Author's response to Referee #1

General Comments to the Author

The author reports two years of NHx and NH_4^+ data collected in Nagoya, Japan, and uses it to infer local sources of NH_3, such as traffic, plant stomata, soil pore water, and bird droppings. Observations of NH_3 are consistent with other studies (e.g., daytime maximum, strong seasonal variations), and data are presented in a fairly clear manner. The most novel part of the manuscript is the finding that bird droppings could be a relevant local source of NH_3 in urban areas. Although the manuscript is fairly well written, phrasing and grammar could be improved throughout the manuscript. Portions of the data analysis and discussion could be expanded to improve the manuscript, as noted below. Nonetheless, this measurement report contains valuable insight for understanding urban ammonia sources, and publication is recommended once the comments below are addressed.

General Comments:

Most of the data analysis only considers parts of the data set (e.g., July/December 2018, and RH < 70% when wind speed < 3 m/s). A more holistic look at the entire data set might give additional insight on various sources.

For example, the morning NH_3 peak ~2-4 hours after sunrise is decoupled from the maximum ambient temperature which is inconsistent with bi-directional exchange (i.e., stomata and soil) driving NH_3 emissions, since these emissions should peak with temperature. Is it possible the lack of a coincident peak of NH_3 and temperature is caused by enhanced vertical mixing (i.e., dilution) later in the day?

Furthermore, examining days with presumed surface wetness (i.e., RH > 70%) might provide insight on whether or not the morning peak in Fig. 4 (top left) is related to evaporation of surface wetness. In other words, the different peak times for NH_3 and temperature, as well as the impact of surface wetness evaporation should be explored further.

Response:

I thank anonymous Referee #1 for constructive comments exploring the cause of the morning NH_3 peak described in the manuscript. I asked a native-English proofreader to review the revised manuscript, particularly for clarity in preference to subjective style. Modified words and sentences in the text have been highlighted as yellow in the manuscript.

To cover a longer span and details of seasons, I modified Fig. 4 including the monthly average of diurnal variations for every 3 months from December 2017 through September 2019. I also added a new Fig. 5 to discuss the effects of direct sunshine on the morning peak. Related to the new figures, I have added additional discussion of the boundary layer height (BLH). Unfortunately, data related to BLH were not available for this study. I agree that dilution effects

during daytime reduce the NH_3 concentration. Diurnal variation of NH_3 concentrations for cloudy days shows a coincident peak with air temperature. In addition, strong effects of the inversion layer on NH_3 concentration must be limited for days of calm winds in winter, when the morning peak was absent.

Specific comments

Comment #1:

Line 108 – what was the measurement height above the ground?

Response:

The inlet height was ca. 26 m above the ground. I have added this explanation to the text and to the caption of Figure 1d.

Comment #2:

Lines 108 to 124 – what is the approximate residence time of the air sample, and distance it travels from the inlet, before it comes into contact with the water droplets (i.e., is dissolved)? Is it possible that some relevant fraction of NH_3 partitions to the surface of the sampling inlet, which could desorb later at high temperatures and/or lower NH_3 concentrations? In other words, has collection efficiency of the system been tested?

Response:

The distance from the end of the denuder glass tube to the mixing point of water droplets is approximately 10 cm. Because the sample air is transported through the PTFE tube (id: 3 mm) at a flow rate of 1 L min^{-1}, the residence time from the end of the denuder to the mixer is ca. 0.04 s, which means that water droplets immediately contact with the sample air after leaving the denuder glass tube. The collection efficiency of the system was higher than 95% for the condition employed in this study. I added these points to the revised text.

Comment #3:

Lines 144 to 145 – presumably diurnal variation in wind speed is not as clear in winter time due to the lack of sea breeze circulations, although the current phrasing implies a direct link between sunlight and wind speed. Recommend rephrasing to clarify that it's not sunlight that's directly impacting wind speed.

Response:

I revised this part of the text as suggested.

Comment #4:

Section 3.1 – the analysis focuses on only two months (July and December 2018). Is there a reason that more months weren't considered (e.g., Dec 2017, July 2019, Nov/Jan, June/Aug) when trying to interpret seasonal differences? Considering these additional months would likely make the analysis more representative of the winter/summer seasons.

Response:
To present more data, I renewed Fig. 4 to include the monthly average of diurnal variations for every 3 months from December 2017 through September 2019.

Comment #5:
Section 3.2 – there is a lot of discussion about mist/droplet pH; however, the impact of pH on NH_3 release from evaporating mist/droplets is not made clear. It would be helpful to provide a few sentences explicitly stating how NH_3 emissions from droplets are impacted by pH.

Response:
Additional explanations of chemical composition and pH were added to the manuscript, highlighting effects on NH_3 emission after the evaporation of mist droplets.

Comment #6:
Lines 226 to 227 – the assumption is that the air being sampled before sunrise under low wind conditions reflects local sources. However, is it possible that the nocturnal boundary layer is sufficiently shallow during these times, such that the sampling inlet on the 7th floor is above the nocturnal boundary and is decoupled from surface sources?

Response:
Although a detailed time evolution of the nocturnal boundary layer was not known for the site, the sampling inlet (26 m above the ground) is presumed to be located well within the boundary layer. I added discussion specifically related to the controlling factors of NH_3 concentration related to the boundary layer height, dry deposition of NH_3, and local emissions.

Comment #7:
Lines 303 to 306 – the description of crow abundance and behavior is very anecdotal. A more detailed description on what is meant by terms like "visual impression" and "rarely observed" would be useful.

Response:
I modified the sentence related to appendix photograph 1 and deleted the sentence that used

“rarely observed” from the revised manuscript.

Comment #8:
Line 322 – is this a unit conversion error (3.4 mol m^{-2} day^{-1} to 100 mmol m^{-2} $month^{-1}$)?

Response:
I corrected the unit of deposition (3.4 mmol m^{-2} day^{-1}).

Comment #9:
Figure 1b – please add a scale for distance.

Response:
I added a scale for distance in Figure 1b to the revised manuscript.

Author's response to Referee #2

General Comments to the Author

The author presents the analysis of 2 year hourly NHx data in Nagoya, Japan suggesting trends in ambient NH_3 are due to mist evaporation and the N input of bird dropping into the surrounding vegetation. This manuscript aims at better characterizing NH_3 emission sources in urban areas, which is needed. This study shows the increasing importance of bird guano as a significant source of NH_3 is also true for urban areas where high populations of fowl can congregate. The long-term measurements of NHx for this region are valuable and the analysis is sound but somewhat incomplete. I would recommend publishing this manuscript after some revisions.

Response:

I thank anonymous Referee #2 for valuable comments on the overall clarity of the intended message conveyed by the manuscript. We have improved the manuscript according to comments from reviewers. Modified words and sentences have been highlighted as yellow in the revised manuscript.

Major comment #1:

What was the measurement height of NHx? Could the repeated morning increase also be due to the increase in the boundary layer height?

Response:

The inlet height was 26 m above the ground. I added this point to the manuscript and the caption of Fig. 1d. Referee #1 also pointed out the aspects of time change of the boundary layer height. I agree that the dilution effect during daytime reduces NH_3 concentration. Unfortunately, no micrometeorological observation was conducted during this study. Instead, I added some discussion about the controlling factors of NH_3 concentration related to boundary layer height, dry deposition of NH_3, and local emissions.

Major comment #2:

The correlation to NOx measurements is useful in getting a sense of how much vehicles are contributing to total NH_3 emissions. Since, as the author mentions, NH_3 can easily react to form NH_4^+, do the correlations of NOx to NHx look similar? since NHx is a better-conserved tracer for all emitted NH_3.

Response:

As the lowest panels in Figs. 2 and 3 show, temporal variation of NH_3 concentration did not correlate well with NOx concentration. Similarly, NHx and NOx showed no good correlation. I added more discussion on this point using supplemental Figure 1, which shows scatter plots between NHx and NOx as well as CO and NOx in December 2018 and 2019, respectively.

Major comment #3:

Related to the comment above, the discussion around seasonal and interannual variations is focused on NH_3, which may underestimate the impact of local sources if any NH_3 is reacted to form NH_4^+ - especially at the time resolution of the measurements. Since the study includes measurements of NH_3 and NH_4^+ (not an easy task) for such an extensive period, what do the variations in total NHx (and what % NHx is NH_3) look like? are the conclusions the same?

