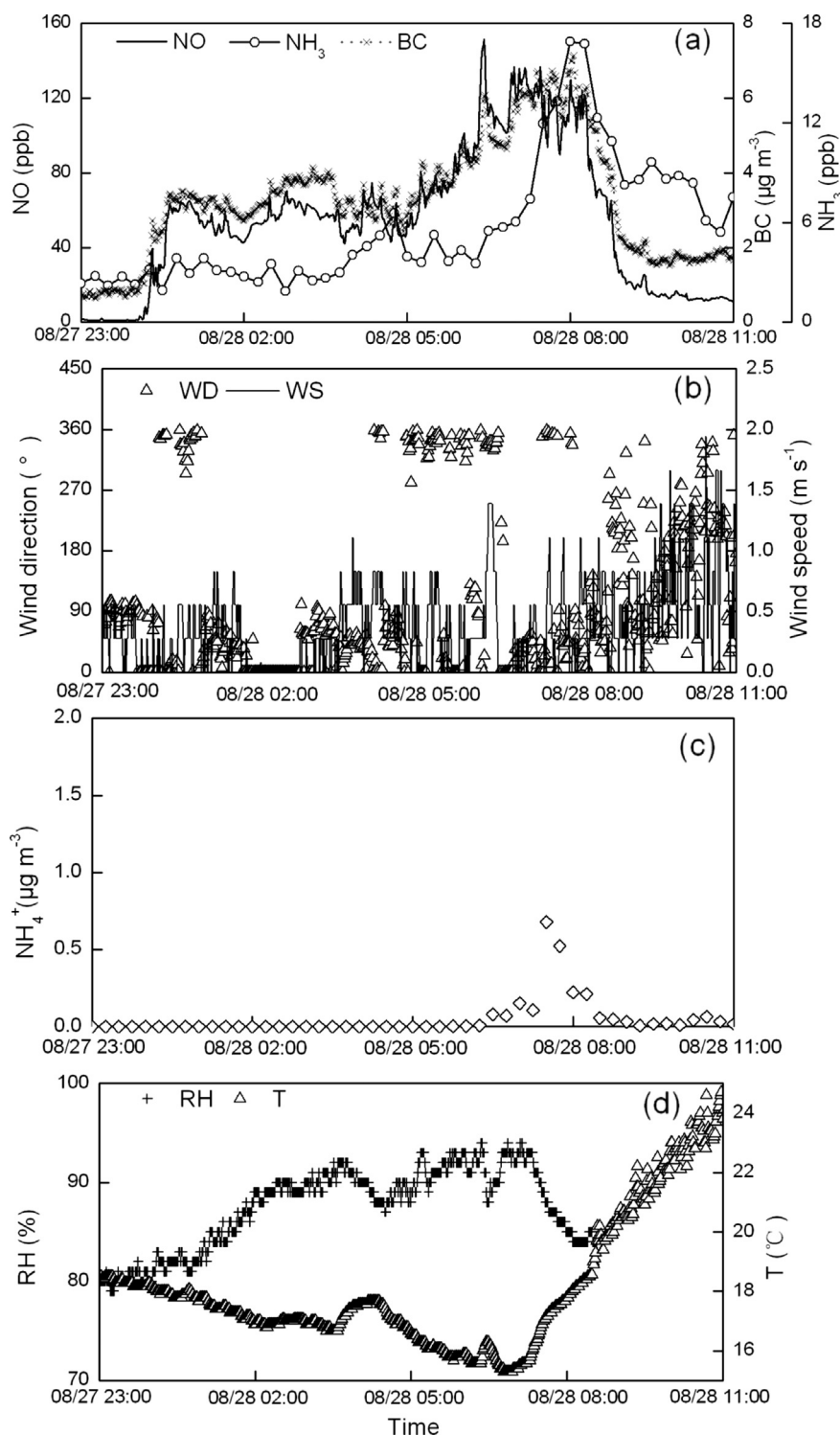
### 3. Results and discussion

#### 3.1. The relationship between air pollutants and wind during the campaign

Due to the fast titration reaction between NO and  $\text{O}_3$ , freshly emitted NO is converted to  $\text{NO}_2$  in a few minutes. Thus, the observed NO in ambient air is commonly believed to be due to local emissions. The higher mixing ratios of NO ( $> 50$  ppb) were generally associated with low wind speeds ( $< 2 \text{ m s}^{-1}$ ) and wind directions were mostly from the northwest, north and northeast (Fig. 2a). At these wind directions, 401 Highway was located upwind of the sampling site. When the wind speed was larger than  $4 \text{ m s}^{-1}$ , the mixing ratio of NO was generally less than 10 ppb due to dilution. Higher concentrations of BC ( $> 4 \mu\text{g m}^{-3}$ ) were generally associated with lower wind speeds ( $< 2 \text{ m s}^{-1}$ ) and wind directions were mostly from the northwest, north and northeast (Fig. 2b). However, the moderately higher concentrations of BC ( $2\text{--}4 \mu\text{g m}^{-3}$ ) were sometimes associated with wind directions from the southwest and the south, suggesting that BC could be from regional transport. Thus, NO was a better indicator than BC to reflect the influence of the on-road vehicle emissions at the sampling site. Higher mixing ratios of  $\text{SO}_2$  ( $> 4$  ppb) were overwhelmingly from the southwest because major industrial sources of  $\text{SO}_2$  were located in that direction (Fig. 2c). Thus,  $\text{SO}_2$  was a good indicator of regionally transported pollutants.

The relationship between mixing ratios of  $\text{NH}_3$  and winds was complicated (Fig. 2d), unlike that for NO, BC and  $\text{SO}_2$ . Most of the





**Fig. 3.** Temporal variations of gas and particle concentrations and meteorological conditions between 27 and 28 August 2007 (a: NO, NH<sub>3</sub> and BC; b: WD and WS; c: NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub>; d: RH and T).

