Revisiting Nitrous Acid (HONO) Emission from On-road Vehicles: A Tunnel Study with a Mixed Fleet

Abstract

Nitrous acid (HONO) is an important precursor of OH radicals in the atmosphere. In urban areas, emissions from vehicles are the main source of air pollutants including reactive nitrogen. Previously reported emission ratios of HONO ($HONO/NO_x$) from vehicles were measured in the late 1990s which needs to be updated due to the significant changes in emission control technologies. We measured the emission ratio of a fleet of vehicles (38% diesel on average) from 11 to 21 March, 2015 in a road tunnel in Hong Kong. The emission ratio $1.24\% \pm 0.35\%$ obtained is greater than the commonly adopted 0.8% or 0.3%. The elevated emission ratio is likely to be related to the presence of vehicles equipped with Diesel Particle Filters (DPFs). Positive correlation between HONO and Black Carbon (BC) shows that HONO and BC were emitted together, while the lack of correlation or even anti-correlation between $HONO/NO_x$ and BC indicates that the BC-mediated conversion of NO_2 to HONO in the dark was insignificant in the immediate vicinity of the emission sources.

Implications

Vehicular emission is a key source for HONO in the urban atmosphere. However, the most commonly used emission ratio $HONO/NO_x$ in modeling studies were measured more than 15 years ago. Our tunnel study suggests that a mixed fleet nowadays has a higher emission ratio, possibly as a result of the Diesel Particle Filter (DPF) retrofit program and the growing share of Euro IV or more advanced diesel vehicles. Our study also provides new insight into the role of Black Carbon in HONO formation from vehicles.

Revisiting Nitrous Acid (HONO) Emission from On-road Vehicles: A Tunnel Study with a Mixed Fleet

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Introduction

Nitrous acid (HONO) is an important reservoir of radicals in the atmosphere. Upon its photolysis at wavelengths smaller than 390 nm, hydroxyl radical (OH), which acts as an important cleansing agent in the atmosphere and promotes the formation of photo-oxidants such as ozone and peroxyacetylnitrates (PANs) will be produced (Kleffmann, 2007). The mechanisms by which HONO accumulates in the atmosphere are still not well understood. The homogeneous reaction between NO and OH alone cannot fully explain the high concentration (up to ppbv level) of daytime HONO present in the atmosphere (e.g. Kleffmann, 2007). For primary HONO emitted by vehicles, the emission ratio ($ER_{HONO} = HONO/NO_x$, in which $NO_x = NO + NO_2$), is the most commonly used parameter to quantify HONO emission from vehicles. Previous measurement studies showed the emission ratios fell between 0.3% and 0.8% (Pitts et al., 1984, Sjödin and Ferm, 1986, Kirchstetter et al., 1996, Kurtenbach et al., 2001). Since these values are significantly lower than $HONO/NO_x$ observed in the atmosphere, a number of secondary HONO sources were proposed (Spataro and Ianniello, 2014). Although incorporating these sources into models can improve the simulation of HONO (e.g. Wong et al., 2013), the uncertainties in quantifying these sources and inability of the models to simulate certain cases necessitate a re-evaluation of the traditional sources, in addition to the search for new emission and formation pathways.

Emission Ratios (ERs) from vehicles ($HONO/NO_x$) can be determined in several ways, such as dynamometer tests, roadside measurements and tunnel measurements. The tunnel measurement has advantages of being able to capture a large enough sample of on-road vehicles and not influenced by chemical processes triggered by sunlight (Ropkins, 2009). Kirchstetter et al. (1996) measured HONO using denuders in a road tunnel in California (with over 99% gasoline vehicles), and derived an ER of 0.3%. Kurtenbach et al. (2001) used Differential Optical Absorption Spectroscopy (DOAS) to measure HONO in a tunnel in Germany with 24.3% share of diesel vehicles in traffic, which yielded an ER of 0.8%. These two ratios, although obtained in an era with only relatively primitive emission control technologies, have been used in many recent modeling studies. For instance, in the MOVES model for traffic emission used by the EPA, the 0.8% ratio was assigned to all the on-road vehicles throughout the day (Rappenglück et al., 2013). The low emission ratios made researchers exclude traffic emission as an important source of HONO (Pusede et al., 2015). However, the vehicle fleets of in the two tunnels were both gasoline dominated, which may not reflect the composition of fleet today and elsewhere. In the last two decades, the heavy tax on gasoline has made diesel vehicles increasingly popular in the European countries. According to European Automobile Manufacturers Association (available at: http://www.acea.be/statistics), the share of diesel in new passenger cars has grown from 23.1% in 1994 to 52.1% in 2015. It is commonly believed that diesel vehicles have a higher emission ratio of HONO because the semi-volatile organics in diesel exhaust can enhance secondary HONO formation at tailpipe by reaction 1, where $[C-H]_{red}$ stands for the reductive functional groups on soot surfaces (Gutzwiller et al., 2002, Khalizov et al., 2010).

