Vehicular exhaust contributions to high NH_3 and $PM_{2.5}$ concentrations during winter in Tokyo, Japan

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Abstract. Concentrations of $PM_{2.5}$ in Tokyo, a densely populated megacity, often increase because of NH_4NO_3 formation under low-wind conditions during winter. To obtain source information of NH_3 as a NH_4NO_3 precursor, hourly NH_3 and NH_4^+ concentrations were measured at an urban site in Tokyo in December 2017. Results show that $PM_{2.5}$ and NH_4^+ concentrations increased simultaneously under low-wind and low-temperature conditions along with NH_3, NOx, CO, and optical black carbon (OBC) concentrations. The remaining NH_4^+ (herein, ΔNH_4^+) subtracted from observed NH_4^+ to equivalent SO_4^{2-} concentration correlated well with NO_3^- in $PM_{2.5}$, indicating the existence of fine NH_4NO_3 particles. Regression analysis of hourly NH_3 + ΔNH_4^+ concentrations with CO, NOx, and OBC showed significant correlation. Virtual emission rates (VER) of NH_3 per motor vehicle in Tokyo were estimated using observed relations between NH_3 + ΔNH_4^+ and OBC, etc. with data from vehicular statistics: they were 3.7–32 mg/km. The regression of NH_3 + ΔNH_4^+ with OBC concentrations indicated an intercept of about 3.2 ppb, which is about half of the monthly average in December. This result implies that the non-vehicular source strength was nearly the same strength as the bulk vehicular emissions of NH_3 during winter in Tokyo.

Key words: hourly measurement, motor vehicle exhaust, NH_3, urban source

Highlights:

* Considering excess NH_4^+ concentrations over SO_4^{2-} was useful to study urban NH_3.
* Virtual emission rates of NH_3 per vehicle in Tokyo were 3.7–32 mg/km.
* Non-vehicular NH_3 sources contributed almost equally to winter vehicular emissions.

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1 Introduction

Ammonia (NH_3) in the atmosphere plays an important role in various chemical, climatic, and environmental processes including neutralization of acidic substances (gases, particles, and droplets), formation of secondary aerosol particles, soil acidification, and water eutrophication (Behera et al., 2013; Seinfeld and Pandis, 2016). In fact, atmospheric NH_3 has been recognized as the major precursor of fine particles such as ammonium sulfate and ammonium nitrate (Seinfeld and Pandis, 2016), which might affect human health, visibility, and the Earth's radiation balance. Wet and dry deposition of NH_3 and particles containing ammonium salts to the Earth's surface might markedly alter the nitrogen cycle of natural ecosystem, engendering alteration of plant community composition, and causing other ill effects (Cape et al., 2009; Behera et al., 2013).

Various natural and anthropogenic sources emit NH_3 (Sutton et al., 2008; Behera et al., 2013). Agriculture is the dominant source on a global scale, contributing more than 80% of global NH_3 emissions. For urban areas, non-agricultural NH_3 sources have been reported as major contributors to the concentration levels. They include emissions from related anthropogenic wastes (sewage disposal, etc.; Pandolfi et al., 2012; Reche et al., 2012, 2015), green spaces with plants and soils located in street canyons (Hu et al., 2014; Teng et al., 2017), and motor vehicles (e.g., Perrino et al., 2002; Cape et al., 2004; Li et al., 2006; Matsumoto et al., 2006; Nowak et al., 2006; Chang et al., 2016). Evaporation of NH_3 from waste materials, plants, and soils is mainly related to pH and temperature: higher temperatures allow higher atmospheric concentrations, leading to diurnal flux and concentration variation synchronized with air temperature peaking near noon time (Roelle and Aneja, 2002; Kruit et al., 2007). Regarding emissions from motor vehicles, however, the emission strength (the number of active motor vehicles) in urban areas is expected to show large diurnal variation, with maximum concentrations occurring during the morning rush hour (Perrino et al., 2002; Li et al., 2006; Nowak et al., 2006).

To reduce CO, hydrocarbon, and NO_x emissions from gasoline-powered vehicles, three-way catalytic converters (TWC) have been widely introduced since the 1980s. When using the TWC, however, NH_3 has been emitted as a side product in the NO_x reduction process, thereby contributing as an NH_3 source in the urban atmosphere (e.g., Fraser and Cass, 1998; Kean et al., 2009). In addition, to reduce NOx emission from heavy-duty and light-duty diesel powered vehicles, application of selective catalytic reduction (SCR) systems using urea started in the mid-2000s in Japan and later in other countries, often contributing even more NH_3 to the atmosphere (Suzuki et al., 2008; Carslaw and Rhys-Tyler, 2013; Yamamoto et al., 2013; Suarez-Bertoa et al., 2016). Because of the short lifetime of ammonia in the atmosphere, the influence of even a strong point source such as a livestock facility is mostly limited to a few kilometers (Asman et al., 1989; Hojito et al., 2006; Shen et al.,

2016). Such agricultural facilities are usually absent from urban areas. Therefore, gasoline-powered and diesel-powered vehicles might be the dominant contributors of atmospheric NH_3 within urban areas.

In urban areas, air pollution episodes resulting from local emissions have often occurred during cold seasons (e.g., Kukkonen et al., 2005). Development of strong temperature inversion layers under low-wind conditions is responsible for many cases of heightened concentrations of pollutants such as NOx and $PM_{2.5}$.