high mixing ratios of NH<sub>3</sub> (>5 ppb) were associated with lower wind speed (<2 m s<sup>-1</sup>) regardless of wind direction, suggesting that local emissions could have been the major sources of NH<sub>3</sub> during these episodes. Soil emissions could be one of the important sources of NH<sub>3</sub> (Sutton et al., 2009) since they universally exist regardless of wind direction. Hu et al. (2008) reported that evaporation of dew droplets in the morning could also release NH<sub>3</sub> gas.

Based on the industrial emission inventory of air pollutants developed in 2007 (<http://www.ec.gc.ca/inrp-npri/>), industrial emissions of NH<sub>3</sub> were negligible in a 5 km range from the sampling site. Emissions of NH<sub>3</sub> from on-road vehicles could also have been a source (Burgard et al., 2006; Bishop et al., 2010, 2012) when the wind was from the northwest, north and northeast. Pandolfi et al. (2012) and Reche et al. (2012) proposed that emissions from

waste containers could be important sources of  $\text{NH}_3$  in the urban atmosphere in summer. Wednesday is garbage collection day in Toronto. The sources of  $\text{NH}_3$  could be particularly important on Tuesday evenings and early Wednesday mornings. A residential area is situated to the north of the sampling site (Fig. 1) and the waste containers could be a source of  $\text{NH}_3$ . Sewage water systems in Toronto include municipal sewage wastewater systems and rainwater drainage systems. Sewage lines running below streets often have open gates on top which can release gases. Rainwater drainage systems can release gases through holes on well caps to ambient air. Emissions of  $\text{NH}_3$  from sewage water systems in urban areas are poorly understood.

In addition, the moderately higher mixing ratios of  $\text{NH}_3$  (5–10 ppb) were sometimes associated with the higher wind speed ( $>4 \text{ m s}^{-1}$ , e.g., with wind directions between  $300^\circ$  and  $330^\circ$  and between  $240^\circ$  and  $270^\circ$  where strong emission sources of  $\text{NH}_3$  existed (Zbieranowski and Aherne, 2012). At this wind speed, much lower mixing ratios of NO were observed (Fig. 2a). Thus, the elevated  $\text{NH}_3$  at the higher wind speed could be mainly from regional transport.

