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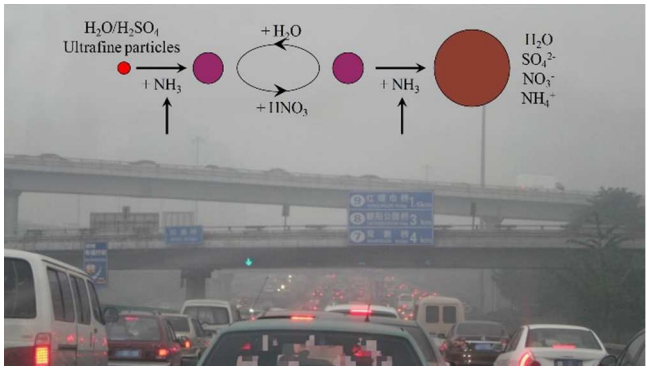


ABSTRACT

Ammoniated aerosols are important for urban air quality, but emissions of the key precursor NH_3 are not well quantified. Mobile laboratory observations are used to characterize fleet-integrated NH_3 emissions in six cities in the US and China. Vehicle NH_3:CO_2 emission ratios in the US are similar between cities (0.33–0.40 ppbv/ppmv, 15% uncertainty) despite differences in fleet composition, climate, and fuel composition. While Beijing, China has a comparable emission ratio (0.36 ppbv/ppmv) to the US cities, less developed Chinese cities show higher emission ratios (0.44 and 0.55 ppbv/ppmv). If the vehicle CO_2 inventories are accurate, NH_3 emissions from US vehicles (0.26 ± 0.07 Tg/yr) are more than twice those of the National Emission Inventory (0.12 Tg/yr), while Chinese NH_3 vehicle emissions (0.09 ± 0.02 Tg/yr) are similar to a bottom-up inventory. Vehicle NH_3 emissions are greater than agricultural emissions in counties containing near half of the US population and require reconsideration in urban air quality models

due to their co-location with other aerosol precursors and the uncertainties regarding NH_3 losses from upwind agricultural sources. Ammonia emissions in developing cities are especially important because of their high emission ratios and rapid motorizations.

INTRODUCTION

Atmospheric ammonia (NH_3) reacts with nitric and sulfuric acids to form nitrate and sulfate aerosols, a key component of fine particulate matter ($PM_{2.5}$). Ammoniated aerosols degrade urban air quality,[1] affect human health,[2] and impact the global radiation budget.[3,4] Long range transport of NH_3 and ammoniated aerosols threatens ecosystem health by contributing to critical load exceedance of nitrogen in remote ecosystems.[5] Because of its low molecular weight, NH_3/ammonium has a more significant impact on molar-based aerosol chemical and optical properties than the same mass of nitrate, sulfate, or organic compounds.

Although agriculture is the dominant NH_3 source at continental to global scales,[6,7] in urban areas a significant NH_3 source is gasoline vehicles equipped with three-way catalysts (TWC).[8] The presence of NH_3 in vehicle exhaust greatly enhances the formation and growth of secondary inorganic aerosols.[9] With the growing efficiency of TWC to reduce NO_x emissions and the recent introduction of selective catalytic reduction (SCR) system in diesel vehicles, NH_3 is now the dominant reactive nitrogen species emitted by vehicles produced in the recent decade.[10,11] Except for the Euro VI standard on heavy duty diesel vehicles,[12] there are no vehicle emission standards to regulate NH_3 worldwide. Reductions in fleet NH_3 emissions are slow or insignificant in US cities in recent years due to modest reduction in NH_3 emissions from new vehicles and increasing emissions from older vehicles (though with their TWCs still active).[10] In contrast, the emissions of SO_2 and NO_x have been regulated effectively in many countries and are projected to decrease even further in the upcoming decades.[13]

While high concentrations of NH_3 measured in cities have been attributed to vehicle emissions,[14–22] current inventories rely on laboratory studies and tunnel/roadside measurements to estimate vehicle emission factors (NH_3 emitted per unit mass of fuel).[23–26] Vehicle NH_3 emissions depend on road grade, driving mode, and vehicle age.[27] Therefore, the representativeness of laboratory tests or stationary measurements at single locations for an entire metropolitan area is not well-characterized.[28,29] The tunnels or freeway ramps where previous studies were carried out were often characterized by significant road grade, slow traffic movement, and/or high acceleration (see Table 1 for a summary of stationary measurements). To this end, Sun et al.[30] found that when road grade increased from 0 to 7%, the NH_3 emission factor more than doubled, thereby helping to explain the large range of emission factors reported in the literature. The only study to compare regional urban measurements from aircraft with the roadside tests showed good agreement in Los Angeles, although only NH_3:CO emission ratios were compared.[31] Emission factors have been reported for only a few US cities, all located in the western US. It is unclear how well individual stationary measurements represent an entire urban area in general and whether these cities are representative of vehicle emissions elsewhere in the US.

China has the second largest vehicle population of 0.15 billion, and together with the US (0.25 billion vehicles), the two countries account for about one third of the world vehicle population.[32] The vehicle fleet in Chinese cities has been rapidly developing and evolving, contributing significant amount of secondary inorganic aerosols in strong haze events.[33] Nonetheless, very few vehicle NH_3 emission measurements have been performed in China. One tunnel study reported an NH_3 emission factor one order of magnitude larger than those in the US.[34]

It is important to understand how vehicle emissions contribute to NH_3 and aerosol budgets in urban regions with diverse driving habits, fleet composition, topography, and vehicle emission/fuel standards. In this study, we characterize vehicle NH_3 emissions at the city scale in both the US and China through measurements of fleet-integrated vehicle NH_3:CO_2 emission ratios. To assess the representativeness of this method, the on-road emission ratios are compared with those derived from city-scale background and tunnel-based approaches. Overall, the results will be synthesized to help understand the accuracy of existing NH_3 emission inventories widely used in atmospheric chemical transport modeling.