Tokyo is among the largest metropolitan areas in the world (The United Nations, 2016). In addition, Tokyo is among of the most densely populated megacities in the world (population density of about 6,200 persons km^{-2} in 2015; http://www.metro.tokyo.jp/ENGLISH/ABOUT/HISTORY/history03.htm). In light of the high density of population, industries, and motor vehicles in megacities, air quality in Tokyo has often not been healthy, but it has improved gradually during recent decades (Minoura et al., 2006; Hara et al., 2013; Wakamatsu et al., 2013). Nevertheless, for particulate matter in Tokyo, high-$PM_{2.5}$ episodes with concentrations greater than the daily regulatory value in Japan still occur, especially in winter. Nitrate and ammonium have been reported as dominant ions in fine particles during such episodes, especially in winter (Minoura et al., 2006; Saito et al., 2012). To investigate the origin and cause of high $PM_{2.5}$ related to reactive nitrogen species, detailed time variation data of NH_3 and NH_4^+ must be obtained with other tracer species of motor vehicle exhaust. This report presents results of such observations conducted in December 2017 in Tokyo. These data are expected to elucidate ambient NH_3 levels, the relation with $PM_{2.5}$, and their contributions to high-$PM_{2.5}$ events from vehicular emissions in this area. We also attempted to quantify annual NH_3 emissions from bulk vehicles in the Tokyo metropolitan area because of the importance of obtaining realistic data on the NH_3 budget in the urban atmosphere.

2 Observation

Gaseous NH_3 and NH_4^+ concentrations in fine particles were measured using a semi-continuous microflow analytical system (ANH-16; Kimoto Electric Co. Ltd.; Osada et al., 2011) at the sixth floor of the main building of Tokyo Metropolitan Research Institute for Environmental Protection (35.67°N, 139.83°E, Fig. 1) located in the southern Tokyo metropolitan area. Two identical sampling lines were used to differentiate total ammonium (NH_3 and NH_4^+) and NH_4^+ alone using a H_3PO_4 denuder to remove NH_3 from the sample air stream. An impactor having a 50% cut-off diameter at about 2 μm was installed at the inlet. The sample air was introduced into an inner frosted glass tube (3 mm inner diameter, 50 cm long) at a flow rate of 1 L min^{-1}. One was coated inside by H_3PO_4. The

other was uncoated. After passage through the glass tube, water droplets were added to the sample air at 100 μl min^{-1} and were mixed in a 5-m-long Teflon tube. The sample water was separated using an air–liquid separator and was injected into the microflow fluorescence analyzer to quantify the NH_4^+ concentration (Osada et al., 2011; Osada et al., 2018). Analysis of the sample solution took 15 min. Consequently, the dataset of NH_4^+ plus NH_3 and NH_4^+ alone was obtainable at 30 min intervals. The detection limit of NH_3 concentration was about 0.1 ppbv (Osada et al., 2011) under stable atmospheric NH_3 and NH_4^+ concentrations. Equivalence of two sample lines and the span of the calibration slope were checked periodically using NH_3 standard gas at about 4 ppbv diluted from 100 ppmv (Taiyo Nippon Sanso Corp.). The ANH-16 was calibrated periodically with a standard NH_4^+ solution prepared from a certified 1000 ppm solution (Fujifilm Wako Pure Chemical Corp.).

Just as NO and NOx were measured (APNA-370; Horiba Ltd.), CO was measured (48i TLE; Thermo Fisher Scientific Inc.). We measured $PM_{2.5}$ and optical black carbon (OBC, PM712; Kimoto Electric Co. Ltd.). Hourly concentrations of NO_3^- and SO_4^{2-} in $PM_{2.5}$ were measured (ACSA-14; Kimoto Electric Co. Ltd., Saito et al., 2012). Measurement methods for NO_3^- and SO_4^{2-} used in ACSA-series were evaluated by Osada et al. (2016). For this study, we adjusted ACSA-based daily mean values to daily mean values based on the reference method (Federal Reference Method, EPA, 1999), if necessary. Meteorological data were obtained at the Japan Meteorological Agency's Tokyo regional headquarters, located about 6 km northwest of the site (JMA, 2018).

3 Results and Discussion

Figure 2 presents results of observations conducted in December 2017. In Tokyo, days of low wind speed were frequent in December, 2017. Indeed, the hours below 3 m s^{-1} were 543 out of 744 hr in December, comprising about 73% of the month. Because of low winds during winter, a surface inversion layer often developed, preventing the vertical diffusion of locally emitted pollutants. Therefore, atmospheric concentrations of CO, OBC, and NOx, mainly emitted from automobile exhausts, were often higher under low-wind conditions in winter. In Fig. 2, for example, the concentration peaks on December 7th–8th, 10th–11th, 15th–16th, 18th–19th, and 22nd–24th were associated with low winds. High NOx correlates well with high NO concentrations, suggesting that emissions from internal combustion are the dominant source of NOx enhancement. Moreover, the NH_3 concentration increased under low winds. The similarity of NH_3 temporal variation with those of species emitted from motor vehicles suggests that NH_3 was emitted from motor vehicles. Correlation between NH_3 and vehicle-emitted species in the urban area has been reported for many cities (Perrino et al., 2002; Li et al., 2006; Nowak et al., 2006).

