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# Vehicle Emissions as an Important Urban Ammonia Source in the United States and China

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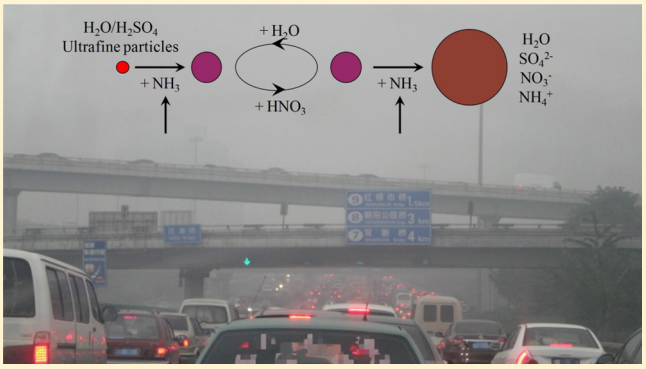
Supporting Information

**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 U.S. and China. Vehicle $NH_3$:$CO_2$ emission ratios in the U.S. 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 U.S. 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 U.S. 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 U.S. population and require reconsideration in urban air quality models due to their colocation 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) systems 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 U.S. cities in recent years due to modest reduction in $NH_3$ emissions from new vehicles and increasing emissions from older vehicles

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Table 1. Comparison of Tunnel, Roadside, and Mobile-Based $NH_3$:$CO_2$ Emission Ratio Measurements in the U.S. 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 (exit) | 4.2 | 0.3 | Kean et al. (2000)[41] |
| 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 and 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 SI 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 toward 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.



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(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 U.S. cities, all located in the western U.S. 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 U.S.

China has the second largest vehicle population of 0.15 billion, and together with the U.S. (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 a 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 1 order of magnitude larger than those in the U.S.[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 U.S. 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 U.S. (Houston, Denver, and Philadelphia) and three major cities in China (Beijing, Shijiazhuang, and Baoding) with over 4000 km and 100 h of urban sampling.[35] Detailed measurement time, sampling routes, and demographic information on each city are shown in Supporting Information (SI) 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 (CARE-Beijing/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 SI Section S2 for details of instruments).

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

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

## RESULTS AND DISCUSSION

**On-Road Emission Ratios in the U.S. and Chinese Cities.** Table 1 summarizes the $NH_3$:$CO_2$ emission ratios measured in this study and measurement conditions in the six U.S./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


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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.

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 U.S. 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 U.S., 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 ppm 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 interannual consistency (see Table 1 and SI Figure S4). The interannual 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 (SI Figure 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 data sets for each year will be analyzed together.

The on-road emission ratio distributions in the six cities are presented in Figure 1. The developed cities showed similar

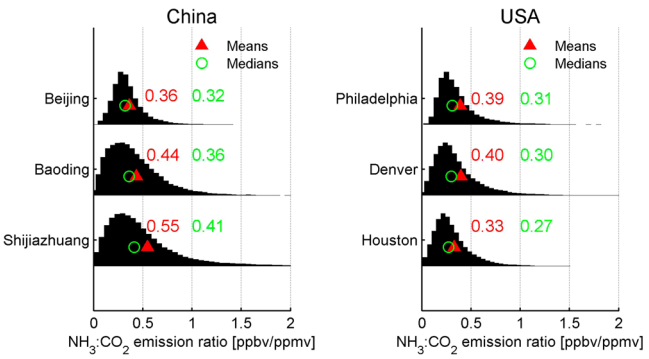


**Figure 1.** Distribution of on-road emission ratios in the six sampled cities. Mean (red) and median (green) values are labeled.

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 U.S.), 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 U.S., 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]

**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 Fourth Ring Road in Beijing (labeled in Figure 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 U.S. cities, except that heavy-duty trucks were banned on the Fourth 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 Figure 2. The mean values and 95th percentiles of both $NH_3$ and $CO_2$ mixing ratios (Figure 2a,b) peaked at 7:00−9:00 and 17:00−18:00, clearly showing the emissions of rush hour traffic. The driving speed (Figure 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 < ±10% of the diurnal mean (0.35 ± 0.03 ppbv/ppmv, Figure 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 PBL, as also observed in stationary measurements away from local traffic in Beijing.[22,53]