Response:

I added more data and discussion on NH_4^+ and NHx, such as average diurnal variation of NH_4^+ in new Fig. 4, seasonal variation of NH_4^+, and the fraction of NH_3 to NHx in the new Fig. 7.

Major comment #4:

In section 3.2, there is a brief mention of some of the other chemical components in rain. The NH_4^+ content is reported later in section 3.3. Based on the reported pH and assuming the rain and mist content have similar NH_4^+ content, could the fraction of NH_3 emitted from mist evaporation be calculated using the expression for dew? Does this match the observed increase in NH_3?

Response:

According to an acid rain report by Nagoya City Institute of Environmental Sciences (NCIES), the volume weighted mean pH of the weekly collected rain samples from 13–20 November, 2017 was 6.00. Based on major ionic data reported for the sample, Frac (NH_4^+) proposed in Wentworth et al. (2016) was estimated as 0.14, which suggests the possibility of NH_3 evaporation. However, rain was observed twice on the 14th (9 mm) and 18th (16.5 mm) during the sampling period. Unfortunately, the chemical composition of individual rain was not known. In addition, the amount of mist droplets of the event was unavailable. Therefore, the amount of NH_3 evaporated from mist droplets could not be estimated. The statement of "A similar rapid NH_3 increase up to 15 ppb during 4 hr" was related to another event which occurred in December 11, 2015. For the event in 2015, detailed data about the rain composition were collected; we were able to use it. In the present manuscript, the date of the event in 2015 was added. The description of sea salt and Ca^{2+} for the rain in 2015 was deleted to avoid confusion. In addition, the explanation of NCIES data was rewritten as presented above.

Major comment #5:

There is no discussion on the role of cuticular deposition, which is generally represented as a constant NH_3 sink (Sutton et al. 1995, 1998; Flechard et al. 1999) in forest canopies. From the photograph of bird dropping, there also appears to be an increase in vegetation. The increase in leaf surface area could potentially increase the amount of NH_3 dry deposited to the cuticles, also reducing overall ambient NH_3 concentrations. The author discusses the potential difference in N inputs between years and is correct that both soil and leaf stoma can act as reservoirs. Can the author also comment on changes in the local NH_3 sinks between years as well that would also affect the overall ambient NH_3 concentrations?

Response:

I agree with the importance of cuticular deposition on NH_3 concentration. Brief discussion of the importance of cuticular deposition and its variation in 2018 and 2019 were added to the revised manuscript.

Major comment #6:

Work by Decina S.M. et al (Ponette-González A.G., Rindy J.E. (2020) Urban Tree Canopy Effects on Water Quality via Inputs to the Urban Ground Surface. In: Levia D., Carlyle-Moses D., Iida S., Michalzik B., Nanko K., Tischer A. (eds) Forest-Water Interactions. Ecological Studies (Analysis and Synthesis), vol 240. Springer, Cham) shows vegetation in urban environments tend to concentrate pollutants and input them into the ground surface. The author makes an important point that for NH_3 this exchange is bi-directional.

Response:

I added relevant discussion with this reference to the last part of section 3.3.

Major comment #7:

The discussion around comparing the estimated compensation point of soil/leaf surface with ambient NH_3 concentration does not account for the transfer velocity that ultimately determines the magnitude (and likelihood) of the exchange. Massad et al. (2010) provide a detailed description of this parameter. Would the conclusions be the same when accounting for the transfer velocity?

Response:

I agree that the ambient NH_3 concentration depends on various parameters including the transfer

velocity. Data related to flux estimation were not available for this study. Further study including flux estimations is necessary to evaluate the impact of bird droppings on urban NH_3 emissions. Nonetheless, important suggestions can be made for potential sources at the site. I added need of further data to evaluate NH_3 exchange.

Minor suggested edits #1:
The article would benefit from another round of general grammar and writing edits.

Response:
I asked an experienced native-English speaking proofreader for further improvement and clarification of the text of the revised manuscript. Although preferences for style can be subjective, we hope that the changes will clarify all points for all readers.

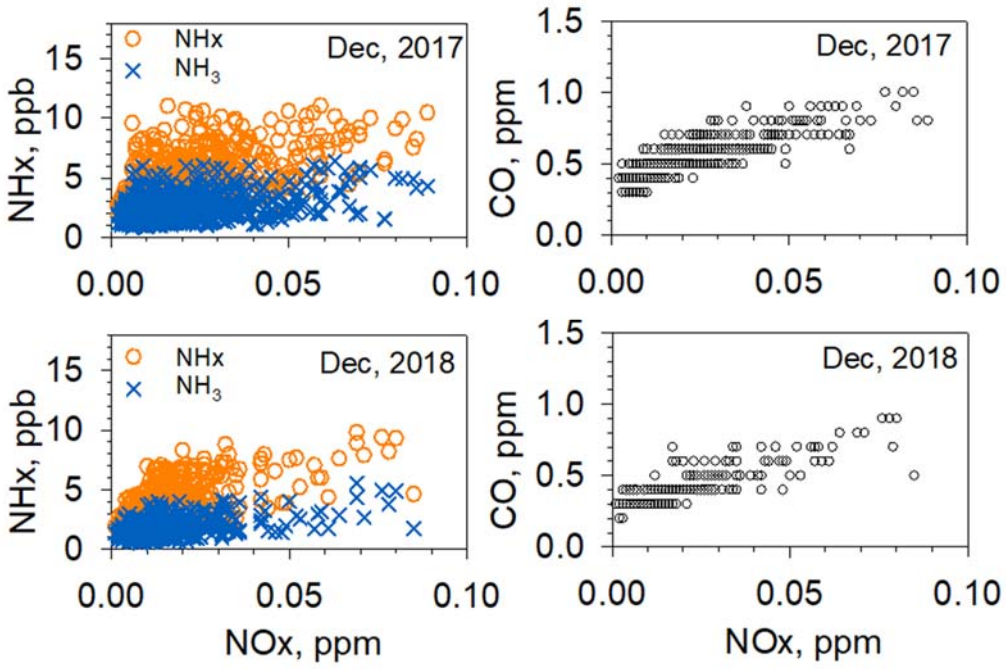
Minor suggested edits #2:
Include dates in Figure captions: Figure 5. Impact of the rain–mist event on the ambient NH_3 concentrations from 14 to 17 November 2017.

Response:
The caption of the new Fig. 6 (previously Fig. 5) was modified as the reviewer has suggested.

Minor suggested edits #1:
Measurements highlighting the importance of bird guano as a significant NH_3 source is relatively recent, the authors should also include the work of Croft, B.; Wentworth, G. R.; Martin, R. V.; Leaitch, W. R.; Murphy, J. G.; Murphy, B. N.; Kodros, J. K.; Abbatt, J. P. D.; Pierce, J. R. Contribution Of Arctic Seabird-Colony Ammonia To Atmospheric Particles And Cloud-Albedo Radiative Effect. Nature Communications 2016, 7, 13444.
Work by Hrdina, A. H. I.; Moravek, A.; Schwartz-Narbonne, H.; Murphy, J. G. Summertime Soil-Atmosphere Ammonia Exchange In The Colorado Rocky Mountain Front Range Pine Forest. Soil Systems 2019, 3(1) (Special Issue "Formation and Fluxes of Soil Trace Gases") also supports the dynamic range of soil emission potentials chosen by the author

Response:
These references were cited in the revised manuscript.

Supplement Figure



Supplement Figure 1 Scatter plots between NOx and NHx (NH_3 + NH_4^+), and NOx and CO concentrations. Upper row, December, 2017; lower row, December, 2018.

