Emission factor of ammonia (NH$_3$) from on-road vehicles in China: tunnel tests in urban Guangzhou

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Abstract

Ammonia (NH$_3$) is the primary alkaline gas in the atmosphere that contributes to formation of secondary particles. Emission of NH$_3$ from vehicles, particularly gasoline powered light duty vehicles equipped with three-way catalysts, is regarded as an important source apart from emissions from animal wastes and soils, yet measured emission factors for motor vehicles are still not available in China, where traffic-related emission has become an increasingly important source of air pollutants in urban areas. Here we present our tunnel tests for NH$_3$ from motor vehicles under ‘real world conditions’ in an urban roadway tunnel in Guangzhou, a central city in the Pearl River Delta (PRD) region in south China. By attributing all NH$_3$ emissions in the tunnel to light-duty gasoline vehicles, we obtained a fuel-based emission rate of 2.92 ± 0.18 g L$^{-1}$ and a mileage-based emission factor of 229.5 ± 14.1 mg km$^{-1}$. These emission factors were much higher than those measured in the United States while measured NO$_x$ emission factors (7.17 ± 0.60 g L$^{-1}$ or 0.56 ± 0.05 g km$^{-1}$) were contrastingly near or lower than those previously estimated by MOBILE/PART5 or COPERT IV models. Based on the NH$_3$ emission factors from this study, on-road vehicles accounted for 8.1% of NH$_3$ emissions in the PRD region in 2006 instead of 2.5% as estimated in a previous study using emission factors taken from the Emission Inventory Improvement Program (EIIP) in the United States.

Keywords: emission factors, tunnel tests, ammonia, nitrogen oxide, emissions, vehicles

1. Introduction

Ammonia (NH$_3$) is the third abundant nitrogen-containing gas in the atmosphere, after N$_2$ and N$_2$O (Seinfeld and Pandis 1998). As the primary alkaline gas in ambient air, NH$_3$ can neutralize nitric and sulfuric acid to form ammonium nitrate and sulfate (Pinder et al 2007), which are important constituents of airborne fine particles or PM$_{2.5}$ (Chow et al 1994). China, for example, has serious air quality problem due to PM$_{2.5}$ pollution in the recent decade (Chan and Yao 2008, Zhang et al 2012a), and ammonium alone had contributed over 5% of the PM$_{2.5}$ mass in its megacities (He et al 2001, Pathak et al 2009, Ianniello et al 2011, Meng et al 2011, Yang et al 2011, Wang et al 2012). Another important role played by NH$_3$ is that it enhances the nucleation of sulfuric acid particles, and thus influences new particle formation events (Ortega et al 2008, Kirkby et al 2011). In addition, wet and dry deposition of NH$_3$ and ammonium may cause eutrophication and even
perturbation of ecosystems (Pearson and Stewart 1993, Seinfeld, Pandis 1998).

The major sources for atmospheric NH$_3$ include animal wastes, biological processes in soils and ammonia-based chemical fertilizers, followed by biomass burning, and sewage treatment plants (Bouwman et al 1997, Asman 1998). The contribution of on-road mobile sources has been considered to be negligible (Pierson and Brachaczek 1983). However, recent highway tunnel (Moeckli et al 1996, Fraser and Cass 1998, Emmenegger et al 2004, Kean et al 2000, 2009) and classis dynamometer (Durbin et al 2002, Huai et al 2003) studies indicate that NH$_3$ emissions from vehicles may be larger than previously estimated, which is mainly attributed to the chemistry over three-way catalysts (TWC) equipped on gasoline powered light duty vehicles (Bradow and Stumpf 1977, Cadle and Mulawa 1980). Therefore, road traffic is now recognized as an important source of NH$_3$ in the urban environment (Sutton et al 2000, Battye et al 2003). Chitijian et al (2000) estimated mobile sources might be responsible for as much as 18% of total NH$_3$ emissions in the South Coast Air Basin of California. US EPA concluded mobile sources contributed 8% of NH$_3$ emissions nationwide in 2006 (US EPA 2007).

In China, however, NH$_3$ emissions from vehicle exhaust were rarely measured and estimated. Huang et al (2012) estimated road traffic only contributed 1% of the total NH$_3$ emissions in 2006 in China. A high-resolution NH$_3$ inventory developed by Zheng et al (2012) for the Pearl River Delta region of China in 2006 indicated that on-road mobile source accounted for 2.5% of the total NH$_3$ emissions. The above-mentioned two studies in China all adopted emission factors from the same research by Roe et al (2004): Zheng et al (2012) used the factor for three-way catalyst light-duty gasoline vehicles (63.2 mg km$^{-1}$) while Huang et al (2012) used the average (26 mg km$^{-1}$) of non-catalyst, oxidation catalyst, and three-way catalyst gasoline vehicles. Though both Huang et al (2012) and Zheng et al (2012) got negligible contributions from vehicle exhausts to the total ammonia emissions, Ianniello et al (2011) and Meng et al (2011) suggested that traffic was an important source of ammonia in urban areas of Beijing, China. Since NH$_3$ in vehicle exhausts may strongly impact the early chemical evolution of exhausts in the ambient, the lack of measured NH$_3$ emissions factor for vehicles in China would not only result in large uncertainty about the role of on-road motor vehicles in NH$_3$ emission inventories, but also impede deep understanding of tropospheric chemistry in urban areas.