EXPERIMENTAL METHODS

Data sets and instrumentation

Vehicle-based, mobile measurements of NH_3 (10% uncertainty), CO_2 (1 ppmv uncertainty), CH_4 (5 ppbv uncertainty), and other quantities were conducted in 2013−2014 in three major cities in the US (Houston, Denver, and Philadelphia) and three major cities in China (Beijing, Shijiazhuang, and Baoding) with over 4000 km and 100 hours of urban sampling.[35] Detailed measurement time, sampling routes, and demographic information of each city are shown in Section S1. These mobile measurements were in concert with other airborne and ground-based measurements during the NASA Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) campaigns and the Campaigns of Atmospheric Pollution in Beijing and North China Plain (CAREBeijing/NCP). In Houston, ground-based aerosol composition was measured by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer.[36] Vertical profiles of CO_2 and CH_4 were measured by a modified LI-COR 6252[37] and the Differential Absorption CO Measurement (DACOM)[38] on the NASA P-3B aircraft (see Section S2 for details of instruments).

105 **Methods to calculate emission ratios**

106 Vehicular NH_3:CO_2 emission ratios are used in this study because CO_2 is the primary carbon
107 emission product from vehicles. Constrained by fossil fuel consumption, the vehicle CO_2
108 emission inventories are also more accurate than those for NH_3. We use a similar method as Sun
109 et al.[30] to separate the localized vehicle emission signals from the urban backgrounds by finding
110 the first percentiles of on-road NH_3 and CO_2 mixing ratios within a certain spatial or temporal
111 window. The on-road emission ratios are then calculated by the point-to-point quotients of the
112 enhancements, quantifying emissions from vehicles in the direct vicinity of the mobile laboratory.
113 The arithmetic means of on-road NH_3:CO_2 emission ratios are compared with the literature or
114 other methods. The measurement uncertainty of on-road emission ratios is ± 15%.

115 Our datasets in Houston enable a case study to compare on-road emission ratios with city-scale
116 and tunnel vehicle emission ratios. The city-scale vehicle emission ratio was derived by
117 correlating the monotonically decreasing backgrounds of NH_3 and CO_2 in the urban planetary
118 boundary layer (PBL) during a downtown-suburb transect. We call this the city-scale vehicle
119 emission ratio, due to the dominance of traffic emissions near the transect we took in SW
120 Houston, as justified later. A similar first-percentile method was applied to remove localized
121 emission signals from the backgrounds. The tunnel vehicle emission ratio was measured using
122 the transits through the Washburn tunnel. Each method independently captures vehicle emissions
123 from different spatiotemporal scales, and together the agreement between them provides
124 confidence about the emission ratios observed. Detailed calculations and uncertainty analyses of
125 these three emission ratio methods are shown in Section S3.

RESULTS AND DISCUSSION

On-road emission ratios in the US and Chinese cities

Table 1 summarizes the NH_3:CO_2 emission ratios measured in this study and measurement conditions in the six US/Chinese cities (bold). It also compares our results with previous tunnel/roadside experiments. The on-road measurements in this study sampled all vehicles and did not differentiate between gasoline and diesel vehicles. As shown in Table 1 and the references therein, the majority of on-road traffic is gasoline, the NH_3 emission factors of diesel vehicles are much smaller than those of TWC-equipped gasoline vehicles, and diesel vehicles have very limited overall contribution to on-road NH_3 emissions. The average road grades were not significantly different from zero for all on-road measurements because upslope/downslope driving averages out over large areas. The road topography is thus indicated by the standard deviation of road grades. Most cities sampled in this study had rather flat natural topography, but significant road grades were usually encountered at bridges, freeway ramps, and tunnels. Denver was an exception where its west suburb extended into the Rocky Mountain foothills and therefore had larger road grade standard deviation (2.7%). For on-road measurements, the fleet speed and acceleration distributions were represented by those of the mobile laboratory, which generally followed the traffic pattern. The on-road measurements sampled a much wider range of speed/congestion levels, whereas tunnel/roadside measurements usually sampled free-flowing traffic at moderate to low speed.

Table 1. Comparison of tunnel, roadside, and mobile-based NH_3:CO_2 emission ratio measurements in the US and China

Year	Location	% Gasoline	NH_3:CO_2± uncertainty (ppbv/ppmv)[a]	Mean speed±1σ (km/h)	Mean road grade±1σ (%)[b]	Mean acceleration±1σ (km/h/s)	References
			California				
1993	Van Nuys Tunnel, LA	97.2%	0.45	–	–	–	Fraser and Cass (1998)[39]
1999	Freeway on-ramp, Baldwin Park	–	0.32±0.03	72-90	Slightly uphill	Acceleration onto freeway	Baum et al. (2001)[40]
1999	Caldecott Tunnel, Oakland	99%	0.55±0.04	52±14 (entrance); 71±5	4.2	0.3	Kean et al. (2000)[41]