**Case Studies in Houston.** The presence of additional field measurements in Houston and the existence of a tunnel allowed for three additional analyses to be performed to demonstrate the robustness of the on-road emission approach: (1) comparing the backgrounds derived from the first percentile of the on-road measurements to those measured by an aircraft over a similar spatiotemporal window over Houston; (2) calculation of a city-scale vehicle emission ratio when considering the partitioning 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


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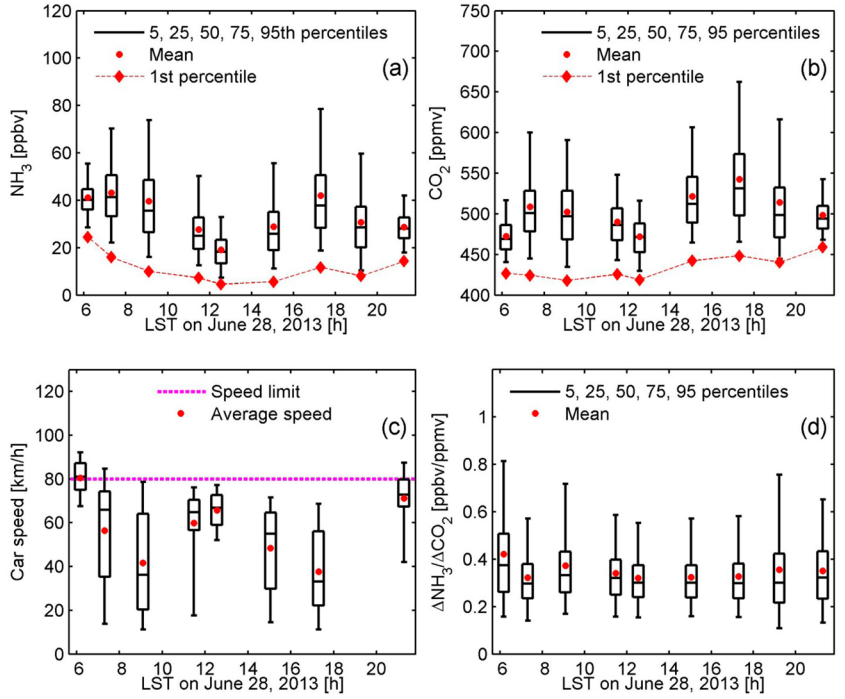


**Figure 2.** Statistics of $NH_3$ mixing ratios (a), $CO_2$ mixing ratios (b), driving speed (c), and emission ratios (d) for each of nine loops around the Fourth Ring Road in Beijing.

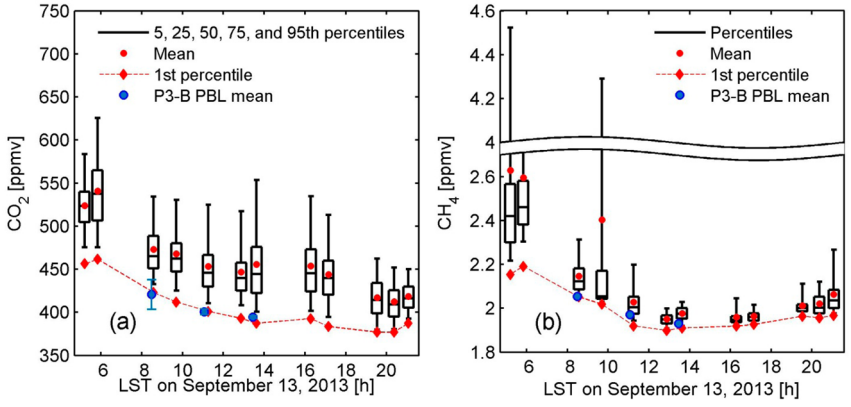


**Figure 3.** Diurnal measurements of $CO_2$ (a) and $CH_4$ (b) during the 12 loops on Houston I-610, similar to Figure 2. The blue circles and errorbars indicate mean and 1$\sigma$ of airborne measurements in the PBL. The extraordinarily high $CH_4$ seen in loop 1 and 4 was from the Houston Ship Channel, upwind to the east side of I-610.

downtown area (similar to the Fourth Ring Road in Beijing), to three PBL spiral measurements above downtown Houston by the P-3B on 13 September 2013 (SI Figure 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 among 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 Figure 3 (see detailed PBL profile evolutions in SI Figure 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 (Figure 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 (Figure 3). Hence with high-frequency, fast-response on-road measurements, it is possible to probe the urban PBL background concentrations.