In the present study, we measured concentration changes of NH$_3$ and NO$_x$ against CO$_2$ and CO inside an urban roadway tunnel in the PRD region, the same region for which Zheng et al (2012) had estimated NH$_3$ emissions from on-road mobile source based on emission factors by Roe et al (2004). With the assumption that NH$_3$ emission from diesel trucks is negligible, fuel-based (mg L$^{-1}$) NH$_3$ and NO$_x$ emission factors for light-duty gasoline vehicles under ‘real world conditions’ were thus calculated and used to estimate and re-evaluate the contribution of on-road vehicles to the total NH$_3$ emissions in the region.

## 2. Methods

### 2.1. Sampling

NH$_3$ emission from motor vehicles can be influenced by many factors, such as vehicle and fuel types, emission control technology and driving patterns (Moeckli et al 1996, Fraser and Cass 1998, Kean et al 2000, 2009, Baum et al 2001, Durbin et al 2002, Heeb et al 2006, 2008, Livingston et al 2009). NH$_3$ emission factors for vehicles can be estimated in road tunnels (Moeckli et al 1996, Fraser and Cass 1998, Emmenegger et al 2004, Kean et al 2000, 2009) or obtained from classis dynamometer studies (Durbin et al 2002, Huai et al 2003). Road tunnels are excellent locations to measure vehicle emissions as the influence of meteorological conditions is minimized and the emissions undergo ‘real world’ dilution effects with minimal interference from other sources, enabling the vehicle emission factors to be determined. More importantly, road tunnel studies provide emissions from a large number of vehicles under ‘real world conditions’, that is, vehicles operating at hot and stable conditions when going through a road tunnel.

We conducted our tests in the Zhujiang Tunnel. It is an underwater tunnel crossing the Pearl River in the western urban area of Guangzhou, the central city in the Pearl River Delta. Figure 1 shows the layout of the tunnel. The tunnel is 1238 m long with a 721 m flat underwater section and two 517 m open slope sections outside both ends; it has two traffic bores of two lanes with traffic in the same direction each (He et al 2008). The vehicle speed limits in the tunnel are 15–50 km h$^{-1}$, and the typical vehicle speed is 40–50 km h$^{-1}$. It is worth noting that during rush hours (7–9 am and 5–8 pm) all trucks are banned; trucks of Guangzhou with vehicle payload weight higher than five tons and trucks from other cities with vehicle payload weight higher than 0.6 tons are banned from 7 am to 10 pm. During this study, the ventilation fans in the tunnel were turned off to prevent the influence of air turbulence.

A video camera was placed at the exit to record the passing vehicles. Numbers of different types of vehicles were determined from the video tapes. Motor vehicles are classified into taxi, cars, mini-trucks (MTs), light-duty trucks (LDTs), medium-duty trucks (MDTs), heavy-duty trucks (HDTs), light-duty buses (LDBs), medium-duty buses (MDBs), heavy-duty buses (HDBs) and motorcycles. During the sampling period, the traffic densities varied between 105 and 2641 vehicles per hour, with an average of 1782 vehicles per hour.

### 2.2. Pollutant measurements

Sampling points were located 50 m from both ends of the tunnel inside the western bore with a cross-sectional area of 52.8 m$^2$. Sampling time lasted from 3 am 10 August to 0 am 15 August 2013, with an average temperature of 33.4 ± 3.4 °C.
and relative humidity of 53.9%. Measured pollutants included NH3, NOx, CO and CO2.