				(exit)			
2006	Caldecott Tunnel, Oakland	~100%	0.34±0.02	57±10[c]	4.1	–	Kean et al. (2009)[42]
2008	Freeway interchange ramp, San Jose	–	0.41±0.02	49	3.1	1.6	Bishop et al. (2010)[27]
2008	Freeway interchange ramp, Fresno	–	0.41±0.01	41	3.1	0.0	Bishop et al. (2010)[27]
2008	Freeway on-ramp, Los Angeles	98.5%	0.66±0.02	28	3.5	3.1	Bishop et al. (2010)[27]
2010	Single lane traffic, Los Angeles	98.3-99.4%	0.49±0.02	51.7	0	0.8	Bishop et al. (2012)[43]
2013	On-road, multiple cities	–	0.42±0.06	77±27	0.0±2.2	0.0±1.2	Sun et al. (2014)[30]
2013	Freeway on-ramp, Los Angeles	98.1%	0.49±0.02	35	3.5	-0.3	Bishop et al. (2015)[10]
				Colorado			
2005	Freeway off-ramp, Denver	96.5%	0.38±0.08	40	8	1.1	Burgard et al. (2006)[44]
2013	Freeway off-ramp, Denver	96.7%	0.37±0.02	37	8	0.0	Bishop et al. (2015)[10]
2014	**On-road, Denver**	–	**0.40±0.06**	**80±32**	**0.0±2.7**	**0.1±1.8**	**This study**
				Oklahoma & Texas			
2005	Freeway interchange ramp, Tulsa	97.5%	0.42±0.01	39	4.7	-0.6	Burgard et al. (2006)[44]
2013	Freeway interchange ramp, Tulsa	97.2%	0.36±0.01	39	4.7	0.0	Bishop et al. (2015)[10]
2013	**On-road, Houston,**	–	**0.33±0.05**	**81±31**	**0.0±1.8**	**0.0±1.5**	**This study**
2013	**Washburn Tunnel, Houston**	91-99% (light-duty)	**0.27±0.05**	**55±9**	**6 or -6[d]**	–	**This study**
2013	**City scale, Houston**	–	**0.35±0.04**	**N/A**	**N/A**	**N/A**	**This study**
				Pennsylvania			
1981	Allegheny Mountain Tunnel	~100%	0.01±0.03	88	-0.5	–	Pierson and Brachaczek (1983)[45]
2013	**On-road, Philadelphia**	–	**0.39±0.06**	**42±18**	**0.0±1.0**	**0.0±1.1**	**This study**
				China			
2013	Zhujiang Tunnel, Guangzhou	75-95% (light-duty)	3.4 ±0.2[e]	40-50	Flat	–	Liu et al. (2014)[34]
2014	Handan Tunnel, Shanghai	85% (light-duty)	0.42±0.07[f]	–	–	–	Chang et al. (2016)[46]
2013	**On-road, Beijing**	–	**0.37±0.06**	**60±26**	**0.0±1.4**	**0.0±1.2**	**This study**
2013	**On-road, Baoding**	–	**0.51±0.08**	**46±24**	**0.0±1.7**	**0.0±1.8**	**This study**
2013	**On-road, Shijiazhuang**	–	**0.48±0.07**	**43±20**	**0.0±1.7**	**0.0±1.8**	**This study**
2014	**On-road, Beijing**	–	**0.36±0.05**	**48±25**	**0.0±1.6**	**0.0±1.7**	**This study**
2014	**On-road, Baoding**	–	**0.43±0.07**	**39±17**	**0.0±1.4**	**0.0±1.6**	**This study**
2014	**On-road, Shijiazhuang**	–	**0.56±0.08**	**42±21**	**0.0±1.7**	**0.0±1.5**	**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 whenever possible (see Section S4 for details).[b]The road grades of on-road measurements are estimated using 1-Hz pressure and car speed data. The absolute uncertainty of road grade is 0.5%.[30] [c]Estimated according to the speed distribution in Ban-Weiss et al.[47] [d]The tunnel has 6% grade outward from the center towards each exit.[48] [e]Calculated from emission factor of 2.92±0.18 g/L and assuming CO:CO_2 emission ratio of 0.05. [f]Calculated from emission factor of 28±5 mg/km and assuming fuel consumption of 7.87 L/100 km and CO:CO_2 emission ratio of 0.05.

The six sampled cities can be separated into developed cities (Houston, Denver, Philadelphia, and Beijing) and developing cities (Baoding and Shijiazhuang) according to their vehicle

emission/fuel regulations and socioeconomic development. The number of vehicles per capita is much higher in the US cities (0.5 – 0.8) than in Chinese cities (0.1 – 0.3, Table S1), and vehicle ownership is generally a positive function of per capita income.[49] However, the vehicle emission standard in Beijing (Euro V) was comparable to that of the US, so we consider Beijing as a developed city. Baoding and Shijiazhuang had less strict vehicle emission regulation (transitioning from Euro III to Euro IV in 2013) and higher gasoline sulfur content (<150 parts per million by weight, ppmw) than Beijing (<10 ppmw).[50] Therefore, they are considered as developing cities.

On-road sampling was carried out in those three Chinese cities in both 2013 and 2014 to check the inter-annual consistency (see Table 1 and Fig. S4). The inter-annual differences in city mean emission ratios were -3%, -10%, and 11%, respectively, without significant trends. The shapes of distributions over the two years were very similar for each city (Fig. S4), implying that despite the large variance and skewness of on-road emission ratios, the mobile sampling strategy represented the patterns of on-road emissions in general. For this reason, the datasets for each year will be analyzed together.

The on-road emission ratio distributions in the six cities are presented in Fig. 1. The developed cities showed similar mean emission ratios (0.33–0.40 ppbv/ppmv) despite the differences in country, climate (Philadelphia was sampled in late autumn but the other cities were in summer), fuel type (regular gasoline in Denver had lower octane rating than the other cities; gasoline sulfur standard was 10 ppmw in Beijing but 30 ppmw in the US), and speed distribution (more highway sampling in Houston/ Denver; more traffic/downtown sampling in Philadelphia/Beijing, see speed distributions in Table 1). The two developing cities showed larger mean emission ratios (0.44 and 0.55 ppbv/ppmv). The distributions of emission ratios in the developing cities were

also characterized by heavier tails; the average 90th percentile of emission ratios in the developing cities was 0.94 ppbv/ppmv, but only 0.64 ppbv/ppmv for the developed cities. Durbin et al. found that the average NH_3 emissions for the 150 ppmw sulfur fuel were 27% higher than those for the 5 ppmw fuel and 12% higher for the 30 ppmw fuel during an aggressive driving cycle test.[51] However, Durbin et al. did not find an effect of sulfur on NH_3 emissions in a smoother driving cycle. The mean speed was lower, and the acceleration was more variable in China than the US, indicating a more aggressive driving cycle in China. Therefore, high fuel sulfur content may be a significant component of elevated emission ratios in the developing cities. The fleet age might also contribute to the difference. Beijing has a newer fleet than Baoding and Shijiazhuang because of its rapid fleet renovation since the 2008 Olympics,[52] and aged TWC generally have higher NH_3 emissions.[27,51]