### 3.2. Estimating the emission factor of $\text{NH}_3$ relative to NO from on-road vehicles

Comparing air masses from different directions can help to identify emission sources. An idea case representing air masses containing highly concentrated vehicle plumes from 401 Highway occurred between 26 and 28, August 2007 (Figs. 3ab and 4ab). Simultaneous increases of the NO mixing ratio and the BC mass concentration were observed on these three days (Fig. 3a and b) and were generally associated with wind speeds less than  $2 \text{ m s}^{-1}$  and with wind directions from the northwest, north and northeast (Figs. 3b and 4b). The temporal trends of NO and BC were almost the same during the three days period. Thus, the elevated NO and BC should be from emissions of vehicles traveling on the 401 Highway. In contrast, low mixing ratios of NO ( $<5 \text{ ppb}$ ) and low concentrations of BC ( $<0.5 \mu\text{g m}^{-3}$ ) were observed when winds were from the east, southeast or southwest, when the labs were situated upwind of the 401 Highway. NO was adopted as a tracer of vehicular plumes in the analysis presented below.

#### 3.2.1. Analyzing vehicular emissions of $\text{NH}_3$ between 27 and 28 August

From 11:00 pm on 27 August to 0:08 am on 28 August, the mixing ratio of NO was lower than 4 ppb (Fig. 3a), indicating a negligible contribution of air pollutants from vehicles on 401 Highway to the sampling site. During the period, the mixing ratio of  $\text{NH}_3$  was almost constant with an hourly average of  $2.5 \pm 0.3 \text{ ppb}$  (average  $\pm$  standard deviation). From 0:08 am to 0:38 am on 28 August, the mixing ratio of NO sharply increased from 2 ppb to 64 ppb with the wind direction changing from east to north, northeast or northwest (Fig. 3b). However, the mixing ratio of  $\text{NH}_3$  varied very slightly with an average of  $2.5 \pm 0.6 \text{ ppb}$ . From 0:45 am to 3:45 am,  $\text{NH}_3$  also varied within a narrow range, with an average mixing ratio of  $3.0 \pm 0.6 \text{ ppb}$ , while the measured mixing ratio of NO ranged from 42 to 65 ppb. Theobald et al. (2012) simulated dispersion of  $\text{NH}_3$  emitted from agricultural sources and found that dry deposition contributed to 7–30% mass loss of  $\text{NH}_3$  at 1000 m distance. When the  $\text{NH}_3$  emitted by vehicles on 401 Highway dispersed to the sampling site over a cement ground surface in  $\sim 190 \text{ m}$  distance, dry deposition of  $\text{NH}_3$  in such short distance were probably negligible. In addition, the concentration of  $\text{NH}_4^+$  in  $\text{PM}_{2.5}$  was less than the detection limit before 5:00 am, 28 August (Fig. 3c), suggesting no significant condensation sink for  $\text{NH}_3$ . Moreover, wet deposition was not expected for  $\text{NH}_3$  because no

rainfall was recorded and fog probably did not occur before 5:00 am on basis of the recorded RH.

Thus, the on-road vehicle emission factor of  $\text{NH}_3$  relative to NO was roughly estimated to be 0.5 ppb  $\text{NH}_3$  per 50 ppb NO (if indeed on-road vehicles emitted  $\text{NH}_3$ ). The estimated low emission factor of  $\text{NH}_3$  was consistent with more evidences observed on 28 August in which emissions of  $\text{NH}_3$  from on-road vehicles were likely a negligible contributor to the  $\text{NH}_3$  observed at the site. For example, the mixing ratio of NO increased from 55 ppb at 5:00 am to 151 ppb at 6:25 am. The net increase of NO was about 100 ppb during this period while no evident increase of  $\text{NH}_3$  was observed, with an average  $\text{NH}_3$  of  $4.7 \pm 0.7 \text{ ppb}$ . In our Supporting information, we compared the  $\text{NH}_3$  measured by the GP-IC with the  $\text{NH}_3$  measured by the denuder  $\text{PM}_{2.5}$  sampler in downtown Toronto and the results showed that a few ppb  $\text{NH}_3$  signal could be effectively detected by the GP-IC. In addition, the mixing ratio of  $\text{NH}_3$  rapidly increased from 6.0 ppb at 7:00 am to 16.9 ppb at 8:15 am. However, the mixing ratio of NO fluctuated and decreased during the period.