$$NO_2 + [C-H]_{red} \rightarrow HONO + [C-H]_{ox} \qquad (1)$$

In addition, many developments of emission control technologies (especially exhaust after-treatment) have taken place since 2000. For example, Diesel Particle Filters (DPFs) at tailpipes, which trap soot and remove them through oxidation, have drastically changed the composition of diesel exhaust. The soot removal in the DPFs is either achieved by active regeneration, in which fuel is injected to burn the carbon, or passive regeneration, in which NO is catalytically oxidized to NO_2 and the latter then oxidizes soot continuously (van Setten et al., 2001). Although the installation of DPFs can reduce the emission of Particulate Matter (PM) by more than 90% (Barone et al., 2010, Herner et al., 2011), it leads to a higher ratio of NO_2/NO_x at tailpipe (Dallmann et al., 2011), which may significantly increase the roadside

oxidative capacity and promote ozone formation (Carslaw, 2005, Millstein and Harley, 2010). Installing DPFs may have affected HONO emission in two ways. First, in the commonly used passive filter regeneration process, a by-product of the NO_2 + soot reaction is HONO (Gerecke et al., 1998, Khalizov et al., 2010). Although this reaction in the dark cannot explain the HONO/NO_x ratio under atmospheric conditions due to the fast deactivation of limited reactive sites on the surface of black carbon, it may have noticeable impact on tailpipe HONO/NO_x (Arens et al., 2001, Aubin and Abbatt, 2007). Second, the DPF-equipped vehicles can also cause increment of secondary HONO formation in the atmosphere because NO_2 is a direct precursor of HONO.

Despite the important role of vehicle emitted HONO in urban atmosphere and the vast change of vehicle exhaust composition, there were only limited studies quantifying HONO emission ratio in the last 15 years. Rappenglück et al. (2013) measured HONO and NO_x at an urban highway junction and a 70 m tower in Houston in 2009. They found that during the morning peak (4 a.m. to 8 a.m. on weekdays), the build-up of HONO was linearly correlated with that of NO_x with a slope 1.7% and $R^2 = 0.75$. Wormhoudt et al. (2015) used the data collected in the same year at a 70-m tower on the campus of University of Houston and derived a slope of 1.4% with $R^2 = 0.67$. Xu et al. (2015) analyzed 21 fresh emission plumes (with NO/$NO_x > 0.80$) near an expressway with 33% diesel vehicles in Tung Chung, a suburban area in Hong Kong. The emission ratios were 0.5%-1.6%, and such ratios were positively correlated with BC emitted.

Hong Kong is a highly urbanized city with heavy traffic density, suffering from severe roadside pollution problems. Although the diesel vehicles only accounts for 18% of vehicles registered, it contributes to over 50% of NO_x emitted by the road transport sector (HK Environment Bureau, 2013). In certain downtown areas, such as the two major roads at Mong Kok (an urban center), the diesel vehicles can exceed 35% in number (Lee et al., 2015), closer to that in the European countries, leading to a greater dominance of diesel NO_x. In Hong Kong, all the pre-Euro and Euro I diesel buses and most Euro II and Euro III buses had been retrofitted with passive regeneration DPF by 2010 and 2012 respectively (HK Environment Bureau 2013, Heimark et al., 2009). For Euro IV or advanced diesel vehicles, DPF has become a common or even required configuration to meet the more stringent emission standards (Johnson, 2008, Tzamkiozis et al., 2010). These changes led roadside

NO$_2$ grow by 20% from 1999 to 2013 and made it the most frequent top pollutant in the three roadside air quality stations (HK Environment Bureau, 2013).

In this paper, we present the measurement result of HONO carried out in a busy road tunnel in Hong Kong. The objectives of this study are to measure the emission ratio of a modern fleet with a higher percentage of diesel vehicles, and to examine whether the new emission control technologies have impact on HONO. We also aim at evaluating the role of soot in HONO emission and formation. Our result will inform the modelers dealing with HONO sources in urban areas with heavy diesel traffic, such as Hong Kong and many European cities.

Methods

Field measurement site

The measurements were conducted at two points (A and B) in the north bore of Shing Mun Tunnel (1600 m in length, cross section area A = 70 m^2), which carries one-way traffic through the Needle Hill, connecting Tsuen Wan and Sha Tin, two densely populated districts in Hong Kong (Figure 1). The tunnel has a 1% gradient from the entrance to the exit. The vehicle speed in the Shing Mun Tunnel was in the 60-70 km/hr range (Ho et al., 2009). As axial ventilation (induced by both the fans overhead and vehicle flow) from A to B was used in the tunnel, no air was lost in the middle of the two sampling points.