A spatial transect from downtown Houston to the southwest suburbs was conducted from 19:20 to 20:00 LST on 12 September 2013 (SI Figure S2). The first percentiles of 2000 m spatial windows were used in the city-scale vehicle emission ratio calculation. Figure 4a and b show the $NH_3$ and $CO_2$ gradients from downtown to the suburbs. Enhanced $NH_3$ (up to 29 ppbv) and $CO_2$ (up to 443 ppmv) background mixing


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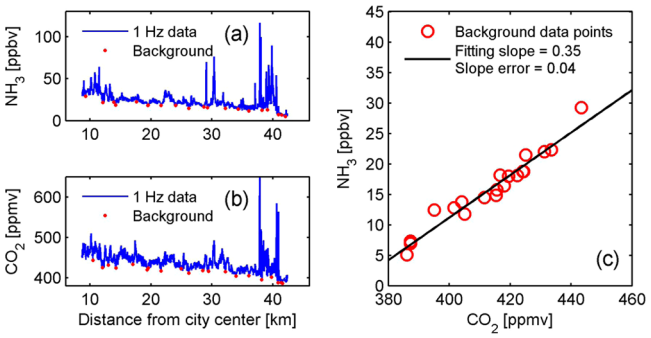


**Figure 4.** $NH_3$ (a) and $CO_2$ (b) mixing ratios from downtown Houston to the suburb. Urban backgrounds (red dots) are determined by taking the first percentiles in 2000 m spatial windows. (c) shows the uncertainty-weighted linear regression between $NH_3$ and $CO_2$ backgrounds.

ratios were observed near the city center and gradually decreased away from the city. This can be largely attributed to regional vehicle emissions in south Houston. The contribution from agricultural emissions in south/southeast Houston (1−3 h upwind) was likely small compared to vehicle emissions that were immediately upwind (see SI Section S7 for detailed analyses). The particulate ammonium mixing ratio measured at Tomball, TX, about 50 km northwest and downwind of Houston, was 0.8 ± 0.1 ppbv from 18:00, 12 September to 4:00, 13 September LST (SI Figure S11). Because the mobile measurements were conducted closer to the urban sources, the ammonium along the sampling route was unlikely to be higher than the more aged air mass measured at Tomball. The contribution of point $NH_3$ sources between Houston and Tomball was small (3 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 (Figure 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 (Figure 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 to 3000 m or changing from the 0.5 percentiles to fifth percentiles, much smaller than the other uncertainties.

According to the U.S. National Emission Inventory (NEI) 2011, on-road vehicle emissions account for 92% of annual nonpoint 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

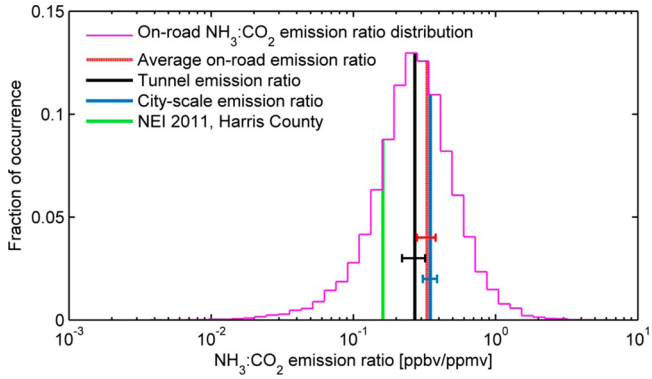


**Figure 5.** $NH_3$:$CO_2$ emission ratios measured by three methods in Houston, TX. The emission ratio in Harris County from NEI-2011 is also shown.

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.

