Environmental Pollution 280 (2021) 116972

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Emission factors of ammonia for on-road vehicles in urban areas from a tunnel study in south China with laser-absorption based measurements☆

Sheng Li [a, b], Tengyu Liu [c], Wei Song [a], Chenglei Pei [b, d], Zuzhao Huang [e], Yujun Wang [d], Yanning Chen [d], Jianhong Yan [f], Runqi Zhang [a, b], Yanli Zhang [a, g], Xinming Wang [a, b, g, *]

[a] State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China
[c] School of Atmospheric Sciences, Nanjing University, Nanjing, 210023, China
[d] Guangzhou Environmental Monitoring Center, Guangzhou, 510030, China
[e] Guangzhou Environmental Technology Center, Guangzhou, 510180, China
[f] Guangzhou Tunnel Development Company, Guangzhou, 510133, China
[g] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China

ARTICLE INFO

Article history:
Received 29 December 2020
Received in revised form
28 February 2021
Accepted 17 March 2021
Available online 20 March 2021

Keywords:
NH_3
Updated emission factor
Vehicle exhaust
Tunnel test
Real-world conditions
Emission standards

ABSTRACT

Vehicle emission is an important source of ammonia (NH_3) in urban areas. To better address the role of vehicle emission in urban NH_3 sources, the emission factor of NH_3 (NH_3-EF) from vehicles running on roads under real-world conditions (on-road vehicles) needs to update accordingly with the increasingly tightened vehicle emission standards. In this study, laser-absorption based measurements of NH_3 were conducted during a six-day campaign in 2019 at a busy urban tunnel with a daily traffic flow of nearly 40,000 vehicles in south China's Pearl River Delta (PRD) region. The NH_3-EF was measured to be 16.6 ± 6.3 mg km^{-1} for the on-road vehicle fleets and 19.0 ± 7.2 mg km^{-1} for non-electric vehicles, with an NH_3 to CO_2 ratio of 0.27 ± 0.09 ppbv $ppmv^{-1}$. Multiple linear regression revealed that the average NH_3-EFs for gasoline vehicles (GVs), liquefied petroleum gas vehicles, and heavy-duty diesel vehicles (HDVs) were 18.8, 15.6, and 44.2 mg km^{-1}, respectively. While NH_3 emissions from GVs were greatly reduced with enhanced performance of engines and catalytic devices to meet stricter emission standards, the application of urea selective catalytic reduction (SCR) in HDVs makes their NH_3 emission an emerging concern. Based on results from this study, HDVs may contribute over 11% of the vehicular NH_3 emissions, although they only share ~4% by vehicle numbers in China. With the updated NH_3-EFs, NH_3 emission from on-road vehicles was estimated to be 9 Gg yr^{-1} in the PRD region in 2019, contributing only 5% of total NH_3 emissions in the region, but still might be a dominant NH_3 source in the urban centers with little agricultural activity.

1. Introduction

Atmospheric ammonia (NH_3) is associated with aerosol formation and growth by reacting with nitric and sulfuric acids to form nitrate and sulfate aerosols, which are the major components of secondary inorganic aerosols (Pinder et al., 2007; Liu et al., 2015; Zhang et al., 2015a). The total ammoniated aerosol accounts for up to 60% of fine particles, especially during severe haze episodes in China's megacities (Pan et al., 2016; Sun et al., 2014). On a global scale, China is the world's leading emitters of NH_3 (Liu et al., 2011, 2013; Meng et al., 2017). Since the 1990s, China shares approximately 20% of global NH_3 emissions from anthropogenic sources (Hoesly et al., 2018). Although more than 80% of NH_3 in China is emitted from livestock breeding and synthetic fertilizer (Bouwman et al., 1997; Kang et al., 2016), road vehicular emissions have been

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☆ This paper has been recommended for acceptance by Pavlos Kassomenos.

* Corresponding author. State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China.

E-mail address: wangxm@gig.ac.cn (X. Wang).

https://doi.org/10.1016/j.envpol.2021.116972
0269-7491/

proposed as an important source of NH_3 in megacities (Chang et al., 2019; Pan et al., 2016). Based on the emission factor of NH_3 (NH_3-EF) measured in recent studies, it was estimated that vehicle exhaust could contribute 4% of total NH_3 emissions in China (Kang et al., 2016), while the proportion could reach up to 12–18% in urban areas (Chang et al., 2016b; Liu et al., 2014). Recent isotope studies suggested that vehicle exhaust could even account for more than 20% of NH_3 in urban areas (Chang et al., 2016a, 2019; Pan et al., 2016).