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

Kazuo Osada[1]

[1] GSES, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

Correspondence to: Kazuo Osada (kosada@nagoya-u.jp)

Abstract. Local meteorological conditions and natural and anthropogenic sources affect atmospheric ~~Short-term variations of~~ NH_3 concentrations in ~~the~~ urban areas~~atmosphere are affected by local meteorological ogical conditions and variations of natural and anthropogenic sources~~. To investigate potential sources and processes of NH_3 variation in ~~an~~ urban areas, ~~hour~~ hourly NH_3 and NH_4^+ concentrations were measured during~~from~~ November 2017 ~~through~~ – October 2019 in Nagoya, a central Japanese megacity ~~located in central Japan~~. ~~Monthly a~~Averages ~~of~~ NH_3 concentrations ~~were~~ are high in summer and low in winter. Daily minimum NH_3 concentrations ~~were~~are ~~almost~~ linearly correlated with daily minimum air temperatures. ~~In~~ By contrast, daily maximum NH_3 concentrations ~~revealed an~~ increase exponentially ~~increase~~ with temperature, suggesting ~~that~~ that different nighttime and daytime processes ~~with~~ and air temperature ~~acted during the~~s affect concentrations ~~nighttime and daytime~~. Short-term increases of NH_3 concentrations of two types were examined closely. ~~The first is a~~Infrequent ~~rare~~ but large increases (11 ppb for 2 hr) occurred after mist evaporation during daytime. During two years of observations ~~It is noteworthy that that an~~only one e~~e~~vent of this magnitude ~~was~~ was identified in Nagoya~~only once during two years of observations~~, ~~at Nagoya even~~ although evaporation of mist ~~or~~ and fog ~~droplets is expected to be~~occurs frequently after rains. ~~The second~~Also, short-term increases ~~was a~~occur with a large morning peak in summer. Amplitudes of diurnal variation of NH_3 concentration (daily maximum minus minimum) were analyzed ~~After~~ on ~~selected~~ days ~~were fulfilled~~ with non-wet and ~~weak~~ low-wind conditions~~, the amplitude of diurnal variation of NH_3 concentration (daily maximum minus minimum) was analyzed~~: ~~the~~ amplitudes ~~was~~ were small (ca. 2 ppb) in winter, but ~~it~~ they increased from early summer along with new leaf growth. ~~It~~ Amplitudes peaked in summer (~~up to~~ ca. 20 ppb) ~~during intense addition of~~because of droppings from hundreds of crows before roosting ~~on~~ in trees ~~in~~ on the campus~~ assembled before roosting~~. ~~The h~~High daily maximum NH_3 concentrations ~~was~~ were characterized ~~by a~~ed ~~using a~~by a rapid increase occurring 2–4 hr after local sunrise. In summer, ~~the~~ peak NH_3 concentrations at around 8 a.m. ~~under fine~~in sunny weather w~~as~~ere ~~larger~~ greater than ~~that that under~~in cloudy weather, suggesting ~~that~~ that ~~receiving~~ direct sunlight particularly ~~is important for~~ boost~~ings~~

the morning peak. Daily and seasonal findings related to the morning peak implicedy that that stomatal emission at the site was responsible for thecauses the increase. The yDearly differences between daily amplitudes during the two summers was explained by thained usingby the differenee in the t input amounts of reactive nitrogen derived from bird droppings and some rain, suggesting that that bird droppings, a temporary rich source of NH_3, affected the small forest canopy of a small forest affected by the bird droppings might act as a temporary but strong source of NH_3.

1 Introduction

Ammonia (NH_3) plays an important role in various atmospheric chemical processes (Behera et al., 2013). In factFor example, NH_3 is the major precursor of fine aerosol particles containing 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. Therefore, reduction and control of its aerosol concentration are desired for able under many most situations circumstances (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 have been identified (Sutton et al., 2008; Behera et al., 2013). Although agricultural NH_3 sources (such as domestic animals, and fertilizestilizer loss, etc.) are dominant emitters on a global scale, non-agricultural sources (such as motor vehicles, industriesindustry, garbage, sewage, humans, and wild animals , etc.) are also also major contributorssources, 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 that comprisedas 19% of the total emissions. As a non-agricultural source, seabirds were also also widely recognized as important contributors (Sutton et al., 2000; Blackall et al., 2007; Riddick et al., 2012; Croft et al., 2016).

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 from densely populated urban areas. Therefore, a mixture of the various small non-agricultural sources is expected to be the the main contributor for local atmospheric NH_3, which 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 (such as CO, hydrocarbons, and NO_x) in vehicular exhausts. However, exhausts from devices often contains 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 concentrations, especially during stagnant calm wind conditions in some megacities (Osada et al., 2019). In fact, ~~In addition,~~ garbage containers have been ~~suggested~~ implicated as a more important contributor than sewage systems in Barcelona, Spain (Reche et al., 2012). ~~Furthermore, e~~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 spaces 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 spaces in Qingdao, a coastal urban area in northern China. Nevertheless, NH_3 emission processes from green spaces are not well known for urban environments. Green spaces in urban areas provide habitable environments for wild animals. Among wild animals found in urban areas, crows have adapted particularly well ~~with~~ to city environment ~~for their lifes~~. As a consequence, ~~numbers of~~quantities of ~~crow~~ populations have increased in many urban areas in 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. Nevertheless, no report has described a study of ~~However,~~ the potential of NH_3 emissions related to bird droppings in urban green areas ~~has not been studied~~.

Analysis of ~~hour~~ hourly concentrations in the atmosphere is useful to ~~explain~~ ascertain 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~~ found 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 grassland areas, ~~which~~ which have ~~allowed elucidation of the~~revealed a 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~~ ~~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; Hrdina et al., 2019) because NH_3 transfer is governed by rapidly changing meteorol~~ogical~~ ogical (sunlight availability, temperature, relative humidity, etc.) and plant physiol~~ogical~~ ogical (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 ~~hour~~ hourly measurements of related parameters.

To investigate potential sources and processes controlling the variation of NH_3 concentration, ~~hour~~ hourly data of NH_3 and NH_4^+ were ~~measured~~ recorded from November 2017 ~~to~~ through October 2019 in Nagoya, central Japan. The data were analyzed by particularly ~~addressing~~ examining 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~~ were expected to elucidate effects of large amounts of bird droppings on ambient NH_3 con~~levels~~centrations in urban areas with scattered forests ~~affected by large amounts of bird droppings~~.

2 Observation

Atmospheric observations ~~was~~ were ~~conducted~~ made at Nagoya University in Nagoya city located in the central area of Honshu Island of Japan (Fig. 1a). ~~Industrial~~ This industrial area with a 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~~ various industrial activities, ~~the~~ air pollution ~~level is~~concentrations are not so high. Recent ~~levels of the~~ annual mean $PM_{2.5}$ concentrations ~~are~~ have been approximately 12 μg/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~~ that burnable waste including food waste and other materials be packed into predesignated plastic bags and 2) ~~that~~ that the garbage bags ~~must~~ be put out in a specified collection place by 8:00 a.m. on ~~the~~ a regular (twice per week) collection day, 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~~ presenting ~~the~~ a possib~~ility of~~le food supply for the adaptation of omnivorous animals, such as crows, in urban areas (Kurosawa et al., 2003). The observation site is located within the campus. Therefore, the effects of residential garbage are expected to be small. The annual mean air temperature in Nagoya is 15.8°C; ~~the~~ its annual mean rain amount is about 1540 mm (Japan Meteorol~~ogical~~ ogical 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. Meteorol~~ogical~~ ogical data (air temperature, relative humidity, etc.) were obtained from the Nagoya Local Meteorol~~ogical~~ ogical Observatory, ca. 2 km north from Nagoya University (data available from https://www.jma.go.jp/jma/index.html). For this study, NOx and CO 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 up in a room ~~located~~ on the seventh floor (ca. 26 m above the ground) of the Environmental Studies Hall on the main campus of Nagoya University. The northeastern side of the building faced upslope with a small forest with mixed ~~with~~ deciduous and evergreen trees (Fig. 1c). As ~~seen in~~ Fig. 1c shows, the seventh floor height ~~of the seventh floor~~ is ~~almost the same~~almost ~~identical~~ asequal to the ~~level~~ height of the forest canopy growing about 40 m away on the northeastern slope ~~about 40 m apart~~.

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.~~Co.Co. ~~Ltd.~~Co.Ltd.) described in an earlier report~~;~~ (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~~H_3PO_4-coated denuder. The sample air flow rate of the NHx system was 1 L min^{-1}. After passing an ~~impactor~~impactor (about 2 μm cut-off diameter~~ of about 2 μm~~) and an inner frosted glass tube (one coated~~;~~, the other uncoated~~;~~, both ~~are~~ of 3 mm inner diameter and 50 cm long), pure water droplets were added immediately ~~added~~ to the sample air at 100 μl min^{-1}. The collection efficiency of the system was ~~more~~ greater than 95% for the conditions ~~employed~~ used in this study. The equilibrated sample water was analyzed ~~respectively~~respectively using a microflow ~~fluorescence~~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 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.~~Corp.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.~~Corp.Corp.).