**Comparison to Other Emission Ratios in the U.S.** 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 deviation of 1−2.7% and acceleration standard deviation of 1.1−1.8 km/h/s for our on-road measurements in all cites. This might have contributed to its unusually large emission ratios of 0.66 ppbv/ppmv. Higher $NO_x$ emission ratios were also reported in this experiment than other studies.[29]

Overall, despite the differences in methods and spatiotemporal sampling between our study and those in the literature, the stationary and mobile-sampling studies in the U.S. generally agree within their respective uncertainties. The error-weighted average emission ratio is 0.42 ± 0.02 ppbv/ppmv for stationary


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measurements in the U.S. (excluding the 1981 study) and 0.37 ± 0.06 ppbv/ppmv for on-road data in this study. This work hence confirms the previous studies in Western U.S. cities with broader spatial coverage and stronger confidence. The emission ratios are broadly consistent not only within the U.S., but also with stationary measurements in Europe.[57,58]

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

At the national level, fuel sales provide an accurate estimate of on-road $CO_2$ emissions, and at 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 U.S. 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 U.S. cities, the on-road $NH_3$ emission in the U.S. is 0.26 ± 0.07 Tg/yr, a factor of 2 higher than NEI-2011's estimate (0.12 Tg/yr).[55] This increases on-road sources from 3% to 7% of the total U.S. $NH_3$ 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 (Figure 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 U.S., major agricultural sources are largely separated from densely populated areas (see SI Figure S13 for distributions of agricultural/vehicular $NH_3$ sources and the U.S. population). In NEI-2011, only 5% of the U.S. counties have more vehicle $NH_3$ emissions than agricultural emissions, but these counties account for 35% of the U.S. 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 U.S. 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 U.S. emissions in winter (December−February), and 53% of the U.S. 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 U.S. population.

The NEI $NH_3$ inventories have been widely used in atmospheric chemical transport models in the U.S.,[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 U.S.[6] Therefore, agricultural emissions are still relatively more important for mitigating the environmental impact of $NH_3$ in China than in the U.S. 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 more appropriate for other developing cities in the world compared to those in the literature from developed countries.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02805.



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Sections S1−S9, including Figure S1−13 and Table S1−2 (PDF)

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### Notes

The authors declare no competing financial interest.

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## REFERENCES


(1) Pinder, R. W.; Adams, P. J.; Pandis, S. N. Ammonia Emission Controls as a Cost-Effective Strategy for Reducing Atmospheric Particulate Matter in the Eastern United States. *Environ. Sci. Technol.* **2007**, *41* (2), 380−386.

(2) Paulot, F.; Jacob, D. J. Hidden cost of U.S. agricultural exports: particulate matter from ammonia emissions. *Environ. Sci. Technol.* **2014**, *48* (2), 903−908.

(3) Shindell, D. T.; Faluvegi, G.; Koch, D. M.; Schmidt, G. A.; Unger, N.; Bauer, S. E. Improved Attribution of Climate Forcing to Emissions. *Science* **2009**, *326* (5953), 716−718.

(4) *IPCC, 2013: Climate Change 2013. The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovern- mental Panel on Climate Change*; Stocker, T. F., Stocker, T. F., Stocker, T. F., Qin, D.., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M. Eds.; Cambridge University Press: Cambridge, United Kingdom and New York, USA, 2013, pp 1535.

(5) Obbink, R. B.; Hicks, K.; Galloway, J.; Spranger, T.; Alkemade, R.; Ashmore, M.; Bustamante, M.; Cinderby, S.; Davidson, E.; Dentener, F.; et al. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecol. Appl.* **2010**, *20* (1), 30−59.

(6) Paulot, F.; Jacob, D. J.; Pinder, R. W.; Bash, J. O.; Travis, K.; Henze, D. K. Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH3). *J. Geophys. Res. Atmos.* **2014**, *119*, 4343−4364.

(7) Sutton, M. A.; Reis, S.; Riddick, S. N.; Dragosits, U.; Nemitz, E.; Theobald, M. R.; Tang, Y. S.; Braban, C. F.; Vieno, M.; Dore, A. J.; et al. Towards a climate-dependent paradigm of ammonia emission and deposition. *Philos. Trans. R. Soc., B* **2013**, *368*, 20130166.

(8) Shelef, M.; Gandhi, H. S. Ammonia Formation in the Catalytic Reduction of Nitric Oxide. III. The Role of Water Gas Shift, Reduction by Hydrocarbons, and Steam Reforming. *Ind. Eng. Chem. Prod. Res. Dev.* **1974**, *13* (1), 80−85.

(9) Liu, T.; Wang, X.; Deng, W.; Zhang, Y.; Chu, B.; Ding, X.; Hu, Q.; He, H.; Hao, J. Role of ammonia in forming secondary aerosols from gasoline vehicle exhaust. *Sci. China: Chem.* **2015**, *58* (9), 1377−1384.

