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Measurement report: Short-term variation of ammonia concentration in an urban area: contributions of mist evaporation and emissions from a forest canopy with bird droppings

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Abstract. Short-term variations of NH_3 concentrations in the urban atmosphere are affected by local meteorological conditions and variations of natural and anthropogenic sources. To investigate potential sources and processes of NH_3 variation in an urban area, hourly NH_3 and NH_4^+ concentrations were measured from November 2017 through October 2019 in Nagoya, a megacity located in central Japan. Monthly averages of NH_3 concentrations were high in summer and low in winter. Daily minimum NH_3 concentrations were almost linearly correlated with daily minimum air temperature. In contrast, daily maximum NH_3 concentrations revealed an exponential increase with temperature, suggesting that different processes with air temperature acted during the nighttime and daytime. Short-term increases of NH_3 concentrations of two types were examined closely. The first is a rare but large increase (11 ppb for 2 hr) after mist evaporation during daytime. It is noteworthy that an event of this magnitude was identified only once during two years of observations at Nagoya even though evaporation of mist or fog droplets is expected to be frequent after rain. The second short-term increase was a large morning peak in summer. After selected days were fulfilled with non-wet and weak wind conditions, the amplitude of diurnal variation of NH_3 concentration (daily maximum minus minimum) was analyzed: the amplitude was small (ca. 2 ppb) in winter but it increased from early summer along with new leaf growth. It peaked in summer (up to ca. 20 ppb) during intense addition of droppings from hundreds of crows on trees in the campus assembled before roosting. The high daily maximum NH_3 concentration was characterized by a rapid increase occurring 2–4 hr after local sunrise. Daily and seasonal findings related to the morning peak implied that stomatal emission at the site was responsible for the increase. The yearly difference between daily amplitudes during the two summers was explained by the difference in the input amounts of reactive nitrogen derived from bird droppings and some rain, suggesting that the canopy of a small forest affected by the bird droppings might act as a temporary but strong source of NH_3.

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1 Introduction

Ammonia (NH_3) plays an important role in various atmospheric chemical processes (Behera et al., 2013). For example, NH_3 is the major precursor of fine aerosol particles of constituents such as ammonium sulfate and ammonium nitrate (Seinfeld and Pandis, 2016). In addition, aerosol particle acidity is modified by neutralization with NH_3 (e.g. Murphy et al., 2017; Song and Osada, 2020). Aerosol particles affect human health and climate; therefore, reduction and control of aerosol concentration are desired for many situations (Dockery et al., 1993; IPCC, 2013). As an important gaseous precursor of aerosol particles, NH_3 sources and factors affecting concentrations have been studied for decades. Various natural and anthropogenic sources of NH_3 are known (Sutton et al., 2008; Behera et al., 2013). Although agricultural NH_3 sources (domestic animals, fertilizer loss, etc.) are dominant emitters on a global scale, non-agricultural sources (motor vehicles, industries, garbage, sewage, humans, wild animals, etc.) are also major contributors, especially in urban areas (e.g., Perrino et al., 2002; Pandolfi et al., 2012; Reche et al., 2012; Sutton et al., 2000). For example, in the UK, Sutton et al. (2000) estimated non-agricultural NH_3 emissions that comprised 19% of the total emissions. As a non-agricultural source, seabirds were also recognized as important contributors (Sutton et al., 2000; Blackall et al., 2007; Riddick et al., 2012).

According to the source-receptor analysis of atmospheric NH_3, the effective distance of a strong point source is mostly limited to within a few kilometers (Asman et al., 1989; Hojito et al., 2006; Theobald et al., 2012; Shen et al., 2016). Agricultural facilities and seabird colonies acting as strong NH_3 sources are normally absent in densely populated urban areas. Therefore, a mixture of the various small non-agricultural sources is expected to be the main contributor for local atmospheric NH_3, which potentially acts as a precursor of aerosol particles.

Three-way catalytic converters and selective catalytic reduction systems have been applied as after-treatment devices to reduce air pollutant emissions (CO, hydrocarbons, and NO_x) in vehicular exhausts. However, exhausts from devices often contain NH_3 as a side product created under non-ideal conditions of the after-treatments (Kean et al., 2009; Suarez-Bertoa et al., 2017). Vehicular emissions of NH_3 engender local and regional increases of ambient concentration, especially during stagnant calm wind conditions in some megacities (Osada et al., 2019). In addition, garbage containers have been suggested as a more important contributor than sewage systems in Barcelona, Spain (Reche et al., 2012). Furthermore, emissions from humans and pets, etc., have been implicated as a major nonagricultural urban source of NH_3 (Sutton et al., 2000). Recently, Hu et al. (2014) reported the green space in downtown Toronto, Canada as a potential source of ambient NH_3 based on analyses of local, regional, and temporal variations of NH_3 concentrations. Similarly, Teng et al. (2017) pointed out the importance of NH_3 emissions from urban green space in Qingdao, a coastal urban area in northern China. Nevertheless, NH_3 emission processes from green spaces are not well known for urban environments. Specifically because of green spaces in urban areas, urbanization of the landscape has modified habitable environments of wild animals. Among wild animals found in urban area, crows have adapted well. Numbers of crows have increased in many urban areas in

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recent years (Ueta et al., 2003; Vuorisalo et al., 2003). They form large roosts in scattered forests in urban areas and drop excreta from trees and wires to the ground during pre-roosting assembly and when resting in roosts. However, the potential of NH_3 emissions related to bird droppings in urban green areas has not been studied.