Figure 3 presents concentrations of NH_4^+, SO_4^{2-}, NO_3^-, and ΔNH_4^+ in $PM_{2.5}$. Concentrations of SO_4^{2-} were much lower than that of NO_3^- or NH_4^+. Actually, the SO_2 concentrations (not shown) in Tokyo were also low (ca. 1 ppb; MOE, 2018a) in December. The oxidation speed of SO_2 was expected to be low in winter. Therefore, the amount of in-situ formation of SO_4^{2-} from local SO_2 oxidation is expected to be limited. Long-range transport of fine particles containing $(NH_4)_2SO_4$ might contribute to NH_4^+ to some degree in Tokyo. As Fig. 3 shows, NH_4^+ resulting from such $(NH_4)_2SO_4$ accounts for about 30% at most because of the low SO_4^{2-} concentrations observed during this period. Here we define ΔNH_4^+ concentrations as

$$[\Delta NH_4^+] = [NH_4^+] - [2\ SO_4^{2-}]\ , \qquad (1)$$

where [x] denotes the concentration of x species in nanomoles per cubic meter. The ΔNH_4^+ concentration indicates an extra amount of NH_4^+ after subtracting the fully neutralized amount as forming $(NH_4)_2SO_4$. In other words, the amount of NH_4^+ potentially existed as ammonium nitrate (NH_4NO_3). Temporal variation of the ΔNH_4^+ correlates very well with NO_3^- concentrations, indicating that most of the NO_3^- existed as NH_4NO_3. A slightly higher ΔNH_4^+ concentration suggests potential on other counterpart anions (such as Cl^- and organic acids) to neutralize or slightly overestimating NO_3^-concentrations because of interference from water-soluble organics (Osada et al., 2016). As Fig. 2 shows, NOx concentrations often exceeded 100 ppb, which can produce high levels of N_2O_5 or HNO_3. High NH_3 concentrations with HNO_3 in the atmosphere promote NH_4NO_3formation, especially under cold temperatures (Mozurkewich, 1993). The mean air temperature in Tokyo was 6.6°C during December 2017 (Japan Meteorological Agency, 2018). According to monitoring data for acid-rain-related species by the Ministry of Environment in Japan (MOE, 2018a), the monthly average HNO_3 concentration was about 0.3 ppb in December (2011–2016) in Tokyo. The mean NH_3 concentration observed for this study was 4.1 ppb. On average, the concentration products of gaseous NH_3 and HNO_3 were higher (about a factor of 4) than the gas–solid equilibrium value for NH_4NO_3 at 6.6°C based on parameters reported by Mozurkewich (1993). This result strongly suggests the frequent formation of NH_4NO_3 in the atmosphere and an increasing contribution of NH_4NO_3 to $PM_{2.5}$ concentration, which is consistent with high NH_4NO_3 fraction to $PM_{2.5}$ under high NOx, NH_3, and low-wind conditions.

Sewage disposal plants are potential sources of urban NH_3. The nearest such plant, the Sunamachi sewage plant, is located 1 km southeast from the observation site. To detect any influence of plant emissions, hourly NH_3 concentrations were taken by wind direction as a polar plot portrayed in Fig. 4. Higher NH_3 concentrations were observed from west to north winds as opposed to the direction of the sewage plant. The area of north to west from the site is covered by densely populated metropolitan areas, whereas Tokyo Bay lies to the south (Fig. 1). Anthropogenic NH_3 emissions such

as those from humans themselves, pets, sewage treatment, and garbage are known as major contributors to the urban atmosphere, especially during warm seasons (Reche et al., 2012). Our study was conducted in winter. Therefore, emission flux from these sources is limited because of the prevailing low temperatures. Reche et al. (2012) pointed out that the number of garbage containers per unit of area affects the local NH_3 concentration in Barcelona. However, domestic waste collection in Japan generally requires 1) that burnable waste including food waste, etc. be packed into plastic bags and 2) that stringent rules be applied for public collection (e.g., garbage bags must be put out in a specified collection place by 8:00 a.m. on the collection day), preventing unnecessary NH_3 emissions during garbage collection.

For polar plots on NOx, OBC, and CO, higher concentrations were also observed for west to north winds, implying that motor vehicle emissions from metropolitan areas are greater than those from the Tokyo Bay area. The similarity of higher directions for these with NH_3 suggests that, for NH_3 in winter, motor vehicle exhausts are potentially the major contributor at the site, rather than sewage plant emissions.

Figure 5 portrays scatter plots of $NH_3 + \Delta NH_4^+$ among hourly concentrations for vehicular exhaust markers in December 2017. All panels in Fig. 5 depict significant correlation at a 99% confidence level (n=663). Regarding conversion of concentrations from OBC to elemental carbon (EC), daily relations between those at Nagoya were used (Osada et al., 2019). The EC concentrations were estimated as OBC concentrations multiplied by 1.25. They are expressed as mole fractions (ppb) in the air for comparative purposes. A higher coefficient of determination (R^2 >0.8) was obtained for pairs of vehicular marker species (EC, CO, and NOx). The R^2 (0.48) between NOx and $NH_3 + \Delta NH_4^+$ was higher than that (0.36) for the relation between NH_3 and NOx, suggesting that the concentration of $NH_3 + \Delta NH_4^+$ is useful to study the NH_3 budget considering NH_4NO_3 formation in the atmosphere. The highest R^2 found for $NH_3 + \Delta NH_4^+$ was obtained for OBC (0.60). As the panel shows, the intercept of the regression line for $NH_3 + \Delta NH_4^+$ with OBC is about 3.2 ppb, which suggests the existence of a non-vehicular source for NH_3. The monthly average of $NH_3 + \Delta NH_4^+$ was 6.7 ppb. Therefore, the non-vehicular source contribution accounts for about 48% of the average. In turn, vehicular emissions contribute to about half of the average concentration of $NH_3 + \Delta NH_4^+$ in December.