(10) Bishop, G. A.; Stedman, D. H. Reactive Nitrogen Species Emission Trends in Three Light-/Medium-Duty United States Fleets. *Environ. Sci. Technol.* **2015**, *49* (18), 11234−11240.

(11) Stritzke, F.; Diemel, O.; Wagner, S. TDLAS-based NH3 mol fraction measurement for exhaust diagnostics during selective catalytic reduction using a fiber-coupled 2.2-$\mu$m DFB diode laser. *Appl. Phys. B: Lasers Opt.* **2015**, *119* (1), 143−152.

(12) Suarez-Bertoa, R.; Zardini, A.; Astorga, C. Ammonia exhaust emissions from spark ignition vehicles over the New European Driving Cycle. *Atmos. Environ.* **2014**, *97*, 43−53.

(13) European Environment Agency. *Assessment of Global Mega-trends—An Update*, 2014.

(14) Whitehead, J. D.; Longley, I. D.; Gallagher, M. W. Seasonal and diurnal variation in atmospheric ammonia in an urban environment measured using a quantum cascade laser absorption spectrometer. *Water, Air, Soil Pollut.* **2007**, *183* (1−4), 317−329.

(15) Li, Y.; Schwab, J. J.; Demerjian, K. L. Measurements of ambient ammonia using a tunable diode laser absorption spectrometer: Characteristics of ambient ammonia emissions in an urban area of New York City. *J. Geophys. Res.* **2006**, *111* (D10), 10.1029/2005JD006275.

(16) Livingston, C.; Rieger, P.; Winer, A. Ammonia emissions from a representative in-use fleet of light and medium-duty vehicles in the California South Coast Air Basin. *Atmos. Environ.* **2009**, *43* (21), 3326−3333.

(17) Reche, C.; Viana, M.; Karanasiou, A.; Cusack, M.; Alastuey, A.; Artiñano, B.; Revuelta, M. A.; López-Mahía, P.; Blanco-Heras, G.; Rodríguez, S.; et al. Urban NH3 levels and sources in six major Spanish cities. *Chemosphere* **2015**, *119*, 769−777.

(18) Phan, N.-T.; Kim, K.-H.; Shon, Z.-H.; Jeon, E.-C.; Jung, K.; Kim, N.-J. Analysis of ammonia variation in the urban atmosphere. *Atmos. Environ.* **2013**, *65*, 177−185.

(19) Toro, R. A.; Canales, M.; Flocchini, R. G.; Morales, R. G. E. Urban atmospheric ammonia in Santiago city, Chile. *Aerosol Air Qual. Res.* **2014**, *14* (1), 33−44.

(20) Sharma, S. K.; Kumar, M.; Gupta, N. C.; Saxena, M.; Mandal, T. K. Characteristics of ambient ammonia over Delhi, India. *Meteorol. Atmos. Phys.* **2014**, *124* (1−2), 67−82.

(21) Gong, L.; Lewicki, R.; Griffin, R. J.; Flynn, J. H.; Lefer, B. L.; Tittel, F. K. Atmospheric ammonia measurements in Houston, TX using an external-cavity quantum cascade laser-based sensor. *Atmos. Chem. Phys.* **2011**, *11* (18), 9721−9733.

(22) Meng, Z. Y.; Lin, W. L.; Jiang, X. M.; Yan, P.; Wang, Y.; Zhang, Y. M.; Jia, X. F.; Yu, X. L. Characteristics of atmospheric ammonia over Beijing, China. *Atmos. Chem. Phys.* **2011**, *11* (12), 6139−6151.

(23) Huang, X.; Song, Y.; Li, M.; Li, J.; Huo, Q.; Cai, X.; Zhu, T.; Hu, M.; Zhang, H. A high resolution ammonia emission inventory in China. *Global Biogeochem. Cycles* **2012**, *26* (1), 10.1029/2011GB004161.

(24) Zheng, J. Y.; Yin, S. S.; Kang, D. W.; Che, W. W.; Zhong, L. J. Development and uncertainty analysis of a high-resolution NH3 emissions inventory and its implications with precipitation over the Pearl River Delta region, China. *Atmos. Chem. Phys.* **2012**, *12*, 7041−7058.




