The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai

Yunhua Chang1,2, Zhong Zou3, Congrui Deng1,2, Kan Huang1,2,5, Jeffrey L. Collett4, Jing Lin1,2, and Guoshun Zhuang1,2

1Center for Atmospheric Chemistry Study, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China
2Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China
3Pudong New Area Environmental Monitoring Station, Shanghai 200135, China
4Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA
5Department of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN 37996, USA

Correspondence to: Congrui Deng (congruideng@fudan.edu.cn) and Guoshun Zhuang (gzhuang@fudan.edu.cn)

Received: 1 December 2015 – Published in Atmos. Chem. Phys. Discuss.: 10 December 2015
Revised: 14 February 2016 – Accepted: 11 March 2016 – Published: 17 March 2016

Abstract. Agricultural activities are a major source contributing to NH3 emissions in Shanghai and most other regions of China; however, there is a long-standing and ongoing controversy regarding the contributions of vehicle-emitted NH3 to the urban atmosphere. From April 2014 to April 2015, we conducted measurements of a wide range of gases (including NH3) and the chemical properties of PM2.5 at hourly resolution at a Shanghai urban supersite. This large data set shows NH3 pollution events, lasting several hours with concentrations 4 times the annual average of 5.3 µg m−3, caused by the burning of crop residues in spring. There are also generally higher NH3 concentrations (mean ± 1 σ) in summer (7.3 ± 4.9 µg m−3; n = 2181) because of intensive emissions from temperature-dependent agricultural sources. However, the NH3 concentration in summer was only an average of 2.4 µg m−3 or 41 % higher than the average NH3 concentration of other seasons. Furthermore, the NH3 concentration in winter (5.0 ± 3.7 µg m−3; n = 2113) was similar to that in spring (5.1 ± 3.8 µg m−3; n = 2198) but slightly higher, on average, than that in autumn (4.5 ± 2.3 µg m−3; n = 1949). Moreover, other meteorological parameters like planetary boundary layer height and relative humidity were not major factors affecting seasonal NH3 concentrations. These findings suggest that there may be some climate-independent NH3 sources present in the Shanghai urban area. Independent of season, the concentrations of both NH3 and CO present a marked bimodal diurnal profile, with maxima in the morning and the evening. A spatial analysis suggests that elevated concentrations of NH3 are often associated with transport from regions west–northwest and east–southeast of the city, areas with dense road systems. The spatial origin of NH3 and the diurnal concentration profile together suggest the importance of vehicle-derived NH3 associated with daily commuting in the urban environment. To further examine vehicular NH3 emissions and transport, sampling of the NH3 concentration was performed in (from the entrance to the exit of the tunnel) and out (along a roadside transect spanning 310 m perpendicular to the tunnel) of a heavily trafficked urban tunnel during the spring of 2014. NH3 concentrations in the tunnel exit were over 5 and 11 times higher than those in the tunnel entrance and in the ambient air, respectively. Based on the derived mileage-based NH3 emission factor of 28 mg km−1, a population of 3.04 million vehicles in Shanghai produced around 1300 t NH3 in 2014, which accounts for 12 % of total NH3 emissions in the urban area. Collectively, our results clearly show that vehicle emissions associated with combustion are an important NH3 source in Shanghai urban areas and may have potential implications for PM2.5 pollution in the urban atmosphere.
Ammonia (NH$_3$) is one of the most abundant nitrogen-containing substances and the principal reduced nitrogen component in the atmosphere. It plays a strong role in local and regional-scale tropospheric chemistry and air quality by serving as a precursor to particulate ammonium (pNH$_4^+$) (Seinfeld and Pandis, 2006). Although major efforts have been made to regulate NO$_x$ and SO$_2$ emissions to improve air quality in China (Wang et al., 2014; Zhao et al., 2013), a major portion of the nation’s population presently lives in environments of non-compliance with national standards for fine particulate matter (PM$_{2.5}$, representing particles with aerodynamic diameters smaller than 2.5 microns) (Huang et al., 2014; Lin et al., 2010; Ma et al., 2014, 2016). NH$_3$ emissions have been proposed as a cost-effective strategy to lower ambient PM$_{2.5}$ levels (Heald et al., 2012; Pinder et al., 2007; Wang et al., 2011, 2013; Ye et al., 2011). However, the emission sources of NH$_3$ and their relative contributions to ambient concentrations, especially in urban atmospheres, remain uncertain (Chang, 2014; Felix et al., 2014; Yao et al., 2013).

Emission sources of NH$_3$ have been previously reviewed (e.g., Asman et al., 1998; Reis et al., 2009; Sutton et al., 2008). Major sources include volatilization of N-containing fertilizers and excreta from animal husbandry, which together contribute over 80% of total global NH$_3$ emissions (Bouwman et al., 1997; Clarisse et al., 2009; Olivier et al., 1998; Schlesinger and Hartley, 1992). Thus, it is not surprising that previous investigations of NH$_3$ emissions were mainly performed adjacent to dairy operations (Mount et al., 2002), animal housing (Gay et al., 2003), livestock facilities (Kawashima and Yonemura, 2001), slurry lagoons (Aneja et al., 2000), pit latrines (Rodhe et al., 2004), and croplands (Yan et al., 2003), where elevated levels of NH$_3$ are often observed. Varying significantly in time and space, biomass burning (including agricultural waste, savanna, and forest fires) may contribute up to 12% of the global NH$_3$ emissions flux (Behera et al., 2013; Lamarque et al., 2010). Despite the focus on ammonia sources mainly from agricultural and rural environments, a number of studies reveal that ambient NH$_3$ concentrations in urban areas can be comparable to (Cao et al., 2009; Stanier et al., 2012) or even higher than (Bettez et al., 2013; Meng et al., 2011; Singh and Kulshrestha, 2014) those in rural areas. These observations strongly suggest that there must be other non-agricultural NH$_3$ sources present in urban areas.