Analysis of hourly concentrations in the atmosphere is useful to explain the sources and processes of ambient NH_3. For example, a temporal correlation between vehicular exhaust species such as NOx, CO, and elemental carbon in urban area has been inferred for vehicular emissions of NH_3 (e.g. Perrino et al., 2002; Nowak et al., 2006; Osada et al., 2019). Moreover, temporal analyses have been made of NH_3 concentrations at grasslands, which have allowed elucidation of the link between the morning peaks and dew formed on plant surfaces during the previous night (Wentworth et al., 2014; 2016). Hourly NH_3 measurements are also a key technique to ascertain the bidirectional exchange of NH_3 through the canopy layer (e.g. Wyers and Erisman, 1998; Nemiz et al., 2004; Kruit et al., 2007; Hansen et al., 2013) because NH_3 transfer is governed by rapidly changing meteorological (sunlight availability, temperature, relative humidity, etc.) and plant physiological (stoma opening and closing, etc.) parameters (Schjoerring et al., 1998; 2000). In fact, NH_3 exchange between plants and ambient air occur mainly through stoma when they open during daytime for photosynthesis (Farquhar et al., 1980). Therefore, the degree and direction of the NH_3 exchange are expected to vary diurnally, highlighting the importance of hourly measurements of related parameters.

To investigate potential sources and processes controlling variation of NH_3 concentration, hourly data of NH_3 and NH_4^+ were measured from November 2017 to October 2019 in Nagoya, central Japan. The data were analyzed by particularly addressing various time scales and the amplitude of diurnal variation in relation to potential reactive nitrogen sources and plant physiology near the site. These data are expected to elucidate ambient NH_3 levels in urban areas with scattered forest affected by large amounts of bird droppings.

2 Observation

Atmospheric observation was conducted at Nagoya University in Nagoya city located in the central area of Honshu Island of Japan (Fig. 1a). Industrial area with busy port is located at about 10 km southwest from the campus of Nagoya University (Fig. 1b). The Nagoya city population is about 2.3 million. Despite the large city population engaged in numerous industrial activities, the air pollution level is not so high. Recent levels of the annual mean $PM_{2.5}$ concentration are approximately 12 $\mu g/m^3$ (Nagoya City, 2019: http://www.city.nagoya.jp/kankyo/page/0000117927.html). The nearest agricultural activities (farming land) are done about 4 km southeast from the campus. Garbage collection in the city requires 1) that burnable waste including food waste and other materials be packed into predesignated plastic bags and 2) that the garbage bags must be put out in a specified collection place by 8:00 a.m. on the regular (twice per week) collection day,

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preventing unnecessary NH_3 emissions during garbage collection. However, the garbage bags might be pecked by crows when deterrents to bird pecking are insufficient, providing the possibility of food supply for adaptation of omnivorous animals, such as crows, in urban areas (Kurosawa et al., 2003). The observation site is located within the campus. Therefore, effects of residential garbage are expected to be small. The annual mean air temperature in Nagoya is 15.8°C; the annual mean rain amount is about 1540 mm (Japan Meteorological Agency: http://www.jma.go.jp/jma/index.html). Seasons in Nagoya have warm-humid summers with southern winds from the Pacific Ocean and cold-dry winters with winds from the northwest, originating from continental Eurasia.

Measurements of NHx (NH_3 and NH_4^+ in fine particles) were taken at Nagoya University (35.16°N, 136.97°E), located in an eastern residential area of Nagoya city. Meteorological data (air temperature, relative humidity, etc.) were obtained from the Nagoya Local Meteorological Observatory, ca. 2 km north from Nagoya University (data available from https://www.jma.go.jp/jma/index.html). NOx concentrations were observed at the Nagoya national air pollution monitoring site located ca. 2 km north from Nagoya University (data available from http://soramame.taiki.go.jp/).

The equipment used for NHx measurements was set in a room located on the seventh floor of the Environmental Studies Hall on the main campus of Nagoya University. The northeastern side of the building faced upslope with a small forest mixed with deciduous and evergreen trees (Fig. 1c). Scattered trees and buildings are located on the other side of the hall. Hourly measurements of NHx were conducted using a semi-continuous microflow analytical system (MF-NH3A; Kimoto Electric Co. Ltd.; Osada et al., 2011). Two identical sampling lines were used to differentiate total ammonium (NH_3 and NH_4^+) and NH_4^+(p) alone after removal by a H_3PO_4 coated denuder. After passing an impactor (cut-off diameter of about 2 μm) and an inner frosted glass tube (one coated; the other uncoated; both are 3 mm inner diameter and 50 cm long), pure water droplets were added to the sample air at 100 μl min^{-1}. The equilibrated sample water was analyzed respectively using a microflow fluorescence analyzer to quantify NH_4^+ in the lines of NH_4^+ and total ammonium. The NH_3 concentration was calculated based on their difference. The sample air flow rate of the NHx system was 1 L min^{-1}. The temporal resolution was ca. 30 min for one pair of NH_4^+ and total ammonium measurements. 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 was checked monthly using NH_3 standard gas at about 4 ppb diluted from 100 ppm (Taiyo Nippon Sanso Corp.). The NHx system was calibrated monthly using a standard NH_4^+ solution prepared from a certified 1000 ppm solution (Fujifilm Wako Pure Chemical Corp.).

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3 Results and Discussion

3.1 Diurnal variation during summer and winter

Results of measurements taken in summer (July, 2018; Fig. 2) and winter (December, 2018; Fig. 3) are presented to explain the relation between NH_3 concentrations and other parameters. In summer (Fig. 2), the Pacific high-pressure system dominates the Japan archipelago, engendering continuous good weather with land−sea breeze cycles: south−southwest winds during afternoon and north−northeast winds after midnight to early morning. When good weather continued, for example of 14–24 July, regular diurnal variations were visible in air temperature and wind speed: high in the afternoon and low in the midnight to early morning. For this period, the diurnal variation of NH_3 concentration was extremely wide. In other words, the difference between maximum and minimum concentration ranges from nearly 10 to more than 20 ppb. In contrast, the NH_3 concentration dropped to a few ppb and remained constantly low for the duration of the rain with small diurnal variation as that found in 4–7 July when Baiu front (East Asian rainy front) was active near the site. A similar tendency of low NH_3 concentration during rainy days was also found during observations, as reported at other places (Roelle and Aneja, 2002; Ellis et al., 2011). Increased contents of soil pore water dilute NH_4^+ in liquid phase and inhibit evaporation as NH_3. Furthermore, wet surfaces of cuticular of leaf absorb ambient NH_3 under high relative humidity during rain. Moreover, NH_3 concentrations were low during the day of higher wind, such as 23 July. The NOx concentrations in July were mostly below 0.02 ppm with no clear correlation with NH_3 variation.