NH3 and NOx were continuously measured by a chemiluminescence analyzer (EC9842, Ecotech, Austria). The EC9842 chemiluminescence NH3 analyzer combines a high performance ammonia converter (HTO-1000) and proven chemiluminescence detection to measure NH3, NOx and total nitrogen compounds (N). N is the sum of NO, NO2 and NH3. To measure N2 concentration, NO2 and NH3 are converted to NO in a quartz converter by Pt catalyst at a temperature range of 580–820 °C. In a separate reaction, NOx is passed through a molybdenum converter heated to approximately 325 °C to convert NO2 to NO. NO is then detected by the analyzer. The resulting NH3 concentration is determined by subtracting the N2 result from the NOx. Measured NH3 concentration may be interfered by basic gases, such as organic amines or the like. McCulloch and Shendrikar (2000) compared experimental results of concurrent sampling using this method with a Model 17C analyzer (Thermo Environmental Instruments, Franklin, MA) and collocated citric acid denuders (URG, Chapel Hill, NC). Their results demonstrated that this method reliably measured ambient NH3 concentrations with a high degree of accuracy. This method was also successfully employed to measure NH3 in the southeastern US (Hansen et al. 2003, Edgerton et al. 2007). The instrument was calibrated using a certified cylinder of NO (Foshan Kodi Gas Chemical Industry, China). NH3 converter efficiency was determined to be 91.28% using a certified cylinder of NH3 (Beijing AP BAIF Gases Industry, China). The detection limit and accuracy of the NH3 instrument are 0.5 ppb and ±0.5%, respectively, and the time resolution is 1 min.

For accurately determining CO2 and CO concentrations during a time interval, two-hour integrated air samples were collected by pumping air into the cleaned aluminum foil bags at a constant rate of 100 ml min⁻¹. Samples were collected every two hours from 6 am 10 August to 4 am 11 August and from 4 am 12 August to 0 am 13 August for two days. CO concentrations in these air samples were determined using a gas chromatography (Agilent 6890GC, USA) with a flame ionization detector and a packed column (5A Molecular Sieve 60/80 mesh, 3 m x 1/8 inch). Details of this instrument can be found elsewhere (Zhang et al. 2012b). CO2 was analyzed with HP 4890D gas chromatography (Yi et al. 2007). For CO and CO2 the detection limits were <30 ppb and the relative standard deviations were all less than 5% based on seven duplicates running with CO and CO2 standards of 1.0 ppm.

3. Results and discussion

3.1. Diurnal variations of NH3 and NOx concentrations

Concentrations of NH3 and NOx measured at the tunnel inlet and outlet are presented in Table 1. Averaged concentrations of NH3 and NOx measured at the outlet were 13.8 and 8.0 times that at the inlet, respectively. The average concentration of NH3 at the tunnel outlet was 729 ppb, much higher when compared to ~390 ppb reported by Moeckli et al. (1996) at the outlet of Gubrist Tunnel for a one-day exposure period, or 34 µg m⁻³ (48.9 ppb NTP) measured by Fraser and Cass (1998) inside the Van Nuys Tunnel, or 369 ppb observed by Kean et al. (2000) at the exit of Caldecott Tunnel from 4–6 pm.

As shown in Figure 2, NH3 and NOx at the tunnel outlet all exhibited diurnal patterns quite similar to that of the total traffic density. Each day both NH3 and NOx concentrations had two peaks at the rush hours of 7–9 am and 5–8 pm, and they were higher during evening rush hours than during the morning ones, consistent with about 10% higher total traffic densities during evening rush hours. The maximum concentrations occurred during the evening rush hours with levels over 4000 ppb and 2500 ppb for NOx and NH3, respectively. The concentration valleys were reasonable during the nighttime of 0–6 am when traffic density was also the lowest.

Figures 2(b) and (c) show the traffic density profiles for taxi, MTs, LDTs, MDTs, HDTs, cars, LDBs, MDBs, HDBs and motorcycles inside the tunnel. Diurnal patterns of cars and LDBs exhibited two peaks in rush hours, the same as that of the total traffic density. Taxi showed a quite different pattern with a peak at midnight. Densities of MDTs and HDTs showed no significant differences between rush hours and other time periods. As MDTs and HDTs only contributed about 0.5% of the total traffic, the restrictions on trucks might have a negligible effect on the composition of vehicle fleet. Percentages of light-duty (LD) vehicles (cars, taxi, MTs, LDTs and LDBs) were relatively stable during 10 am–10 pm (figure 2(d)) and the sum of cars, LDBs and taxi contributed approximately 82.5% of the total traffic, which was quite near a share of 79.6% for small passenger vehicles in all civil vehicles in Guangzhou in 2012 (Guangdong Provincial Bureau of Statistics (GPBS) and Guangdong Survey Office of National Bureau of Statistics (GSONBS) 2013).
consistency means, if cars and LDBs were major contributors of NH$_3$ as discussed below, our tunnel test results would be largely representative ones for Guangzhou.