Table 1 presents annual emission amounts of the vehicular markers in Tokyo and slope values of regression analysis in Fig. 5. Vehicular emissions were taken from the latest report for 2015 (Bureau of Environment Tokyo Metropolitan Government, 2017). The report, which has been compiled every five years, is based on various chassis dynamometer experiments and traffic surveys in Tokyo. The emission amount of EC was estimated as 70% of particle emissions from vehicular exhausts (Hagino

et al., 2010; Yamagami et al., 2019). Based on these emissions and observed slopes, annual emission amounts of NH_3 from motor vehicles are estimated. For example, because the slope value on (NH_3 + ΔNH_4^+)/OBC (EC) and EC emissions are, respectively, 1.46 and 69 ton/yr, proportional NH_3 emissions are calculated as 143 ton/yr. Similarly, data based on CO and NOx respectively provide 456 and 1245 ton/yr. Actually, NH_3 emissions based on the slope with NOx were much larger than others. The accuracy of these estimates depends on the correctness of emissions inferred from vehicular emission markers and regression slopes. Other than these sources of uncertainty, larger estimates based on NOx might be attributed to one or more of the following: 1) low emissions for 2017 than those compiled for 2015 and 2) rapid oxidation of NOx and efficient removal from the atmosphere. First, emission controls of NOx for new vehicles in Japan have strengthened for these years, especially for diesel heavy vehicles (from 2.0 g/kWh in 2005 to 0.7 g/kWh at 2009, 0.4 g/kWh in 2016; MOE, 2018b). According to the latest report for 2015 (Bureau of Environment Tokyo Metropolitan Government, 2017), NOx emission factors (EFs) estimated for passenger and freight vehicles decreased respectively about 56% and 24% during 2010–2015. Older high-emission vehicles are gradually being replaced by newer and lower emission vehicles. Therefore, the decreasing trend of EF continues from 2015 through 2017. Second, regarding behavior in the atmosphere, atmospheric residence time is about two months for CO and more than several days for fine particles, representing about OBC (Warneck, 2000). In contrast, NOx is unstable in the atmosphere because of its rapid oxidation. In fact, the NOx lifetime has been estimated to be as short as 8 hr, even in winter (Beirle et al., 2011), which is much shorter than that of either CO or OBC. Therefore, the observed slope to NOx might be overestimated; consequently, NH_3 emissions might be overestimated.

As shown in Table 1, virtual emission rates (VERs) of NH_3 per motor vehicles in Tokyo were also estimated as annual emission amounts divided by the running number of vehicles and road distance in 2015. The value of traffic surveys was taken from a report by the Bureau of Environment Tokyo Metropolitan Government (2017). The VER estimation results show large dispersion (3.7–32), which is likely to be attributable to the reasons described above. Table 2 presents the VER obtained in this study and EFs from other studies obtained using various methods and at various places. Although the VER calculation method differs from EFs based on direct observations on single or many sample vehicles, comparison of these values is useful to elucidate bulk emissions from motor vehicles in an area. The EF data presented in Table 2 were selected from recent (after 2009) published data because of the rapid evolution of emissions control technologies worldwide. The range of the VERs obtained in this study is within the range of reported values. Actually, NH_3 EFs have been estimated from observations at tunnels and measurements of chassis dynamometers, both of which are expensive and which require much equipment. In contrast, once hourly relations of NH_3 + ΔNH_4^+

with vehicular markers and their areal emission strengths in an area are available. Our method might be useful to estimate NH_3 emission rates for bulk motor vehicle activities in the area.

In Japan, implementation of the SCR system using urea started for heavy-duty trucks and other vehicles after the mid-2000s. An older SCR system in use might produce more NH_3 (Suzuki et al., 2008; 2014; Carslaw and Rhys-Tyler, 2013) and would enhance the EF of NH_3 from diesel vehicles. Further simultaneous observations of $NH_3 + \Delta NH_4^+$ and vehicular exhaust markers must be conducted to estimate VERs for NH_3 more precisely across urban areas.