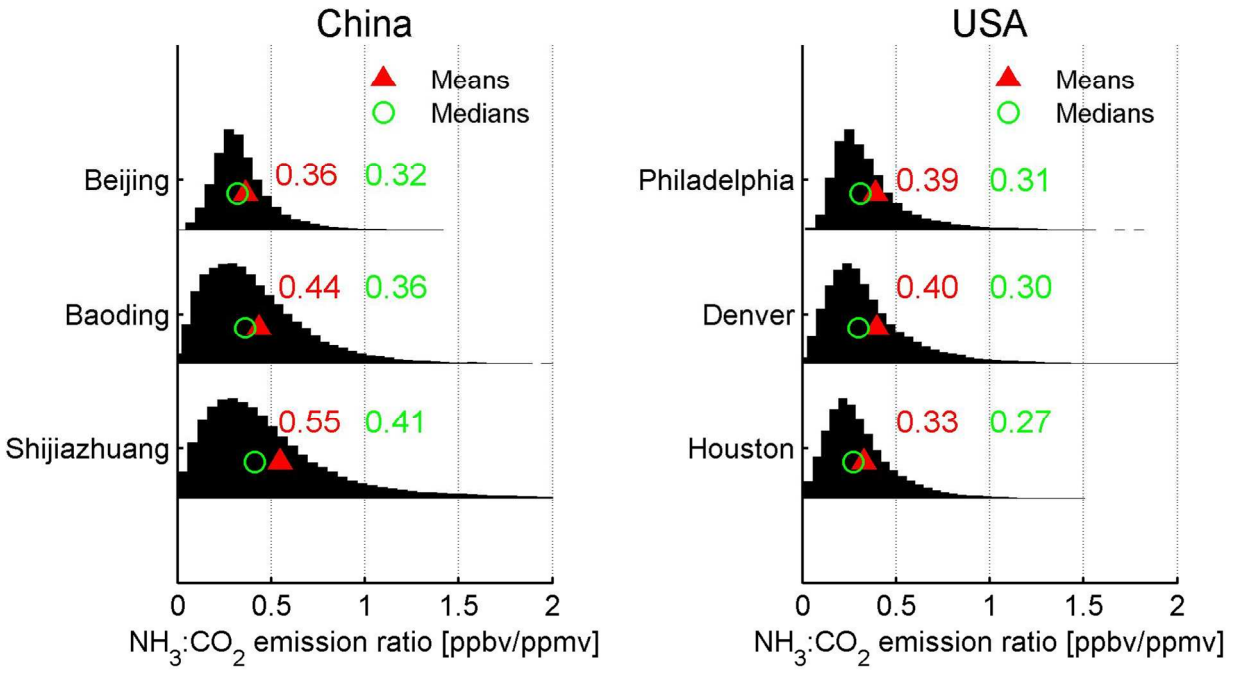
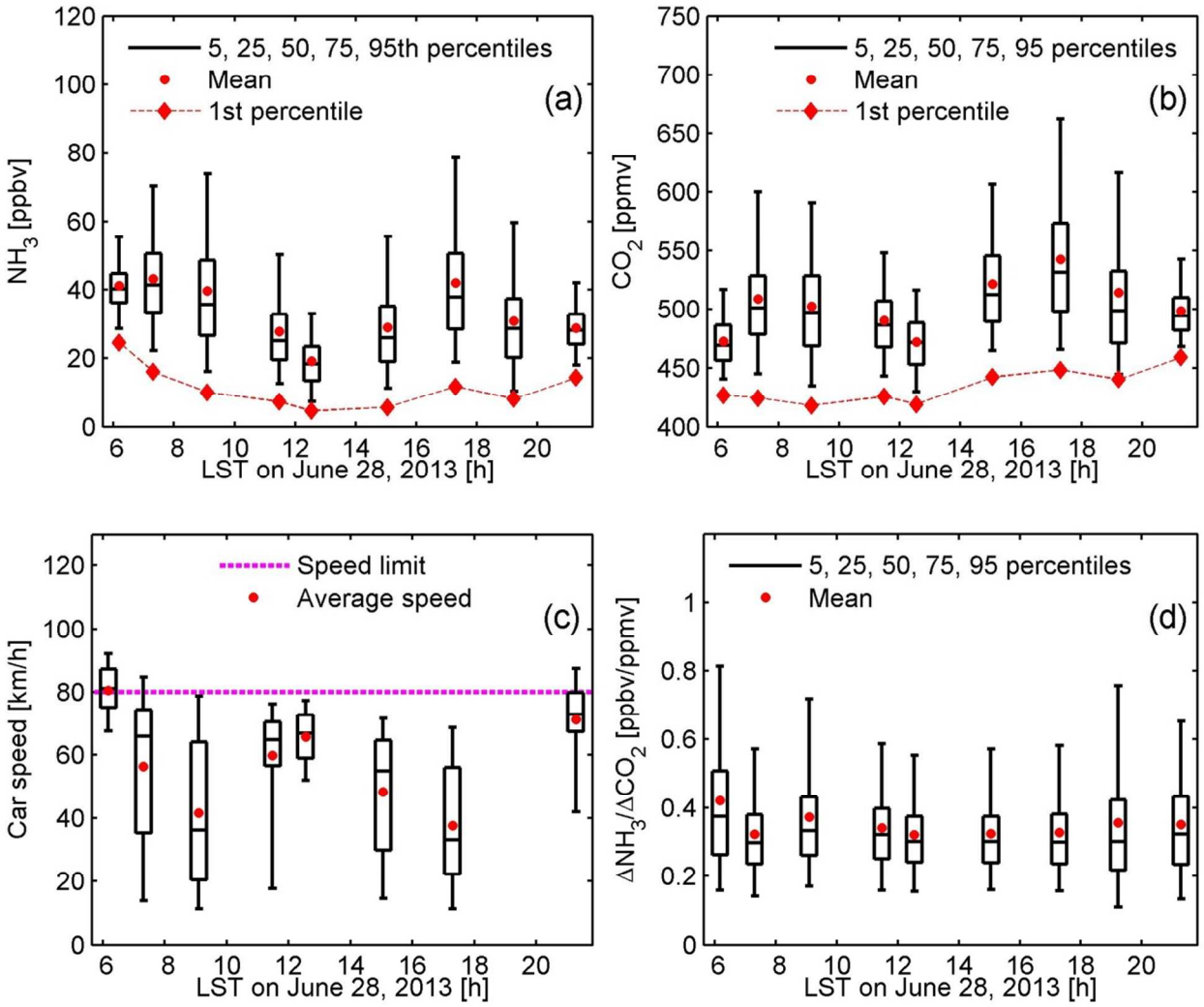


Figure 1. Distribution of on-road emission ratios in the six sampled cities. Mean (red) and median (green) values are labeled.