Figure 1 here

Measurement period and instruments

The measurement took place from March 11 to Mach 21 2015. HONO was continuously measured by a commercial LOng-Path Absorption Photometer (LOPAP) at Point B. Detailed description of the LOPAP system can be found elsewhere (Heland et al., 2001, Zha et al., 2014; Xu et al., 2015). To fit the polluted environment, the upper range of our LOPAP was changed from ~2 ppbv to ~40 ppbv by reducing the sensitivity through adjusting the detecting wavelength from 550nm to 610nm) (Personal communication with Dr. J. Kleffman at Bergische Universität Wuppertal). The detection limit of this system was approximately 20

pptv with effective time resolution around 5 min and an accuracy of ~10%. Automatic zero checks with synthetic air were performed for 3 times per day, and manual calibrations with 0.4 µg L^{-1} liquid NO_2^- standard were conducted on March 11, 12, 16, and 19. Time delay and response time of the LOPAP were corrected in data analysis each day. The 10-min averaged data was used in the following analysis.

NO and NO$_2$ were simultaneously at both Point A and Point B, while BC and HONO were measured at Point B . NO$_x$ was measured by an API-T200 chemiluminescence analyzer with a molybdenum converter with the time resolution of 1 min. Our previous study has demonstrated that the thermal catalytic conversion gives similar NO$_2$ results with those obtained from a more selective photolytic method when the sampling point is very close to the emission source (Xu et al., 2013); therefore the data measured by the Mo-oxide NO$_x$ analyzers in the present tunnel study were used without correction. BC was measured by an AE-51 aethalometer with time resolution of 10 s. It is worth noting that the aethalometer, which measures attenuation of light through a filter where particles deposit, may report a lower BC concentration especially when highly absorbing aerosols (like diesel soot) are present. So eq 2 proposed by Kirchstetter and Novakov (2007) was used for the correction of BC:

$$BC = \frac{BC_{raw}}{0.88 \exp(-ATN/100) + 0.12} \tag{2}$$

Here, BC$_{raw}$ is the raw concentration of BC reported by the aethalometer, and ATN refers to the light attenuation at the measurement wavelength of 880 nm in this instrument. Due to the malfunctioning of the aethalometer, BC data were only available from 11-14 March.

Table 1 here

Results and Discussion
Traffic Counting

Figure 2a shows the diurnal hourly vehicle flow during the measurement period. Each day 26970 vehicles on average passed through the tunnel, with two apparent peaks in the morning and afternoon rush hours. We therefore define 6:00 a.m. to 11:59 p.m. as "emission intensive

hours", during which the average hourly vehicle flow was larger than 1000 vehicles/h. This time period also corresponds well with the hours with average wind velocity (in vehicle flow direction) larger than 3.6 m/s, making the tunnel like a plug flow reactor. Figure 2b displays the composition of traffic fleet monitored on March 13 and March 14 during the emission intensive hours. The share of diesel vehicles in the tunnel was 38%, around half of which were DPF-equipped (buses and Euro IV or above goods vehicles) in our estimation using data from HK Environment Bureau (2013).

Figure 2 here

Emission Ratio

Two approaches have been used to determine the emission ratio of HONO based on measurements in tunnel. Kurtenbach et al. (2001) performed least square linear regression of measured [HONO] vs. [NO_x], and reported the slope as the emission ratio. This approach might underestimate the emission ratio due to the very large intercept on the [HONO] axis (~10 ppbv). Kirchstetter et al. (1996) calculated the emission ratio by:

$$ER_{HONO} = \frac{\Delta[\text{HONO}]}{\Delta[\text{NO}_x]} \qquad (3)$$

where Δ[HONO] and Δ[NO_x] are the background-subtracted concentration of HONO and NO_x, respectively. Since the ambient concentration of HONO and NO_x were much lower than that in the tunnel, the authors found that HONO/NO_x measured in the middle of the tunnel was nearly the same as ER_{HONO}. In the present study, we choose the method by Kirchstetter et al. (1996), which we believe is more appropriate for emission ratio calculation.

The mean concentrations of HONO and NO_x measured at Point B deep inside the tunnel were 15.7 ($\pm$ 4.2) ppbv and 1.31 ($\pm$ 0.32) ppmv respectively, significantly higher than that those measured at the suburban Tung Chung site (mean HONO = 0.35 ppbv, mean NO_x = 0.16 ppmv) in Hong Kong (Xu et al., 2015), which can be seen as a proxy for the background of the Shing Mun Tunnel. Therefore, we believe that HONO/NO_x measured at Point B can provide a reasonable representation of tailpipe emission ratio, which is close to Δ[HONO]/Δ[NO_x].