As discussed earlier, the intercept of the regression line suggests that non-vehicular sources accounted for about half the monthly average. The wide scatter shown in the plot between $NH_3 + \Delta NH_4^+$ and vehicular markers suggests that the non-vehicular source strength might vary with parameters other than vehicular rush and vertical mixing. Using the regression results with OBC, the residual concentration (observed minus estimated) of $NH_3 + \Delta NH_4^+$ is shown with air temperature in Fig. 6. Some larger positive deviations marked by asterisks are found for days of higher daytime temperature. Furthermore, detailed examination indicates that the daily peak of the residual value was found before the maximum of air temperature but after the morning. This indication suggests that the variation of residual $NH_3 + \Delta NH_4^+$ resulted not only from air temperature but also because of other parameters. Dissociation of NH_4NO_3 under higher temperatures has already been regarded as the use of $NH_3 + \Delta NH_4^+$. Evaporation of dew has been implicated as a cause of morning NH_3 peak from grassland areas (Wenworth et al., 2014; 2016) and building walls (Osada et al., 2018). Prior deposition of NH_4^+ species with water (dew, fog, etc.) during the nighttime under high relative humidity is a key process promoting morning evaporation. According to Wenworth et al. (2014 and 2016), higher morning NH_3 peaks were observed after higher relative humidity (>90%) during the previous nighttime. However, nighttime relative humidity did not reach such high values in this study, mostly around 70% except for the early morning of December 5. This finding implies that dew evaporation might not be the major cause at these events. Teng et al. (2017) reported that emissions from urban soils in green space likely caused the spikes of atmospheric NH_3 occurring 1–4 hr after morning rush hours. Such timing of morning peak after morning rush hours accords with results of this study. Relations with air temperature also partly support emanation from soil. However, areas of green space around the observation site are few. Moreover, input of NH_4^+ species to soil surface, such as wet deposition of NH_4^+, was slight during this study: rain was observed only on December 8 and 25. Given these limitations, although soil emissions at green space might be a possible urban NH_3 source, it might not be sufficient to provide the NH_3 peaks that require similar or greater magnitudes larger than those of vehicular emissions of 143 ton/yr or more.

4 Summary and Conclusions

Simultaneous and continuous measurements of gaseous NH_3 and NH_4^+ in fine particles were conducted at an urban site in Tokyo in December 2017. Together with results found for $PM_{2.5}$, NOx, CO, and OBC concentrations, both NH_3 and NH_4^+ concentrations were increased simultaneously under low-wind conditions. Analyses of NO_3^- and SO_4^{2-} in $PM_{2.5}$ with NH_4^+ indicated that residual amounts (defined as ΔNH_4^+) subtracted for equivalent concentration of SO_4^{2-} from observed NH_4^+ concentrations correlated well with NO_3^-, suggesting the formation of NH_4NO_3 in the atmosphere. Considering the high fraction of particulate NH_4NO_3, vehicular emissions of both NOx and NH_3 contribute to high $PM_{2.5}$ events during winter in metropolitan Tokyo.

Several analyses were conducted to elucidate NH_3 source contributions. Based on the polar plot of hourly NH_3 concentrations by wind direction, the NH_3 concentration from densely populated areas is higher than that from a local sewage plant. Regression analysis of hourly NH_3 + ΔNH_4^+ concentrations with vehicular exhaust markers (CO, NOx, and OBC) showed significant correlation. Annual NH_3 emission amounts from bulk (gasoline and diesel) vehicles in Tokyo were estimated using the regression slope and vehicular emission of CO, NOx, and OBC. Furthermore, the virtual emission rate (VER) of NH_3 per vehicle in Tokyo was calculated from running numbers of vehicles and road distances in 2015. The VER was 3.7–32 mg/km, which is within the range of recently reported emission factors based on measurements taken at tunnels and chassis dynamometers. The regression of NH_3 + ΔNH_4^+ concentrations with OBC indicated the intercept as about 3.2 ppb, which is about half of the monthly average in December. This indication implies that non-vehicular sources are nearly the same strength as the vehicular emission of NH_3. Non-vehicular and time-variable sources were discussed including soil emissions from green spaces.

Because of frequent calm wind conditions during winter at Tokyo, regression analysis of hourly data of NH_3 and NH_4^+ together with $PM_{2.5}$, NOx, CO, and OBC concentrations provide clues to separate vehicular and non-vehicular contribution of NH_3. Although plausible non-vehicular sources varying with temperature in winter were not specified, similar observations at multiple sites across an urban area might provide more clues revealing urban non-vehicular sources.

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Table 1 Vehicular emissions in Tokyo at 2015, slope of regression analysis, vehicular emissions of NH_3 and virtual emission rates of NH_3.

	CO	NOx	EC
Emissions (ton/yr)*	32,588	17,297	69
	slope to CO	slope to NOx	slope to EC (OBCx1.25)
$NH_3+\Delta NH_4^+$	0.014 (0.55)	0.072 (0.48)	1.46 (0.60)
	from CO	from NOx	from EC (OBCx1.25)
Vehicular NH_3 # (ton/yr)	456	1,245	143
Virtual Emission Rate$ of NH_3 (mg/km)	12	32	3.7

*: Bureau of Environment Tokyo Metropolitan Government, 2017

Slopes are calculated using mol units.

Numbers in parentheses denote coefficients of determination.

#: estimated for Tokyo as emissions multiplied in 2015 by the slope observed.

$: estimated as NH_3 emissions divided by the number of running vehicles and distance (39,122 million vehicles•km) in Tokyo, 2015 (Bureau of Environment Tokyo Metropolitan Government, 2017).