Diurnal variation of on-road NH_3 emissions in Beijing

Most mobile sampling was conducted during the daytime. To characterize the representativeness of daytime measurements, the 4th Ring Road in Beijing (labeled in Fig. S1) was continuously sampled from 5:50 to 21:40 local standard time (LST) on Friday, 28 June 2013. The traffic pattern in Beijing was similar to many US cities, except that heavy-duty trucks were banned on the 4th Ring Road between 6:00 and 23:00 LST. The distributions of quantities measured during each of the nine loops around the ring road are illustrated in Fig. 2. The mean values and 95th percentiles of both NH_3 and CO_2 mixing ratios (Fig. 2a-b) peaked at 7:00–9:00 and 17:00–18:00, clearly showing the emissions of rush hour traffic. The driving speed (Fig. 2c) had two minima during the rush hours with large variability due to stop-and-go conditions. The speed was close to the regulatory limit (80 km/h) in the early morning and late evening, indicating free-flowing traffic. Despite the large diurnal variations of driving conditions, the difference of emission ratios among the nine loops was $< \pm 10\%$ of the diurnal mean (0.35 ± 0.03 ppbv/ppmv, Fig. 2d).

The first percentiles of NH_3 and CO_2 mixing ratios were not significantly influenced by the rush hours. As justified later, the first percentiles are largely controlled by the variation of urban backgrounds and insensitive to local traffic emissions. The high NH_3 background at night was due to the accumulation of regional-scale emissions under the stable, shallow mixing layer, as also observed in stationary measurements away from local traffic in Beijing.[22,53]



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205 **Figure 2. Statistics of NH_3 mixing ratios (a), CO_2 mixing ratios (b), driving speed (c), and emission ratios (d) for each of**
206 **nine loops around the 4th Ring Road in Beijing.**

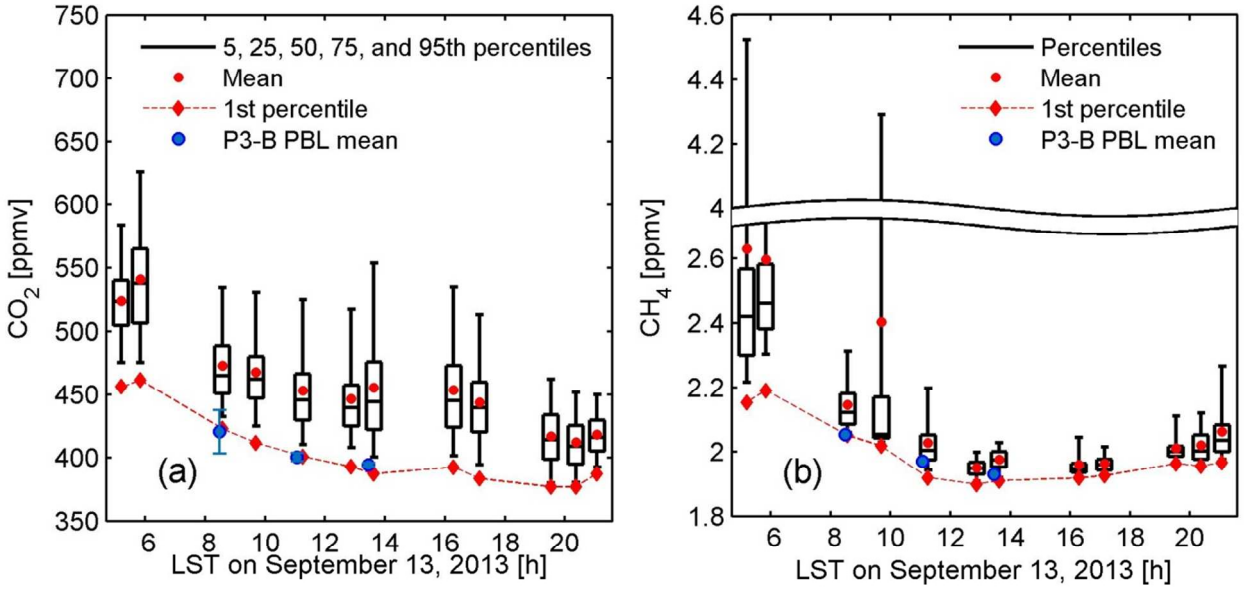
207 **Case studies in Houston**

208 The presence of additional field measurements in Houston and the existence of a tunnel allowed
209 for three additional analyses to be performed to demonstrate the robustness of the on-road
210 emission approach: 1) comparing the backgrounds derived from the first percentile of the on-
211 road measurements to those measured by an aircraft over a similar spatiotemporal window over
212 Houston; 2) calculation of a city-scale vehicle emission ratio when considering the partitioning
213 of NH_3 into particulate ammonium; and 3) direct measurements of emission ratios from transits

through the Washburn Tunnel. Emission ratios from the latter two methods are directly comparable to the on-road emission ratios in Houston.

To assess whether the background concentrations derived from the first percentiles of measurements on busy urban roads represent the urban PBL, we compared our continuous mobile measurements around I-610, a freeway around the Houston downtown area (similar to the 4th Ring Road in Beijing), to three PBL spiral measurements above downtown Houston by the P-3B on 13 September 2013 (Fig. S2). Because NH_3 was not measured on the P-3B, we compared CO_2 and CH_4 measured by the aircraft and the mobile laboratory. Although the lifetime of NH_3 (0.5 day to several days[54]) is considerably shorter than CO_2 and CH_4, it is still longer than the time scale of emission pattern change. Both CO_2 and CH_4 had strong and localized emission sources on or near the sampling routes and hence can be used to assess whether the mobile measurements could indeed deduce the urban PBL backgrounds amongst the intensive, localized emission signals.