However, a good correlation between  $\text{NH}_3$  and NO was observed ( $[\text{NH}_3] = 0.093[\text{NO}] + 6.9, R^2 = 0.93$ ) when the mixing ratio of  $\text{NH}_3$  decreased from 16.9 ppb to 8.3 ppb from 8:00 am to 9:15 am during which period NO also decreased from 116 ppb to 20 ppb. The simultaneous decreases of  $\text{NH}_3$  and NO were due to the changes in wind directions from the north or northeast to the southeast, south or southwest (Fig. 3b). Thus, the good correlation between  $\text{NH}_3$  and NO during this short period were caused by meteorological factors and did not imply they were from the same emission sources.

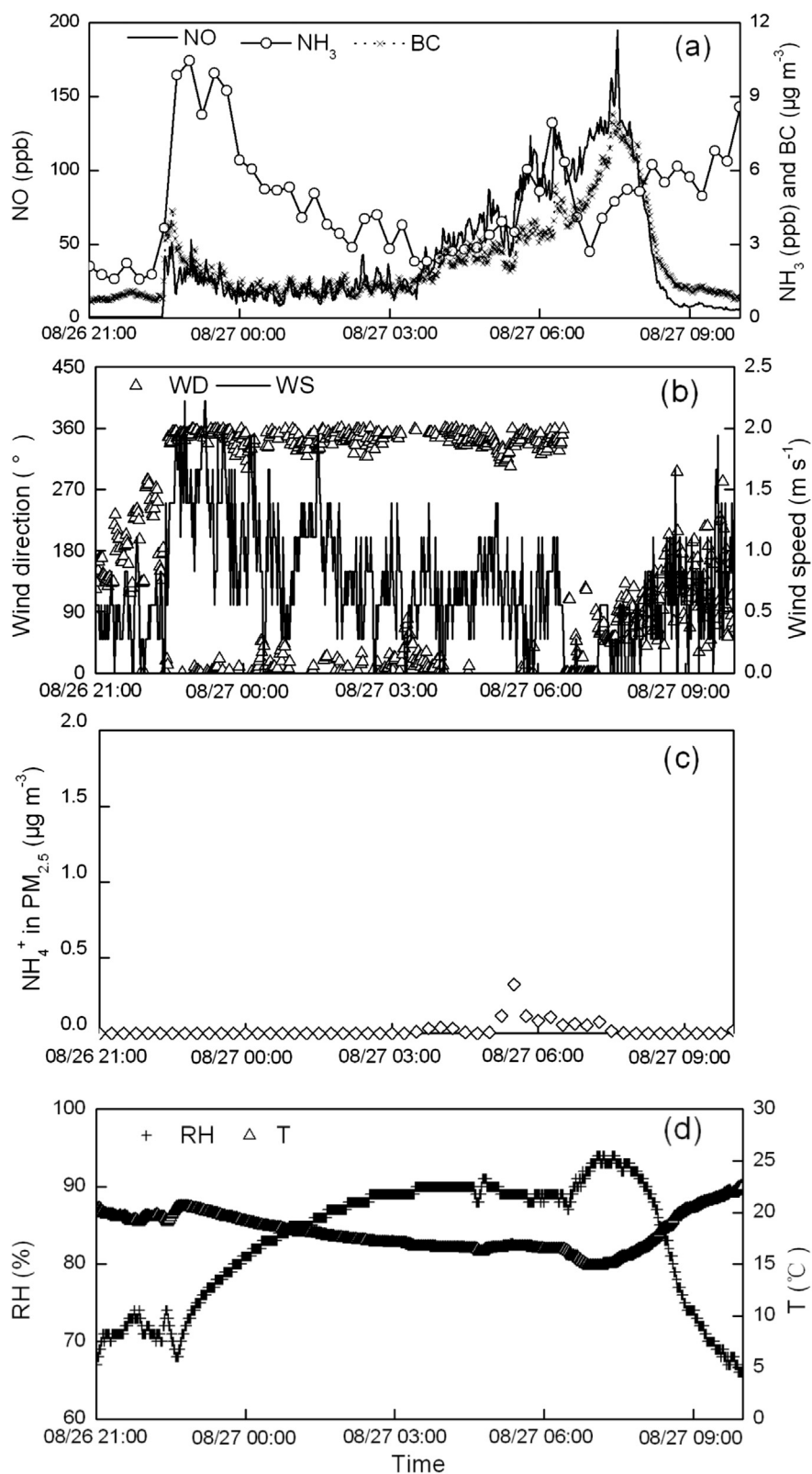
#### 3.2.2. Analyzing vehicular emissions of $\text{NH}_3$ between 26 and 27 August