Diurnal pattern of HONO/NO$_x$ at Point B is shown in Figure 3a. This ratio was highest in the period between midnight and dawn, when traffic flow was minimal, and dropped quickly after the start of morning traffic, and remained stable from 6 a.m. to 11 p.m. (the emission intensive hours). The high HONO/NO$_x$ ratios in the early hours are attributed to additional sources of HONO in incoming ambient air, apart from vehicle emissions. Therefore, the average HONO/NO$_x$ in the emission intense period, 1.24% ($\pm$ 0.35%), can be taken as the emission ratio of HONO. We also compute the above emission ratio with an alternative approach. The 10-min averaged HONO (between 7 a.m. and 11 p.m.) was plotted against NO$_x$ (Figure 3b). To take account of measurement uncertainties in both HONO and NO$_x$, the reduced major axis regression was used to determine the slope and intercept (Cantrell, 2008). The resulting slope 1.31% is very close to the emission ratio we determined based on the ratio of concentrations, with the y-intercept close to 0. In the remaining analysis, we use the concentration ratio as the emission ratio. The emission ratio measured in this study is 50% higher than that reported in Kurtenbach et al. (2001), but smaller than that measured at the highway junction in Houston (Rappenglück et al., 2013), despite in Shing Mun tunnel the share of diesel vehicles was more than 3 time higher compared with that junction.

Nitrous acid can be produced by the uptake of NO$_2$ on humid wall surfaces by reaction 4, which needs to be considered in ER$_{HONO}$ calculation. This reaction is first order to NO$_2$ Finlayson-Pitts et al. (2003).

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \tag{4}$$

The overall rate of this reaction can be calculated by:

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[HONO]}{dt} = k_{het}^*[NO_2] = \frac{1}{8}\bar{v}_{NO2}\frac{S}{V}\gamma_{geo}[NO_2] \tag{5}$$

where $\bar{v}_{NO2}$ is the mean speed of NO$_2$ molecules, S/V is the surface to volume ratio, and γ_{geo} is the uptake coefficient of NO$_2$ on wall surface. Kurtenbach et al. (2001) measured $\gamma_{geo} \approx 10^{-6}$ in a road tunnel with similar wall composition to Shing Mun Tunnel (both steel sheets covered by enamel). Using this value as NO$_2$ uptake coefficient, and given that S/V equals

0.436 m^{-1} in the Shing Mun tunnel (estimated according to Ho et al. 2009), the pseudo-first-order rate constant k^*_{het} in eq 5 was found to be 1.31×10^{-3} min^{-1}. The residence time of gases between the tunnel entrance and point B can be estimated as $\tau = L_{entrance-to-B}/v_{wind} = 4.4$ min (length from the entrance to B divided by average wind speed). Thus it is reasonable to assume that NO$_x$, after being emitted from vehicles, stayed half of τ, i.e. 2.2 min on average in the tunnel before reaching Point B. Substitute these parameters and $[NO_2]/[NO_x] \approx 0.15$ as measured into eq 5, the increment of HONO/NO$_x$ via the heterogeneous reaction is estimated as 0.04%. This correction can be neglected because it is much smaller than the variation in HONO/NO$_x$ itself ($\sigma = 0.35\%$).

The increase in HONO emission ratio can have a significant impact on the HONO mixing ratio and oxidative capacity in urban areas. For example, Czader et al. (2015) compared two emission ratios, i.e. 0.8% and 1.6% in a WRF-CMAQ model for Houston. They found that in the increased emission ratio case, the modeled mean HONO level increased by 0.11 ppbv at the 70 m Moody Tower in Houston, which was 16% closer to the observed value. The increased HONO emission also led to a 14% increase of OH on that tower, and 3% if averaged over the whole urban area. Though the increment of emission ratio in our study is smaller, it may still have a noticeable impact on the oxidative capacity of urban atmosphere, especially in street canyons. This topic warrants further investigation.