Previous studies have demonstrated that the three-way catalytic (TWC) converters equipped in vehicles are significant NH_3 emitters (Fraser and Cass, 1998; Heeb et al., 2006). Heeb et al. (2006) showed that the pre-catalyst NH_3 emission rate was below 0.1 mg s^{-1}, while the post-catalyst NH_3 emission rate reached levels up to 10 mg s^{-1}. Besides, driving speed also has a significant influence on vehicular NH_3 emission. Chassis dynamometer tests suggested that vehicular NH_3 emissions would reduce significantly from idling to cruising at approximately 60 km h^{-1} (Heeb et al., 2006; Park et al., 2019), and would however increase with driving speed when the speed exceeds 60 km h^{-1} (Heeb et al., 2006). Based on measurements in a highway tunnel in the San Francisco Bay area, NH_3 emissions from light-duty gasoline vehicles (equipped with the converters) decreased by 38 ± 6% between 1999 and 2006 (Kean et al., 2000, 2009), largely due to driving speed (Kean et al., 2009). As many factors, including vehicle type, catalytic converter, and driving condition, would impact vehicular NH_3 emissions, the individual and combined influence of these factors are difficult to formulate, and estimating NH_3 emission from vehicles running on roads under real-world conditions (on-road vehicles) is a highly challenging task.

Feasible methods to measure NH_3-EF for vehicles include the chassis dynamometer test, portable emissions measurement, and tunnel test. Among these methods, tunnel test is proved more powerful in acquiring absolute emission levels and reflecting real operating conditions (Franco et al., 2013; Gentner and Xiong, 2017). In an early study in 1995, NH_3-EF was determined to be 15 ± 4 mg km^{-1} for vehicles traveling through the Gubrist Tunnel in Switzerland (Moeckli et al., 1996), and the vehicle fleet was made up of mostly light-duty vehicles and a small portion of large trucks (4.4%). Vieira et al. (2016) carried out measurements in 2011 at Jânio Quadros Tunnel, São Paulo, Brazil, and found an EF of 42 ± 22 mg km^{-1} for a fleet consisting of motorcycles and light-duty vehicles (burning gasohol). Up to now, there have been quite limited tunnel studies measuring the NH_3 emission from on-road vehicles in China. An earlier tunnel test in 2013 in the Zhujiang Tunnel, the same tunnel where this present study was carried out, revealed an average vehicle NH_3-EF of 230 ± 14 mg km^{-1} (Liu et al., 2014), and later Chang et al. (2016b) reported NH_3-EF of 28 mg km^{-1} from on-road vehicles based on tests inside a Shanghai roadway tunnel in 2014.

In recent years, the total number of vehicles in China grew rapidly from 127 million in 2013 to 348 million in 2019. Meanwhile, emission standards have been upgraded from China IV in 2010 to China V in 2015, and to China VI in 2020 (MEEPRC, 2013–2020). Along with the upgrading of emission standards, the proportion of China V vehicles has increased by 30.9% during 2013–2018 in China (MEEPRC, 2013–2020). It is worth noting that in Guangzhou, a central city in south China's Pearl River Delta region, the China VI emission standard has been implemented since 2019. Many recent studies via chassis dynamometer experiments or portable emissions measurement revealed that vehicles with higher emission standards emit less NH_3 (He et al., 2020; Huang et al., 2018; Wang et al., 2019). Therefore, it is urgently needed to reevaluate the real-world vehicle emission of NH_3 with the latest vehicle emission standards, vehicle population, and fleet compositions. The main objectives of this study are: (1) to reevaluate the real-world NH_3 emission for on-road vehicles via tunnel test; (2) to derive the NH_3-EFs for different vehicle types from regression analysis between changing NH_3-EFs and fleet compositions; and (3) to estimate the contribution of vehicular NH_3 emission based on updated NH_3-EFs.

2. Material and methods

2.1. Tunnel site

The sampling campaign in this study was conducted in the Zhujiang Tunnel, which is an underwater tunnel crossing the Pearl River in the western urban area of Guangzhou. The tunnel consists of two independent bores with two traffic lanes in the same direction. It has a total length of 1,238 m with a flat underwater section (721 m) and two open slope sections outside both ends (517 m) (He et al., 2008). The sampling site includes two monitoring stations located at both ends of the flat underwater section, 50 m away from the inlet and the outlet (see Fig. 1). A more detailed description can be found elsewhere (Liu et al., 2014; Zhang et al., 2015b). Traffic rules associated with this tunnel are: (1) the upper limit speed is 50 km h^{-1}; (2) all diesel vehicles are forbidden to enter during rush hours (7:00–9:00 and 17:00–20:00); (3) local and ecdemic trucks with payload weights of >5 and >0.6 tons, respectively, are permitted to enter the tunnel only during night hours (22:00–7:00).