Starting in the 1980s, the introduction of three-way catalytic converters (TWCs) on automobiles dramatically mitigated pollutant emissions from vehicle tailpipes (Shleef and McCabe, 2000). An unwanted side effect of the use of TWCs for gasoline powered vehicles and selective catalytic reduction (SCR) for control of nitrogen oxide emissions from diesel-powered vehicles, has been an increase in NH$_3$ emissions from motor vehicles, a significant source of non-agricultural NH$_3$ that has been documented directly through laboratory dynamometer studies (Durbin et al., 2002; Heeb et al., 2006, 2008; Huai et al., 2005; Livingston et al., 2009; Suarez-Bertoa et al., 2014, 2015) and on-road measurements (including mobile chase systems and tunnel tests) (Brito et al., 2013; Fraser and Cass, 1998; Kean et al., 2009; Liu et al., 2014; Moeckli et al., 1996; Pierson and Brachaczek, 1983; Pierson et al., 1996; Sun et al., 2014), or indirectly through correlation analysis between ambient NH$_3$ concentrations and other recognized traffic tracers (e.g., CO, NO$_x$) (Bishop and Stedman, 2015; Gong et al., 2011, 2013; Ianniello et al., 2010; Nowak et al., 2010; Pandolfi et al., 2012; Phan et al., 2013; Reche et al., 2012). In the US, it is estimated that 5% of the national NH$_3$ emissions are due to motor vehicles (Kean et al., 2009), while this figure is estimated at 12% for the UK (Sutton et al., 2000), with almost all the remaining NH$_3$ coming from agricultural processes. At a regional level, motor vehicle emissions make a small contribution to the total. Nevertheless, they are locally concentrated in urban areas where agricultural sources of NH$_3$ are mostly absent. Therefore, a disproportionately greater impact of motor vehicles on the urban NH$_3$ budget and subsequent secondary PM$_{2.5}$ formation can be expected (Chang, 2014). On the other hand, we notice that several important studies did not detect evidence of an influence of on-road traffic on ambient NH$_3$ concentrations (Pryor et al., 2004; Saylor et al., 2010; Yao et al., 2013). Therefore, more efforts needed to be made to elucidate the contribution of vehicle-emitted NH$_3$ to the urban atmosphere.

Shanghai, like many other cities in eastern China, is suffering severe air pollution problems, such as high PM$_{2.5}$ concentrations and resulting poor visibility (Huang et al., 2012, 2013b). Although there are many studies aimed at understanding PM pollution, little is known about the characteristics of NH$_3$ in the largest city of China. In an effort to curb its severe air pollution, China recently launched an air pollution monitoring research program (known as the supersite program) in several major cities. In 2014, a new in situ atmospheric station equipped with state-of-the-art instruments was installed in the Shanghai region, allowing comprehensive characterization of PM$_{2.5}$ and associated precursor gases. Here, seasonal trends, diurnal variations, and pollution episodes retrieved from 1 year of real-time measurement of NH$_3$ are presented and interpreted in order to explore the sources and parameters controlling the NH$_3$ concentrations across Shanghai. Meanwhile, an additional source-specific campaign was performed to examine the emission and transport of vehicle-emitted NH$_3$ from an urban, heavily trafficked tunnel in Shanghai.
2 Methods

2.1 Long-term monitoring at Pudong supersite

In situ continuous observations of the chemical and optical properties of atmospheric aerosols and associated precursor gases were made on the rooftop (18 m above ground level) of the Pudong Environmental Monitoring Center (PEMC; 121.5446° E, 31.2331° N), 5 km east of the Shanghai urban center (the People’s Square) (Fig. 1). The site is located in a mixed-use urban area (office, commercial, residential, and traffic) east of downtown Shanghai, with no obvious NH3 point source within 5 km (Zou et al., 2015). As one of the state-controlled sites, Pudong (PD) supersite was designed by the Ministry of Environmental Protection of China and operated by the Shanghai Environmental Monitoring Center, being responsible for the release of hourly air-quality data for PM10, PM2.5, and other criteria pollutants (CO, SO2, NOx, and O3).

From 3 April 2014 to 2 April 2015, using a MARGA instrument (measurement of aerosols and reactive gases analyzer, Metrohm Applikon B.V., NL), water-soluble gases (NH3, HNO3, HONO, HCl, and SO2) and PM2.5 components (NO3−, Cl−, SO42−, Na+, NH4+, K+, Mg2+, and Ca2+) were measured with hourly temporal resolution. The MARGA removes soluble gases in a rotating, wet-walled denuder, while a steam-jet aerosol collector is used for fine particle collection. Meanwhile, aerosol light absorption coefficients (βabs) were retrieved every 5 min from an AE31 aethalometer using seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) with a PM2.5 cut-off inlet. Black carbon (BC) concentrations for the whole data set were calculated from the absorption coefficient at 880 nm. The measurement process was subjected to rigorous quality assurance and quality control procedures according to the Technical Guideline of Automatic Stations of Ambient Air Quality in Shanghai based on the national specification HJ/T193-2005. Meteorological parameters including temperature, relative humidity, and rainfall were monitored by an automatic meteorological station (Met One Instruments, US), which was co-located at the rooftop of the PD supersite.

To explore the comparability between on-line and off-line methods for NH3 measurement, an Ogawa passive sampling device (PSD) was co-located with MARGA at PD to passively measure weekly ambient NH3 concentration from May 2014 to June 2015. The Ogawa PSD is a double-sided passive sampler equipped with two 14 mm quartz filters (serving as duplicates) impregnated with phosphoric acid provided by the manufacturer. Following the manufacturer’s protocols (http://www.ogawausa.com), exposed filter samples were soaked with 8 mL ultra-pure water (18.2 MΩ cm) and analyzed by an ion chromatography system (883 Basic IC plus, Metrohm Co., Switzerland). The detection limit for NH4+ in the passive sampler extracts was 2.8 µg L−1; this corresponds to an ambient NH3 concentration detection limit of approximately 0.1 ppb for a 7-day sample. The NH3 concentrations measured by the MARGA (ppb) were averaged over the same time period as the Ogawa PSDs (ppb).

Figure S1 in the Supplement shows a good correlation (y = 0.82 x +0.56, R2 = 0.84) between the MARGA and Ogawa PSD measurements.
Y. H. Chang et al.: The importance of vehicle emissions as a source of atmospheric ammonia

\[ n = 53, \ R^2 = 0.84, \ p < 0.001 \] between the two NH\textsubscript{3} measurement methods, validating the reliability of NH\textsubscript{3} data from the MARGA platform.

2.2 On-road measurement of NH\textsubscript{3} concentration in and out of a tunnel

To complement the information obtained from the main monitoring campaign described above, additional measurements of NH\textsubscript{3} concentration were performed at eight sites inside and outside of the Handan tunnel from 9 April to 21 May 2014. The Handan tunnel is a 720 m long urban freeway in the northeast of Shanghai, separating the campus of Fudan University into two parts (Fig. 9a). It contains an array of ventilation orifices in the middle section of the tunnel, 200 m in total. The tunnel has two traffic bores; each bore has a cross section of 70 m\textsuperscript{2} and four lanes with typically 120 000 vehicles (of which 85% are light-duty vehicles) passing per day (Li, 2007). Driven by a group of high power fans, the average wind speed measured at the exit of the tunnel was approximately 5 ± 1 m s\textsuperscript{-1}. The maximum vehicle speed limit in the tunnel is 80 km h\textsuperscript{-1}, with typical driving speeds of 50–60 km h\textsuperscript{-1}. Inside the northern bore of the tunnel, four sampling points were located at both ends of the tunnel (10 m from the exit and entrance of the tunnel, or T-d and T-a, for short) and the two ends of an array of ventilation orifices located in the middle section of the tunnel (Fig. 9a; the site near the entrance and the exit, named T-b and T-c for short, respectively). Outside the tunnel, a roadside transect involving four sites perpendicular to the tunnel was established, spanning the distance from 0 m (O\textsubscript{0m}, for short), 20 m (O\textsubscript{20m}), 150 m (O\textsubscript{150m}), to 310 m (O\textsubscript{310m}). Figure 9a shows the layout of the tunnel and the sampling points.