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~~. When good weather continued, for example of 14–24 July, regular diurnal variations were ~~visible in~~found for air temperature and wind speed: high in the afternoon and low in the midnight to early morning. During ~~For~~ this period, the difference between maximum and minimum NH_3 concentrations was large~~ and ranged~~; from nearly 10 ~~to more~~to more than 20 ppb. ~~In contrast,~~However, the NH_3 concentration dropped to a few ~~ppb~~ parts per billion. It~~and~~ remained constantly low for the duration of the rain with small diurnal variation ~~as that~~ because, during~~that found in~~ 4–7 July ~~when~~, the Baiu front (East Asian rainy front) was active near the site. A similar tendency of low NH_3 concentration during rainy days was ~~also~~ ~~also~~ found during observations, as reported ~~at other places~~from other studies (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~~cuticular ~~of~~

leafves absorb ambient NH_3 under high relative humidity during rain. Moreover, NH_3 concentrations were low during the days 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 for December 2018. The maximum value of the vertical axis of NH_3 concentrations is 15 ppb, which which is half of that that in Fig. 2. In winter, the amplitude of the diurnal variation of NH_3 concentration was much smaller than those in summer. Diurnal variation of wind speed was also also not unclear in winter because of the lack of sea breeze circulations. In contrast to summer, wind speed dependence of NH_3 concentrations were shownis more clearly clearer, showingas higher concentrations under calm winds and lower concentrations under strong wind conditionsconditions, because the local sources contributed more effectively understrongly affect local conditions under stagnant air conditions. Under With 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 that temporal variations of daily minimum NH_3 concentrations 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 which corresponds to a decreasing trend of high to low air temperatures for these days.

In contrast to the modest variation in found for July, NOx concentrations in December showed large variation: it was concentrations were displayed frequently as found to be more greater 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 concentrations were correlated wellwere strongly associated with high CO concentrations (Suppl. Fig.. Figure . Figure 1), suggesting strong contributions of vehicular emissions for both species. In addition In addition, toIn addition toSimilarly to the NOx, the NH_3 concentrations increased also also under low winds. The similarity of NH_3 temporal variation with NOx suggests that that motor vehicle emissions from motor vehicles partly contribute to ambient NH_3 concentration in winter (Osada et al., 2019). However, neither NH_3 nor NHx (NH_3 and NH_4^+) did not show showed no a strong correlation with NOx (Suppl. Fig.. Figure . Figure 1), suggesting that that a source other than vehicular emissions contributes more to NH_3 concentrations in winter.

Figure 4 depicts average diurnal variations of NH_3 and NH_4^+ concentrations, air temperature, solar radiation, relative humidity (RH), wind speed (WS), NOx and CO concentrations from December 2017 to through September 2019 for every 3 months. For NH_3 variation, seasonal change was clearly seenreadily apparent. Broad and modest maximum of NH_3 concentrations were observed at around noon in December and March. On the contraryBy contrast, in June and September, sharp peaks at around 8 o'clock in the morning was were superimposed to on the broad and modest variation during colder season. The start timing of the NH_3 increase in the morning during the warm season was similar to the hour hours of rising air temperature and dropping relative

humidity. In contrast to diurnal variations of NOx and CO concentrations, NH_3 concentrations in December and March showed no large morning peak at rush ~~hour~~ hour around 7–9 o'clock, suggesting ~~that~~ that contributions of NH_3 from motor vehicular emissions are apparently limited ~~for only~~to those days under calm wind conditions, even in December.

Diurnal variation of NH_4^+ concentration was nearly flat for all examples ~~shown in Fig. 4~~portrayed in Fig. 4. Regarding the relation between NH_4^+ concentrations and air 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, the NH_4^+ concentrations in ~~Fig.~~Fig.~~.~~ Fig.ure 4 were not simply a mirror of diurnal temperature variations. Therefore, NH_3 increases at around noon during the~~in~~ cold season ~~was~~ are not attributable to dissociation of NH_4NO_3. Solar radiation showed higher values around noon. Wind speed was low from mid-night to the morning and high during afternoon and early evening.

Diurnal variation of NH_3 concentration is controlled mainly ~~controlled~~ by time variations of 1) atmospheric boundary layer ~~dynamics~~dynamics, 2) dry deposition to ~~euticular~~cuticular of vegetation and other surfaces, and 3) local emission strength (Sutton et al., 1995; Saylor et al., 2010; Hrdina et al., 2019). First, the boundary layer height ~~of boundary layer~~ increases with surface heating by solar radiation, leading ~~more~~ to greater dilution of the NH_3 concentration ~~in~~ at noon~~. If~~. If this is the case, then diurnal variation of NH_3 ~~is~~ resembles ~~to~~ those of NOx and CO. However, it ~~looks~~ appears to be different in Fig. 4, suggesting dominance of other factors. Second, dry deposition velocity of NH_3 varies with wetness of the surfaces. Diurnal variation of RH shows minimum values around noon, implying ~~that~~ that the NH_3 dry deposition in day~~time is slower~~time is greater than ~~that~~ that during~~in~~ nighttime. Evaporation of dew and that from ~~other~~ wet surfaces is ~~also~~ also a potential source of NH_3,~~which~~ ~~which will be~~as discussed in greater detail in section 3.2. Lastly, time variation of local emissions is ~~also~~ ~~also~~ important, especially for a low wind conditions. ~~However, r~~Rush ~~hour~~ hour emissions from motor vehicles ~~was~~ were not the major contributor, as discussed earlier. To seek an effective source creating the morning peak, diurnal variations were analyzed again for days selected by weather condition (more specifically duration of sunshine) as presented~~noticed~~ in Fig. 2.

Figure 5 depicts the ~~impact~~ effects of sunshine on the morning peak of NH_3 concentrations during July and August for 2018 and 2019. ~~Left~~ The left column represents fine weather of ~~the~~ days receiving direct sunlight longer than 10 hr (~~namely~~ clear sky for ~~the~~ most of the day). ~~Right~~ The right column shows cloudy weather with sunshine duration shorter than 5 hr and daily rain of less than 3 mm. The NH_3 concentration showed a strong peak at 8 a.~~m.~~ under fine weather, ~~while~~ although~~whereas~~ the peak concentration was slightly lower in 2019. ~~In~~ By contrast, a strong peak was absent ~~in~~ on the mornings ~~for~~ of cloudy days. This evidence ~~relating~~ related to direct solar radiation suggests ~~that~~ that the morning peak is attributed ~~from~~ to plant physiol~~ogical~~ ogical activities such

as photosynthesis or stoma opening. ~~Importance~~ The importance of stomatal NH_3 emissions ~~will be~~is discussed ~~later again~~ further in section 3.3.

3.2 Peak after mist evaporation

Figure 6 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~~. This magnitude of NH_3 increase after rain was only rarely observed during the two year study period ~~of two years~~. Mist is defined as reduced horizontal visibility to ~~between~~ 1 ~~and~~ 10 km ~~by~~because of ~~suspending~~ suspended water droplets in the atmosphere. In Nagoya, mist ~~is~~ often ~~observed~~ occurs before or after rain. In this case, rain ceased in the early evening of November 14, but the mist ~~continued~~ persisted until 10 am ~~of~~ on 15 November ~~15~~. Associated with relative humidity ~~dropped~~ dropping sharply from ca. 90% at 10 ~~AM~~ am to ca. 40% at noon, the mist disappeared ~~and~~. The NH_3 concentration increased 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~~ Those reports presented ~~discussed~~ discussion of 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 rain cessation ~~of rain~~ to decrease soil moisture; then, it is too slow to raise the atmospheric NH_3 concentration. In contrast, Wentworth et al. (2014, 2016) reported ~~that~~ that a rapid increase of NH_3 in the morning was attributed to evaporation of dew containing ~~relatively~~ elatively high concentrations of NH_4^+ with ~~the~~ nearly neutral pH. They ~~pointed out~~reported ~~that~~ that the amount of NH_3 vol~~atilize~~seatilized from dew is governed by the ionic composition (excess amount of NH_4^+ rather than forming less-volatile salts from constituents) and pH (gas–aqueous partitioning and chemical equilibria in solution). Although the magnitude of the morning increase reported ~~in~~ by Wentworth et al. (2016) was less than half that of the present case, the~~ir~~ timing and quickness of NH_3 increase were similar to ~~the aspect~~those ~~shown in Fig. 6~~depicted in Fig. 6, suggesting ~~that~~ that mist droplet evaporation ~~of mist droplets~~ is a major source process for ~~the~~ high NH_3. A similar rapid NH_3 increase up to 15 ppb during 4 hr was ~~previously~~ observed earlier on 11 December ~~11~~, 2015 in Nagoya (Osada et al., 2018). According to an acid rain report in 2017 published by the Nagoya City Institute of Environmental Sciences (NCIES, 2018), the volume weighted mean pH of the weekly collected rain sample from 13–20 November, 2017 was 6.00. Based on major ionic data reported for the sample, Frac (NH_4^+) proposed by Wentworth et al. (2016) was estimated as 0.14 ~~that~~ ~~that~~, which suggests the possibility of NH_3 evaporation after drying of the rain. However, rain was observed twice during the sampling period~~,~~; ~~in~~ on 14 November ~~14th~~ (~~9mm~~9 mm) and 18 November ~~18th~~ (16.5 mm). Unfortunately, the chemical composition of rain ~~in~~ on 14 November ~~14~~ was not known, so ~~and~~ further discussion is ~~thus~~ difficult ~~to discuss more~~. Instead, the duration of mist after the rain might