The distributions of CO_2 and CH_4 mixing ratios measured by the mobile laboratory during each loop and by the P-3B in the PBL are shown in Fig. 3 (see detailed PBL profile evolutions in Fig. S5). The mean and upper percentiles of on-road measurements were strongly influenced by localized emissions, mainly vehicle emissions for CO_2 and petrochemical emissions for CH_4. In contrast, the first percentiles represented a general diurnal pattern with a strong accumulation effect overnight and dilution during the daytime as the PBL grew, similar to the diurnal measurements in Beijing (Fig. 2). The average PBL mixing ratios from three P-3B vertical profiles agreed with the first percentiles of the on-road data within 1% and show similar temporal variations (Fig. 3). Hence with high-frequency, fast-response on-road measurements, it is possible to probe the urban PBL background concentrations.



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238 **Figure 3. Diurnal measurements of CO_2 (a) and CH_4 (b) during the twelve loops on Houston I-610, similar to Fig. 2. The**
239 **blue circles and errorbars indicate mean and 1σ of airborne measurements in the PBL. The extraordinarily high CH_4**
240 **seen in loop 1 and 4 was from the Houston Ship Channel, upwind to the east side of I-610.**

241 A spatial transect from downtown Houston to the southwest suburbs was conducted from 19:20
242 to 20:00 LST on 12 September 2013 (Fig. S2). The first percentiles of 2-km spatial windows
243 were used in the city-scale vehicle emission ratio calculation. Figure 4a and b show the NH_3 and
244 CO_2 gradients from downtown to the suburbs. Enhanced NH_3 (up to 29 ppbv) and CO_2 (up to
245 443 ppmv) background mixing ratios were observed near the city center and gradually decreased
246 away from the city. This can be largely attributed to regional vehicle emissions in south Houston.
247 The contribution from agricultural emissions in south/southeast Houston (1-3 hours upwind) was
248 likely small compared to vehicle emissions that were immediately upwind (see Section S7 for
249 detailed analyses). The particulate ammonium mixing ratio measured at Tomball, TX, about 50
250 km northwest and downwind of Houston, was 0.8 ± 0.1 ppbv from 18:00, 12 September to 4:00,
251 13 September LST (Fig. S11). Because the mobile measurements were conducted closer to the
252 urban sources, the ammonium along the sampling route was unlikely to be higher than the more
253 aged air mass measured at Tomball. The contribution of point NH_3 sources between Houston and

Tomball was small (three orders of magnitude smaller than on-road emissions).[55] Therefore, an upper limit of 0.8 ppbv ammonium was added to the background NH_3 during the transect when calculating the NH_3:CO_2 emission ratio. The ground-based ammonium sampled over the Houston area was 0.7 ± 0.5 ppbv during the entire campaign, also much smaller than the observed background NH_3 mixing ratio. The deposition loss of NH_3 should also be small on these times scales of transport, because the NH_3:CO_2 emission ratio did not change significantly along the route (Fig. 4c).

The city-scale vehicle emission ratio, determined by a linear regression between the background NH_3/CO_2 mixing ratios, was 0.35 ± 0.04 ppbv/ppmv (Fig. 4c). The resulting slope was insensitive to the percentiles and window sizes used to derive urban backgrounds. For example, the slope only varied < ± 1.5% when changing the spatial window size from 500 m to 3000 m or changing from the 0.5th percentiles to 5th percentiles, much smaller than the other uncertainties.

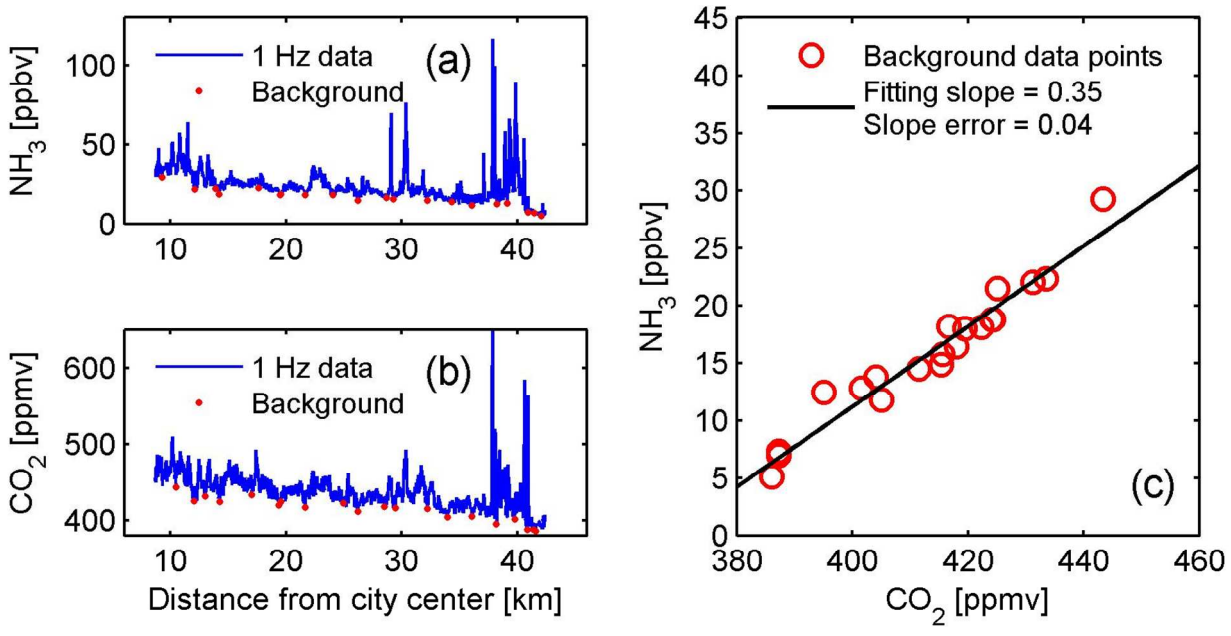

Figure 4. NH_3 (a) and CO_2 (b) mixing ratios from downtown Houston to the suburb. Urban backgrounds (red dots) are determined by taking the first percentiles in 2000 m spatial windows. (c) shows the uncertainty-weighted linear regression between NH_3 and CO_2 backgrounds.