Using US EPA Method 207.1 (Determination of Ammonia Emissions from Stationary Sources), the NH\textsubscript{3} concentration at each site was measured. Briefly, for each sample, ambient air was pumped through two fritted glass bubblers (containing 10 mL 0.005 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} absorbing solution in each bubbler) for 2 h at a flow rate of 1 L min\textsuperscript{-1}. These two bubblers were connected in series, and the NH\textsubscript{3} collection efficiency of the sampling trains was 95% or better (checked by using four bubblers in series in our pilot study, the collection efficiency = 100 × ([the sum of the values of the first two bubblers])/(the sum of the values of the four bubblers)). Measurements were made during the morning (between 08:00 and 11:00 local time) and afternoon (between 14:00 and 19:00). Due to the proximity of the monitoring sites to the laboratory, all samples could be collected and analyzed by IC swiftly to avoid potential contamination, and field blanks were below the detection limit. Due to the dangers to personnel of sampling at the T-a, T-b, and T-c sites, six samples were collected synchronously at these three sites. Nineteen paired samples were successfully collected and determined at the site of T-d, O\textsubscript{0m}, O\textsubscript{20m}, O\textsubscript{150m}, and O\textsubscript{310m}.

2.3 Planetary boundary layer height simulation

The Weather Research and Forecasting (WRF) model v3.5.1 (Skamarock et al., 2008) is used for simulating the height of planetary boundary layer. The WRF simulation was performed from a mother domain with a 45 × 45 km horizontal resolution over Asia, and nested down to a second domain of 15 × 15 km covering eastern China, the Korean Peninsula, and Japan, and further nested down to a third domain of 5 × 5 km covering the Yangtze River Delta region. Lambert conformal conic projection was used with true latitude limits of 4 and 44° and standing longitude of 115°. The coverage of three domains is shown in Fig. S4. We chose the RRTM longwave radiation scheme and the Dudhia shortwave radiation scheme. The Yonsei University scheme was used for the planetary boundary layer option. The WRF model configurations can be found elsewhere (Huang et al., 2013a). The National Center for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis data set (http://rda.ucar.edu/datasets/ds083.2/) with a horizontal resolution of a resolution of 1.0 × 1.0° are incorporated as initial and boundary conditions for the model. A one-way nested approach with four-dimensional data assimilation (FDDA) in WRF is applied. We have performed model evaluations of major meteorological parameters against the NCDC surface meteorological network (National Climate Data Center, http://www7.ncdc.noaa.gov/CDO/cedo) within the YRD region (red dots marked in Fig. S4). The evaluation results of surface wind speed, temperature, and humidity are shown in Table S2 in the Supplement. It could be seen that these meteorological parameters are within the benchmarks during most of the months, suggesting our WRF modeling results are reliable. A Meteorology–Chemistry Interface Processor (MCIP) (Otte and Pleim, 2010) v4.1 is used to postprocess the WRF results by outputting the atmospheric height of the planetary boundary layer field, one of the standard MCIP outputs. The simulation period is consistent with the observation, i.e., from April 2014 to April 2015. In this study, planetary boundary layer height (PBLH) derived from the third domain is used. Additionally, the planetary boundary layer depths at 3 h resolution were obtained from the US National Oceanic and Atmospheric Administration (NOAA) Real-time Environmental Applications and Display System (READY) archived Global Data Assimilation System (GDAS) meteorological data (1° × 1°) based on Coordinated Universal Time (UTC). All UTC values are converted to local time (UTC + 8).

2.4 Potential source contribution analysis

Back trajectories of 24 h, arriving at the PD supersite at a height of 500 m, were calculated at 1 h time intervals for each of the four seasons using NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model with GDAS one-degree archive meteorological data (Draxler...
and Rolph, 2015). An in-depth back trajectory analysis, the potential source contribution function (PSCF), is useful for identifying the possible geographic origin of emission sources; this method calculates the ratio of the number of points with concentration higher than a threshold value \(m_{ij}\) to the total number of points \(n_{ij}\) in the \(i/j\)th grid cell. Higher PSCF values indicate higher potential source contributions to the receptor site. In this study, the domain for the PSCF was set within the range of \((26–42^\circ\text{N}, 112.5–125.5^\circ\text{E})\) in \(0.1^\circ \times 0.1^\circ\) grid cells. The 75th percentile for CO and NH\(_3\) during the four seasons was used as the threshold value \(m_{ij}\). To reduce the uncertainties of \(m_{ij}/n_{ij}\) for those grid cells with a limited number of points, a weighting function recommended by Polissar et al. (2001) was applied to the PSCF in each season. Visualizations of the PSCF were mapped using ArcMap 10.2.

### 3 Results and discussion

#### 3.1 Temporal evolution of NH\(_3\) concentrations

The temporal patterns of hourly gaseous NH\(_3\) concentrations determined by the MARGA at the Pudong supersite are reported in Fig. 2. Summary statistics for NH\(_3\) concentrations (\(\mu\text{g m}^{-3}\)) during 3 April 2014–2 April 2015 are shown in Table 1. Using a variety of chemical, physical, and optical techniques, numerous studies have examined ambient NH\(_3\) concentrations over the last 3 decades; however, few of them were conducted in urban areas. As a comparison, we compiled previous work related to the measurement of urban NH\(_3\) concentrations in Table 2.