DOI: 10.1021/acs.est.6b02805
*Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

(25) Bouwman, A. F.; Lee, D. S.; Asman, W. A. H.; Dentener, F. J.; Van Der Hoek, K. W.; Olivier, J. G. J. A global high-resolution emission inventory for ammonia. *Global Biogeochem. Cycles* **1997**, *11* (4), 561−587.
(26) Roe, S. M.; Spivey, M. D.; Lindquist, H. C.; Thesing, K. B.; Strait, R. P. *Estimating ammonia emissions from anthropogenic nonagricultural sources−Draft final report. Emiss. Invent. Improv. Program*; U.S. Environmental Protection Agency, 2004.
(27) Bishop, G. A.; Peddle, A. M.; Stedman, D. H.; Zhan, T. On-Road Emission Measurements of Reactive Nitrogen Compounds from Three California Cities. *Environ. Sci. Technol.* **2010**, *44* (9), 3616−3620.
(28) Lee, T.; Frey, H. C. Evaluation of representativeness of site-specific fuel-based vehicle emission factors for route average emissions. *Environ. Sci. Technol.* **2012**, *46* (12), 6867−6873.
(29) Hudda, N.; Fruin, S.; Delfino, R. J.; Sioutas, C. Efficient determination of vehicle emission factors by fuel use category using on-road measurements: downward trends on Los Angeles freight corridor I-710. *Atmos. Chem. Phys.* **2013**, *13* (1), 347−357.
(30) Sun, K.; Tao, L.; Miller, D. J.; Khan, M. A.; Zondlo, M. A. On-Road Ammonia Emissions Characterized by Mobile, Open-Path Measurements. *Environ. Sci. Technol.* **2014**, *48* (7), 3943−3950.
(31) Nowak, J. B.; Neuman, J. A.; Bahreini, R.; Middlebrook, A. M.; Holloway, J. S.; McKeen, S. A.; Parrish, D. D.; Ryerson, T. B.; Trainer, M. Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation. *Geophys. Res. Lett.* **2012**, *39*. DOI: 10.1029/2012GL051197.
(32) The World Bank. World Bank Data: Motor vehicles (per 1000 people) http://data.worldbank.org/indicator.
(33) Huang, R.-J.; Zhang, Y.; Bozzetti, C.; Ho, K.-F.; Cao, J.-J.; Han, Y.; Daellenbach, K. R.; Slowik, J. G.; Platt, S. M.; Canonaco, F.; et al. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* **2014**, *514* (7521), 218−222.
(34) Liu, T.; Wang, X.; Wang, B.; Ding, X.; Deng, W.; Lü, S.; Zhang, Y. Emission factor of ammonia (NH3) from on-road vehicles in China: tunnel tests in urban Guangzhou. *Environ. Res. Lett.* **2014**, *9* (6), 64027.
(35) Tao, L.; Sun, K.; Miller, D. J.; Pan, D.; Golston, L. M.; Zondlo, M. A. Low-power, open-path mobile sensing platform for high-resolution measurements of greenhouse gases and air pollutants. *Appl. Phys. B: Lasers Opt.* **2015**, *119* (1), 153−164.
(36) DeCarlo, P. F.; Kimmel, J. R.; Trimborn, A.; Northway, M. J.; Jayne, J. T.; Aiken, A. C.; Gonin, M.; Fuhrer, K.; Horvath, T.; Docherty, K. S.; et al. Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* **2006**, *78* (24), 8281−8289.
(37) Vay, S. A.; Woo, J. H.; Anderson, B. E.; Thornhill, K. L.; Blake, D. R.; Westberg, D. J.; Kiley, C. M.; Avery, M. A.; Sachse, G. W.; Streets, D. G. Influence of regional-scale anthropogenic emissions on CO2 distributions over the western North Pacific. *J. Geophys. Res.* **2003**, *108* (D20), 10.1029/2002JD003094
(38) Sachse, G. W.; Hill, G. F.; Wade, L. O.; Perry, M. G. Fast-response, high-precision carbon monoxide sensor using a tunable diode laser absorption technique. *J. Geophys. Res.* **1987**, *92* (D2), 2071−2081.
(39) Fraser, M. P.; Cass, G. R. Detection of Excess Ammonia Emissions from In-Use Vehicles and the Implications for Fine Particle Control. *Environ. Sci. Technol.* **1998**, *32* (8), 1053−1057.
(40) Baum, M. M.; Kiyomiya, E. S.; Kumar, S.; Lappas, A. M.; Kapinus, V. A.; Lord, H. C., III Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. Direct on-road ammonia measurements. *Environ. Sci. Technol.* **2001**, *35* (18), 3735−3741.
(41) Kean, A. J.; Harley, R. A.; Littlejohn, D.; Kendall, G. R. On-Road Measurement of Ammonia and Other Motor Vehicle Exhaust Emissions. *Environ. Sci. Technol.* **2000**, *34* (17), 3535−3539.