According to the US National Emission Inventory (NEI) 2011, on-road vehicle emissions account for 92% of annual non-point anthropogenic CO_2 emissions in Harris County, where Houston is located.[55] A top-down inventory also shows that CO_2 emissions in southwest Houston are mainly from vehicles.[56] This makes it possible to directly compare the city-scale vehicle emission ratio with on-road/tunnel emission ratios.

In addition, we measured emission ratios in the Washburn tunnel in Houston. Seven transits were performed through the tunnel on 5, 8, and 15 September 2013. Our measurements spanned from the early afternoon, when a higher proportion of the passing fleet was diesel, to the evening rush hours, when light-duty vehicles dominated the tunnel travel.[48] The tunnel results are also summarized in Table 1.

Figure 5 shows the mean values of on-road (0.33 ± 0.05 ppbv/ppmv), city-scale vehicle (0.35 ± 0.04 ppbv/ppmv), and tunnel (0.27 ± 0.05 ppbv/ppmv) emission ratios and the distribution of on-road emission ratios in Houston. The relatively lower tunnel emission ratio was likely due to smoother driving pattern compared to normal on-road driving and also possibly to deposition of NH_3 on the tunnel wall. Overall, the three different methods yielded similar results within their uncertainties, providing confidence about the range and average emission ratios observed and suggesting that fleet-integrated, on-road measurements are representative of the city.

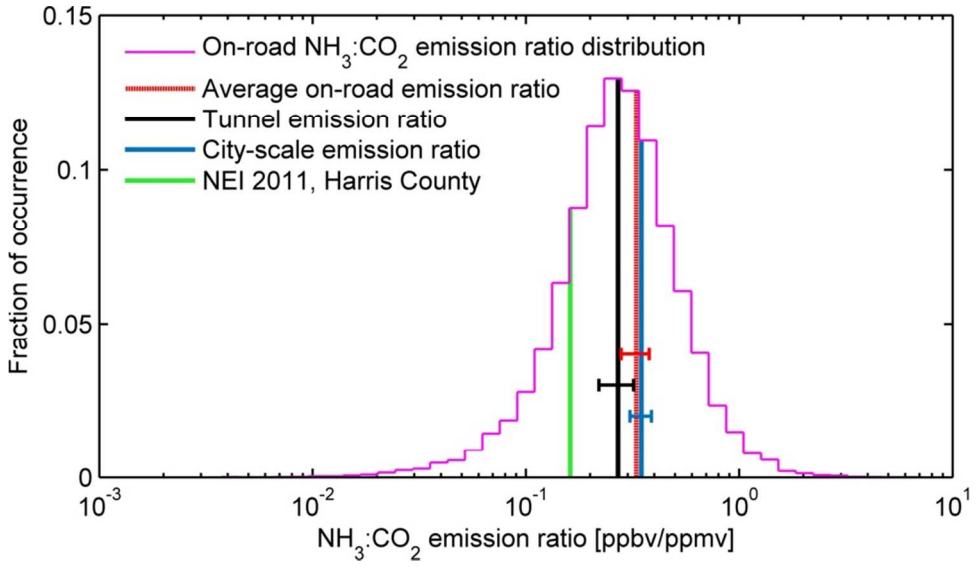

Figure 5. NH_3:CO_2 emission ratios measured by three methods in Houston, TX. The emission ratio in Harris County from NEI-2011 is also shown.

Comparison to other emission ratios in the US

For previous studies (Table 1), vehicle NH_3 emissions were undetectable in the tunnel in 1983, when less than 10% of vehicles were equipped with TWC.[45] The 1993 study in Van Nuys Tunnel at Los Angeles, CA reported 81% TWC-equipped vehicles and an NH_3:CO_2 emission ratio of 0.45 ppbv/ppmv,[39] comparable to most of the recent studies (e.g., Bishop et al. measured 0.49 ppbv/ppmv in LA in 2013[10]). The similarity between NH_3:CO_2 emission ratios measured 20 years ago and recent results from multiple cities again demonstrates that the reduction and regulation of vehicle NH_3 emissions have greatly fallen behind the other critical pollutants. The closest comparison between this study and the literature is in Denver, CO, where Bishop et al.[10] reported 0.38 ± 0.08 ppbv/ppmv in June 2005 and 0.37 ± 0.02 ppbv/ppmv in December 2013–January 2014, seven months before our measurements (0.40 ± 0.06 ppbv/ppmv).

Some roadside data in Table 1 were acquired under significantly higher road grade and acceleration conditions than normal. For example, the 2008 roadside measurement site in LA had a road grade of 3.5% and mean acceleration of 3.1 km/h/s,[10] compared to the road grade standard

304 deviation of 1–2.7% and acceleration standard deviation of 1.1–1.8 km/h/s for our on-road
305 measurements in all cites. This might have contributed to its unusually large emission ratios of
306 0.66 ppbv/ppmv. Higher NO_x emission ratios were also reported in this experiment than other
307 studies.[29]

308 Overall, despite the differences in methods and spatiotemporal sampling between our study and
309 those in the literature, the stationary and mobile-sampling studies in the US generally agree
310 within their respective uncertainties. The error-weighted average emission ratio is 0.42 ± 0.02
311 ppbv/ppmv for stationary measurements in the US (excluding the 1981 study) and 0.37 ± 0.06
312 ppbv/ppmv for on-road data in this study. This work hence confirms the previous studies in
313 Western US cities with broader spatial coverage and stronger confidence. The emission ratios are
314 broadly consistent not only within the US, but also with stationary measurements in Europe.[57,58]

315 **Comparison to emission inventories**

316 Also shown in Fig. 5 is the molar ratio of on-road NH_3 and CO_2 emissions for Harris County
317 from NEI-2011 (0.16 ppbv/ppmv),[55] about half of the observed values. Similarly, the NEI on-
318 road NH_3:CO_2 emission ratios are 0.19 and 0.17 ppbv/ppmv in Denver and Philadelphia County,
319 respectively, compared to the observations of 0.40 and 0.39 ppbv/ppmv. Nationally, the on-road
320 emission ratio is 0.18 ppbv/ppmv from NEI-2011. The standard deviation of the NEI on-road
321 emission ratios at the county level is 0.03 ppbv/ppmv (see Fig. S12 for the county level
322 distribution), much smaller than the differences between the inventory and the observations. The
323 previous studies (Table 1) show similar differences from the inventory values.