The 1-year data set \((n = 8441; \text{data availability } 96.4\%)\) in the current study represents one of the longest on-line continuous measurement series of atmospheric NH\(_3\) in China. During the study period, the NH\(_3\) concentrations varied between 0.1 and 39.2 \(\mu\text{g m}^{-3}\), with an average \((\pm 1 \sigma)\) of 5.5 \(\pm 3.9 \mu\text{g m}^{-3}\). Domestically, the annual average NH\(_3\) concentrations in Beijing and Xi’an were much higher than in Shanghai (see Table 2). This might be expected since Beijing and Xi’an are located in the North China Plain (NCP) and the Guanzhong Plain (GZP), respectively. The NCP and GZP are two of the most intensive agricultural production regions in China. Moreover, the NH\(_3\) loss from soil increases with an increase in soil pH value (Ju et al., 2009). Shanghai and its surrounding regions are dominated by the acid soils of paddy fields (Fig. 1) (Zhao et al., 2009), while Beijing and Xi’an are dominated by the alkaline soils of dry land (Wei et al., 2013). Internationally, the NH\(_3\) concentration level in Shanghai was similar to observations from cities in developed and middle-income countries, but much lower than those cities in emerging countries. This is particularly true when comparing with cities in South Asia (e.g., Delhi in India and Lahore in Pakistan), where there is a lack of basic sanitation facilities (e.g., public flush toilets), and significant animal populations (such as cows) coexist with people in urban areas. The higher NH\(_3\) concentrations measured at surface sites in South Asia are consistent with spatial patterns from recent satellite remote sensing observations (Clarisse et al., 2009; Van Damme et al., 2014).

The variations of NH\(_3\) in spring and summer were generally consistent with fluctuations of temperature (Fig. 2a). In winter, their correlations turned out to be much weaker (Fig. 4a). While in autumn, no significant correlation between temperature and NH\(_3\) was observed (Fig. 4a). Monthly, from March to September, the NH\(_3\) concentration first increased steadily, with the highest value in July, then decreased gradually, along with falling temperature (Fig. 2c). In summer (June–August), high temperatures favor NH\(_3\) volatilization from urea and other N fertilizers applied to croplands (Fu et al., 2013; Huang et al., 2011; Ianniello et al., 2010; Meng et al., 2011). High temperatures in summer also favor NH\(_3\) emission from other sources, such as animal housing, landfills, laystalls and pit latrines, animal manure, natural and fertilized soils, vegetation, and municipal solid waste (Fu et al., 2013; Huang et al., 2011). Moreover, given that the equilibrium between ammonium nitrate particles and gaseous ammonia and nitric acid favors the gas-phase compounds at higher temperature, warmer summer conditions promote dissociation of ammonium nitrate particles, shifting the ammonium/ammonia partitioning toward the gas phase (Behera et al., 2013). In this study, the average NH\(_3\) concentration in summer \((7.3 \pm 4.9 \mu\text{g m}^{-3}; n = 2181)\) was 2.4 \(\mu\text{g m}^{-3}\) or 41 % higher than the average of other seasons. The gap between summer and winter in Shanghai was similar to New York, but generally much lower than many other cities. Taking Beijing for example, according to Ian-

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
<th>Minimum</th>
<th>P10</th>
<th>Medium</th>
<th>P90</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>8441</td>
<td>5.5</td>
<td>3.9</td>
<td>0.10</td>
<td>2.0</td>
<td>4.6</td>
<td>10.2</td>
<td>39.2</td>
</tr>
<tr>
<td>Spring</td>
<td>2198</td>
<td>5.1</td>
<td>3.8</td>
<td>0.10</td>
<td>1.7</td>
<td>4.1</td>
<td>9.6</td>
<td>25.1</td>
</tr>
<tr>
<td>Summer</td>
<td>2181</td>
<td>7.3</td>
<td>4.9</td>
<td>0.65</td>
<td>2.6</td>
<td>6.3</td>
<td>12.7</td>
<td>39.2</td>
</tr>
<tr>
<td>Autumn</td>
<td>1949</td>
<td>4.5</td>
<td>2.3</td>
<td>0.57</td>
<td>2.3</td>
<td>3.9</td>
<td>7.2</td>
<td>19.7</td>
</tr>
<tr>
<td>Winter</td>
<td>2113</td>
<td>5.0</td>
<td>3.4</td>
<td>0.43</td>
<td>1.8</td>
<td>4.3</td>
<td>9.3</td>
<td>30.7</td>
</tr>
</tbody>
</table>
niello et al. (2010), the NH₃ concentration in summer was 460% higher than in winter; this figure was 320% in Xi’an between 2006 and 2007 (Cao et al., 2009). Smaller seasonal temperature differences and less agricultural activity in Shanghai could be the contributing factors.

Based on the “bottom-up” methodologies, previous emission inventories indicate that livestock feeding and N-fertilizer application contribute around 50% (48–54.9%) and 35% (33.4–40%) of the total NH₃ emissions in the Yangtze River delta region (YRD for short, including Shanghai as well as 24 cities in the provinces of Jiangsu and Zhejiang), respectively (Fu et al., 2013; Huang et al., 2011, 2012). Agricultural production is also the dominant source of NH₃ emissions in most other regions worldwide (Bouwman et al., 1997; Olivier et al., 1998; Reis et al., 2009). However, performed at an urban level, many studies in Table 2 concluded that the concentrations and evolution of ambient NH₃ in urban areas were influenced by traffic emissions. As one of the world’s largest megacities, Shanghai might expect contributions of vehicle-emitted NH₃ as well. NH₃ concentrations in the atmosphere, however, are also sensitive to other important factors such as changes in temperature, wind speed or direction, and boundary layer depth; other influential factors might include local or regional NH₃ emissions, dry and wet deposition, and gas-to-particle partitioning. The relative importance of such factors in controlling ambient NH₃ concentration may vary seasonally. For example, the highest and lowest daily NH₃ concentrations in Shanghai were observed on 10–11 July 2014 (23.4 ± 6.7 µg m⁻³) and 10–11 March 2015 (0.5 ± 0.4 µg m⁻³), respectively. For the two periods, there was no significant difference between them in terms of wind speed and planetary boundary layer height (the relative humidity data for the March period were missed). Although 19.6 mm of rainfall in the July period would be expected to lower NH₃ levels, the temperature on this high concentration date (28.4 °C) was much higher than on the low concentration March date (4.7 °C). Over a longer time frame, even though rainfall in summer was around twice the amount of rainfall in other seasons, other factors such as greater NH₃ emissions at higher temperature outweigh the wet scavenging effects of rainfall yielding higher summertime NH₃ concentrations. High NH₃ concentration episodes during burning of agricultural wheat residues, indicated by a strong and synchronous rise of trace aerosols from biomass burning (e.g., K⁺ and BC), were also evident in late spring (Fig. 2b). The evolution of this pollution episode induced by biomass burning and its influence on the air quality of Shanghai has been examined in our recent paper (Zou et al., 2015).
3.2 Effects of meteorological parameters

In the following, we will examine the (synergistic) effects of various meteorological parameters on measured NH$_3$ concentrations in Shanghai, because these factors may mask the effect of vehicular emissions on the measured NH$_3$ concentrations. Summary statistics for meteorological parameters during 3 April 2014–2 April 2015 are shown in Table 3.