be an important factor to form a favorable composition for releasing NH_3. In fact, the duration of mist after the rain was unusually long (16 hr). Therefore, ambient NH_3 during the mist was able to dissolve into the droplets ~~more better into the droplets~~. 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 Emissions from the tree canopy ~~around~~ surrounding the site: relation to bird droppings

Figure 7 presents results of data analysis of NH_3 and NH_4^+ concentrations. Monthly NHx (NH_3 + NH_4^+) concentrations (Fig. 7a) are high in summer and low in winter. Daily and monthly NH_4^+ (Fig. 7b) concentrations show higher values from spring to summer and lower in fall and winter, whereas daily and monthly NH_3 concentrations (Fig. 7c) depict clear seasonal variation: high in summer (maximum in August) and low in winter (minimum in January). Amplitudes of seasonal variations of NH_3 ~~is~~ are larger than ~~that~~ those of NH_4^+~~, thus~~. Consequently, ~~thereby,~~ NH_3 ~~is~~ controllings the seasonal variation of the NH_3 fraction (Fig. 7b): ca. 60–75% in late summer (maximum in August–September) and 40–50%~~&~~ in late winter to early spring (minimum in February and March). For the NH_3 concentration, the monthly minimum (1.6 ppb) in January 2018 was almost equal to ~~that~~ that (1.7 ppb) in January 2019, although the monthly maximum (7.0 ppb) in August 2018 was higher than ~~that~~ that (4.9 ppb) in August 2019. Furthermore, day-to-day variation was ~~also~~ also greater in 2018 than in 2019. To examine the relation with source factors, ~~hour~~ hourly NH_3 concentrations were analyzed for two subjects: the daily minimum and the diurnal range (maximum minus minimum) under dry (RH <70%) and weak wind (<3 m s^{-1}) conditions ~~as fulfilled~~ for days with both daily mean values. Reasons for the meteorol~~ogical~~ogical limitations were the following. Wet surfaces on building walls, litter, soil, and leaves can act as a NH_4^+ reservoir, ~~which~~ 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. 7d). As briefly described earlier for Fig. 3, day-to-day variation of daily minimum NH_3 concentration in December covaries with the baseline trend in daily minimum temperature. Analogously to this, the seasonal variation of daily minimum NH_3 concentrations follows 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 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). Although vertical profiles of NH_3 concentration and meteorol~~ogical~~ogical parameters were not available, the ambient NH_3

at the time of daily minimum is presumably derived from local ~~in~~ origin under low wind. The NH_3 in the air is equilibrated with the local surfaces of plants and soils. Stomata of plants do not open before sunrise. Therefore, stomatal gas exchange is expected to be negligible before sunrise. Furthermore, ~~the~~ plant surface ~~is~~s are less effective as ~~the~~ NH_4^+ reservoirs because ~~of~~ RH <70%. However, pore water or moisture in soil can remain. ~~They~~ That moisture 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, important parameters aside from the atmospheric NH_3 level include the 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 more details related to this point later ~~in greater detail~~.

Another point is analysis of the amplitude of diurnal variation as the difference between the maximum and minimum of the day ~~(~~, denoted as daily max−min ~~)~~ (Fig. 7e). As anticipated from the difference between summer and winter in daily NH_3 variations portrayed in Fig. 4, the daily max−min values were larger in warm months than ~~those~~ in cold months. The daily max−min values were found to be quite large in summer (12.8 ppb as averages during ~~from~~ July ~~to~~ August in 2018 and 9.2 ppb in 2019) and small in winter (2.3 ppb as the average during ~~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~~ a connection with the leaf growth stage of deciduous trees around the site. Although evergreen trees (*Quercus glauca*, *Pinus*, *Machilus thunbergii*, etc.) are ~~mixing~~mixed, deciduous trees (*Quercus variabilis*, *Zelkova serrata*, Japanese cherry, *Liquidambar*, *Metasequoia glyptostroboides*, *Aphananthe aspera*, etc.) ~~are~~ grow~~ing~~ in the ~~a~~ small forest (ca. 380 × 30 m) near the site~~. Fig.~~. ~~Figure~~ . Figures 1c and 1d ~~respectively~~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~~ estimation from temperature and thermodynamic equilibrium among various surfaces and the atmosphere. The compensation point (X) is predicted as ~~to~~ the following.

$$X = \frac{161000}{T} \exp\left(-\frac{10380}{T}\right) \Gamma \qquad (1)$$

Therein, T denotes the surface reservoir 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~~ represents higher equilibrium NH_3 concentration with the surface for the same temperature. Higher temperature raises the equilibrium NH_3 concentration present as gas phase.

Apoplastic fluid in stomata of plants and pore water in soil are assumed as the major reservoirs of NH_4^+. To equilibrate apoplastic fluid with ambient atmosphere, stomata must be opened, ~~which~~ which is regulated by the plant physiology ~~relating~~ related to photosynthesis. Consequently, ~~the~~ daily maximum NH_3 concentrations were observed at about 2−4 hr ~~later from~~after sunrise. In other words, the initial stage of stomata 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. 8a). ~~The l~~Leaf temperatures ~~was~~ were not measured ~~in~~ for this study. The ambient temperature was used as a surrogate of ~~the~~ leaf temperature. In Fig. 8a, two hypothetical compensation curves are ~~also~~ also shown using Γ of 1500 and 200. ~~Above an~~At air temperatures ~~of~~ higher than about 10–15°C, most observed data ~~were~~ are shown between these two curves, suggesting ~~that~~ that the Γ of the forest canopy around the site ~~was~~ is in the range of 200–1500. According to the literature ~~regarding~~ related to compensation points (Massad et al., 2010; Zhang et al., ~~(~~2010~~), ; Massad et al. (2010), and~~ Hrdina et al. ~~(~~, 2019~~)~~), Γ was several tenths to 10^5 depending on the type of ground, vegetation, and richness of reactive nitrogen available for ~~the~~ plant~~, types of~~s ~~types of ground, and vegetation~~. For stomatal emission potential of NH_3, the range of 300–3000 for trees of deciduous and evergreen forests was proposed by Zhang et al. (2010). A similar range of ~~the~~ values was ~~also~~ ~~also~~ listed by Massad et al. (2010).

Furthermore, daily minimum NH_3 concentrations are ~~also~~ ~~also~~ shown versus the minimum air temperature of the day (Fig. 8b). As described earlier, the condition observed for daily minimum NH_3 concentration is ~~connected~~ related to the emission potential from soil around the site because stomatal emissions are negligible. Although soil temperatures were not measured ~~in~~ for this study, the minimum air temperature was used as a surrogate for nighttime soil temperatures. In Fig. 8b, 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 temperatures ~~above~~ higher than 20°C. Below 20°C, most observed data were over the curve for Γ of 500. Two possibilities ~~are~~ can be considered for these relations. One is ~~that~~ that higher Γ for soil is responsible for winter because litter from deciduous trees can be decomposed by microbial activity~~. Also,~~, In addition, subsequent NH_4^+ production raised Γ higher than 500. Another possibility is ~~a~~ that the contribution from vehicular emissions was enhanced by stagnant air pollution in winter (Yamagami et al., 2019).