The measurements were carried out from October 14th to October 19th, 2019. During this period, the air temperature inside the tunnel was 30.9 ± 1.6 °C, and the horizontal wind speed along the direction of traffic flow was at 3.8 ± 0.4 m s^{-1}. A video camera fixed at the tunnel inlet was used to identify vehicle types and count their numbers. The average traffic flow during the whole campaign was 1,509 vehicles per hour, varying between 470 and 2,263 vehicles per hour. To understand how fleet compositions affect NH_3-EF, vehicles were classified into four categories based on their fuel types: (1) electric vehicles (EVs), referring to those labeled with green license plate and omnibuses in urban area; (2)

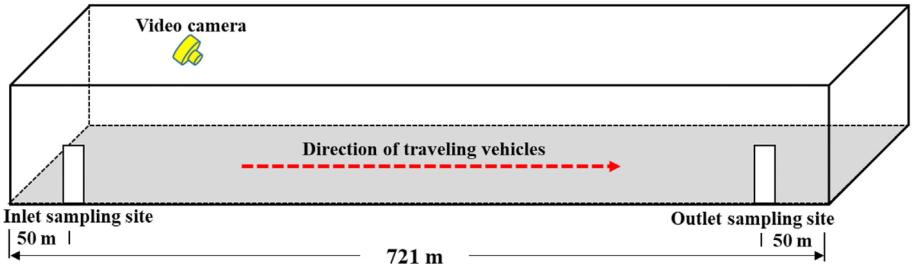

Fig. 1. Schematic diagram of the sampling site in the Zhujiang Tunnel.

gasoline vehicles (GVs), including cars, mini-trucks, mini-buses and motorcycles with non-green license plate; (3) diesel vehicles (DVs), involving trucks and buses (medium-duty and heavy-duty types) (He et al., 2005); and (4) liquefied petroleum gas vehicles (LPGVs), referring to all taxis except those with the green license plates. In this study, GVs shared a majority (73.7%) of the total traffic flow, followed by EVs (12.5%), LPGVs (9.7%), and DVs (4.2%).

2.2. Instrumentation and field measurements

NH_3, NO_x, CO, and CO_2 were simultaneously measured at the inlet and outlet stations. All gas analyzers were placed inside containers with a constant-temperature ~25 °C. Two LGR-NH_3 analyzers (Model 902-0016, Los Gatos Research, USA) were employed to measure gaseous NH_3 concentrations with a time resolution of 1 s. The analyzers directly quantify NH_3 concentration based on the laser-absorption spectroscopy. They have a high-finesse optical cavity serving as an absorption cell, which could sufficiently trap laser photons and guarantee an effective optical path length of several thousand meters to enhance the measured absorbance. The standard gaseous NH_3 (Messer, Germany) was used for instrument calibration. The detection limit was 0.3 ppbv (1 s) at a signal-to-noise ratio of 3. Compared to offline analysis and indirect online measurements in the previous tunnel tests, the NH_3 analyzers used in this study enable fast and accurate in situ observations of NH_3. NH_3 was typically having long equilibration times with surface and adsorbed water. To avoid sampling line interference, we set the NH_3 analyzers' inlet lines as shorter as possible and used high flow rates of air passing through the system. A detailed description of the operation principle, calibration, and data analysis can be found elsewhere (Leen et al., 2013).

NO_x and CO concentrations were measured by the Model 42i and 48i analyzers (Thermo Electron Inc., USA), respectively. The detection limit of the NO_x analyzer is 0.05 μg m^{-3}. The operating wavelength and detection limit of the CO analyzer was 4.6 μm and 0.04 mg m^{-3}, respectively. CO_2 concentrations at the inlet and outlet stations were measured by Model 410i analyzer (Thermo Electron Inc., USA) and Li-7100 analyzer (Li-COR, USA), respectively, with a detection limit of 2.0 mg m^{-3} for both CO_2 analyzers. The time resolution of these instruments was all set at 5 min. A 3-D Sonic Anemometer (Campbell, USA) was used to measure wind speed and direction in the tunnel with a time resolution of 1 s.

2.3. Emission factor and emission ratio

The mean EF for vehicles traveling through the tunnel during a time interval T can be expressed as below (Pierson and Brachaczek, 1983; Pierson et al., 1996; Zhang et al., 2015b):

$$EF_{fleet} = \frac{\Delta[P] \times V_{air} \times T \times A}{N \times L} \tag{1}$$

where EF_{fleet} is the emission factor per vehicle for a given species expressed as emitted mass per kilometer (mg km^{-1}). *Δ[P]* represents the increase in the concentration of pollutants between tunnel inlet and outlet. V_{air} represents the velocity parallel to the tunnel sensed by the 3-D Sonic Anemometer. *A* is the area of tunnel cross-section area (52.8 m^2). *N* is the number of vehicles passing through the tunnel during the time interval *T* (1 h in this study), and *L* (0.621 km) is the length between two sampling sites in the tunnel.

In this study, CO_2 contributed more than 99% of the carbon emissions. The vehicular NH_3:CO_2 emission ratio (NH_3/CO_2, ppbv ppmv^{-1}) can also be used to estimate the contribution of vehicle exhaust to NH_3 given that vehicle CO_2 emission inventories are relatively accurate (Sun et al., 2017).