Planetary boundary layer (PBL) height plays a vital role in determining the vertical dispersion of air pollutants that are emitted from the Earth’s surface. Decreasing height of PBL can normally hold the pollutants within the shallow surface

<table>
<thead>
<tr>
<th>Location</th>
<th>Period</th>
<th>Methodology</th>
<th>Time resolution</th>
<th>Concentration (µg m$^{-3}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Asia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shanghai, CN</td>
<td>Apr 2014–Apr 2015</td>
<td>MARGA online monitor</td>
<td>hourly</td>
<td>5.5 ± 3.9</td>
<td>This study</td>
</tr>
<tr>
<td>Beijing, CN</td>
<td>Jan–Feb, Aug 2007, Apr 2006–Apr 2007</td>
<td>Annular diffusion denuder</td>
<td>daily/weekly</td>
<td>12.9 ± 4.2/0.3 (annual/summer)</td>
<td>Ca et al. (2009)</td>
</tr>
<tr>
<td>Nanjing, CN</td>
<td>Aug–Sept 2012</td>
<td>HRT-ToF-CIMS (a)</td>
<td>1 Hz</td>
<td>1.3 ± 1.8 (industrial area)</td>
<td>Zheng et al. (2015)</td>
</tr>
<tr>
<td>Nanjing, CN</td>
<td>Jul–Aug 2013</td>
<td>Portable NH$_3$ online detector</td>
<td>hourly</td>
<td>6.7 (near road)</td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td>Guangzhou, CN</td>
<td>Nov 2010</td>
<td>OP-DOAS (b)</td>
<td>2.5 min</td>
<td>1.6</td>
<td>Wang et al. (2012)</td>
</tr>
<tr>
<td>Urumqi, CN</td>
<td>Sep 2009–Aug 2010</td>
<td>Radiello passive sampler</td>
<td>biweekly</td>
<td>6.5</td>
<td>Li et al. (2013)</td>
</tr>
<tr>
<td>Hong Kong, CN</td>
<td>Oct 2003–May 2006</td>
<td>Ogawa passive sampler</td>
<td>weekly</td>
<td>0.7 (rooftop) – 7.1 (near road)</td>
<td>Tanner (2009)</td>
</tr>
<tr>
<td>Taichung, TW</td>
<td>Jan–Dec 2002</td>
<td>Annular diffusion denuder</td>
<td>12 h</td>
<td>8.5 ± 3.0</td>
<td>Lin et al. (2006)</td>
</tr>
<tr>
<td>Seoul, KP</td>
<td>Oct 1996–Sept 1997</td>
<td>Annular diffusion denuder; MARGA online monitor</td>
<td>10 min</td>
<td>3.4/0.7/38.6 (annual/summer/mean)</td>
<td>Lee et al. (1999)</td>
</tr>
<tr>
<td>Seoul, KP</td>
<td>Jan–Dec 2010</td>
<td>MARGA online monitor</td>
<td>hourly</td>
<td>6.8 ± 3.3 (spring), 11.2 ± 3.9 (summer)</td>
<td>Shon et al. (2013)</td>
</tr>
<tr>
<td>Seoul, KP</td>
<td>Sep 2010–Aug 2011</td>
<td>MARGA online monitor</td>
<td>hourly</td>
<td>8.4 ± 3.3</td>
<td>Phan et al. (2013)</td>
</tr>
<tr>
<td>North America</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New York, US</td>
<td>Jan–Feb 2004</td>
<td>TDLAS (c)</td>
<td>&lt;1 min</td>
<td>0.6 (winter)</td>
<td>Li et al. (2006)</td>
</tr>
<tr>
<td>Farmington, US</td>
<td>Dec 2006–Dec 2007</td>
<td>Ogawa passive sampler</td>
<td>3 week</td>
<td>1.2 ± 0.4</td>
<td>Sather et al. (2008)</td>
</tr>
<tr>
<td>Morehead, US</td>
<td>Jan–Dec 2000</td>
<td>Annular diffusion denuder</td>
<td>12 h</td>
<td>0.3 (winter), 0.7 (summer)</td>
<td>Walker et al. (2004)</td>
</tr>
<tr>
<td>Houston, US</td>
<td>Aug 2010</td>
<td>Quantum laser spectrometer</td>
<td>10 min</td>
<td>2.3 (winter), 1.9 (summer)</td>
<td>Gong et al. (2011)</td>
</tr>
<tr>
<td>Vinton, US</td>
<td>May–Sep 1995</td>
<td>Ogawa passive sampler</td>
<td>biweekly</td>
<td>1.3 ± 0.4 (summer)</td>
<td>Leaderer et al. (1999)</td>
</tr>
<tr>
<td>Mexico City, MX</td>
<td>Mar 2006</td>
<td>Quantum laser spectrometer</td>
<td>6 min</td>
<td>17.7 ± 11.0 (spring)</td>
<td>Fountoukis et al. (2009)</td>
</tr>
<tr>
<td>Europe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edinburgh, UK</td>
<td>Apr–May 2002</td>
<td>ALPHA passive sampler</td>
<td>bimonthly</td>
<td>4.8 (spring)</td>
<td>Cape et al. (2004)</td>
</tr>
<tr>
<td>Munster, DE</td>
<td>Mar–Jul 2004</td>
<td>AMANDA (d)</td>
<td>10 min</td>
<td>3.9 (spring/summer)</td>
<td>Vogt et al. (2005)</td>
</tr>
<tr>
<td>Rome, IT</td>
<td>May 2001–Mar 2002</td>
<td>Annular diffusion denuder</td>
<td>30 min</td>
<td>17.2 ± 2.7 (near road)</td>
<td>Perrino et al. (2002)</td>
</tr>
<tr>
<td>Al-Ain, AE</td>
<td>Apr 2005–Apr 2006</td>
<td>Ogawa passive sampler</td>
<td>biweekly</td>
<td>9.7 ± 4.8</td>
<td>Salem et al. (2009)</td>
</tr>
<tr>
<td>Barcelona, ES</td>
<td>May–Sep 2011</td>
<td>Ammonia online analyzer</td>
<td>1 min</td>
<td>2.2 ± 1.0 (near road), 5.6 ± 2.1 (mixed)</td>
<td>Pandolfi et al. (2012)</td>
</tr>
<tr>
<td>Madrid, ES</td>
<td>Mar–Jul 2011</td>
<td>ALPHA passive sampler</td>
<td>biweekly</td>
<td>2.3 ± 1.3 (winter), 2.6 ± 1.8 (summer)</td>
<td>Reche et al. (2015)</td>
</tr>
<tr>
<td>Valencia, ES</td>
<td>Jun 2010, Feb–Mar 2011</td>
<td>ALPHA passive sampler</td>
<td>biweekly</td>
<td>1.5 ± 0.9 (winter), 0.5 ± 0.4 (summer)</td>
<td>Reche et al. (2015)</td>
</tr>
<tr>
<td>Huelva, ES</td>
<td>Nov 2010, May–Jun 2011</td>
<td>ALPHA passive sampler</td>
<td>biweekly</td>
<td>2.8 ± 3.8 (winter), 1.2 ± 0.9 (summer)</td>
<td>Reche et al. (2015)</td>
</tr>
<tr>
<td>South America</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Santiago, CL</td>
<td>Apr–Jun 2008</td>
<td>Ogawa passive sampler</td>
<td>monthly</td>
<td>15.0 ± 3.8 (spring)</td>
<td>Toro et al. (2014)</td>
</tr>
<tr>
<td>South Asia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dayalbagh, IN</td>
<td>Jul 1997, Feb 1998</td>
<td>Annular diffusion denuder</td>
<td>3 h</td>
<td>12.5 ± 2.2</td>
<td>Parmar et al. (2001)</td>
</tr>
<tr>
<td>Delhi, IN</td>
<td>Apr 2010–Nov 2011</td>
<td>Glass flask sampling</td>
<td>5 h</td>
<td>35.0 ± 16.8</td>
<td>Singh and Kulshreshtha (2012)</td>
</tr>
<tr>
<td>Delhi, IN</td>
<td>Oct 2012–Sep 2013</td>
<td>Glass flask sampling</td>
<td>8 h</td>
<td>40.7 ± 16.8</td>
<td>Singh and Kulshreshtha (2014)</td>
</tr>
</tbody>
</table>