Table 2 Virtual emission rate (VER) and emission factors (EFs) of NH_3 reported after 2009

Method	Location	VER (mg/km) EF (mg/km)	Reference
Regression analysis	Tokyo	3.7–32	this study
tunnel	Shanghai	28	Chang et al. (2016)
tunnel	São Paulo	44	Vieira-Filho et al. (2016)
tunnel	Guangzhou	230	Liu et al. (2014)
tunnel	California	49	Kean et al. (2009)
chassis dynamometer	Italy	2–8 (on-road) 45–134 (cold start)	Suarez-Bertoa et al. (2017)
chassis dynamometer	Italy	4–70	Suarez-Bertoa et al. (2014)
chassis dynamometer	California	46	Livingston et al. (2009)

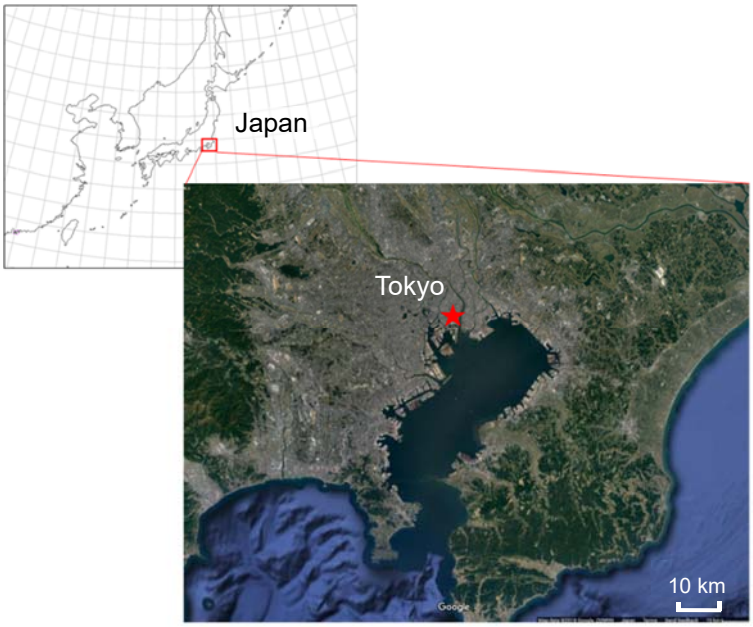

Figure 1 Map showing observation site (red asterisk, 35.67°N, 139.83°E) in Tokyo, Japan.

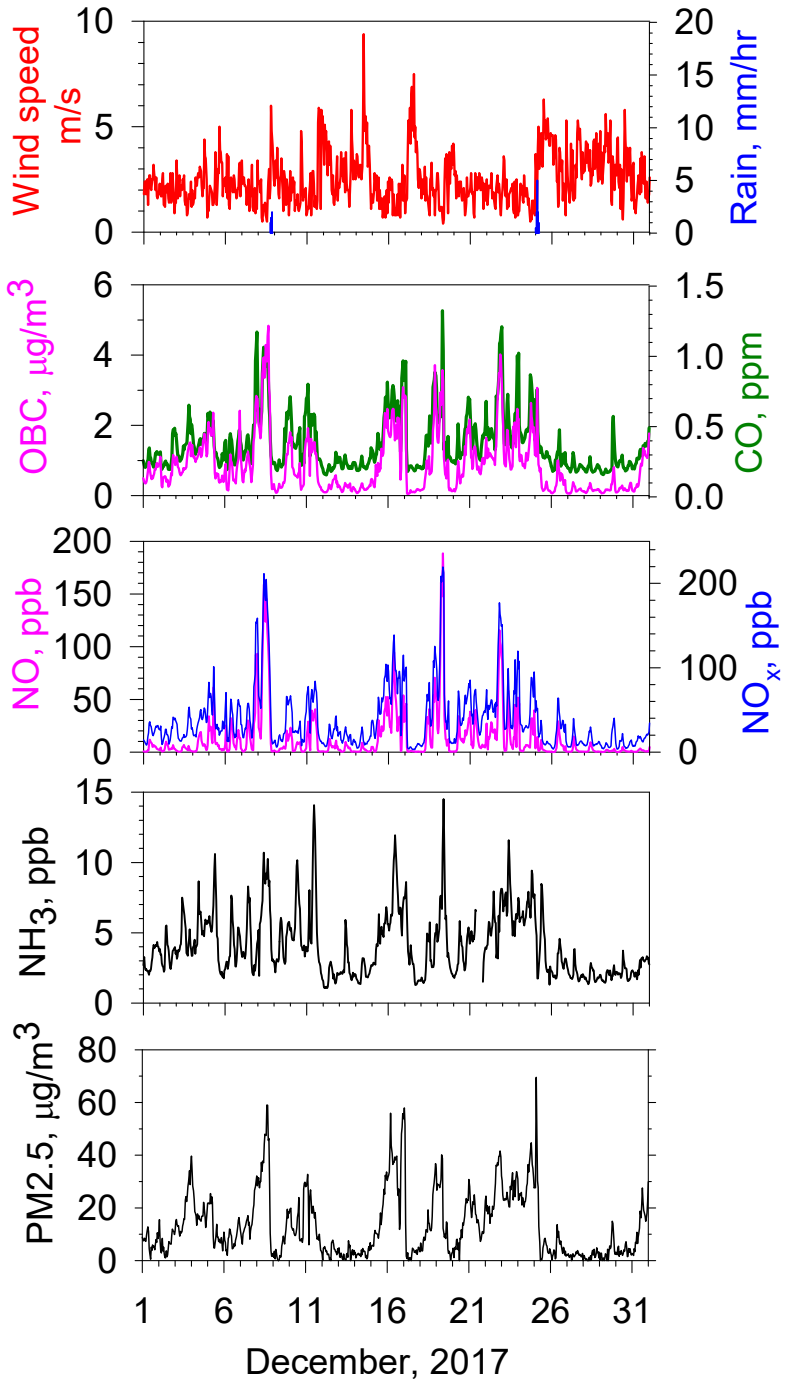

Figure 2 Observation results obtained in Tokyo during December, 2017. Meteorological data are from the Japan Meteorological Agency. OBC represents optical black carbon.