3. Results and discussion

3.1. Incremental concentrations between outlet and inlet

Fig. 2 shows the mean concentration and ranges of NH_3, NO_x, CO, and CO_2 at tunnel inlet and outlet. The mean concentrations of NH_3, NO_x, CO, and CO_2 were 43.7 μg m^{-3}, 617.5 μg m^{-3}, 1.5 mg m^{-3}, and 1,057 mg m^{-3} at the tunnel outlet, and were 21.8 μg m^{-3}, 268.4 μg m^{-3}, 0.7 mg m$^{-3,}$ and 824.6 mg m^{-3} at tunnel inlet, respectively. The inlet-outlet incremental concentrations of NH_3 (ΔNH_3) measured in this study was less than 1/10 of that measured previously in 2013 in the same tunnel (Liu et al., 2014). The average traffic flow and speed were similar to those during the campaign in 2013, so the traffic volumes and their speeds might not be the major

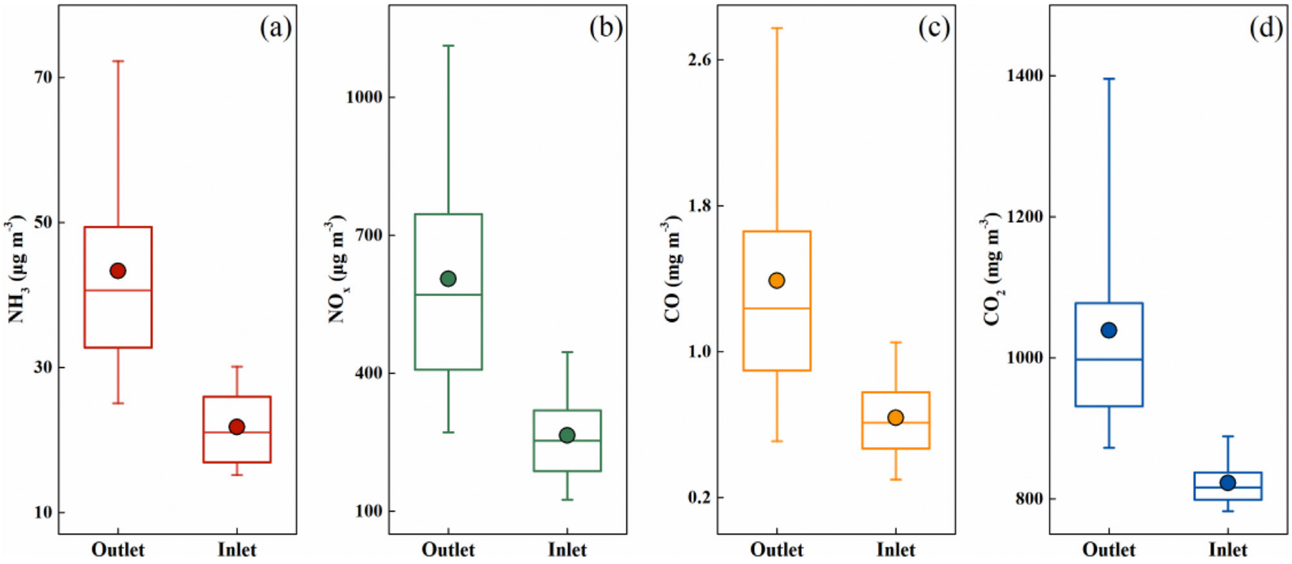

Fig. 2. The concentration of a) NH_3, b) NO_x, c) CO, and d) CO_2 at the tunnel outlet and inlet. Error bars represent 5% and 95% percentiles, box represent 25%, 50% and 75% percentiles, scatter point in the box represent average value.

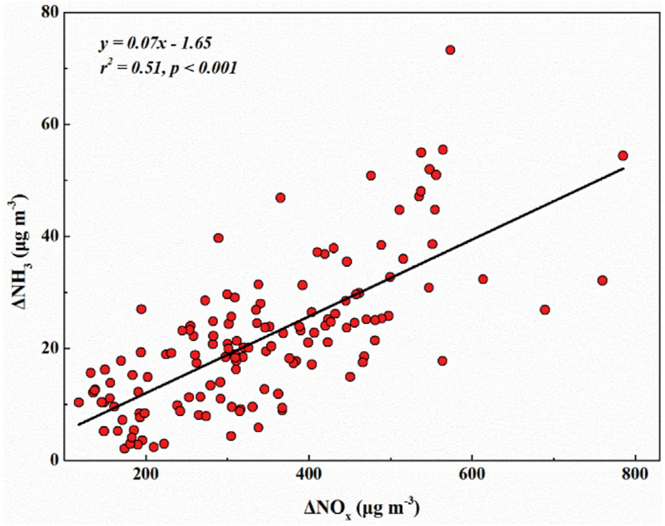

Fig. 3. Relationship between ΔNH_3 and ΔNO_x.

factors causing the decline.