(42) Kean, A. J.; Littlejohn, D.; Ban-Weiss, G. A.; Harley, R. A.; Kirchstetter, T. W.; Lunden, M. M. Trends in on-road vehicle emissions of ammonia. *Atmos. Environ.* **2009**, *43* (8), 1565−1570.
(43) Bishop, G. A.; Schuchmann, B. G.; Stedman, D. H.; Lawson, D. R. Multispecies remote sensing measurements of vehicle emissions on Sherman Way in Van Nuys, California. *J. Air Waste Manage. Assoc.* **2012**, *62* (10), 1127−1133.
(44) Burgard, D. A.; Bishop, G. A.; Stedman, D. H. Remote Sensing of Ammonia and Sulfur Dioxide from On-Road Light Duty Vehicles. *Environ. Sci. Technol.* **2006**, *40* (22), 7018−7022.
(45) Pierson, W. R.; Brachaczek, W. W. Emissions of ammonia and amines from vehicles on the road. *Environ. Sci. Technol.* **1983**, *17* (12), 757−760.
(46) Chang, Y.; Zou, Z.; Deng, C.; Huang, K.; Collett, J. L.; Lin, J.; Zhuang, G. The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai. *Atmos. Chem. Phys.* **2016**, *16* (5), 3577−3594.
(47) Ban-Weiss, G. A.; McLaughlin, J. P.; Harley, R. A.; Lunden, M. M.; Kirchstetter, T. W.; Kean, A. J.; Strawa, A. W.; Stevenson, E. D.; Kendall, G. R. Long-term changes in emissions of nitrogen oxides and particulate matter from. *Atmos. Environ.* **2008**, *42* (2), 220−232.
(48) McGaughey, G. R.; Desai, N. R.; Allen, D. T.; Seila, R. L.; Lonneman, W. A.; Fraser, M. P.; Harley, R. A.; Pollack, A. K.; Ivy, J. M.; Price, J. H. Analysis of motor vehicle emissions in a Houston tunnel during the Texas Air Quality Study 2000. *Atmos. Environ.* **2004**, *38* (20), 3363−3372.
(49) Wu, T.; Zhao, H.; Ou, X. Vehicle Ownership Analysis Based on GDP per Capita in China: 1963−2050. *Sustainability* **2014**, *6* (8), 4877−4899.
(50) Yue, X.; Wu, Y.; Hao, J.; Pang, Y.; Ma, Y.; Li, Y.; Li, B.; Bao, X. Fuel quality management versus vehicle emission control in China, status quo and future perspectives. *Energy Policy* **2015**, *79*, 87−98.
(51) Durbin, T. D.; Pisano, J. T.; Younglove, T.; Sauer, C. G.; Rhee, S. H.; Huai, T.; Miller, J. W.; MacKay, G. I.; Hochhauser, A. M.; Ingham, M. C.; et al. The effect of fuel sulfur on NH3 and other emissions from 2000−2001 model year vehicles. *Atmos. Environ.* **2004**, *38* (17), 2699−2708.
(52) Zhang, S.; Wu, Y.; Wu, X.; Li, M.; Ge, Y.; Liang, B.; Xu, Y.; Zhou, Y.; Liu, H.; Fu, L.; et al. Historic and future trends of vehicle emissions in Beijing, 1998−2020: A policy assessment for the most stringent vehicle emission control program in China. *Atmos. Environ.* **2014**, *89*, 216−229.
(53) Ianniello, A.; Spataro, F.; Esposito, G.; Allegrini, I.; Rantica, E.; Ancora, M. P.; Hu, M.; Zhu, T. Occurrence of gas phase ammonia in the area of Beijing (China). *Atmos. Chem. Phys.* **2010**, *10* (19), 9487−9503.
(54) Baek, B. H.; Aneja, V. P. Measurement and analysis of the relationship between ammonia, acid gases, and fine particles in eastern north carolina. *J. Air Waste Manage. Assoc.* **2004**, *54* (5), 623−633.
(55) EPA. The National Emission Inventory (NEI) 2011 v2 http://www.epa.gov/ttnchie1/net/2011inventory.html (accessed June 25, 2015).
(56) Brioude, J.; Petron, G.; Frost, G. J.; Ahmadov, R.; Angevine, W. M.; Hsie, E.-Y.; Kim, S.-W.; Lee, S.-H.; McKeen, S. A.; Trainer, M.; et al. A new inversion method to calculate emission inventories without a prior at mesoscale: Application to the anthropogenic CO2 emission from Houston, Texas. *J. Geophys. Res.* **2012**, *117* (D5), D05312.
(57) Carslaw, D. C.; Rhys-Tyler, G. New insights from comprehensive on-road measurements of NOx, NO2 and NH3 from vehicle emission remote sensing in London, UK. *Atmos. Environ.* **2013**, *81*, 339−347.
(58) Emmenegger, L.; Mohn, J.; Sigrist, M.; Marinov, D.; Steinemann, U.; Zumsteg, F.; Meier, M. Measurement of ammonia emissions using various techniques in a comparative tunnel study. *Int. J. Environ. Pollut.* **2004**, *22* (3), 326−341.
(59) EPA. *2011 National Emissions Inventory, version 1 Technical Support Document*; 2014.
(60) EPA. *Using MOVES for Estimating State and Local Inventories of On-Road Greenhouse Gas Emissions and Energy Consumption*; 2012.