*a* High resolution time-of-flight chemical ionization mass spectrometry.

*b* Open-path differential optical absorption spectroscopy.

*c* Tunable diode laser absorption spectrometer.

*d* Horizontal continuous-flow wet denuder.

Table 2. Ambient NH$_3$ concentration measurements in the urban atmosphere of China and other countries/regions.

---

Y. H. Chang et al.: The Importance of Vehicle Emissions as a Source of Atmospheric Ammonia
layer so as to suppress the vertical atmospheric dilution. In many previous studies, as described above, the NH$_3$ concentrations in winter were much lower than those in summer. However, the NH$_3$ concentrations observed here in Shanghai during winter are relatively high. One may argue that weaker vertical mixing and shallow PBL layers in winter could trap NH$_3$ and contribute to elevated concentrations. In Fig. 3a, although the simulated average PBL height in winter is the lowest during our study period, there is no significant difference among different seasons. In Fig. 3b, the average PBL height in winter is even higher than that in spring and summer. Therefore, a relatively high NH$_3$ concentration in winter at PD cannot be fully explained by the strength of vertical mixing or PBL height in this study.

Figure 4a suggests that temperature ($T$) is an important driver of the increase of NH$_3$ concentration in spring. No clear relationship is seen for other seasons. As the transitional period between winter and summer, springtime in Shanghai has the highest standard deviation of temperature during our study period (Table 3). Additionally, spring is known as the sowing season in southern China, with the greatest application of N-containing fertilizers (mainly in the form of urea) of the year. Warming temperature tends to increase the rate of urea hydrolysis and ammonium conversion to NH$_3$, and therefore volatilization. For example, an increase in temperature from 7.2 to 15.6 °C can double volatilization loss when moisture content is kept the same (Ernst and Massey, 1960). For relative humidity (RH), there is no clear evidence to suggest RH as an important factor controlling the dynamics of NH$_3$ concentrations in any of the seasons (Fig. 4b). Figure S2 shows the RH and $T$ dependent distributions of NH$_3$ concentration for each season. Given the generally poor relationship between the NH$_3$ concentration and $T$ and RH as discussed above, NH$_3$ concentrations have no clear dependence on $T$ and RH seasonally.

In Fig. 5a and b the distribution of hourly average wind speeds was calculated for values between 0 and 4.0 m s$^{-1}$ (99.5 % of occurrence). Figure 5a shows that there is a highly significant relationship between WS and NH$_3$ concentration ($R^2 = 0.91$, $p < 0.001$). The highest average NH$_3$ concentrations were measured under the lowest wind speeds and the lowest concentrations were measured at the highest wind speeds. There is no clear relationship between wind frequency (the number of wind occurrence) and average NH$_3$ concentration or WS during the study period (Fig. 5c). Figure S3 shows WS/WD dependence of NH$_3$ concentrations in different seasons. The distribution of NH$_3$ concentration showed an obvious concentration gradient as a function of WS. Seasonally, there are different preferential wind directions for the highest NH$_3$ concentration values. Generally, an overwhelming, higher $T$ in summer tends to greatly enhance the contribution of temperature-dependent emissions to the urban NH$_3$ budget from agricultural areas. And the nearby rural areas around Pudong supersite are in the direction of southeast (Nanhui) and northeast (Chongming) (Fig. 6d). However, it is unexpected that in Shanghai, almost
Figure 4. The relationship between hourly NH$_3$ concentration and hourly temperature (a) and hourly relative humidity (b) in four seasons at Pudong supersite during 3 April 2014–2 April 2015.

Figure 5. (a) Linear fitting of average NH$_3$ concentrations at different ranges of wind speed. The number of occurrences of wind (NOW) within each specific range of wind speed is shown as green columns. (b) Seasonal frequency distribution (%) of NOW at each specific range of wind speed. (c) The green boxes showing a descending order of the number of occurrences of wind at different wind directions. The points in black and the squares in orange represent the average wind speed and NH$_3$ concentration for each specific wind direction, respectively. (d) Seasonal frequency distribution (%) of NOW at each specific wind direction.

all high NH$_3$ concentration values in summer are concentrated in the wind direction range of south–southwest–west (Fig. S3b), which strongly indicates that the urban area is one of the most important NH$_3$ emission regions in Shanghai.

Figure 6a and b show the RH and $T$ dependent distributions of NH$_3$ and WS for the entire study period, respectively. Although the distribution of higher NH$_3$ favors the condition of high $T$ (> 25 °C), low RH (< 60 %), and low WS (< 1.2 m s$^{-1}$), Fig. 6a shows that there is no obvious concentration gradient as a function of RH and $T$. (Note that in Fig. S2d, higher NH$_3$ concentrations in winter tend to occur at higher $T$ for a given RH range of 60–80 %.)
can be explained by the dominance of low WS (often lower than 1.2 m s\(^{-1}\)) during east–southeast and west–northwest wind directions associated with intense local sources for NH\(_3\) within the city (Fig. 6c). In brief, our results suggest that there are some temperature-independent and important NH\(_3\) sources in the urban area of Shanghai.