Figure 3 shows the scatter plots of NH$_3$ concentrations against traffic densities of different types of vehicles. NH$_3$ concentrations show a good positive correlation with the total traffic density. Poor correlations between NH$_3$ concentrations and densities of diesel trucks were probably related to the negligible ammonia emission from diesel vehicles (Burgard et al. 2006). Although taxi contributed about 14.3% of the total traffic in the tunnel from 10 am to 10 pm, its density was also poorly correlated with NH$_3$ concentration. A probable reason is that NH$_3$ concentrations varied with that of major NH$_3$ contributors like cars, and that ammonia emission from taxi was negligible as over 90% of taxis in Guangzhou were

Figure 2. (a) Concentration-time plots of NO$_x$ and NH$_3$ at the tunnel outlet during the sampling period with a time resolution of 1 h. (b) Profile of the total traffic density and traffic densities of taxi, cars, light-duty buses (LDBs) and heavy-duty buses (HDBs) during the sampling period. (c) Profile of traffic densities of mini-trucks (MTs), light-duty trucks (LDTs), medium-duty trucks (MDTs), heavy-duty trucks (HDTs), medium-duty buses (MDBs) and motorcycles during the sampling period. (d) Light-duty vehicles (LDV) and heavy-duty vehicles (HDV) percentages of the total traffic density during the sampling period.

Figure 3. Scatter plots of NH$_3$ concentrations against traffic densities of Taxi, MTs, LDTs, MDTs, HDTs, Cars, LDBs, MDBs, HDBs and motorcycles.
LPG-powered instead of gasoline-powered. The negative correlation between motorcycle densities and NH$_3$ concentrations might be resulted from the fact that motorcycle densities peaked during nighttime when densities of major NH$_3$ contributors, like cars, had valleys instead. The good positive correlations ($p < 0.001$, $R^2 > 0.5$) between NH$_3$ concentrations and densities of cars and buses (LDBs, MDBs and HDBs) might imply that cars and buses were largely responsible for NH$_3$ emissions in the tunnel.

3.2. Emission factors

Light-duty vehicle emission factors were calculated by carbon balance, using the following equation the same as previous studies (Kirchstetter et al 1999, Kean et al 2000, Martins et al 2006):

$$E_p = \frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]} \cdot \frac{MW_p}{MW_c} \cdot w_c \cdot \rho_f \cdot \rho_l \cdot \Delta \rho$$

where $E_p$ is the emission factor of pollutant $P$ in unit of mg kg$^{-1}$ of fuel burned. $\Delta[P]$, $\Delta[CO_2]$ and $\Delta[CO]$ represent the increase in concentration of pollutant $P$, CO$_2$ and CO between the tunnel inlet and outlet, respectively. $MW_p$ and $MW_c$ are molecular weight of pollutant $P$ and carbon, respectively. $w_c = 0.85$ is the mass fraction of carbon of gasoline fuel and $\rho_f$ is the gasoline density (here $\rho_f = 740$ g L$^{-1}$). Since in the vehicle exhausts contribution of hydrocarbons to the total carbon concentrations is known to be negligible compared to that of CO$_2$ (Kirchstetter et al 1998), hydrocarbons have been ignored in equation (1).

As measured CO$_2$ and CO concentrations were 2 h averages for two days, NO$_x$ and NH$_3$ concentrations recorded during the same time intervals at the tunnel inlet and outlet were also averaged to calculate $\Delta[P]$. As shown in figure 2(d), percentages of light-duty (LD) vehicles (cars, taxi, MTs, LDTs and LDBs) and heavy-duty (HD) vehicles (MDTs, HDTs, MDBs and HDBs) were relatively stable from 10 am to 10 pm, so data from 10 am to 10 pm were used to calculate the emission factors of NO$_x$ and NH$_3$.

Given that diesel trucks are found to contribute very little to ammonia (Burgard et al 2006) and that gasoline powered vehicles shared an average of 88.2% in the total traffic densities in the Zhujiang tunnel, gasoline powered vehicles would be the main source of ammonia in the tunnel. Diesel trucks did contribute to CO$_2$ and might have different fuel efficiencies with gasoline powered vehicles. The fraction of fuel burned by light-duty gasoline vehicles is needed when calculating the ammonia emission factor. Using the fuel efficiencies of different kinds of vehicles reported by He et al (2005) and Huo et al (2012) and the fleet distribution in the tunnel, we obtain a rough estimate of 74.2% of fuel burned by light-duty gasoline vehicles. The emission factor of NH$_3$ is thus determined to be 2.92 ± 0.18 g L$^{-1}$ (mean ± 95% C.I.) when all ammonia emission is attributed to light-duty gasoline vehicles. Reported on-road or dynamometer-based NH$_3$ emission factors for motor vehicles in other countries ranged 88.8–503.2 mg L$^{-1}$ (Moeckli et al 1996, Fraser and Cass 1998, Kean et al 2000, Baum et al 2001, Durbin et al 2002, 2004, Huai et al 2003, Burgard et al 2006), less than 1/5 of that determined in this study. Recently, Carslaw and Rhys-Tyler (2013) reported an NH$_3$ emission factor 0.48 g L$^{-1}$ for Euro IV passenger cars in London, and Sun et al (2014) observed an average on-road NH$_3$ emission factor 0.36 ± 0.04 g L$^{-1}$ in California. These factors were quite near that reported by Fraser and Cass (1998) and Kean et al (2000).