Figure 3 presents data of NH_3 concentrations and other parameters in December 2018. The maximum value of the vertical axis of NH_3 concentrations is 15 ppb, which is half of that in Fig. 2. In winter, the amplitude of the diurnal variation of NH_3 concentration was much smaller than those in summer. Similarly, diurnal variation of wind speed was also not clear in winter because of less sunshine. In contrast to summer, wind speed dependence of NH_3 concentrations were shown more clearly as high concentration under calm wind and low concentration under strong wind conditions because the local source contributed more effectively under stagnant air conditions. Under low winds during winter, a surface inversion layer often developed in the lower atmosphere, preventing vertical diffusion of locally emitted pollutants (e.g., Kukkonen et al., 2005, Osada et al., 2019). It is particularly interesting that temporal variation of daily minimum NH_3 concentration in winter is roughly following the day to day variation of the daily minimum temperature. For example, a higher minimum NH_3 concentration of about 3 ppb during 2−4 December decreased to ca. 1 ppb around 10 December, which corresponds to a decreasing trend of high to low air temperatures for these days.

In contrast to the modest variation in July, NOx concentrations in December showed large variation: it was displayed frequently as more than 0.05 ppm during calm winds. In Fig. 3, the concentration peaks on 3–4, 11, 19–23, and 25–26 December were associated with low winds. High NOx correlates well with high NO concentrations (not shown), suggesting strong contributions of emissions from internal combustion. In addition

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to the NOx variation, the NH_3 concentration increased also under low winds, as described earlier. The similarity of NH_3 temporal variation with NOx suggests that emissions from motor vehicles partly contribute to ambient NH_3 concentration in winter, as reported in Tokyo, Japan (Osada et al., 2019).

Figure 4 depicts average diurnal variations of NH_3 and NH_4^+ concentrations, air temperature (Ta), wind speed (WS) and wind direction for July (left column) and December (right column) in 2018. For July, large NH_3 variation was visible as sharp peaks at around 8 o'clock in the morning. In contrast, broad and modest maximum NH_3 concentrations were observed slightly before noon in December. The start timing of the NH_3 increase was in general accord with the hours of rising temperature and dropping relative humidity. About 2–3 h delay of the NH_3 peak time between summer and winter might be related to the difference of local sunrise: about 4:50 for July and 6:50 for December. The diurnal variation of NH_3 concentration in December showed no large morning peak at rush hour around 7−9 o'clock. Therefore, contributions of rush hour emissions are apparently limited for only those days under calm wind conditions in Nagoya.

Regarding the relations between NH_3 concentration and temperature, dissociation of particulate NH_4NO_3 in the atmosphere is known to be strongly related to temperature: partitioning toward gas phase is favored under higher air temperatures (Mozurkewich, 1993). However, NH_4^+ concentrations in both seasons were not simply a mirror of diurnal temperature variations. Although a small decline of NH_4^+ concentration around noon time in December might result from the dissociation of NH_4NO_3, it is difficult to discern because of the large variation. Another interesting point is the relation between the average air temperature and the lower tenth percentiles for NH_3 concentrations, which both show a maximum at around noon for July and December. This finding is discussed later in greater detail.

3.2 Peak after mist evaporation

Figure 5 presents an example of a sudden increase from 2 ppb to 13 ppb of NH_3 concentration during 2 hr associated with drying mist after rain on 15 November, 2017. This magnitude of NH_3 increase after rain was rarely observed during the study period of two years. Mist is defined as reduced horizontal visibility between 1 and 10 km by suspending water droplets in the atmosphere. In Nagoya, mist is often observed before or after rain. In this case, rain ceased in the early evening of November 14, but the mist continued until 10 am of November 15. Associated with relative humidity dropped sharply from ca. 90% at 10 AM to ca. 40% at noon, mist disappeared and NH_3 concentration abruptly increased as a mirror of temporal variation of relative humidity (RH). Slight enhancement of NH_3 concentration after the rain has been described in some reports of the literature (Roelle and Aneja, 2002; Ellis et al., 2011). They discussed the hypothesis on enhancement associated with the combination of an increase in the ammoniacal nitrogen concentration in the soil and diffusion from the soil to air after the drying pore solution. However, this process requires more time after cessation of rain to decrease soil

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moisture; then, it is too slow to raise the atmospheric NH_3 concentration. In contrast, Wentworth et al. (2014, 2016) reported that rapid increase of NH_3 in the morning was attributed to evaporation of dew containing high concentrations of NH_4^+: the pH of dew was slightly acidic, but near neutral. As their results and the rate shown in Fig. 5, the sudden event of NH_3 concentration increase was regarded as resulting from evaporation of the mist droplets rather than soil-microbe-related processes. A similar rapid NH_3 increase up to 15 ppb during 4 hr was observed in Nagoya after drying hydrometeor and wet surfaces (Osada et al., 2018). During that event, mist was also observed after rain; the rain pH was ca. 5.6 with higher contents of sea salt and Ca^{2+} concentrations. Although the pH of the rain sample of 14 November in this study was unfortunately not known, the volume weighted mean pH of the rain samples from 13–20 November, 2017 was 6.00 at Nagoya City Institute of Environmental Sciences, which is higher than the annual mean (4.99) of rain pH in 2017 (Nagoya City Institute of Environmental Sciences, 2018). In addition, because the duration of mist after the rain was unusually long (16 hr), ambient NH_3 was dissolved more into the mist droplets as a reservoir. Subsequently, a large amount of NH_3 was released from the mist droplets after evaporation, engendering a spike of the NH_3 concentration.