DOI: 10.1021/acs.est.6b02805
*Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

(61) IEA. International Energy Agency $CO_2$ Emissions from Fuel Combustion Statistics http://www.oecd-ilibrary.org/statistics (accessed January 17, 2014).
(62) Howden, L. M.; Meyer, J. A. Age and sex composition: 2010. *2010 Census Briefs, US Dep. Commer. Econ. Stat. Adm. US CENSUS Bur.* 2010.
(63) Zhu, L.; Henze, D.; Bash, J.; Jeong, G.-R.; Cady-Pereira, K.; Shephard, M.; Luo, M.; Paulot, F.; Capps, S. Global evaluation of ammonia bidirectional exchange and livestock diurnal variation schemes. *Atmos. Chem. Phys.* **2015**, *15* (22), 12823−12843.
(64) Sun, K.; Tao, L.; Miller, D. J.; Zondlo, M. A.; Shonkwiler, K. B.; Nash, C.; Ham, J. M. Open-path eddy covariance measurements of ammonia fluxes from a beef cattle feedlot. *Agric. For. Meteorol.* **2015**, *213*, 193−202.
(65) McDonald, B. C.; McBride, Z. C.; Martin, E. W.; Harley, R. A. High-resolution mapping of motor vehicle carbon dioxide emissions. *J. Geophys. Res. Atmos.* **2014**, *119* (9), 5283−5298.
(66) Heald, C. L.; Lee, T.; Benedict, K. B.; Schwandner, F. M.; Li, Y.; Clarisse, L.; Hurtmans, D. R.; Van Damme, M.; Clerbaux, C.; Coheur, P.-F.; et al. Atmospheric ammonia and particulate inorganic nitrogen over the United States. *Atmos. Chem. Phys.* **2012**, *12* (21), 10295−10312.
(67) Schiferl, L. D.; Heald, C. L.; Nowak, J. B.; Holloway, J. S.; Neuman, J. A.; Bahreini, R.; Pollack, I. B.; Ryerson, T. B.; Wiedinmyer, C.; Murphy, J. G. An investigation of ammonia and inorganic particulate matter in California during the CalNex campaign. *J. Geophys. Res. Atmos.* **2014**, *119* (4), 1883−1902.
(68) Bash, J. O.; Cooter, E. J.; Dennis, R. L.; Walker, J. T.; Pleim, J. E. Evaluation of a regional air-quality model with bidirectional $NH_3$ exchange coupled to an agroecosystem model. *Biogeosciences* **2013**, *10* (3), 1635−1645.
(69) Gately, C. K.; Hutyra, L. R.; Sue Wing, I. Cities, traffic, and CO2: A multidecadal assessment of trends, drivers, and scaling relationships. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (16), 4999−5004.


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