Effect of Diesel Particle Filter on HONO emission

To explore the effect of DPF installations on HONO emission, we attempt to isolate the measurements which were heavily affected by the emissions with DPF vehicles. Previous studies have shown that DPF-equipped vehicles emit NO$_2$/NO$_x$ of exceeding 30% (Herner et al., 2009, Khalek et al., 2011, Bishop et al., 2012) and that for other vehicles, the ratio was smaller than 10% (Shorter et al., 2005). The emission ratio of NO$_2$/NO$_x$ can be estimated by:

$$\mathrm{ER}_{NO_2} = \frac{\Delta NO_2}{\Delta NO_x} = \frac{[NO_2]_B - [NO_2]_A}{[NO_x]_B - [NO_x]_A} \tag{6}$$

where the subscript A and B refers to the pollutant concentration at A and B, respectively (Ban-Weiss et al., 2008). This method may not give very accurate emission ratio for NO$_2$ due

to influence of the inflowing ambient ozone via reaction of O_3 with NO (Yao et al., 2005), but it is reasonable for the current study because this ratio is only used as a criterion for selecting NO_2-rich air parcels, and it is the increment of NO_2 and NO_x between A and B, not the NO_2/NO_x at a single point that is utilized. Figure 4 displays mean HONO/NO_x in different bins of $\Delta NO_2/\Delta NO_x$: 0-0.15, 0.15-0.20, 0.20-0.25, 0.25-0.3, 0.3 or above. The number of samples is 458, 254, 59, 10 and 8 respectively. An overall positive correlation between the two ratios indicates that the HONO emission ratios depend on $\Delta NO_2/\Delta NO_x$, with larger values toward the high NO_2/NO_x samples which we believe are indictors of DPF vehicles. For samples with ER_{NO2}>0.25 (77 of out of the 789 data points), the average HONO emission ratio is 1.38% (±0.33%). One-tail z-test shows that the mean emission ratio of these cases is significantly larger than the population mean 1.24% (p<0.001). Since the DPF-equipped vehicles emit lower BC but similar NO_x compared with other diesel vehicles, it is possible that the reaction of NO_2 with trapped BC took place inside the filter, giving larger HONO/NO_x. This reaction is of negligible importance in the atmosphere due to limited surface area of BC (Arens et al., 2001, Aubin and Abbatt, 2007). However, as BC particles are oxidized layer by layer by NO_2 during the regeneration of DPF, the heterogeneous reaction can be significant at tailpipe. The mean BC concentration for the high NO_2/NO_x cases is even smaller than the population mean, suggesting that the higher HONO/NO_x in the high $\Delta NO_2/\Delta NO_x$ samples was probably not caused by the reaction occurring outside the tailpipe while in the tunnel.

HONO emission vs. BC

To assess the role of BC in HONO emission and chemistry, we plotted HONO and NO_x vs. BC and HONO/NO_x vs. BC. The concentrations of HONO and NO_x are positively correlated to BC (Figure 5). However, larger BC was not accompanied by larger HONO/NO_x. In fact, their correlation is almost negative as shown by Figure 6. Several factors may explain this phenomenon:
1. Diesel vehicles without DPF emit large amount of BC, HONO, and NO_x, whereas DPF vehicle, in which BC particles are trapped, would emit high NO_2 and HONO, but low BC. The mixing of the two types of vehicles results in lacking overall correlation between the HONO emission ratios with BC.

2. Reaction 1 seemed to be too weak to alter the HONO/NO$_x$ ratio in the dark. The average amount of HONO generated per unit area by NO$_2$ uptake on fresh soot was 8.2×10^{13} molecules cm^{-2} (Aubin and Abbatt, 2007). If we assume the uptake was limited by BC, and soot particles had a specific surface area of 10^6 cm^2 g^{-1} (Aubin and Abbatt, 2007) and BC = 30 μg m^{-3} in the tunnel (approximately 80 percentile of BC as was measured), then only 0.1 ppbv HONO will be produced, which can be neglected given that the average concentration of HONO in the tunnel was 15.72 ppbv. In addition, DPF can change the surface chemistry of soot by removing the condensed Polycyclic Aromatic Hydrocarbon (PAH) or other aromatics (Heeb et al., 2008). As the aromatic groups are key players in NO$_2$ to HONO conversion both in the dark and under sunlight (Monge et al., 2010, Han et al., 2013a, b), the soot in the effluent of DPF may be even less reactive compared with normal diesel soot.

3. The sampling point was very close to the tailpipe, which means only very fresh BC was sampled. However, the heterogeneous reaction takes more than 10 minutes to induce an observable increase of HONO/NO$_x$, according to uptake experiments (Han et al., 2013b). A previous study of our group reported positive correlation between HONO/NO$_x$ and BC based on measurements made at the top of a 4-storey building 80 m away from the expressway (Xu et al., 2015). It is possible that when air was relatively stagnant, it took 20-30 minutes for fresh plumes to reach the sampling point, and the conversion happened during the transport. We therefore suggest that in the emission based models for HONO budget in urban areas, instead of using BC data to correct for HONO at the emission source, modelers could use precise emission ratio determined at source to account for primary HONO and treat such heterogeneous conversion in the atmospheric chemistry module, no matter in the dark or in sunlight.