As shown separately in Fig. 8, 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 plants'~~s~~ stages 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~~ related to the present ~~this~~ study, new leaves start to grow in April ~~and~~ ; they mature after June. They turn red in November. The duration of active ~~leaf~~ leaves of deciduous trees roughly accords with the season of the higher daily m~~ax min~~ax–min ~~shown in Fig. 7~~portrayed in Fig. 7e. However, the values of the daily

max-minax–min in summer differed between 2018 and 2019, with no great change of trees in on the campus. As discussed in section 3.1, dry deposition of NH_3 is controlled by surface conditions of the soil and euticularcuticular of plant surfaces. In the analysics of portrayed in Figs. 7 and 8, dryer drier days were selected, excluding the complexity of wet processes for NH_3 exchange between air and the various surfaces. In addition, leaf conditions of trees and weeds were almost the samealmost identical for these years, suggesting that that conditions of NH_3 dry deposition did not change. In addition, micrometeorologicalogical factors govern the transfer velocity that that ultimately determines the magnitude of the NH_3 exchange. Unfortunately, meteorologicalogical data required for estimating the transfer velocity were not available in this study. Further data for flux estimations are needed to are necessary to evaluate NH_3 exchange in urban areas. Nonetheless, important suggestions can be made for potential source variation at the site. As input to the system, the amount of reactive nitrogen brought by wet deposition (rain) vary varies slightly year-to-with year. According to annual reports of acid rain (NCIES, 2019; 2020), monthly average wet depositions of NO_3^- duringfrom May to September were 2.3 mmol m^{-2} in 2018 and 2.0 mmol m^{-2} in 2019, respectivelyrespectively. Similarly, monthly average wet depositions of NH_4^+ during May–September were , respectivelyrespectively, 2.9 mmol m^{-2} in 2018 and 2.4 mmol m^{-2} in 2019. Wet depositions of these species during warm months wwere as slightly (ca. 15%) 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 differencethose in wet depositions, requiring more input to explain yearly discrepaneydiscrepancies.

To seek more input to the system, the importance of bird droppings at the site is discussed below. From June or July to through September or October, rooftops of the buildings and trees in on the campus are used frequently by more than several hundreds ofseveral hundred crows for pre-roosting assembly or flight line assembly in early evening before going to roost, located in on or presumably 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 gathereded in the murder in the summer in 2018 than in 2019, which which is seen as regarded as the number density of white fecal remains in photographs under trees at the front of the building (see Appendix Photograph 1).

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 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~~ 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 be the best guess from the dropping situations observed around the building (Appendix Photograph 1). The estimated result is 3.4 mmol m^{-2} day^{-1}, ~~which~~ which is converted as ca. 100 mmol m^{-2} $month^{-1}$. ~~This~~. This value is nearly 40 times higher than the NH_4^+ flux by rain. $Flux_{bd}$ includes large uncertainty depending on the number of crows gathered and their behavior ~~in~~ on the campus. However, it is useful for comparison with reactive nitrogen flux by rain. Even assuming *Freq* ~~w~~as 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~~ on 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~~ 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. For that reason, ~~Therefore,~~ their populations are often increasing in urban areas worldwide (Ueta et al., 2003; Vuorisalo et al., 2003). Through the increase of bird droppings, reactive nitrogen in urban small forests is oversaturated for tree growth and emitted excess nitrogen as NH_3 from the tree canopy. Vegetation in urban environments tends to catch and concentrate gaseous and particulate reactive nitrogen pollutants and to supply them ~~in~~to the ground surface (Decina et al., 2020). The present study ~~made~~ yielded a particularly~~n~~ important point ~~that~~ ~~that~~: this process is bi-directional for NH_3. Furthermore, NH_3 emissions from the tree canopy 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 in summer (7.0 ppb and 4.9 ppb, ~~respectively~~respectively, for August in 2018 and 2019) ~~in summer~~ and low in winter (1.6 ppb and 1.7 ppb for January 2018 and 2019, ~~respectively~~respectively) ~~in winter~~. During the study period, a surge event (11 ppb during 2 hr) was observed after mist evaporation during daytime, ~~which~~ which was very rare at Nagoya, even though evaporation of mist or fog droplets ~~are~~ is expected to be frequent after rain. A plausible condition of the surge

event was discussed in terms of the 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 10 ppb) in summer. The daily max-minax–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 lLarge diurnal variation of NH_3 concentration was characterized by a ced usingby a peak at 2–4 hr after sunrise. In summer, the peak NH_3 concentration at around 8 a.m. under fine weather was larger than that that under cloudy weather, suggesting that that receiving direct sunlight is important for boosting the morning peak. The timing of seasonal and daily increases of the morning NH_3 peak imply that that reactive nitrogen inputs from Crow crow droppings and rain increased NH_3 emissions from the tree canopy. Preliminary estimates suggest that that reactive nitrogen input by crow droppings was greater than the effect of wet deposition. Therefore, as crow populations are of crows increaseing in some urban areas through adaptation., the rReactive nitrogen supplied by crow droppings might become an increasingly important source of NH_3 emissions in urban areas.

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.

5 Acknowledgments

This research was supported by the Environment Research and Technology Development Fund (5-1604) of the Environmental Restoration and Conservation Agency. The author thanks Dr. Y. Hirano for discussion about of soil pH and reactive nitrogen from bird colonies. Constructive comments from two anonymous two referees are also also greatly appreciated.

References

Asman, W. A., Pinksterboer, E. F., Maas, H. F., Erisman, J. W., Waijers-Ypelaan, A., Slanina, J., and Horst, T. W.: Gradients of the Ammonia Concentration in a Nature Reserve: Model Results and Measurements, Atmos. Environ. 23, 2259–2265, 1989.

Behera S. N., Sharma M., Aneja V. P., and Balasubramanian R.: Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies, Environmental Science and Pollution Research International 20, 8092–8131, 2013.

Blackall, T. D., Wilson, L. J., Theobald, M. R., Milford, C., Nemitz, E., Bull, J., Bacon, P. J., Hamer, K. C., Wanless, S., and Sutton, M. A.: Ammonia emissions from seabird colonies, Geophysical Research Letters, 34(10). https://doi.org/10.1029/2006GL028928, 2007.

Croft, B., Wentworth, G. R., Martin, R. V., Leaitch, W. R., Murphy, J. G., Murphy, B. N., Kodros, J. K., Abbatt, J. P. D., & and Pierce, J. R.: Contribution of Arctic seabird-colony ammonia to atmospheric particles and cloud–albedo radiative effect., Nature Comm., 7, 13444, doi.org/10.1038/ncomms13444, 2016.

Decina S. M., Ponette, A. G., and Rindy, J. E.: Urban tree canopy effects on water quality via inputs to the urban ground surface, in: Forest–Water Interactions, edited by: by Levia D., Carlyle-Moses D., Iida S., Michalzik B., Nanko K., Tischer A., Ecological ogical Studies, vol 240, Springer, Cham, https://doi.org/10.1007/978-3-030-26086-6, 2020.

Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., Jr, and Speizer, F. E.: An association between air pollution and mortality in six US cities, New England J. Medicine, 329, 1753–1759, 1993.

Ellis, R. A., Murphy, J. G., Markovic, M. Z., VandenBoer, T. C., Makar, P. A., Brook, J. and Mihele, C.: The influence of gas–particle partitioning and surface–atmosphere exchange during BAQS-Met, Atmos. Chem. Phys., 11, 133–145, doi:10.5194/acp-11-133-2011, 2011.

Farquhar, G. D., Firth, P. M., Wetselaar, R., and Weir, B.: On the gaseous exchange of ammonia between leaves and the environment: determination of the ammonia compensation point, Plant Physiology, 66, 710–714, 1980.

Fujita, M. and Koike, F.: Bird transport nutrients to fragmented forests in an urban landscape, Ecol. Appl., 17: 648–654. doi:10.1890/06-0118, 2007.

Hansen, K., Sørensen, L. L., Hertel, O., Geels, C., Skjøth, C., Jensen, B., and Boegh, E.: Ammonia emissions from deciduous forest after leaf fall, Biogeosciences, 10, 4577–4589, 2013.

