

# 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

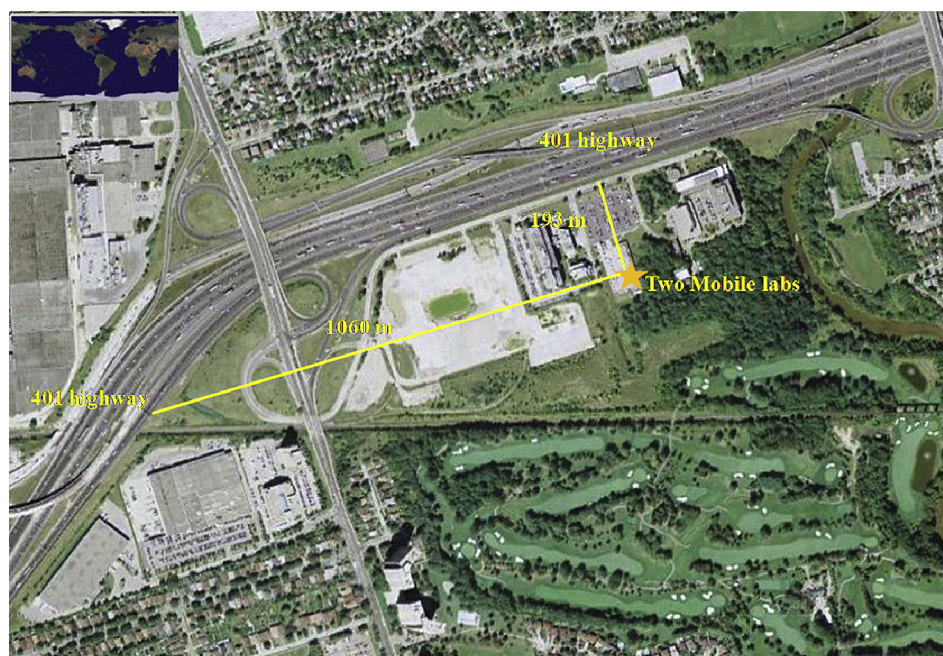


Fig. 1. Map of the sampling site near 401 Highway, Toronto, Canada.

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