As shown in Fig. 3, ΔNH_3 concentrations display significant correlation ($r^2 = 0.51$, $p < 0.001$) with ΔNO_x concentrations. This observation is consistent with previous studies that NH_3 in vehicle exhaust was mainly produced during the catalytic reduction of NO_x by TWC converter (Granger and Parvulescu, 2011). The hourly average concentrations of ΔNH_3 and ΔNO_x show similar trends with the total traffic flow (Fig. 4). Typically there are traffic jams during rush hours (7:00–9:00 and 17:00–19:00). During rush hours, the ΔNH_3 concentrations exhibited a dramatic increase that was not proportional to the increase in traffic flow (Fig. 5), probably due to higher vehicular NH_3 emission at low-speed or idle conditions. This result is supported by a previous study concluding that vehicles had approximately ten times higher NH_3 emission at an average speed of 4.7 km h^{-1} than at an average speed of 34.1 km h^{-1} (Park et al., 2019). It is worth noting that the maximum ΔNH_3 appears at 18:00, which is mainly due to traffic jams that lasted more than 30 min around 18:00 on October 17th and 18th.

3.2. NH_3 emission factor and emission ratio

Table 1 presents NH_3-EF and the NH_3/CO_2 ratios determined in this study in comparison to those from other tunnel studies. The NH_3-EF for all vehicles, NH_3-EF$_{fleet}$, was 16.6 ± 6.3 mg km^{-1} on average from this study. When excluding EVs that have no exhaust emissions, the NH_3-EF for non-EVs was 19.0 ± 7.2 mg km^{-1}. The NH_3-EF$_{fleet}$ in this study was close to 15 ± 4 mg km^{-1} reported by Moeckli et al. (1996) in the Gubrist Tunnel, Zurich, for a fleet with 95.6% short vehicle (78% equipped TWC). The lowest NH_3-EF$_{fleet}$ reported by Moeckli et al. (1996) may result from the fact that 22% of GVs then were not equipped with TWC. The average NH_3/CO_2 ratio (0.27 ± 0.09 ppbv ppmv^{-1}) from this study was almost the same as that (0.27 ± 0.05 ppbv ppmv^{-1}) measured in 2013 by Sun et al. (2017) in the Washburn Tunnel, Houston for the fleet with 91–99% GVs. It is worth noting that almost all on-road vehicles in the US in 2013 met EPA Tier2 emission standards with NO_x emission limit even lower than that of China VI. Due to differences in fuel efficiency, the NH_3/CO_2 identical to that reported by Sun et al. (2017) suggested similar fuel-based NH_3-EF$_{fleet}$, but not mileage-based NH_3-EF$_{fleet}$. Compared with other previous tunnel studies for fleets dominated by GVs, the NH_3/CO_2 measured in this study is the lowest.

Both NH_3-EF$_{fleet}$ and NH_3/CO_2 calculated in this study were much lower than those in the same tunnel in 2013. This reduction in NH_3-EF might be related to the increased proportion of vehicles with stricter emission standards. Recently, due to enhanced vehicle emission control with upgrading emission standards, the proportion of vehicles meeting the China IV standard increased by 57.4% during 2013–2018 (MEEPRC, 2013–2020). The implementation of stricter emission standards directly affects the performance of engines and catalytic converters. The high air-fuel ratio engines are widely used to achieve a significant improvement in fuel economy (Granger and Parvulescu, 2011; Kaspar et al., 2003). The air-fuel ratio of an engine has an important effect on NH_3 emissions, and

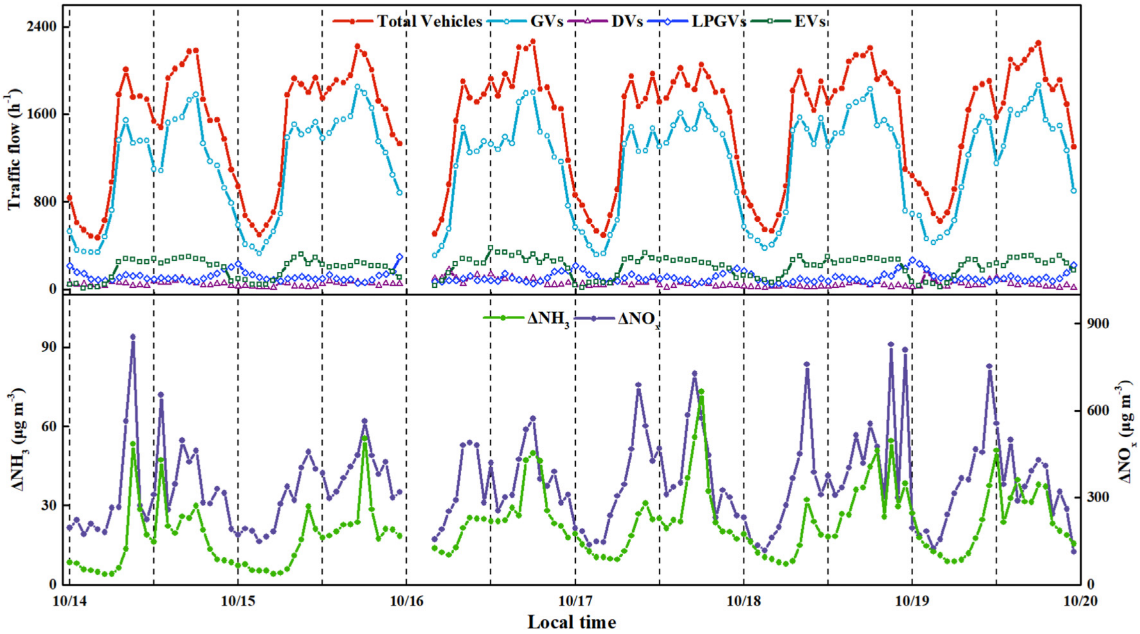

Fig. 4. Time series of traffic flow, ΔNH_3, and ΔNO_x concentrations.