Limitations of the current study

It is important to note that the HONO emission ratio from our study may only be applicable to regions having high share of diesel vehicles with moderate emission control technology, and for vehicle fleet traveling at 60-70 km/hr with little acceleration. As the emission ratio of HONO is dependent on the engine load (Wood et al., 2008, Trinh et al., 2016), and engine load is dependent on acceleration and speed (Kean et al., 2003), the emission ratio in the congested urban area may be different from that determined in the present road tunnel. Also, the exact effect of NO$_2$ + soot reaction in DPF on HONO emission need to be studied in controlled experiments.

Summary and conclusion

In this study HONO, NO_x and BC were continuously measured during March 11-21, 2015 in a road tunnel in Hong Kong. The emission ratio measured (1.24% ± 0.35%) was around 50% higher than the most commonly used 0.8%. Using $\Delta NO_2/\Delta NO_x$ ratios as criteria to identify emission plumes from DPF-equipped vehicles, we found statistically significant increase of ER_{HONO} from these vehicles. Positive correlation between HONO and Black Carbon (BC) suggests that HONO and BC were emitted together, while the lack of correlation between HONO/NO_x and BC, which differs from our previous finding at the suburban Tung Chung site (Xu et al., 2015), suggests that the BC-mediated conversion of NO_2 to HONO in the dark was insignificant immediately after emission. It is suggested that modeling studies handle the BC-mediated HONO formation in the atmospheric chemistry module rather than make correction at the emission source.

In view of the rapid development of emission control technologies nowadays, the emission ratio of HONO needs to be updated regularly. In Hong Kong, Selective Catalytic Reduction (SCR) retrofit program has been implemented in phases since 2015 to further reduce the high NO_2 emissions from diesel vehicles equipped with DPF, and the Government has proposed to enforce Euro VI standard in 2017-2018 (HK ACE, 2013). It will be interesting to observe how HONO emission ratio will change when diesel vehicles with SCR systems become more popular.

Acknowledgment

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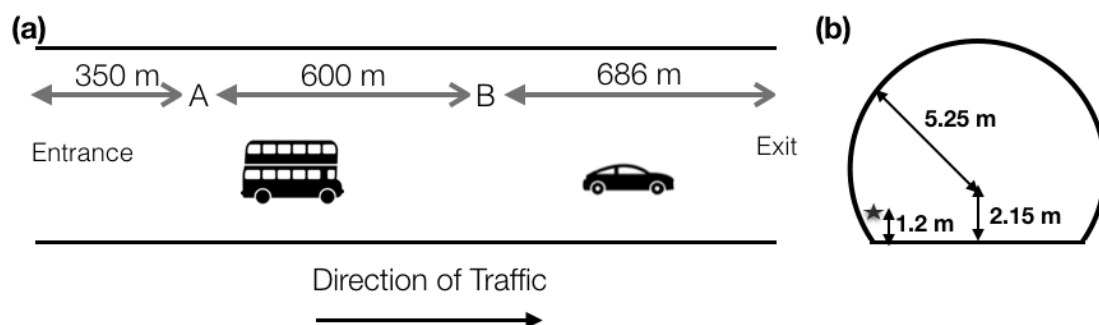
Figure Captions

Figure 1. (a) Schematic diagram of the 2-lane tunnel bore and points at which the pollutants were measured (not to scale). (b) The cross section of the tunnel bore (gases were sampled at the location of the star, around 1.2 m above ground).

Figure 2. (a) Diurnal pattern of vehicle flow during the whole measurement. (b) Mix of engine types counted during the "emission intensive hours" on 13 and 14 March.

Figure 3. (a) Hourly averaged $HONO/NO_x$ as a function of time of day. As an example, the data point at time of day = 7 shows $HONO/NO_x$ averaged over 7:00 a.m. to 8:00 a.m. Error bars on this plot show 1σ variability. (b) 10-min average HONO during 7 a.m. and 11 p.m., plotted against NO_x, RMA regression line is $[HONO] = 0.0134[NO_x] - 1.8169$ (N = 791).

Figure 4. Mean $HONO/NO_x$ with 1σ variance at Point B in different bins of $\Delta NO_2/\Delta NO_x$ (0-0.15, 0.15-0.20, 0.20-0.25, 0.25-0.3, 0.3 or above) between Point A and Point B. The point in each bin is drawn in the middle of that bin on the horizontal axis.

Figure 5. (a) Correlation of BC vs NOx at Point B from 11 March to 14 March. (b) HONO vs BC at Point B from 11 March to 14 March.

Figure 6. $HONO/NO_x$ vs. BC in the "emission intensive hours" from 11 March to 14 March.