324 At the national level, fuel sales provide an accurate estimate of on-road CO_2 emissions, and at
325 the county level, NEI-2011 adopted the Motor Vehicle Emissions Simulator Model (MOVES) to

estimate CO_2 emissions, considering local vehicle activities and environmental conditions.[59,60] Therefore, the uncertainty of CO_2 emissions should be much less than that for NH_3 emissions, and the discrepancy between the inventory and observations is most likely due to underestimation of NH_3 emissions by the inventory. Assuming that the NEI-2011 on-road CO_2 emissions are accurate, the on-road NH_3 emissions in the US can be estimated as the product of the observed emission ratios and the inventory vehicle CO_2 emissions. Estimated using the error-weighted average emission ratios from the three sampled US cities, the on-road NH_3 emission in the US is 0.26 ± 0.07 Tg/yr, a factor of two higher than NEI-2011's estimate (0.12 Tg/yr).[55] This increases on-road sources from 3% to 7% of the total US NH_3 emissions.

The on-road NH_3 emission in China is 0.09 ± 0.02 Tg/yr, calculated similarly using the on-road CO_2 emissions in China (500 Tg in 2011[61]) and our observed emission ratio (0.43 ppbv/ppmv, error-weighted average of three Chinese cities). It is in good agreement with the bottom-up inventory estimate of 0.08 Tg/yr, or 1% of total Chinese NH_3 emissions.[23] Our results in Chinese cities are consistent with tunnel measurements by Chang et al. in Shanghai (0.42 ppbv/ppmv),[46] but much lower than measurements by Liu et al. in Guangzhou (3.4 ppbv/ppmv).[34] Therefore, more on-road measurements in China are necessary to reconcile the existing results.

Implications and future directions

In contrast to agricultural NH_3 emissions, vehicle NH_3 is usually collocated with high emissions of other aerosol precursors such as NO_x (eventually resulting in HNO_3) that directly impact ammonium nitrate formation. Urban backgrounds of 29 ppbv were observed in downtown Houston (Fig. 4), largely attributed to vehicle emissions. The excellent agreement between city-scale and on-road NH_3:CO_2 emission ratios further confirms that the high NH_3 concentrations and strong urban-suburban gradient in Houston were due to vehicle emissions. In the US, major

agricultural sources are largely separated from densely populated areas (see Fig. S13 for distributions of agricultural/vehicular NH_3 sources and the US population). In NEI-2011, only 5% of the US counties have more vehicle NH_3 emissions than agricultural emissions, but these counties account for 35% of the US population (2010 census[62]). When updating vehicle emissions using the observed emission ratios, the counties with more vehicle NH_3 emissions than agriculture account for 45% of the US population. Because the lifetime of NH_3 can be as low as 0.5 day,[54] the local emissions in cities will be disproportionately important to aerosol formation and urban nitrogen deposition than the transport from distant agricultural sources. There are also cases like LA and Denver where substantial agricultural NH_3 emissions are located near or in the city and may dominate ammonium formation. Ultimately, more accurate studies on agricultural NH_3 emissions, transport, deposition, and lifetime are needed to quantify the relative importance of urban vs. upwind agricultural NH_3 emissions for $PM_{2.5}$ formation in each urban area.

The diurnal and seasonal patterns of agricultural vs. vehicular emissions also have significant implications. Agricultural NH_3 emissions are largest in mid/late afternoon and correlate with temperature whereas on-road emissions are strongly dependent upon traffic volume (morning and evening peaks).[63–65] Most agricultural NH_3 emissions occur in the warm season,[6,23] whereas vehicle emissions do not have strong seasonality. This makes NH_3 from vehicles even more critical for air pollution in the cold season, when $PM_{2.5}$ pollution is generally of greater concern. Applying the agricultural NH_3 emission seasonal variation optimized by Paulot et al.[6] and assuming seasonally constant vehicle emissions, vehicles account for 13% of total US emissions in winter (December–February), and 53% of the US population live in counties where vehicle emissions outweigh agriculture in winter. One caveat is that the agricultural emissions are also highly uncertain and could be substantially underestimated.[63,66] Accordingly, vehicular, in

addition to agricultural, NH_3 emissions, transport, and loss merit further investigations for nearly half of the US population.

The NEI NH_3 inventories have been widely used in atmospheric chemical transport models in the US,[66–68] but few have investigated the sensitivity of urban aerosol formation and nitrogen deposition to vehicle NH_3 emissions. The recent development of national level, 1-km resolution on-road CO_2 emission inventories (e.g., Gately et al.[69]) has made it possible to apply the measured NH_3:CO_2 emission ratios and resolve NH_3 emission spatial patterns on the city scale. We expect future modeling efforts to quantify the impact of urban NH_3 sources with a more accurate representation of the absolute value and spatiotemporal variation of vehicle emissions.

Major agricultural regions are collocated with high populations in China, and agricultural NH_3 emissions in China are reportedly three times larger than those for the US.[6] Therefore, agricultural emissions are still relatively more important for mitigating the environmental impact of NH_3 in China than in the US. However, vehicle NH_3 emissions should still be considered because emission ratios are high in the developing cities undergoing rapid urbanization and motorization. This study also provides NH_3 vehicle emission ratios that may be appropriate for other developing cities in the world compared to those in the literature from developed countries.

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Supporting Information

Sections S1−S9, including Fig. S1−13 and Table S1−2.

Notes

The authors declare no competing financial interest.

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