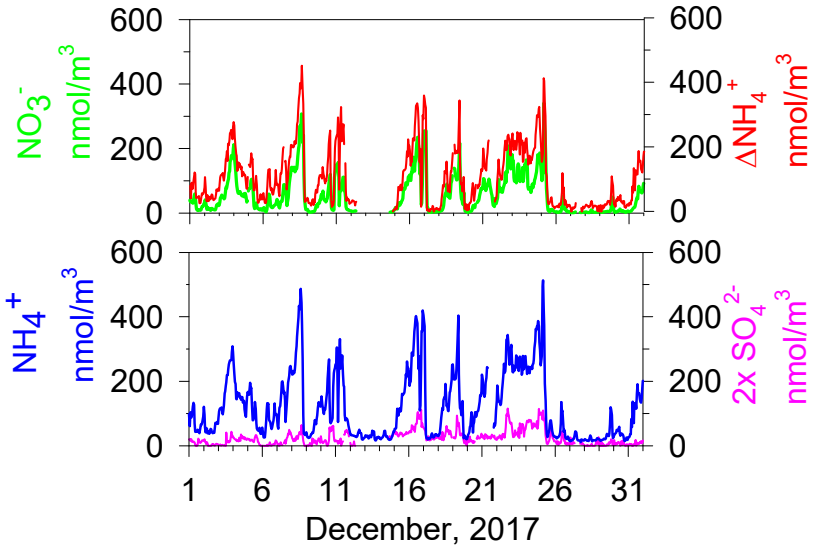

Figure 3 Ionic concentrations of $PM_{2.5}$ in December, 2017. ΔNH_4^+ concentration represents $[NH_4^+]$ minus 2 × $[SO_4^{2-}]$ in nanomoles per cubic meter.

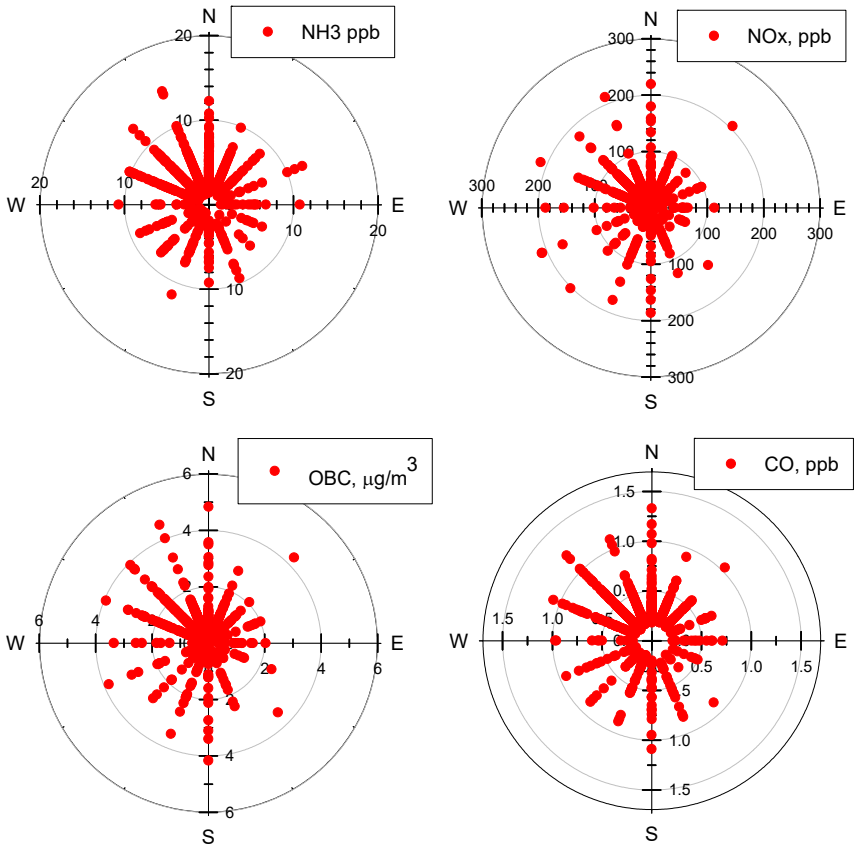

Figure 4 Polar plots of hourly concentrations by wind direction for December, 2017.