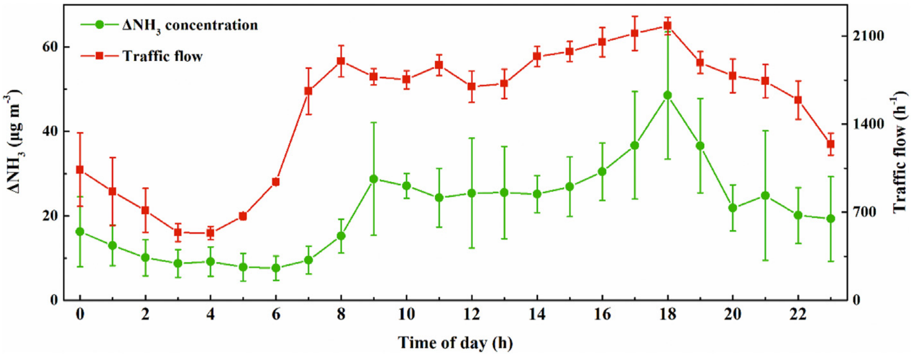

Fig. 5. Hourly averaged ΔNH_3 and traffic flow as a function of time of day, and error bars represent standard deviation (1σ).

Table 1
Comparison of NH_3-EF and NH_3/CO_2 from this study with those from other tunnel studies.

Year	Location	NH_3-EF ($mg\ km^{-1}$)	NH_3/CO_2 ($ppbv\ ppmv^{-1}$)[a]	Fleet compositions	Reference
1993	Vab Buys Tunnel, Los Angeles	61	0.45	97.2% GVs	Fraser and Cass (1998)
1995	Gubrist Tunnel, Zurich	15 ± 4	–	95.6% short vehicle (78% equipped TWC)	Moeckli et al. (1996)
1999	Caldecott Tunnel, San Francisco	49 ± 4	0.55 ± 0.04	99% GVs	Kean et al. (2000)
2002	Gubrist Tunnel, Zurich	31 ± 4	–	light-duty vehicles (length < 6 m)	Emmenegger et al. (2004)
2006	Caldecott Tunnel, San Francisco	–	0.34 ± 0.02	~100% GVs	Kean et al. (2009)
2011	Jânio Quadros Tunnel, São Paulo	42 ± 22	–	~90% motorcycles and light-duty vehicles (burning gasohol)	Vieira et al. (2016)
2013	Zhujiang Tunnel, Guangzhou	230 ± 14	3.45 ± 0.21	88.2% GVs	Liu et al. (2014)
2013	Washburn Tunnel, Houston	–	0.27 ± 0.05	91–99% GVs	Sun et al. (2017)
2014	Handan Tunnel, Shanghai	28 ± 5	–	–	Chang et al. (2016b)
2019	Zhujiang Tunnel, Guangzhou	19 ± 7	0.27 ± 0.09	73.7% GVs, 4.1% DVs, 9.7% LPGVs	This study

[a] The NH_3 emission factors reported in various units in the literature were converted to $NH_3:CO_2$ emission ratio in $ppbv\ ppmv^{-1}$ whenever possible (Sun et al., 2017).

the less fuel-rich combustion in newer vehicles can significantly reduce NH_3 emissions (Granger and Parvulescu, 2011). In addition, low-noble metal loading TWC and lean NO_x trap catalysts are required in China V/VI emission standard vehicles. These catalytic devices could significantly reduce both NO_x and NH_3 emissions (DiGiulio et al., 2014; Huang et al., 2018). As demonstrated by Huang et al. (2018) via chassis dynamometer tests, the average NH_3-EF of Euro V is 10.8 mg km^{-1}, which is only 1/2 of Euro III and 1/3 of Euro II. A recent chassis dynamometer study also revealed that the average NH_3-EF for China VI was only 3.7 mg km^{-1} (0.7–8.0 mg km^{-1}) (Wang et al., 2019). Therefore, stricter emission standards could facilitate the reduction of NH_3 emitted from gasoline vehicles.