3.3 Emission from tree canopy around the site: relation to bird droppings

Figure 6 presents results of data analysis of NH_3 concentrations. Daily and monthly NH_3 concentrations (Fig. 6, top panel) show clear seasonal variation: high in summer (maximum in August) and low in winter (minimum in January). The monthly minimum (1.6 ppb) in January 2018 was almost equal to that (1.7 ppb) in January 2019, although the monthly maximum (7.0 ppb) in August 2018 was higher than that (4.9 ppb) in August 2019. Furthermore, day-to-day variation was also greater in 2018 than in 2019. To examine the relation with source factors, hourly NH_3 concentrations were analyzed for two subjects: daily minimum and diurnal range (maximum minus minimum) under dry (RH <70%) and weak wind (<3 m s^{-1}) conditions as fulfilled for both daily mean values. Reasons for the meteorological limitations were the following. Wet surfaces on building walls, litter, soil, and leaves can act as NH_4^+ reservoir, which might change ambient NH_3 concentration shortly after evaporation. To avoid this effect, the daily average of relative humidity was set to below 70% for extraction as “non-wet days”. As Figs. 2 and 3 show, the wind speed exhibited a strong effect on local source dilution. Therefore, a day of weak wind was selected to illustrate a stronger effect of the local source.

The daily minimum NH_3 concentrations are shown together with the daily minimum air temperature (Fig. 6, middle panel). As briefly described earlier for Fig. 4, day-to-day variation of daily minimum NH_3 concentration in December covaries with the baseline trend in daily minimum temperature. Analogous to this, the seasonal variation of daily minimum NH_3 concentrations follow closely with the seasonal variation of the daily minimum temperature: high in summer with larger variation, and low in winter with less variation during the month. Monthly averages of daily minimum NH_3 concentrations were higher in summer of 2018 (ca. 4 ppb) than those

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of 2019 (ca. 2.8), but almost identical values (0.7−1 ppb) were obtained for the respective winters. Daily minimum values of concentration and temperature were usually observed in the early morning before sunrise (Fig. 4). Therefore, ambient NH_3 observed under these circumstances (early morning under dry and weak wind) is regarded as derived from very local in origin because the ambient air must stay near the site for several hours. Because of this, NH_3 concentrations are equilibrated with local surfaces that can exchange NH_3 bidirectionally, possibly surfaces of plants and soils. Stomata of plants do not open before sunrise. Therefore, stomatal gas exchange is expected to be negligible. Furthermore, the plant surface is less effective as the NH_4^+ reservoir because of RH <70%. However, pore water or moisture in soil can remain. They might act as a bidirectional exchange source of NH_3. For NH_3 equilibrium between soil pore water and air, known as a compensation point, temperature, pH and NH_4^+ concentrations in the solution are important parameters aside from the atmospheric NH_3 level (Farquhar et al., 1980). We discuss this point later in greater detail.

Another is analysis of the amplitude of diurnal variation as the difference between maximum and minimum of the day (denoted as daily max−min; bottom panel of Fig. 6). As anticipated from the difference between summer and winter in daily NH_3 variations portrayed in Figs. 3 and 4, the daily max−min values were larger in warm months than those in cold months. The daily max−min values were quite large in summer (12.8 ppb as averages from July to August in 2018 and 9.2 ppb in 2019) and small in winter (2.3 ppb as the average from January to February in 2018 and 2.2 ppb in 2019). The increase of the daily max−min values began around May and ended gradually in September for these years. The timing of the start and the end for the large amplitude implies the connection with leaf growth stage of deciduous trees around the site. Although evergreen trees (*Quercus glauca*, *Pinus*, *Machilus thunbergii*, etc.) are mixing, deciduous trees (*Quercus variabilis*, *Zelkova serrata*, Japanese cherry, *Liquidambar*, *Metasequoia glyptostroboides*, *Aphananthe aspera*, etc.) are growing in a small forest (ca. 380 × 30 m) near the site. Fig. 1c and 1d respectively show the tree belt and autumn leaves at the front of the building.

To study the emission potential of NH_3 from various reservoirs (i.e. apoplastic fluid of plants and soil pore water), the compensation point model is applied for comparison by estimating from temperature and thermodynamic equilibrium among various surfaces and the atmosphere. The compensation point (X) is predicted as to the following.

$$X = \frac{161500}{T} \exp\left(-\frac{10380}{T}\right) \Gamma \qquad (1)$$

Therein, T denotes the temperature of the surface reservoir in Kelvin, Γ represents the emission potential equal to the concentration ratio between $[NH_4^+]$ and $[H^+]$ in the surface reservoir ($\Gamma = [NH_4^+]/[H^+]$), and X is given in units of parts per billion or in nanamoles per mole (Nemitz et al., 2004). Greater emission potential engenders higher

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equilibrium NH_3 concentration with the surface for the same temperature. Higher temperature raises the equilibrium NH_3 concentration as gas phase.

Apoplastic fluid in stoma of plant and pore water in soil are assumed as the major reservoirs of NH_4^+. To equilibrate apoplastic fluid with ambient atmosphere, stoma must be opened, which is regulated by plant physiology relating to photosynthesis. Consequently, the daily maximum NH_3 concentrations were observed at about 2−4 hr later from sunrise. In other words, the initial stage of stoma opening is synchronized well with the timing of the morning increase. The daily maximum NH_3 concentrations are shown versus the average air temperature of the day (Fig. 7a). The leaf temperature was not measured in this study. The ambient temperature was used as a surrogate of the leaf temperature. In Fig. 7a, two hypothetical compensation curves are also shown using Γ of 1500 and 200. Above an air temperature of about 10–15°C, most observed data were shown between these two curves, suggesting that the Γ of the forest canopy around the site was in the range of 200–1500. According to compilation by Zhang et al. (2010) and by Massad et al. (2010), Γ in the literature was several tenths to 10^5 depending on the richness of reactive nitrogen available for the plant, types of ground, and vegetation. For stomatal emission potential of NH_3, the range of 300–3000 for trees of deciduous and evergreen forest was proposed by Zhang et al. (2010). A similar range of the values was also listed by Massad et al. (2010).