Ammonia emission factor based on mg km$^{-1}$ can be estimated using the fuel efficiency. Wagner et al (2009) estimated the 2006 average fuel consumption of cars in China to be 7.95 L/100 km and projected a 2009 new passenger car average fuel consumption of 7.87 L/100 km. Using 7.87 L/100 km as the average fuel efficiency, we obtained ammonia emission factor of 230 ± 14 mg km$^{-1}$ (mean ± 95% C.I.) for the light-duty gasoline vehicles. A comparison of ammonia emission factor with those from other tunnel studies is given in table 2. Also ammonia emission factor in mg km$^{-1}$ measured in the Zhujiang tunnel was the highest among the studies (Moeckli et al 1996, Fraser and Cass 1998, Kean et al 2000, Emmenegger et al 2004).

Since NH$_3$ is present in human breath in levels ranging 100–200 ppb (Španiel et al 1998, Kearney et al 2002), how much NH$_3$ could be attributed to passengers inside the vehicles? Assuming inhalation rate of 10–15 L min$^{-1}$ for an adult, and taking the NH$_3$ level in human breath as its upper limit of 2000 ppb, the emission of NH$_3$ would be 13.7–20.3 μg min$^{-1}$ for an adult, quite near that of 18.7 μg min$^{-1}$ as reported by Ament et al (1999). Even with the emission rate of 20.3 μg min$^{-1}$, emission factor of NH$_3$ from human breath would be 0.16 mg km$^{-1}$ assuming an average of five passengers per vehicle and an average vehicle speed of 45 km h$^{-1}$ in the tunnel. This factor was negligible compared to the 230 mg km$^{-1}$ from vehicles. Moreover, vehicles passing the tunnels had their windows closed, with a quite limited portion of NH$_3$ from human breath entering the tunnel through indoor/outdoor exchange. The higher gasoline sulfur levels in China may impact the NH$_3$ emission. As observed by Durbin et al (2004), NH$_3$ emission rates were approximately five times higher over the more aggressive US06 test cycle compared to the federal test procedure (FTP) cycle, and sulfur did not affect NH$_3$ emissions over the FTP, but higher NH$_3$ emissions were found for increasing fuel sulfur levels over the US06. Malfunctioning three-way-catalysts might be a major factor causing higher ammonia emissions. Fraser and Cass (1998) reported ammonia emission factors ranging from 67.0 to 166.6 mg km$^{-1}$ for light-duty vehicles equipped with malfunctioning three-way-catalysts. Nevertheless, it is a question that needs further investigation whether the much higher NH$_3$ emission factor in this study was resulted from fuel quality, performance of catalytic converters or driving conditions.

NO$_x$ (as NO) emission factor was determined to be 7.17 ± 0.60 g L$^{-1}$ (0.56 ± 0.05 g km$^{-1}$) when averaged over the entire fleet in the Zhujiang tunnel. As shown in table 2, NO$_x$ emission factor in the Zhujiang tunnel is within the range of other studies. Che et al (2009) estimated
a NO\textsubscript{x} emission factor of 1.40 g km\textsuperscript{-1} for light-duty gasoline vehicles in 2006 in the PRD region using MOBILE and PART5 model, and Liao et al (2011), using COPERT IV model, estimated a NO\textsubscript{x} emission factor of 0.51 g km\textsuperscript{-1} for light-duty gasoline vehicles in Guangzhou in 2008. Our NO\textsubscript{x} emission factor was quite near that by Liao et al (2012) but less than half of that by Che et al (2009).