3.3. NH_3 emission factor for each vehicle type

Previous studies have demonstrated that NH_3 emissions from DVs are negligible (Burgard et al., 2006; Pierson and Brachaczek, 1983). However, to meet increasingly stringent NO_x emission standards, heavy-duty vehicles (HDVs) were equipped with the urea or NH_3 selective catalytic reduction (SCR) (Granger and Parvulescu, 2011; Kean et al., 2009). In China, SCR systems have been widely used since implementing the China IV standard (He et al., 2020). Many studies have shown that NH_3 emissions from HDVs equipped with urea-SCR or NH_3-SCR cannot be ignored (Ciardelli et al., 2007; DiGiulio et al., 2014; He et al., 2020; Salazar et al., 2016; Suarez-Bertoa et al., 2016). To retrieve average EFs for GVs, LPGVs, and HDVs, multiple linear regression followed (Grosjean et al., 2001; Pierson et al., 1996; Zhang et al., 2016):

$$EF_{all-i} = EF_{GV} \times R_{GV-i} + EF_{LPGV} \times R_{LPGV-i} + EF_{HDV} \times R_{HDV-i} \tag{2}$$

where $EF_{all\text{-}i}$ is the measured NH_3 emission factors in time interval i; $N_{GV\text{-}i}$, $N_{LPGV\text{-}i}$, and $N_{HDV\text{-}i}$ and N_i are the number of GV, DV, LPGV, and non-EVs passing the tunnel during the time interval i, respectively; and EF_{GV}, EF_{LPGV}, and EF_{HDV} represent the average EF for GV, LPGV, and HDV,respectively. Multiple linear regression based on the observed data from this study revealed that EF_{GV}, EF_{LPGV}, and EF_{HDV} were 18.8 mg km^{-1}, 15.6 mg km^{-1}, and 44.2 mg km^{-1}, respectively. Based on eq (2), NH_3-EF for the fleet could be calculated with retrieved average emission factors for each vehicle type. The calculated NH_3-EF was highly correlated with the observed NH_3-EF ($p < 0.001$) with a slope of 1.09 (Fig. 6), indicating that the fitting results were reasonable.

LPG vehicles in this study were retrofitted from original gasoline engines to LPG-gasoline bi-fuel engines and were also equipped with TWC devices. The NH_3-EF for LPGVs was reasonably close to that for GVs in this study. A chassis dynamometer study in Korea also showed that the NH_3-EFs for LPGVs (12–120 mg km^{-1}) was

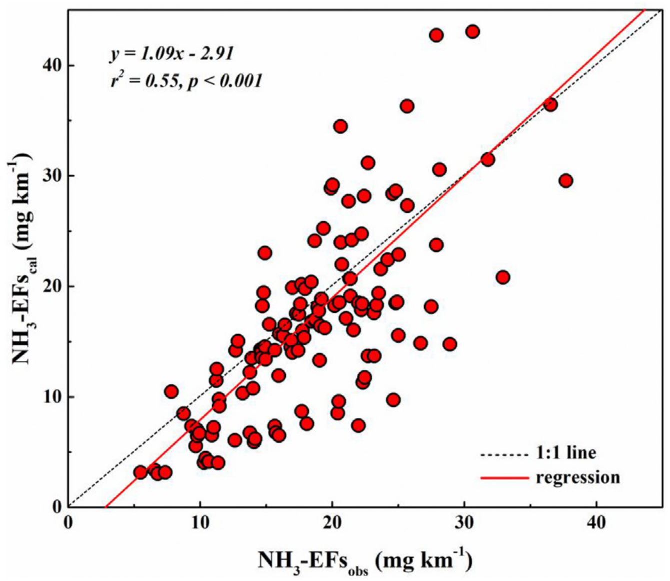

Fig. 6. Scatter plot of calculated NH_3-EFs based on regression results against the observed NH_3-EFs.

close to that for GVs (5–110 mg km^{-1}) under the same driving conditions (Park et al., 2019), and our NH_3-EFs for GVs and LPGVs fell in their low ranges.

It is worth noting that NH_3-EF for HDVs was significantly higher than that for other vehicle types. For the comparison of EF-NH_3 with that in previous studies, we used a conversion factor of 0.9 kWh km^{-1} for HDVs (USEPA, 2002) to convert the brake-specific emission factors (mg $kW^{-1}h^{-1}$) from previous studies into mileage-based emission factors (mg km^{-1}). A previous study reported an NH_3-EF of 5.4 mg km^{-1} for a Euro V engine tested over the European Steady Cycle (Tadano et al., 2014). Suarez-Bertoa et al. (2016) reported average NH_3-EFs of 17.1–56.7 mg km^{-1} for an on-road Euro V HDV without the ammonia oxidation catalyst (AMOX) system, while a number of studies reported average NH_3-EFs of 1–17 mg km^{-1} for Euro VI equipped with AMOX system (Khalek et al., 2015; Mendoza-Villafuerte et al., 2017; Suarez-Bertoa et al., 2020), suggesting AMOX system has a significant effect on reducing non-reacted NH_3 in HDV exhaust. In China, AMOX system has been installed in a part of China V HDVs. A recent study found that the average NH_3-EF for China IV HDVs and China V HDVs were 176.9 mg km^{-1} and 12.0 mg km^{-1}, respectively (He et al., 2020). At present, China III and IV DVs account for the largest proportion of DVs in China (MEEPRC, 2013–2020). The contribution of China III HDVs without the urea/NH_3-SCR to NH_3 can be negligible (Burgard et al., 2006; Pierson and Brachaczek, 1983), which may be a factor for relatively lower NH_3-EF for HDVs derived from this study. To meet stricter emission standards, SCR will be more widely used in HDVs, and thereby may increase the contribution of NH_3 from DVs. The NH_3-EF of HDVs (17 mg km^{-1}) used in current emission inventories (Ma, 2020; Wang et al., 2018) was much lower than that derived from regression in this study, implying that the NH_3-EF for HDVs might be underestimated in the emission inventories.