From 9:00 pm on 26 August to 10:00 am on 27 August, there were two time slots in which the mixing ratios of  $\text{NH}_3$  were relatively stable, i.e., from 9:00 pm to 11:30 pm on 26 August and from 3:30 am to 5:00 am on 27 August (Fig. 4a). The average  $\text{NH}_3$  measured during the period 9:00 pm to 11:30 pm on 26 August was  $1.8 \pm 0.3 \text{ ppb}$ , while the average was  $2.7 \pm 0.2$  during the period 3:30 am to 5:00 am on 27 August. The difference (0.9 ppb) between the two averages is statistically significant at the 99% confidence level. The mixing ratio of NO was less than 1 ppb before 10:27 pm on 26 August when the wind direction was from the southwest, south or southwest. The average NO mixing ratio was  $50 \pm 15 \text{ ppb}$  during the period 3:30 am to 5:00 am on 27 August, when the wind direction was from the northwest, north or northwest. Again, sinks of  $\text{NH}_3$  were found to be negligible when the  $\text{NH}_3$  emitted by vehicles on 401 Highway arrived at the sampling site during the later time slot (Fig. 4bc). Thus, based on the data of  $\text{NH}_3$  and NO measured during the two time slots, the on-road vehicle emission factor of  $\text{NH}_3$  relative to NO was roughly estimated to be only 0.9 ppb  $\text{NH}_3$  per 50 ppb NO.

More evidence on 27 August also suggests that emissions of  $\text{NH}_3$  from on-road vehicles were negligible contributors to the  $\text{NH}_3$  observed at the site. For example, the mixing ratio of NO decreased from the maximum value (195 ppb) at 7:33 am to  $<10 \text{ ppb}$  at 8:50 am on 27 August. The mixing ratio of  $\text{NH}_3$  increased slightly from 4.7 ppb between 7:30 and 7:45 am to 6.2 ppb between 8:45 and 9:00 am.

However, when the time slot from 4:00 am to 6:30 am on 27 August was considered separately, a moderately good correlation between NO and  $\text{NH}_3$  was obtained ( $[\text{NH}_3] = 0.072[\text{NO}] - 1.27, R^2 = 0.81$ ). This good correlation should be caused by common accumulation process instead of common emission sources.

Overall, the observed mixing ratio of  $\text{NH}_3$  varied from 0.9 to 16.9 ppb with an average of  $4.0 \pm 2.4 \text{ ppb}$  between 26 and 28 August. The average mixing ratio of NO during the three days was



**Fig. 4.** Temporal variations of gas and particle concentrations and meteorological conditions between 26 and 27 August 2007 (a: NO, NH<sub>3</sub> and BC; b: WD and WS; c: NH<sub>4</sub><sup>+</sup> in PM<sub>2.5</sub>; d: RH and T).

$23 \pm 33$  ppb. When 0.5–0.9 ppb NH<sub>3</sub> per 50 ppb NO was used as the emission factor of NH<sub>3</sub> from on-road vehicles, the NH<sub>3</sub> derived from on-road vehicles contributed less than 10% (on average) to the observed NH<sub>3</sub> during the three days.

### 3.2.3. Comparison to vehicular emission factors of NH<sub>3</sub> reported in literature

The estimated on-road vehicle emission factor of NH<sub>3</sub> relative to NO was approximately 0.5–0.9 ppb NH<sub>3</sub> per 50 ppb NO in this study.