Hojito, M., Hayashi, K., Murano, K., and Mori, A.: The Status of Atmospheric Concentrations of Ammonia in an Intensive Dairy Farming Area in Central Japan, Japanese J. Soil Sci. Plant Nutrition, 77, 53–57, 2006. (in Japanese).

Hrdina, A. H. I., Moravek, A., Schwartz-Narbonne, H., and Murphy, J. G.: Summertime Soil–Atmosphere Ammonia Exchange In The Colorado Rocky Mountain Front Range Pine Forest, Soil Systems, 3, 15, doi.org/10.3390/soilsystems3010015, 2019.

Hu, Q., Zhang, L., Evans, G. J., and Yao, X.: Variability of atmospheric ammonia related to potential emission sources in downtown Toronto, Canada, Atmos. Environ., 99, 365–373, 2014.

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

Kean, A. J., Littlejohn, D., Ban-Weiss, G. A., Harley, R. A., Kirchstetter, T. W., and Lunden, M. M.: Trends in on-road vehicle emissions of ammonia, Atmos. Environ., 43, 1565–1570, 2009.

Kruit, R. R. W., Van Pul, W. A. J., Otjes, R. P., Hofschreuder, P., Jacobs, A. F. G., and Holtslag, A. A. M.: Ammonia fluxes and derived canopy compensation points over non-fertilizetilizsed agricultural grassland in The Netherlands using the new gradient ammonia – high accuracy – monitor (GRAHAM), Atmos. Environ., 41, 1275–1287, 2007.

Kukkonen, J., Pohjola, M., Sokhi, R. S., Luhana, L., Kitwiroon, N., Fragkou, L., and Denby, B.: Analysis and evaluation of selected local-scale PM10 air pollution episodes in four European cities: Helsinki, London, Milan and Oslo, Atmos. Environ., 39, 2759–2773, 2005.

Kurosawa, R., Kanai, Y., Matsuda, M., and Okuyama, M.: Conflict between humans and crows in greater Tokyo – garbage management as a possible solution –. Global Environmental Research – English edition –, 7, 139–148, 2003.

Massad, R. S., Nemitz, E., and Sutton, M. A.: Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere, Atmos. Chem. Phys., 10, 10359–10386, https://doi.org/10.5194/acp-10-10359-2010, 2010.

Mattsson, M., and Schjoerring, J. K.: Senescence-induced changes in apoplastic and bulk tissue ammonia concentrations of ryegrass leaves, New Phytologist, 160, 489–499, 2003.

Mozurkewich, M.: The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size, Atmos. Environ. 27A, 261–270, 1993.

Murphy, J. G., Gregoire, P. K., Tevlin, A. G., Wentworth, G. R., Ellis, R. A., Markovic, M. Z., and VandenBoer, T. C.: Observational constraints on particle acidity using measurements and modelling of particles and gases, Faraday Discussions, 200, 379–395, 2017.

Nagoya City Institute for Environmental Sciences: Acid rain report 2017, 24p, http://www.city.nagoya.jp/kankyo/page/0000076867.html, 2018. (in Japanese)

Nagoya City Institute for Environmental Sciences: Acid rain report 2018, 24p, http://www.city.nagoya.jp/kankyo/page/0000076867.html, 2019. (in Japanese)

Nagoya City Institute for Environmental Sciences: Acid rain report 2019, 24p, http://www.city.nagoya.jp/shisei/category/53-5-22-8-1-2-0-0-0-0.html, 2020. (in Japanese)

Nakamura, S.: Dynamics of flight line assemblies of crows in the Osaka area, Jpn. J. Ornithol., 53: 77–86, 2004. (in Japanese)

Nakamura, M., and Yuyama, Y.: Development of a composition database for various ~~types of~~ types of biomass, Technical report of the National Research Institute of Agricultural Engineering, No. 203, 57–80, 2005. (in Japanese)

Nemitz, E., Sutton, M. A., Wyers, G. P., and Jongejan, P. A. C.: Gas–particle interactions above a Dutch heathland: I. Surface exchange fluxes of NH_3, SO_2, HNO_3 and HCl, Atmos. Chem. Phys., 4, 989–1005, https://doi.org/10.5194/acp-4-989-2004, 2004.

Nowak, J. B., Huey, L. G., Russell, A. G., Tian, D., Neuman, J. A., Orsini, D., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Weber, R. J., Nenes, A., Edgerton, E., and Fehsenfeld, F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), J. Geophys. Res. 111, D17308, doi:10.1029/200~~6J6-J~~D007113, 2006.

Osada, K., Ueda, S., Egashira, T., Takami, A., and Kaneyasu, N.: Measurement of gaseous NH_3 and particulate NH_4^+ in the atmosphere by fluorescent detection after continuous air–water droplet sampling, Aerosol and Air Quality Res., 11, 170–178, 2011.

Osada, K., Yamagami, M., Ikemori, F., Hisatsune, K., Nakashima, H., Miwa, A., and Yabutani, S.: Sudden increase in atmospheric NH_3 concentration after drying hydrometeor, J. Japan Soc. Atmos. Environ., 53, 130–135, 2018. (in Japanese)

Osada, K., Saito, S., Tsurumaru, H., and Hoshi, J.: Vehicular exhaust contributions to high NH_3 and $PM_{2.5}$ concentrations during winter in Tokyo, Japan, Atmos. Environ., 206, 218–224, 2019.

Pandolfi, M., Amato, F., Reche, C., Alastuey, A., Otjes, R. P., Blom, M. J., and Querol, X. Summer ammonia measurements in a densely populated Mediterranean city, Atmos. Chem. Phys., 12, 7557–7575, 2012.

Perrino, C., Catrambone, M. D., Di Bucchianico, A. D. M., and Allegrini, I.: Gaseous ammonia in the urban area of Rome, Italy and its relationship with traffic emissions, Atmos. Environ., 36, 5385–5394, 2002.

Reche, C., Viana, M., Pandolfi, M., Alastuey, A., Moreno, T., Amato, F., and Querol, X.: Urban NH_3 levels and sources in a Mediterranean environment, Atmos. Environ., 57, 153–164, 2012.

Riddick, S. N., Dragosits, U., Blackall, T. D., Daunt, F., Wanless, S., and Sutton, M. A.: The global distribution of ammonia emissions from seabird colonies, Atmos. Environ., 55, 319–327, 2012.

Roelle. P. A. and Aneja. V. P.: Characterization of ammonia emissions from soils in the upper coastal plain, North Carolina, Atmos. Environ., 36, 1087–1097, 2002.

Saylor, R. D., Edgerton, E. S., Hartsell, B. E., Baumann, K., ~~&~~ and Hansen, D. A.: Continuous gaseous and total ammonia measurements from the southeastern aerosol research and characterization (SEARCH) study~~. .~~. Atmos. Environ., 44(38), 4994–5004, 2010.

Schjoerring, J. K., Husted, S., and Mattsson, M.: Physiol~~ogical~~ ogical parameters controlling plant–atmosphere ammonia exchange, Atmos. Environ., 32, 491–498, 1998.

Schjoerring, J. K., Husted, S., Mäck, G., Nielsen, K. H., Finnemann, J., and Mattsson, M.: Physiol~~ogical~~ ogical regulation of plant–atmosphere ammonia exchange, Plant and Soil, 221, 95–102, 2000.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change. John Wiley & Sons, 2016.

Shen, J., Chen, D., Bai, M., Sun, J., Coates, T., Lam, S. K., and Li, Y.: Ammonia deposition in the neighbourhood of an intensive cattle feedlot in Victoria, Australia, Sci. Rep., 6, 32793, 2016.

Song, Q. and Osada, K.: Seasonal variation of aerosol acidity in Nagoya, Japan and factors affecting it, Atmos. Environ.: X, 5, 1000622020, 2020.

Suarez-Bertoa, R., Mendoza-Villafuerte, P., Riccobono, F., Vojtisek, M., Pechout, M., Perujo, A., and Astorga, C.: On-road measurement of NH_3 emissions from gasoline and diesel passenger cars during real world driving conditions, Atmos. Environ., 166, 488–497, 2017.

Sutton, M. A., Fowler, D., Burkhardt, J. K., ~~&~~ and Milford, C.: Vegetation atmosphere exchange of ammonia: canopy cycling and the impacts of elevated nitrogen inputs, Water, Air, and Soil Pollution, 85(4), 2057–2063. 1995.