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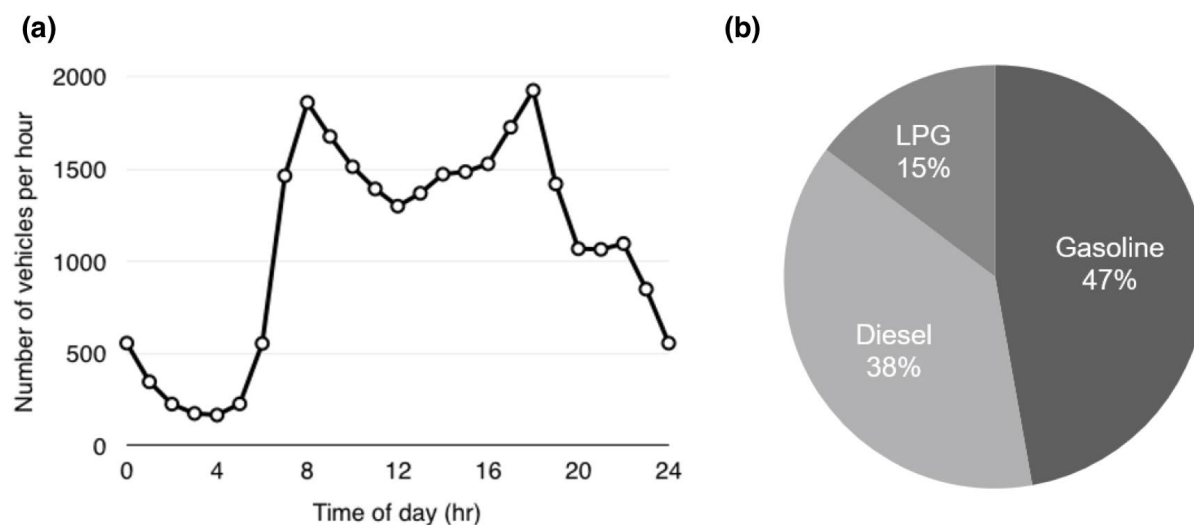

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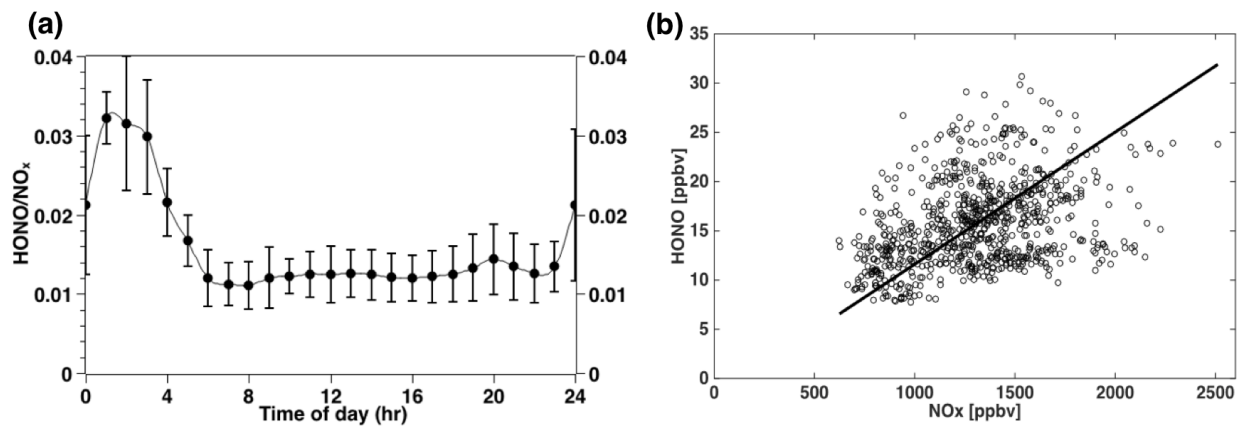
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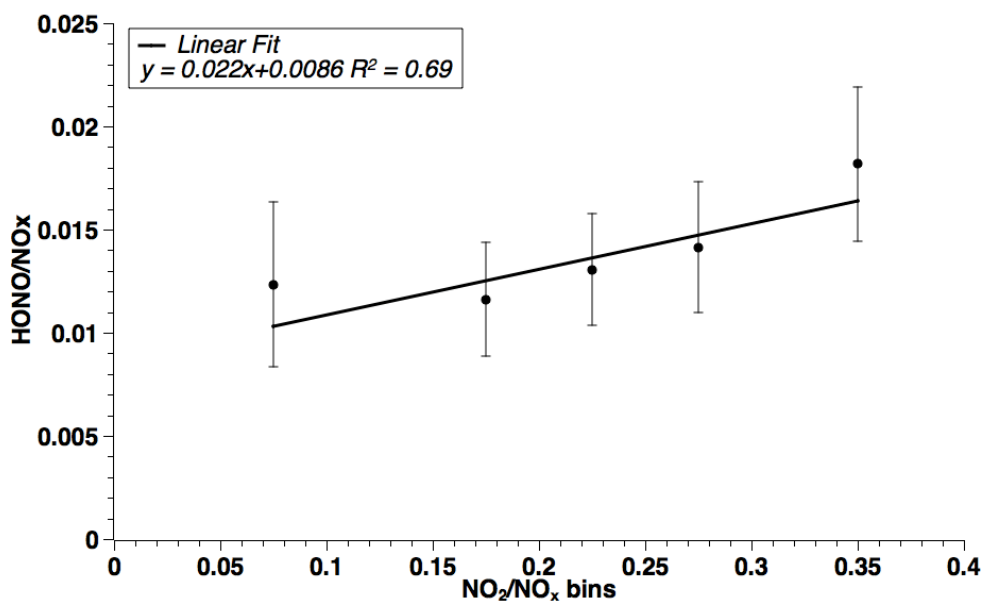