3.3 NH\(_3\) diurnal profiles and insight into sources

Hourly observations over long-term periods offer a unique opportunity to provide robust diurnal profiles for each season. Figure 7 shows the average diurnal profiles of NH\(_3\) and CO concentrations across seasons. Historically, CO emissions in Shanghai and its surrounding YRD region mainly came from iron and steel manufacturing and on-road vehicles, which contributed 34 and 30% of the total, respectively, in 2007 (Huang et al., 2011). Due to changing economic activity, emission sources of air pollutants in China are changing rapidly. For example, over the past several years, China has implemented a portfolio of plans to phase out its old-fashioned and small steel mills, and raise standards for industrial pollutant emissions (Chang et al., 2012). In contrast, China continuously experienced double digit growth in terms of auto sales during the same period, and became the world’s largest automobile market since 2009 (Chang, 2014). Consequently, on-road traffic has overtaken industrial sources as the dominant source of CO emissions in eastern China (Zhao et al., 2012). In Fig. 7, CO shows a well-marked bimodal diurnal profile, with maxima in the morning (starting at 05:00 local time) and the evening (starting at 16:00), consistent with the variation of traffic flow in Shanghai (Liu et al., 2012). Therefore, CO variation can be utilized as a robust indicator of vehicle emissions. NH\(_3\) also displays a clear bimodal profile during all four seasons, similar to the CO diurnal profile, suggesting a significant influence of on-road traffic (with daily commuting) on ambient NH\(_3\) concentrations in the urban environment of Shanghai. We also notice that pools of surface water (i.e., dew or fog), which form on nights that have a high RH, can act as NH\(_3\) reservoirs that release NH\(_3\) upon evaporation in the midmorning, particularly in spring seasons.

Interestingly however, NH\(_3\) shows different degrees of a positive relationship with CO as a function of season (Fig. 8b). Specifically, during summertime, NH\(_3\) displays a significant relationship with CO \((R^2 = 0.48, p < 0.001)\), while this positive relationship is not observed during the winter season, when heavy traffic volume also occurs. As discussed above, the seasonal variation of NH\(_3\) concentration in Shanghai during our study period was quite flat. The seasonal average CO concentrations at PD were 0.71, 0.61,
Figure 7. Seasonal diurnal profiles of NH$_3$ and CO concentrations in Shanghai. Color coded by hourly temperature and circle radius coded by hourly relative humidity.

Figure 8. PSCF of CO (a) and NH$_3$ (c) during four seasons. The cities marked in each panel are Beijing (BJ) and Shanghai (SH). The color scales indicate the values of PSCF. (b) Relationship between hourly NH$_3$ and CO during four seasons.

0.58, and 1.1 ppmv in spring, summer, autumn, and winter, respectively. And the CO level in wintertime was higher than other seasons. Moreover, Fig. 8c suggests that for all seasons, the source region of NH$_3$ in Shanghai is locally dominated. However, the atmospheric lifetime of CO is much longer than that of NH$_3$ (typically several hours depending on meteorology) (Asman et al., 1998). PSCF analysis for CO in winter suggests important contributions from north of Shanghai (Fig. 8a), a region that does not appear as important as a NH$_3$ source (Fig. 8c). Consequently, elevated
regional background levels of CO from long-range transport appear to yield a poorer relationship between NH$_3$ and CO in wintertime (Fig. 8b).

3.4 The emission and transport of vehicle-sourced NH$_3$

Table S1 summarizes statistics of the NH$_3$ concentrations (µg m$^{-3}$) measured at each sampling point in and out of the Handan tunnel, which have been also been visualized in Fig. 9b. As expected, the highest average NH$_3$ concentration occurred at the exit of the tunnel (T-d). Although NH$_3$ concentration varied temporally, throughout the 2 months of observations, a large spatial gradient in NH$_3$ concentration at near-road sites was present in every sampling event, suggesting that an intensive NH$_3$ source from on-road traffic (not meteorological parameters) is the leading factor in governing the variation of ambient NH$_3$ concentration in a road-side environment. The NH$_3$ concentrations in the tunnel were increased with distance from the entrance of the tunnel (T-a). The NH$_3$ concentration at T-d (64.9 ± 11.5 µg m$^{-3}$) was over 5 times that at T-a (12.6 ± 3.3 µg m$^{-3}$). Moreover, the lowest NH$_3$ concentration value obtained at T-d (47.0 µg m$^{-3}$) was still nearly 10 µg m$^{-3}$ or 20 % higher than the highest value of other sites (Table S1). These observations provide compelling evidence that on-road traffic is an important emission source of NH$_3$ in the urban atmosphere. Given that there is a significant loss of vehicle exhaust from the tunnel through an open tunnel, the NH$_3$ concentration at the exit of the tunnel (T-d) has been also been visualized in Fig. 9b. Although NH$_3$ concentrations were highly dependent on wind speed (WS; 5 m s$^{-1}$), and traffic flow (TF; 120 000 vehicles day$^{-1}$), we can obtain an approximate mileage-based NH$_3$ emission factor (EF) of 28 ± 5 mg km$^{-1}$ for a single vehicle using the following equation:

$$EF = \frac{CG \times CS \times WS \times 86 400}{TF \times PD}$$

(1)

where 86 400 is the number of seconds in a day. This NH$_3$ emission factor was similar to that observed for the Gurbrist tunnel in Switzerland (31 ± 4 mg km$^{-1}$) (Emmenegger et al., 2004) and the Caldecott tunnel in California (49 ± 3 mg km$^{-1}$) (Kean et al., 2000), while much lower than that recently measured in Guangzhou, China (230 ± 14 mg km$^{-1}$) (Liu et al., 2014). Based on the emission factor we developed, a population of 3.04 million vehicles (average mileage of 15 000 km yr$^{-1}$) in Shanghai would produce around 1300 t NH$_3$ in 2014. This is very close to the “bottom-up” emission inventory for Shanghai for 2010 (1581.1 t) (Chang, 2014). Previous emission inventories in Shanghai (e.g., Huang et al., 2011 and Fu et al., 2012) made a significant underestimation of the NH$_3$ emissions from city areas. When compared with the NH$_3$ emissions from city areas, the contribution of on-road traffic can reach 12 % of the total NH$_3$ emissions in Shanghai city areas (10 742 t) (Chang, 2014). Moreover, model results have shown that over half of agricultural NH$_3$ emissions would be deposited downwind of their source within 10 km, depending on local meteorological conditions (Asman et al., 1998). Therefore, the relative contribution of NH$_3$ emissions from on-road traffic to urban PM pollution could be higher than the share of its mass contribution. Given that precisely estimating the EF of NH$_3$ from on-road traffic is beyond the scope of this paper, more research is needed to pinpoint this parameter in order to accurately quantify the amount of NH$_3$ emissions from vehicles.