3.4. Implication

From the above results, the NH_3-EF from vehicles in China has significantly decreased in recent years. A recent study estimated that vehicle NH_3 emission was ~250 Gg in 2017 in China (Ma, 2020). Replacing the NH_3-EF used in Ma (2020) with the NH_3-EF_{fleet} from this study, we could estimate annual vehicular NH_3 emission of ~150 Gg in 2017 in China. Applying this NH_3-EF_{fleet} to the vehicle population in 2019 (SBGD, 2020) in the Pearl River Delta (PRD) region, we can have an NH_3 emission estimate of 9 Gg yr^{-1} for on-road mobile source. If the total NH_3 emissions from all sources in 2019 in the PRD region were ~180 Gg as same as in 2015 estimated by Bian et al. (2019), on-road vehicle exhaust would contribute only 5% of total NH_3. The contribution of agricultural sources to total NH_3 emissions in the PRD region remained stable at ~80% (Bian et al., 2019). Therefore, vehicles could still contribute more than 20% to the total nonagricultural NH_3 emissions, and in the urban areas with little agricultural activities, vehicle emissions might contribute substantially to ambient NH_3. Moreover, a chamber study has demonstrated that if NH_3 in gasoline vehicle exhaust is removed by a denuder, the number and mass concentrations of particles formed from the exhaust under photo-oxidation would be significantly reduced (Liu et al., 2015). Therefore, reducing NH_3 emissions from vehicles might be of greater importance in control traffic-related fine particle emissions in urban areas.

NH_3 emissions from GVs in China will continue to decline if China VI or stricter emission standards are implemented. However, HDVs account for only 1.9% of the total vehicles in this study, but they can contribute 5% of the total NH_3 from vehicles. This implies that HDVs, which is only 4% of the total vehicles in China (MEEPRC, 2013–2020), might contribute ~11% of NH_3 from all on-road vehicles in 2019 if applying the emission factors from this study. Therefore, to meet stricter emission standards, the continued efforts to upgrade the performance of engines and catalytic devices will significantly reduce NH_3 emission from GVs, but the application of urea-SCR system may make HDVs an increasingly important contributor to NH_3 from vehicles. While reducing NO_x emission from HDVs, the by-producing NH_3 emission is an emerging concern.

4. Conclusions

Based on tests in 2019 in the Zhujiang Tunnel involving over 200,000 passing vehicles, we updated the EF of NH_3 for real-world on-road vehicles with the rapidly changing vehicle emission standards, vehicle population, and fleet compositions in recent years. The NH_3-EF_{fleet} was measured to be 16.6 ± 6.3 mg km^{-1} on average, and it was 19.0 ± 7.2 mg km^{-1} for non-EVs if the non-emitting EVs were excluded. ER (NH_3/CO_2) was measured to be 0.27 ± 0.09 ppbv $ppmv^{-1}$ on average. Both NH_3-EF_{fleet} and ER from in this study were less than 1/10 of that measured in the same tunnel in 2013. Based on multivariate linear regression with the observed data in this study, the average NH_3-EFs of GVs, LPGVs, and HDVs were derived from 18.8 mg km^{-1}, 15.6 mg km^{-1}, and 44.2 mg km^{-1}. The results revealed that LPGVs had an average NH_3-EF comparable to that of GVs. Moreover, HDVs showed the largest NH_3-EF, probably due to the SCR application. Based on results from this study, HDVs may contribute over 11% of the vehicular NH_3 emissions, although they only share ~4% by vehicle numbers in China. While reducing NO_x emission from HDVs with the application of SCR system, the by-producing NH_3 emission is an emerging concern.

Authorship contribution statement

Sheng Li, Writing – original draft, Methodology, Formal analysis, Writing – review & editing. Tengyu Liu, Writing, Methodology, Formal analysis, Writing – review & editing. Wei Song, Writing, Methodology, Formal analysis, Writing – review & editing. Chenglei Pei, Methodology. Zuzhao Huang: Methodology. Yujun Wang, Methodology. Yanning Chen, Methodology. Jianhong Yan, Methodology. Runqi Zhang, Investigation, Data curation. Yanli Zhang, Writing – review & editing. Xinming Wang, Project administration, Conceptualization, Writing, Funding acquisition, Supervision-Writing – review & editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was funded by Natural Science Foundation of China (41530641/41961144029), the Chinese Academy of Sciences (QYZDJ-SSW-DQC032), and Department of Science and Technology of Guangdong Province (2017B030314057/2017BT01Z134/2019B121205006).

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