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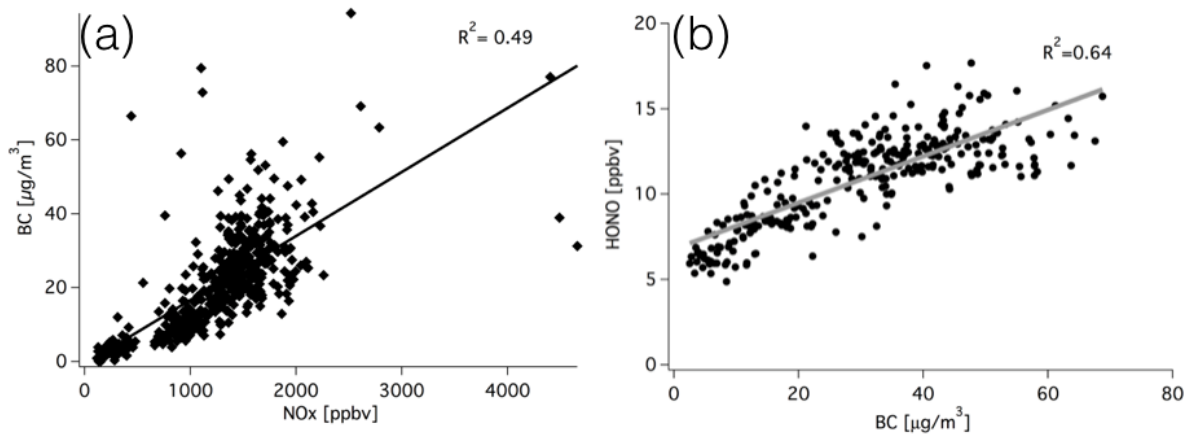
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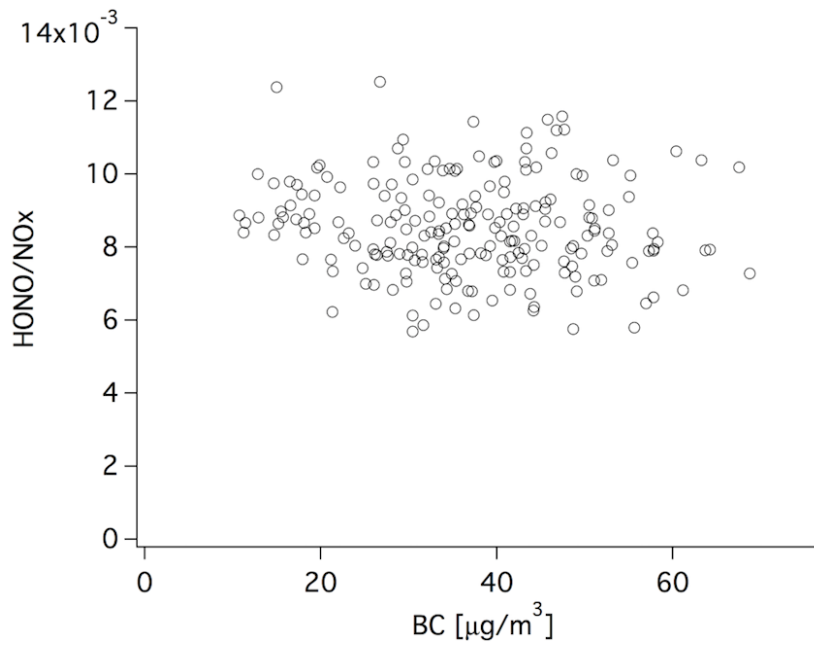

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