Furthermore, daily minimum NH_3 concentrations are also shown versus the minimum air temperature of the day (Fig. 7b). As described earlier, the condition observed for daily minimum NH_3 concentration is connected to the emission potential from soil around the site because stomatal emissions are negligible. Although soil temperatures were not measured in this study, the minimum air temperature was used as a surrogate for nighttime soil temperatures. In Fig. 7b, two hypothetical compensation curves are shown using Γ of 500 and 200. Observed data were in the range of the hypothetical compensation curves only for minimum air temperature above 20°C. Below 20°C, most observed data were over the curve for Γ of 500. Two possibilities are considered for these relations. One is that higher Γ for soil is responsible for winter because litter from deciduous trees can be decomposed by microbial activity. Also, subsequent NH_4^+ production raised Γ higher than 500. Another possibility is a contribution from vehicular emissions because of frequent stagnant air pollution on elemental carbon in winter in Nagoya (Yamagami et al., 2019).

As shown separately in Fig. 7, concentrations of NH_3 in summer of 2018 were higher than those of 2019 for comparison with the same temperature. Γ for the canopy of a site varies with various parameters such as seasonal variation of plant's stage of growth and supply of reactive nitrogen (Schjoerring et al., 1998; 2000; Massad et al., 2010). Senescent and mature leaves have high potential for NH_3 emissions (Mattsson and Scjoerring, 2003). For deciduous trees in this study, new leaves start to grow in April and mature after June. They turn red in November. The duration of active leaf of deciduous trees roughly accords with the season of the higher daily max-min shown in Fig. 6c. However, the values of the daily max-min in summer differed between 2018 and 2019, with no great

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change of trees in the campus. Therefore, deposition of reactive nitrogen at the site might be the reason for the difference. Wet deposition (rain) is the major input of reactive nitrogen. According to reports of rain composition in Nagoya City (http://www.city.nagoya.jp/shisei/category/53-5-22-8-1-2-0-0-0-0.html. Personal communication from Yamagami and Nakashima, 2019), monthly average wet depositions of NO_3^- from May to September were 2.3 mmol m^{-2} in 2018 and 2.0 mmol m^{-2} in 2019, respectively. Similarly, monthly average wet depositions of NH_4^+ during May–September were, respectively, 2.9 mmol m^{-2} in 2018 and 2.4 mmol m^{-2} in 2019. Wet depositions of these species during warm months were slightly higher (ca. 15%) in 2018 than those in 2019. However, the observed differences (ca. 30%) in the average daily max-min between 2018 and 2019 were almost double for the difference of wet depositions, requiring more input difference.

To fill the gap of the yearly difference, the possibility of bird droppings at the site is discussed below. From June or July to September or October, rooftops of the buildings and trees in the campus are used frequently by large numbers, actually hundreds, of crows for pre-roosting assembly or flight line assembly in early evening before going to roost, presumably located near the campus. Normally, a murder of crows stays a short time (mostly less than 2 hr). They then leave to their primary roost area (Nakamura, 2004). More crows gathered in the murder in the early evening in 2018 than in 2019 based on visual impressions of the crow density on the trees and building rooftops. Some crows unusually stayed overnight on the campus in the summer of 2018, but that behavior was rarely observed in 2019.

Bird droppings are rich in reactive nitrogen: nitrogen contents in dry weight of droppings are 3.5% for chickens (Nakamura and Yuyama, 2005) and 4.7% for crows (Fujita and Koike, 2007). The major reactive nitrogen of bird droppings is the uric acid, which is readily transformed into NH_4^+ by microbial activity in the soil. It is later incorporated and used by plants through roots. To evaluate the effects of bird droppings at the site, the flux of reactive nitrogen added by bird droppings over the unit area ($Flux_{bd}$, mol m^{-2} day^{-1}) is estimated as shown below.

$$Flux_{bd} = \frac{Freq \cdot W \cdot R}{14} \quad (2)$$

In that equation, *Freq.* (number m^{-2} day^{-1}) represents the input frequency of excreta shot per day over unit area, *W* (g $shot^{-1}$) stands for the dry weight of excreta per an excreta shot, *R* (%) denotes the nitrogen content per dry excreta weight, and 14 is the atomic weight of nitrogen for conversion. For simplicity, the following values are used to estimate $Flux_{bd}$: *Freq* is once per day per square meter, *W* is 1 g per shot, and *R* is 4.7% (Fujita and Koike, 2007). Evaluating the relevance to the assumptions is difficult, but it is believed to the best guess from the dropping situations observed around the building (Appendix Photograph 1). The estimated result is 3.4 mol m^{-2} day^{-1}, which is converted as ca. 100 mmol m^{-2} $month^{-1}$. This value is nearly 40 times higher than the NH_4^+ flux

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by rain. $Flux_{bd}$ includes large uncertainty depending on the crow density and their habitat in the campus. However, it is useful for comparison with reactive nitrogen flux by rain. Even assuming *Freq* was one-tenth of the initial assumption above (0.1 number m^{-2} day^{-1}), $Flux_{bd}$ is still larger than the NH_4^+ flux by rain. In this study, the dense area of bird droppings was not so large in the campus. However, the excess inputs of reactive nitrogen brought by crows to a small area might engender strong local emissions of NH_3 from the soil and through the forest canopy. Indeed, Fujita and Koike (2007) pointed out that jungle crows brought substantial amounts of nutrients to their roost of fragmented forests in an urban area. Populations of crows and the distribution of crow roosts vary with food availability and trees for sleeping and breeding. Crows have adapted well to urban areas. Therefore, they are ubiquitous. Their populations are often increasing (Ueta et al., 2003; Vuorisalo et al., 2003). Through their habits of roosting in scattered small forests in urban areas, reactive nitrogen supplied by crows might be oversaturated for tree growth and emitted from the canopy. Large and continuous NH_3 sources are limited for recent urban areas, except for automobile exhaust. Therefore, emissions from the tree canopy reinforced by bird droppings have become more important for neutralizing acidic urban aerosol particles.