### 3.3. Implications

The most comprehensive NH\textsubscript{3} emission inventory for on-road mobile source in the PRD region was recently compiled by Zheng et al (2012). This inventory, however, was based on the emission factors taken from the Emission Inventory Improvement Program (EIIP) by Reo et al (2004), which were 63.2, 4.2, 28.0, 16.8, and 7.0 mg km\textsuperscript{-1} for light-duty gasoline, light-duty diesel, heavy-duty gasoline, heavy-duty diesel vehicles, and motorcycles, respectively. They obtained NH\textsubscript{3} emission of 4.9 kt yr\textsuperscript{-1}, or 2.5% of the total NH\textsubscript{3} emissions, from on-road mobile source in the PRD region in 2006. If we just replace the emission factor for light-duty gasoline vehicles with 230 mg km\textsuperscript{-1} determined in this study, NH\textsubscript{3} emission from on-road mobile sources by Zheng et al (2012) would then reach 16.8 kt yr\textsuperscript{-1} and account for 8.1% of the total NH\textsubscript{3} emission in the region, comparable to 10% obtained by Yao et al (2013) near a highway with the highest traffic density in Canada. As all newly manufactured light-duty vehicles in China are equipped with TWC for exhaust control, and meanwhile in recent decades vehicle population in the PRD region is increasing rapidly at a rate of over 10% per year (Che et al 2011), NH\textsubscript{3} emission from vehicle exhausts would become increasingly important. Applying this emission factor to the vehicle population in 2012 in the PRD region, for NH\textsubscript{3} emission from on-road mobile source we would get an estimate of 44.2 kt yr\textsuperscript{-1}, which is about 2.6 times that in 2006. If the total agricultural NH\textsubscript{3} emissions in 2012 were the same as that in 2006 as estimated by Zheng et al (2012), NH\textsubscript{3} emission from vehicle exhausts would occupy a share as high as 18.8% in the total NH\textsubscript{3} emission. In urban areas where on-road vehicle density is relatively higher and there is much less agricultural activity, NH\textsubscript{3} emission from on-road vehicles would be more distinctive and thus greatly influence the near-surface atmospheric chemistry. Further studies are needed to make clear the reason for the much higher emission factors determined from our tunnel tests in Guangzhou.