The ratio was only 1/20–1/30 of the ratio ( $\sim 1$  ppb  $\text{NH}_3$ : 3 ppb NO) in on-road light-duty vehicular plumes obtained by remote sensing measurements (Burgard et al., 2006; Bishop et al., 2010, 2012) and was approximately one order of magnitude less than those ratios measured in tunnels and dynamometer studies (Kean et al., 2009). NO in the plume from 401 Highway mixed contributions from light-duty and heavy-duty vehicles, while heavy-duty vehicles do not emit  $\text{NH}_3$ . The estimated emission factor of  $\text{NH}_3$  relative to NO in this study would be smaller than that in light-duty vehicular plumes. In addition, Kean et al. (2009) summarized that  $\text{NH}_3$  emissions from vehicles could be related to a variety of factors such as vehicle technology and operating mode, catalyst technology and age, and the air/fuel ratio. For example, the emission factor of  $\text{NH}_3$  from vehicles on the Federal Test Procedure (FTP75) was 1/4–1/5 of that on the US06 cycle (vehicles operating on aggressive, high-speed, and/or high-acceleration driving behavior, rapid speed fluctuations, and driving behavior that is not included in the FTP, Huai et al., 2003). The emission factor of  $\text{NH}_3$  from vehicles measured at the Gubrist Tunnel (Switzerland) in 1995 was approximately 1/3 of that measured at the Caldecott Tunnel (California) in 1999 (Moeckli et al., 1996; Kean et al., 2000). Bishop et al. (2012) reported that the emission factor of  $\text{NH}_3$  from vehicles with vehicle age less than 10 years at West LA in 2008 was approximately two times higher than those at San Jose and Fresno in 2008. All these suggested that the emission factor of  $\text{NH}_3$  from vehicles could be highly variable. The low on-road vehicle emission factor of  $\text{NH}_3$  measured in this study could be related to a combination of these factors, but it also could be due to some unidentified factors either in previous studies or in this study. However, our study strongly indicates that the vehicle-derived  $\text{NH}_3$  was a negligible source of  $\text{NH}_3$  relative to other sources in the urban atmosphere of Toronto.

#### 4. Conclusion

An intensive campaign using a complementary suite of gas and particle analyzers was performed to study on-road vehicle emissions of  $\text{NH}_3$  near 401 Highway, which has the highest traffic density in Canada. A few vehicle plumes with elevated NO and BC were observed when the sampling site was downwind of 401 Highway and the wind speed was less than  $2 \text{ m s}^{-1}$ . A low mixing ratio of NO and a low concentration of BC were observed when the sampling site was upwind of 401 Highway. The differences allowed an estimation of the on-road vehicle emission factor of  $\text{NH}_3$ . Using NO as a reference, the estimated emission factor of  $\text{NH}_3$  from on-road vehicles relative to NO was 0.5–0.9 ppb  $\text{NH}_3$  per 50 ppb NO. However, a good correlation between  $\text{NH}_3$  and NO was observed in some time slots. When regression equations were used to estimate the emission factor of  $\text{NH}_3$  from on-road vehicles relative to NO, the values reached 3.5–5 ppb  $\text{NH}_3$  per 50 ppb NO. The higher values were physically meaningless because  $\text{NH}_3$  and NO were probably not from the same source.

Between 26 and 28 August, the observed mixing ratio of  $\text{NH}_3$  varied from 0.9 to 16.9 ppb, with an average of  $4.0 \pm 2.4$  ppb. The mixing ratio of  $\text{NH}_3$  (on average) derived from on-road vehicles was estimated to be  $\sim 0.4$  ppb. On the other hand, a few spikes in  $\text{NH}_3$  ( $>8$  ppb) were sometimes observed. The elevated  $\text{NH}_3$  was probably due to non-traffic emissions of  $\text{NH}_3$  near the sampling site. Overall, we conclude that emissions of  $\text{NH}_3$  from on-road vehicles yield a negligible contribution to atmospheric ammonia in Toronto, compared to other sources.

However, negligible emissions of  $\text{NH}_3$  from vehicles in Toronto could be associated with its local traffic composition; it might or might not be true for other urban environments. The negligible emissions could also be due to unknown loss of  $\text{NH}_3$  in the GP-IC, although it is not found so far.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2013.08.028>.

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