4 Summary and Conclusions

Hourly measurements of NH_3 and NH_4^+ were conducted from November 2017 through October 2019 in Nagoya, central Japan. Monthly average NH_3 concentrations were high (7.0 ppb and 4.9 ppb, respectively, for August in 2018 and 2019) in summer and low (1.6 ppb and 1.7 ppb for January 2018 and 2019, respectively) in winter. During the study period, a surge event (11 ppb during 2 hr) was observed after mist evaporation during daytime, which was very rare at Nagoya, even though evaporation of mist or fog droplets are expected to be frequent after rain. A plausible condition of the surge event was discussed in terms of composition and pH of rain. The amplitude of diurnal variation of NH_3 concentration (daily maximum minus minimum) was small (ca. 2 ppb) in winter and large (ca 20 ppb) in summer. The daily max-min increased from late spring synchronized with new leaf growth and peaked in summer during intense addition of droppings from hundreds of crows assembled on trees and rooftops near the site before going to their roosts. The large diurnal variation of NH_3 concentration was characterized by a peak at 2–4 hr after sunrise. The timing of seasonal and daily increases of the late morning NH_3 peak imply that reactive nitrogen inputs from crow droppings and rain increased NH_3 emissions from the tree canopy. Preliminary estimates suggest that reactive nitrogen input by crow droppings was greater than the effect of wet deposition. Therefore, as populations of crows increase in some urban areas through adaptation, the reactive nitrogen supplied by crow droppings might become an increasingly important source of NH_3 emissions in urban areas.

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355 *Data availability.* All data supporting these study findings are available in this article and its Supplement or from the corresponding author on request.

Author contributions. KO conducted all of this research.

Competing interests. The author has no conflict of interest related to this report or the study it describes.

360 **5 Acknowledgments**

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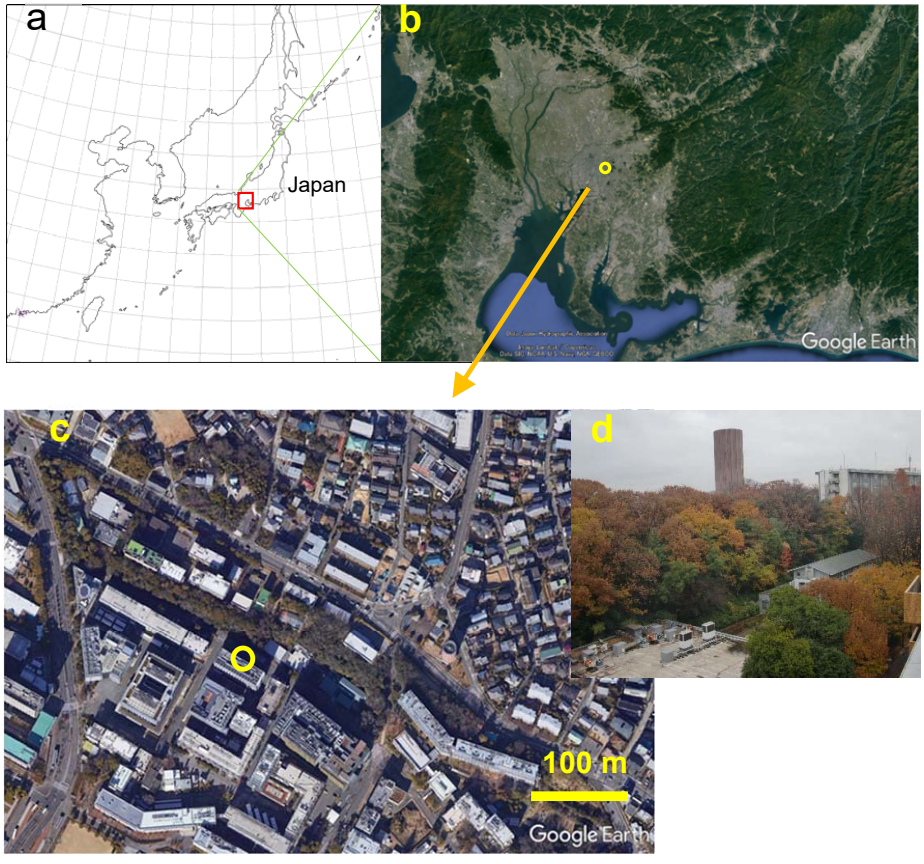

Figure 1(a): Map of the area around the observation site. (b): Satellite image (from © Google Earth) near Nagoya University (open circles: 35.67°N, 139.83°E) in Nagoya, Japan. Local meteorological station (air temperature, relative humidity, rain, wind speed and direction, weather records) and national air pollution monitoring site (NOx) are located at about 2 km north from the site. (c): © Google Earth close up image of the campus. NHx measurements were conducted at the Environmental Studies Hall (open circle in c). d: Outside view from the seventh floor to the northeast taken in early December.