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### References

Ament W, Huizenga J R, Kort E, van der Mark T W, Grevink R G and Verkerke G J 1999 Respiratory ammonia output and blood ammonia concentration during incremental exercise Int. J. Sports. Med. 20 71–7
Asman W A H 1998 Factors influencing local dry deposition of gases with special reference to ammonia Atmos. Environ. 32 415–21
Battye W, Aneja V P and Roelie P A 2003 Evaluation and improvement of ammonia emissions inventories Atmos. Environ. 37 3873–83
Baum M M, Kiyomiya E S, Kumar S, Lappas A M, Kapinus V A and Lord H C 2001 Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. direct on-road ammonia measurements Environ. Sci. Technol. 35 3735–41
Bowman A F, Lee D S, Asman W A H, Dentener F J, Van Der Hoek K W and Olivier J G J 1997 A global high-resolution emission inventory for ammonia Glob. Biogeochem. Cycles 11 561–87
Bradow R L and Stump F D 1977 Unregulated emissions from three-way catalyst cars SAE Technical Paper No 770369
Burgh D A, Bishop G A and Stedman D H 2006 Remote sensing of ammonia and sulfur dioxide from on-road light duty vehicles Environ. Sci. Technol. 40 7018–22
Cadle S H and Mulawa P A 1980 Low-molecular-weight aliphatic amines in exhaust from catalyst-equipped cars Environ. Sci. Technol. 14 718–23
Carslaw D C and Rhys-Tyler G 2013 New insights from comprehensive on-road measurements of NOx, SO2 and NH3 from vehicle emission remote sensing in London, UK Atmos. Environ. 81 339–47
Chan C K and Yao X H 2008 Air pollution in mega cities in China Atmos. Environ. 42 1–42
Chang S C, Lin T H and Lee C T 2009 On-road emission factors from light-duty vehicles measured in hushed tunnel (12.9 km), the longest tunnel in Asia Environ. Monit. Assess. 153 187–200
Che W W, Zheng J Y and Zhong L J 2009 Mobile source emission characteristics and contributions in the pearl river delta region Res. Environ. Sci. 22 456–61
Che W, Zheng J, Wang S, Zhong L and Lau A 2011 Assessment of motor vehicle emission control policies using model-3/CMAQ model for the pearl river delta region, China Atmos. Environ. 45 1740–51
Chiang H L, Hwu C S, Chen S Y, Wu M C, Ma S Y and Huang Y S 2007 Emission factors and characteristics of criteria pollutants and volatile organic compounds (VOCs) in a freeway tunnel study Sci. Total. Environ. 381 200–11
Chitjian M, Koizumi J, Botsford C W, Mansell G and Vinegar E 2000 Final 1997 gridded ammonia emission inventory update for the south coast air basin Final report to the south coast air quality management district
Chow J C, Watson J G, Fujita E M, Lu Z, Lawson D R and Ashbaugh L L 1994 Temporal and spatial variations of PM2.5 and PM10 aerosol in the southern California air quality study Atmos. Environ. 28 2061–80
Durbin T D et al 2004 The effect of fuel sulfur on NH3 and other emissions from 2000–2001 model year vehicles Atmos. Environ. 38 2699–708
Durbin T D, Wilson R D, Norbeck J M, Miller J W, Huai T and Rhee S H 2002 Estimates of the emission rates of ammonia from light-duty vehicles using standard chassis dynamometer test cycles Atmos. Environ. 36 1475–82
Edgerton E S, Saylor R D, Hartsell B E, Jansen J J and Alan Hansen D 2007 Ammonia and ammonium measurements from the southeastern United States Atmos. Environ. 41 3339–51
Emmenegger L, Mohn J, Sigrist M, Marinov D, Steineumann U, Zumsteg F and Meier M 2004 Measurement of ammonia emissions using various techniques in a comparative tunnel study Int. J. Environ. Pollut. 22 326–41
Fraser M P and Cass G R 1998 Detection of excess ammonia emissions from in-use vehicles and the implications for fine particle control Environ. Sci. Technol. 32 1053–7
Guangdong Provincial Bureau of Statistics (GPBS) and Guangdong Survey Office of National Bureau of Statistics (GSONBS) 2013 Guangdong Statistical Yearbook, (Beijing: China Statistics Press)
Hansen D A, Edgerton E S, Hartsell B E, Jansen J J, Kandasamy N, Hidy G M and Blanchard C L 2003 The southeastern aerosol research and characterization study: part 1—overview J. Air Waste Manage. Assoc. 53 1460–71
He K, Huo H, Zhang Q, He D, An F, Wang M and Walsh M P 2005 Oil consumption and CO2 emissions in China’s road transport: current status, future trends, and policy implications Energy Policy 33 1499–507
He K, Yang F, Ma Y, Zhang Q, Yao X, Chan C K, Cadle S, Chan T and Mulawa P 2001 The characteristics of PM2.5 in Beijing, China Atmos. Environ. 35 4599–70
He L Y, Hu M, Zhang Y H, Huang X F and Yao T T 2008 Fine particle emissions from on-road vehicles in the zhujiang tunnel, China Environ. Sci. Technol. 42 4461–6
Hебе N V, Saxer C J, Fors A-M and Bruhlmann S 2006 Correlation of hydrogen, ammonia and nitrogen monoxide (nitric oxide) emissions of gasoline-fueled euro-3 passenger cars at transient driving Atmos. Environ. 40 3750–63
Heeb N V, Saxer C J, Fors A-M and Bruhlmann S 2008 Trends of NOx, NO2-, and NH3-emissions from gasoline-fueled euro-3 to euro-4 passenger cars Atmos. Environ. 42 2543–54
Hua T, Durbin T D, Miller J W, Pisano J T, Sauer C G, Rhee S H and Norbeck J M 2003 Investigation of NH3 emissions from new technology vehicles as a function of vehicle operating conditions Environ. Sci. Technol. 37 4841–7
Huang X, Song Y, Li M, Li J, Huo Q, Cai X, Zhu T, Hu M and Zhang H 2012 A high-resolution ammonia emission inventory in China Glob. Biogeochem. Cycles 26 GB1030
Huo H, He K, Wang M and Yao Z 2012 Vehicle technologies, fuel-economy policies, and fuel-consumption rates of chinese vehicles Energy Policy 43 30–6
Hwa M-Y, Hsieh C-C, Wu T-C and Chang L-F W 2002 Real-world vehicle emissions and VOCs profile in the taipei tunnel located at Taiwan taipei area Atmos. Environ. 36 1993–2002
Ianniello A, Spataro F, Esposito G, Allegrini I, Hu M and Zhu T 2011 Chemical characteristics of inorganic ammonium salts in PM2.5 in the atmosphere of Beijing (China) Atmos. Chem. Phys. 11 10803–22
Kean A J, Harley R A, Littlejohn D and Kendall G R 2000 On-road measurement of ammonia and other motor vehicle exhaust emissions Environ. Sci. Technol. 34 3535–9
Kean A J, Littlejohn D, Ban-Weiss G A, Harley R A, Kirchstetter T W and Lunden M M 2009 Trends in on-road vehicle emissions of ammonia Atmos. Environ. 43 1565–70
Kearney D, Hubbard T and Putnam D 2002 Breath ammonia measurement in helicobacter pylori infection Dig. Dis. Sci. 47 2523–30
Kirchstetter T W, Harley R A, Kreisberg N M, Stolzenburg M R and Hering S V 1999 On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles Atmos. Environ. 33 2955–68
Kirchstetter T W, Singer B C, Harley R A, Kendall G R and Traverse M 1998 Impact of California reformulated gasoline on motor vehicle emissions. 1. mass emission rates Environ. Sci. Technol. 32 318–28
Kirkby J et al 2011 Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation Nature 476 429–33
Kristensson A, Johansson C, Westerholm R, Swietlicki E, Gedhagen L, Wideqvist U and Veselý V 2004 Real-world traffic emission factors of gases and particles measured in a road tunnel in Stockholm, Sweden Atmos. Environ. 38 657–73
Liao H B, Yu Z, Zhou B, Liu Y H, Bi S Y, Cai M and Luo W L 2012 Characteristics of motor vehicle exhaust emission in Guangzhou Environ. Sci. Technol. 35 134–8
Livingston C, Rieger P and Winer A 2009 Ammonia emissions from a representative in-use fleet of light and medium-duty vehicles in the California south coast air basin Atmos. Environ. 43 3326–33