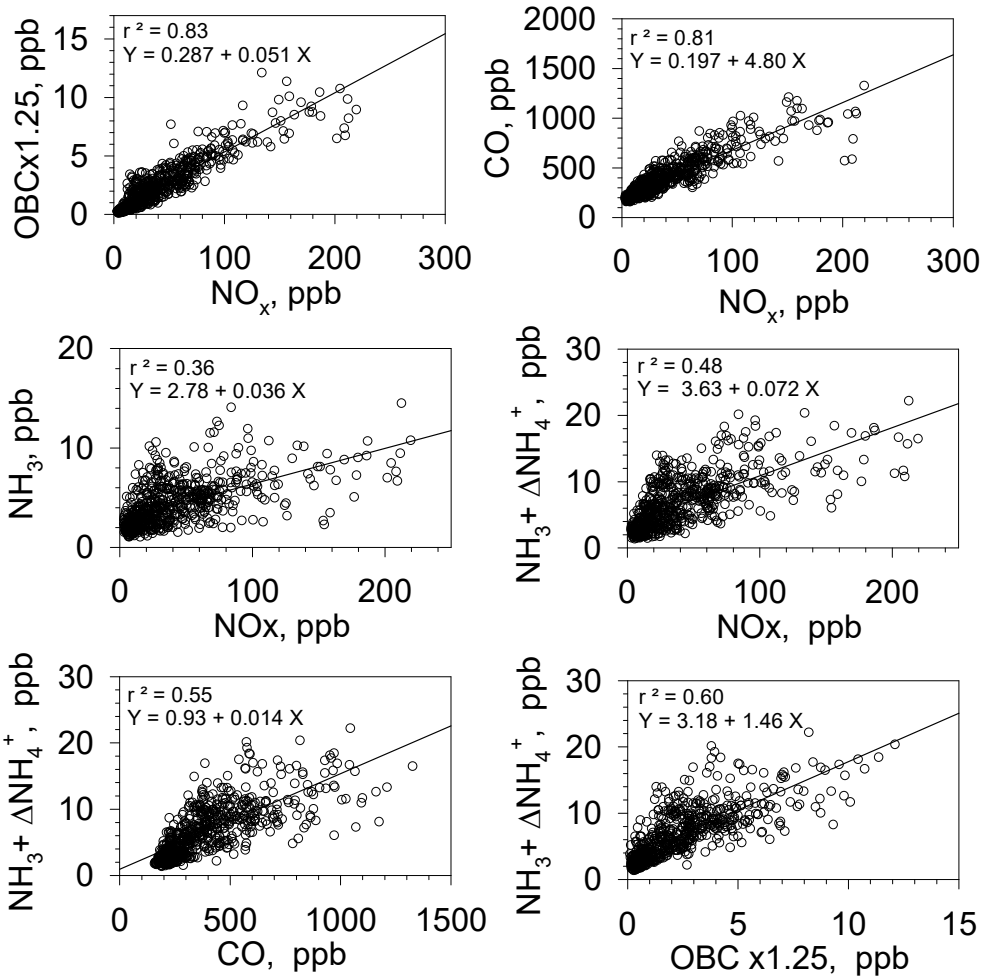

Figure 5 Scatter plots of hourly concentrations in December, 2017. Regression line, equation, and coefficient of determination are also presented in the panels.

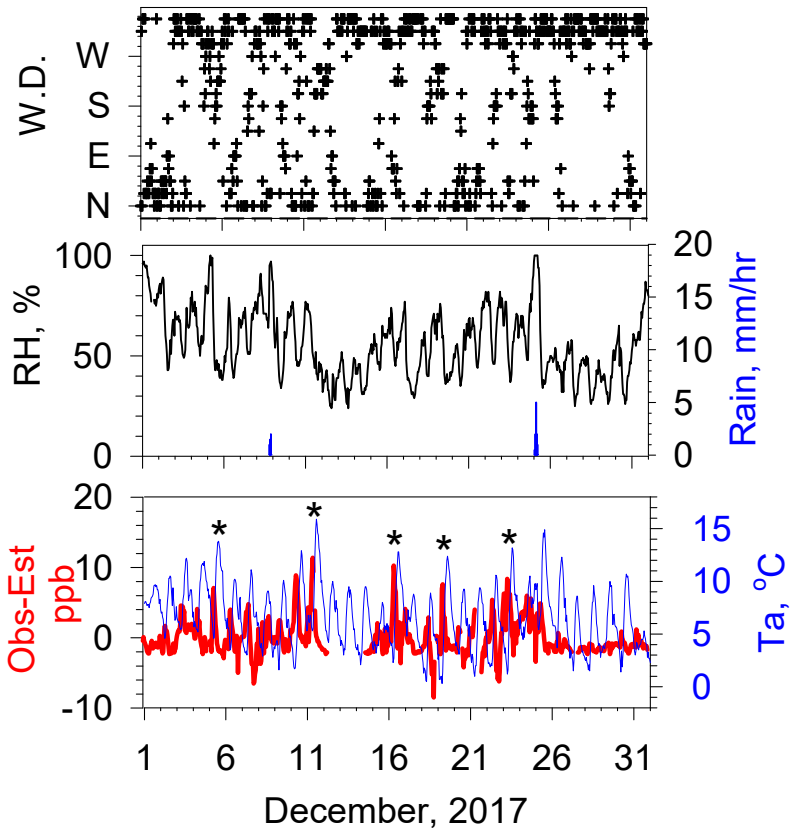

Figure 6 Upper panel: Wind direction. Middle panel: Relative humidity and rain amount. Lower panel: Relation between residual concentration (observed – estimated from the regression with OBC) of NH_3 + ΔNH_4^+ and air temperature. All meteorological data were obtained at the meteorological observatory.