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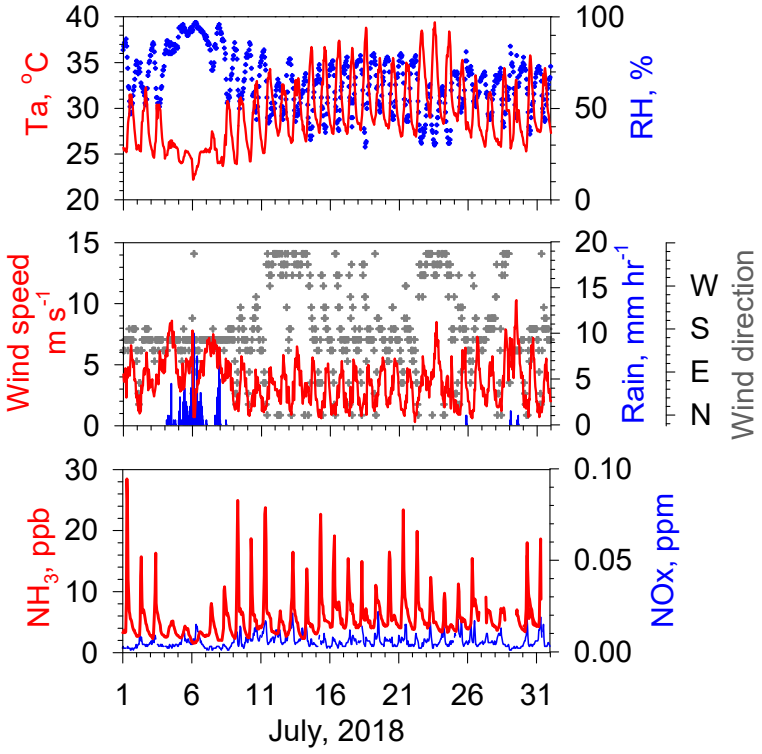

Figure 2 NH_3 and NOx concentrations with meteorological data in Nagoya during July, 2018.

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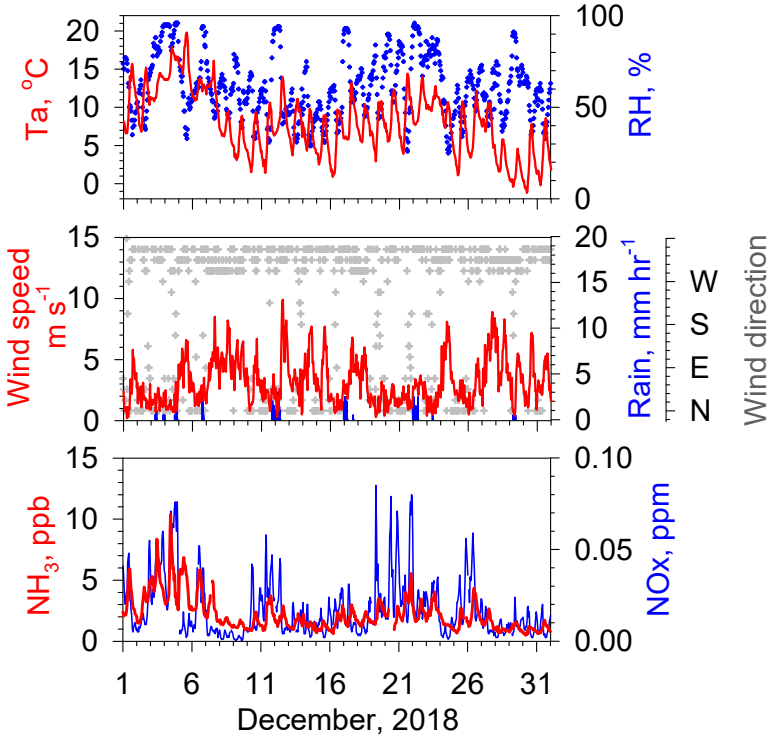

Figure 3 Same as Fig. 2 but for results during December, 2018. The maximum of the vertical axis for NH_3 is reduced to 15 ppb.

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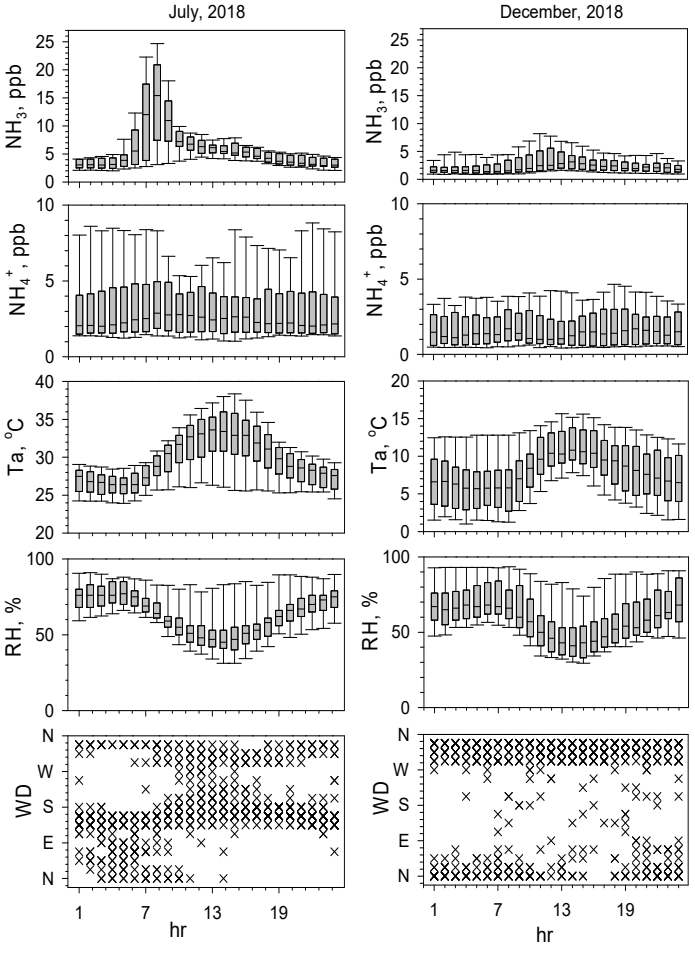

Figure 4 Hourly box plots of NHx concentrations and meteorological parameters (T_a, air temperature; RH, relative humidity; WD, wind direction) during July (left) and December (right), 2018. The lower boundary of the box represents the 25th percentile, the line within the box marks the median, and the upper boundary of the box represents the 75th percentile. Whiskers above and below the box respectively show the 90th and 10th percentiles.