Mancilla Y, Araizaga A E and Mendoza A 2012 A tunnel study to estimate emission factors from mobile sources in Monterrey, Mexico J. Air Waste Manage. Assoc. 62 1431–42

Martins I D et al 2006 Emission factors for gas-powered vehicles traveling through road tunnels in são paulo, Brazil Environ. Sci. Technol. 40 6722–9

McCulloch R B and Shendrikar A D 2000 Concurrent atmospheric ammonia measurements using citric-acid-coated diffusion denuders and a chemiluminescence analyzer Atmos. Environ. 34 4957–8

Meng Z Y, Lin W L, Jiang X M, Yan P, Wang Y, Zhang Y M, Jia X F and Yu X L 2011 Characteristics of atmospheric ammonia over Beijing, China Atmos. Chem. Phys. 11 6139–51

Moeckli M A, Fierz M and Sigrist M W 1996 Emission factors for ethene and ammonia from a tunnel study with a photoacoustic trace gas detection system Environ. Sci. Technol. 30 2864–7

Ortega I K, Kurtén T, Vehkamäki H and Kulmala M 2008 The role of ammonia in sulfuric acid ion induced nucleation Atmos. Chem. Phys. 8 2859–67

Pathak R K, Wu W S and Wang T 2009 Summertime PM$_{2.5}$ ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere Atmos. Chem. Phys. 9 1711–22

Pearson J and Stewart G R 1993 The deposition of atmospheric ammonia and its effects on plants New. Phytol. 125 283–305

Piersma W R and Brachacek W W 1983 Emissions of ammonia and amines from vehicles on the road Environ. Sci. Technol. 17 757–60

Pinder R W, Adams P J and Pandis S N 2007 Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the eastern United States Environ. Sci. Technol. 41 380–6

Roe S M, Spivey M D, Lindquist H C, Thesing K B, Strait R P and Pecham E H and Associates Inc. 2004 Estimating ammonia emissions from anthropogenic nonagricultural sources US Emission Inventory Improvement Program (EIIP)

Seinfeld J H and Pandis S N 1998 Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, (New York: Wiley) pp 74–75, 1056–7

Śpaniel P, Davies S and Smith D 1998 Quantification of ammonia in human breath by the selected ion flow tube analytical method using H$_3$O$^+$ and O$_2^-$ precursor ions Rapid Commun. Mass Spectrom. 12 763–6

Staehelin J et al 1995 Emission factors from road traffic from a tunnel study (gubrist tunnel, Switzerland), part I: concept and first results Sci. Total Environ. 169 141–7

Sun K, Tao L, Miller D J, Khan M A and Zondlo M A 2014 On-road ammonia emissions characterized by mobile, open-path measurements Environ. Sci. Technol. 48 3943–50

Sutton M A, Dragosis U, Tang Y S and Fowler D 2000 Ammonia emissions from non-agricultural sources in the UK Atmos. Environ. 34 855–69

US EPA 2007 1970–2006 average annual emissions All Criteria Pollutants in MS Excel, Accessed 1 February 2008

Wagner D V, An F and Wang C 2009 Structure and impacts of fuel economy standards for passenger cars in China Energy Policy 37 3803–11

Wang X M, Ding X, Fu X X, He Q F, Wang S Y, Bernard F, Zhao X Y and Wu D 2012 Aerosol scattering coefficients and major chemical compositions of fine particles observed at a rural site in the central pearl river delta, south China J. Environ. Sci. 24 72–7

Yang F, Tan J, Zhao Q, Du Z, He K, Ma Y, Duan F, Chen G and Zhao Q 2011 Characteristics of PM$_{2.5}$ speciation in representative megacities and across China Atmos. Chem. Phys. 11 5207–19

Yao X, Hu Q, Zhang L, Evans G J, Godri K J and Ng A C 2013 Is vehicular emission a significant contributor to ammonia in the urban atmosphere? Atmos. Environ. 80 499–506

Yi Z, Wang X, Sheng G, Zhang D, Zhou G and Fu J 2007 Soil uptake of carbonyl sulfide in subtropical forests with different successional stages in south China J. Geophys. Res. 112 D08S02

Zhang Q, He K and Huo H 2012a Policy: cleaning China’s air Nature 484 161–2

Zhang Y L et al 2012b Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the pearl river delta region, south China J. Geophys. Res. 117 D15S06

Zheng J Y, Yin S S, Kang D W, Che W W and Zhong L J 2012 Development and uncertainty analysis of a high-resolution NH$_3$ emissions inventory and its implications with precipitation over the pearl river delta region, China Atmos. Chem. Phys. 12 7041–58