From the tunnel exit to the open environment, the average NH$_3$ concentration at T-d (64.9 ± 11.5 µg m$^{-3}$) was 11 times more than that at O$_{310m}$ (5.6 ± 2.5 µg m$^{-3}$), and a general negative relationship was found between distance and ambient NH$_3$ concentration. Over the total measured distance, the maximum percent decrease was observed between the sites of T-d and O$_{310m}$ (50 m apart), indicating a rapid dispersion of vehicle-emitted NH$_3$ from the road tunnel. Still, Figure 9c clearly shows that 64 % (48 %) of the NH$_3$ concentration we observed at the site of O$_{310m}$(O$_{20m}$) can be explained by the simultaneous measurements of NH$_3$ concentration at T-d. No significant decrease in the gradients of NH$_3$ concentration was observed between the sites of O$_{150m}$ (5.9 ± 2.5 µg m$^{-3}$; n = 6) and O$_{20m}$ (5.6 ± 2.5 µg m$^{-3}$; n = 6), suggesting that the strongest impact of NH$_3$ emission and transport from local traffic flow on ambient NH$_3$ concentrations in the Shanghai urban area lies within 150 m distance.

4 Conclusions and outlook

This study linked a long-term and near real-time measurement of NH$_3$ at one of China’s flagships' supersites with a vehicle source-specific campaign performed inside and outside of a major freeway tunnel in Shanghai. The conclusions are shown as below.

The average NH$_3$ concentration (mean ± 1 σ) between April 2014 and April 2015 was 5.5 ± 3.9 µg m$^{-3}$. Seasonal NH$_3$ concentration levels varied in the following sequence: summer (7.3 ± 4.9 µg m$^{-3}$) > (5.1 ± 3.8 µg m$^{-3}$) ≈ winter (5.0 ± 3.4 µg m$^{-3}$) > fall (4.5 ± 2.3 µg m$^{-3}$).

During spring, ambient NH$_3$ concentrations appeared to be influenced to some extent by temperature-dependent emissions, likely from agricultural activities including crop fertilization. No such relationship was apparent during other seasons. Measured NH$_3$ concentrations were highly dependent on wind speed, while mixing height of planetary boundary layer and relative humidity were not the main factors influencing seasonal NH$_3$ concentrations.

The diurnal profile of NH$_3$ concentrations showed a typical bimodal cycle during four seasons, with maxima in the morning and the evening rush hours, suggesting a persistent
Y. H. Chang et al.: The importance of vehicle emissions as a source of atmospheric ammonia

Figure 9. (a) Location of the eight sampling points inside (labeled in yellow; inside the tunnel from the entrance to the exit) and outside (labeled in green; varying in distance from the tunnel) of the Handan tunnel where atmospheric concentrations of NH\textsubscript{3} were measured using fritted glass bubblers. The campus of Fudan University was separated into north and south parts by the tunnel. (b) Box-whisker plots of the NH\textsubscript{3} concentration sampled at each site, setting 20 as the breaking point of the y axis. The box boundaries represent the 25th and 75th percentile, the horizontal line is the median, and the whiskers mark the 10th and 90th percentiles. (c) Relationship between the NH\textsubscript{3} concentration at T-d (the exit of the Handan tunnel) and the other four sites varying in distance from the Handan road in the open environment.

influence of on-road traffic (with daily commuting) on ambient NH\textsubscript{3} levels in Shanghai.

The NH\textsubscript{3} concentration in the exit of the Handan tunnel (64.9 ± 11.5 µg m\textsuperscript{-3}) was over 5 and 11 times higher than that in the tunnel entrance (12.6 ± 3.3 µg m\textsuperscript{-3}) and the ambient air (5.6 ± 2.5 µg m\textsuperscript{-3}), respectively, providing further compelling evidence that on-road traffic is an important NH\textsubscript{3} source. In 2014, 1300 t vehicle-emitted NH\textsubscript{3} was calculated based on a mileage-based NH\textsubscript{3} emission factor of 28 ± 5 mg km\textsuperscript{-1} that we developed.

A negative relationship was found between the distance and ambient NH\textsubscript{3} concentration in our near-road gradient experiment. Up to 64% of ambient NH\textsubscript{3} concentration out of the tunnel can be explained by the vehicle-emitted NH\textsubscript{3} from the tunnel.

Unlike NH\textsubscript{3} emissions in agricultural areas, the NH\textsubscript{3} emissions in urban areas originate from a variety of stationary sources (industrial coal/oil/gas combustion, wastewater, landfill, compost and incineration), mobile sources and area sources (e.g., humans, green land, domestic fuel combustion). As a start, our study is far from fully elucidating the complex origins of urban NH\textsubscript{3} in Shanghai. Vehicle-emitted NH\textsubscript{3}, while important, is likely not the only major source of NH\textsubscript{3}. Additional useful investigative steps could include:

- Using isotopes as a source apportionment tool. Isotopic techniques have been proven to be useful tools for sources apportionment of gases and PM. Although the δ\textsuperscript{15}N values of NH\textsubscript{4}\textsuperscript{+} in rainwater and aerosols have been examined (Xiao et al., 2012, 2015; Xiao and Liu, 2002), atmospheric NH\textsubscript{3} has received much less attention. According to Felix et al., (2013), NH\textsubscript{3} emitted from volatilized sources has relatively low δ\textsuperscript{15}N values, allowing them to be distinctly differentiated from NH\textsubscript{3} emitted from fuel-related sources (e.g., on-road traffic) that are characterized by relatively high δ\textsuperscript{15}N values.

- Using chemical transport modeling (CTM) as a cost-effective analysis tool. CTM has the potential to capture the complex atmospheric behavior of NH\textsubscript{3}. Moreover, NH\textsubscript{3} emission reduction targets are represented as constraints in the optimization problem, and have a major influence on overall costs of a cost-effective solution and their distribution across different sources and economic sectors. Through sensitivity analyses of specific emission source or assuming possible emission control...

Y. H. Chang et al.: The importance of vehicle emissions as a source of atmospheric ammonia


Sutton, M. A., Erisman, J. W., Detener, F., and Möller, D.: Ammonia in the environment: from ancient times to the present, En-