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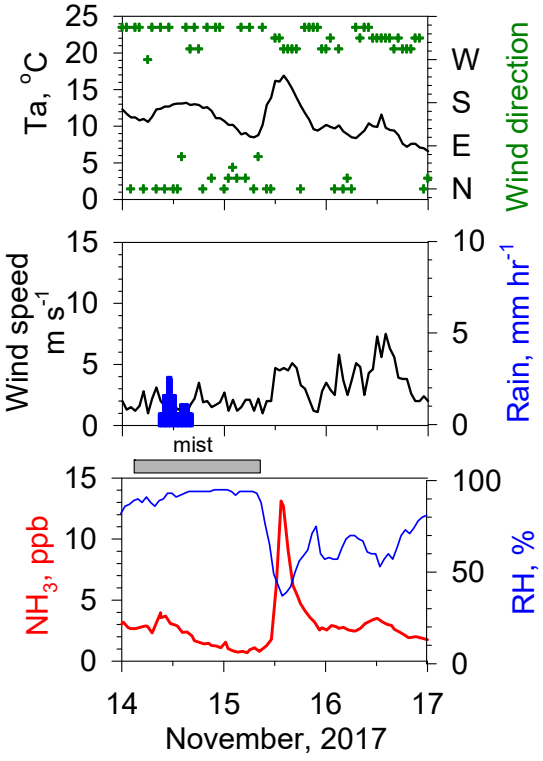

Figure 5 Sudden increase of NH_3 concentrations after a rain–mist event in November, 2017.

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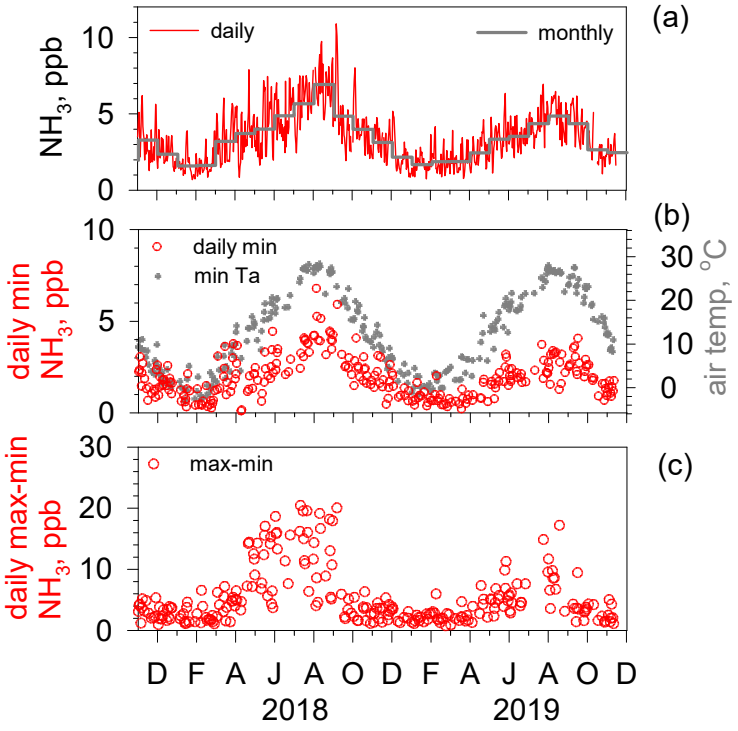

Figure 6(a): Daily (red) and monthly (gray) NH_3 concentrations observed at the site. (b): daily minimum NH_3 concentrations (red circle) and minimum air temperature (gray plus) for the day of both fulfilled average relative humidity below 70% and daily average wind speed below 3 m s^{-1}. (c): range of diurnal NH_3 concentrations (max-min: red circle) for the day of both fulfilled average relative humidity below 70% and daily average wind speed below 3 m s^{-1}.

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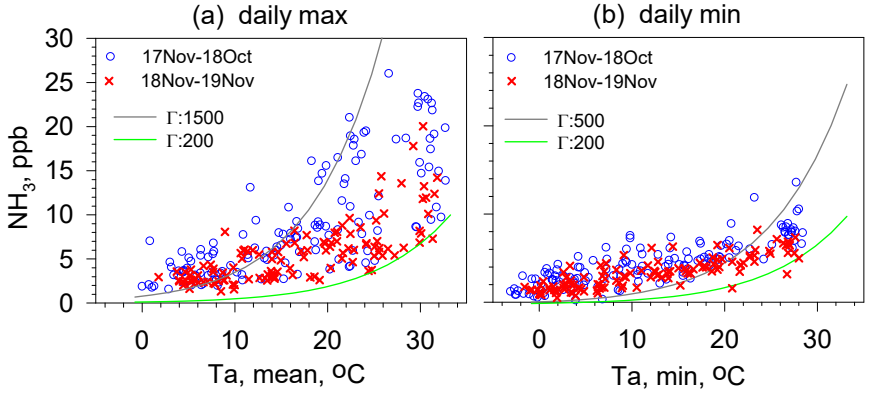

Figure 7(a): Scatter plot showing the maximum NH_3 concentration and average air temperatures for days of both fulfilled average relative humidity below 70% and daily average wind speed below 3 m s^{-1}. (b): Scatter plot showing the daily minimum NH_3 concentration and minimum air temperature for days of both fulfilled average relative humidity below 70% and daily average wind speed below 3 m s^{-1}. Green and gray curves show compensation points for the temperature using Γ values shown in the panels.

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(a) (b)

Appendix Photograph 1 Crow droppings (photographs taken at the same place on (a) July 28, 2018; (b) October 17, 2019) in front of the Environmental Studies Hall of Nagoya University.