Sutton, M. A., Dragosits, U., Tang, Y. S., and Fowler, D.: Ammonia emissions from non-agricultural sources in the UK, Atmos. Environ., 34, 855–869, 2000.

Sutton M. A., Erisman J. W., Dentener F., and Möller D.: Ammonia in the environment: from ancient times to the present, Environ. Poll., 156, 583–604, 2008.

Teng, X., Hu, Q., Zhang, L., Qi, J., Shi, J., Xie, H., Gao, H., and Yao, X.: Identification of major sources of atmospheric NH_3 in an urban environment in northern China during wintertime, Environ. Sci. Technol., 51(12), 6839–6848, 2017.

Theobald, M. R., Løfstrøm, P., Walker, J., Andersen, H. V., Pedersen, P., Vallejo, A., and Sutton, M. A.: An intercomparison of models used to simulate the short-range atmospheric dispersion of agricultural ammonia emissions, Environ. Modelling & Software, 37, 90–102, 2012.

Ueta, M., Kurosawa, R., Hamao, S., Kawachi, H., and Higuchi, H.: Population change of jungle crows in Tokyo, Global Environ. Res-English edition, 7, 131–138, 2003.

Vuorisalo, T., Andersson, H., Hugg, T., Lahtinen, R., Laaksonen, H., and Lehikoinen, E.: Urban development from an avian perspective: causes of hooded crow (*Corvus corone cornix*) urbanisation in two Finnish cities, Landscape and Urban Planning, 62, 69–87, 2003.

Wentworth, G. R., Murphy, J. G., Gregoire, P. K., Cheyne, C. A. L., Tevlin, A. G., and Hems, R.: Soil–atmosphere exchange of ammonia in a non-fer~~tilizes~~tilized grassland: measured emission potentials and inferred fluxes, Biogeosciences, 11, 5675–5686, https://doi.org/10.5194/bg-11-5675-2014, 2014.

Wentworth, G. R., Murphy, J. G., Benedict, K. B., Bangs, E. J., and Collett Jr., J. L.: The role of dew as a night-time reservoir and morning source for atmospheric ammonia, Atmos. Chem. Phys., 16, 7435–7449, 2016.

Wyers, G. P. and Erisman, J. W.: Ammonia exchange over coniferous forest, Atmos. Environ., 32, 441–451, 1998.

Yamagami, M., Ikemori, F., Nakashima, H., Hisatsune, K., and Osada, K.: Decreasing trend of elemental carbon concentration with changes in major sources at Mega city Nagoya, Central Japan, Atmos. Environ., 199, 155–163, 2019.

Zhang, L., Wright, L. P., and Asman, W. A. H.: Bi-directional air–surface exchange of atmospheric ammonia: A review of measurements and a development of a big-leaf model for applications in regional-scale air-quality models, J. Geophys. Res.: Atmos., 115, D20310, doi:10.1029/2009JD013589, 2010.

~~??> Please make sure that the abstract is short enough. Older guidelines show that the limit is 300 words. Yours might be far too long. I was able to cut the length by about 20%+ with very little trouble. Maybe you can cut it by another 15 words, but you will have to cut some meaningful contents.~~

~~You can not claim that something has never been studied, can you? You can very reasonably claim that nobody has reported such a study. Still, it is possible that someone published a report in Chinese, Czech, French or Spanish, right? But an editor and a reader assumes that the second claim is not as strong as the first, so it is acceptable.~~

~~Do not tell readers what they see in a figure. Tell them what you show.~~

~~I think your reviewers were impressed by your use of MURDER of crows. This is a komakai point known by some native speakers, but by few other people. This is a perfect example of a "halo effect." The reviewers know that you use English well in some ways, so they believe you will use it well always. They make kind remarks about your English and only suggest minor revisions. >~~

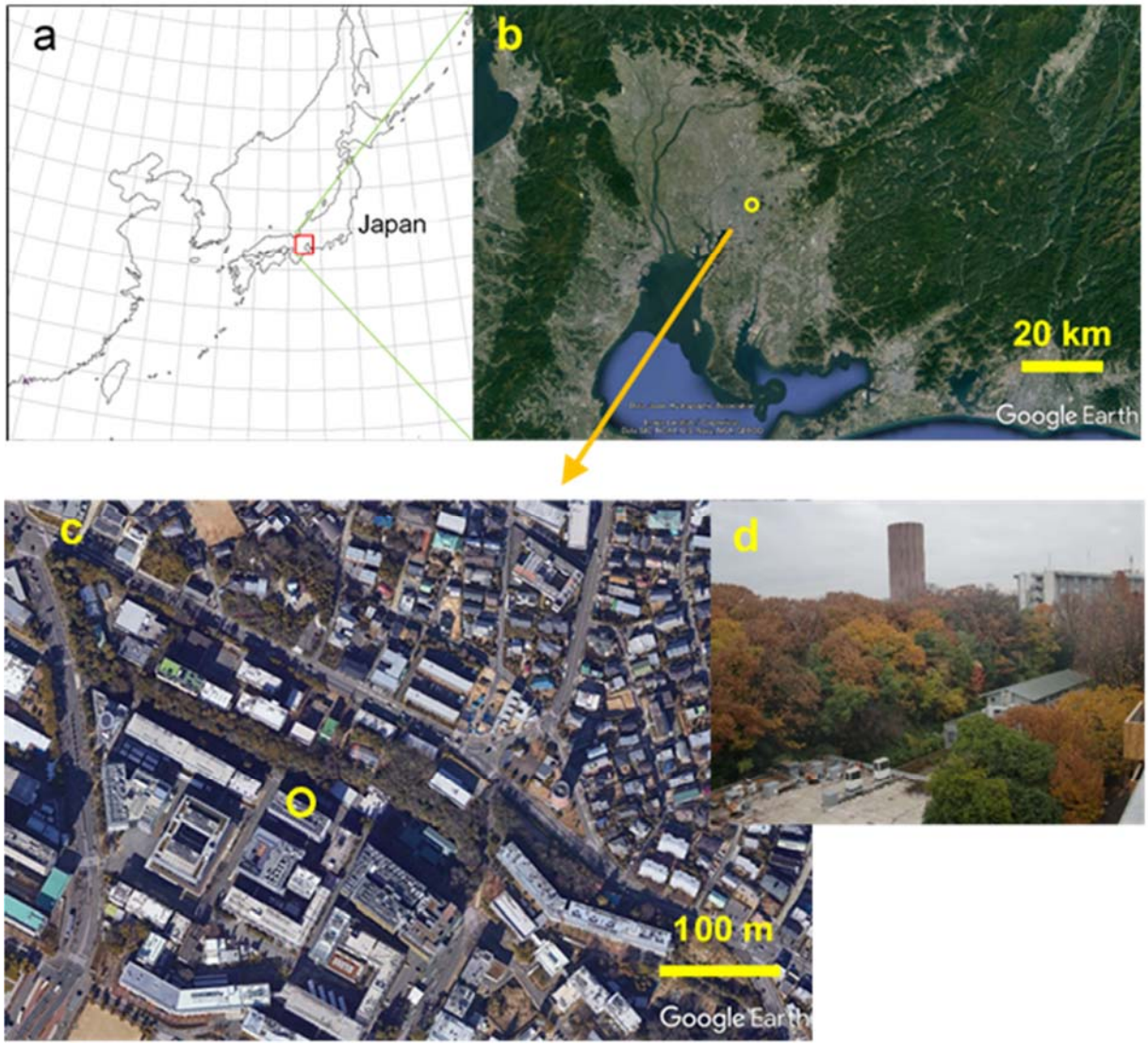


Figure 1(a)~~:~~ Map of the area around the observation site~~.~~ . (b)~~:~~ ~~Satellite~~ Satellite image (from © Google Earth) near Nagoya University (open circles: 35.67°N, 139.83°E) in Nagoya, Japan. ~~Local~~ A local meteorol~~ogical~~ ogical station (air temperature, relative humidity, rain, wind speed and direction, solar radiation, weather records) and a national air pollution monitoring site (NOx and CO) are located at about 2 km north ~~from~~ of the site. (c)~~:~~ © Google Earth ~~close~~ close-up image of the campus. NHx measurements were ~~conducted~~ taken at the Environmental Studies Hall (open circle in c). (d)~~:~~ Outside view from the seventh floor (26 m above the ground) to the northeast taken in early December.

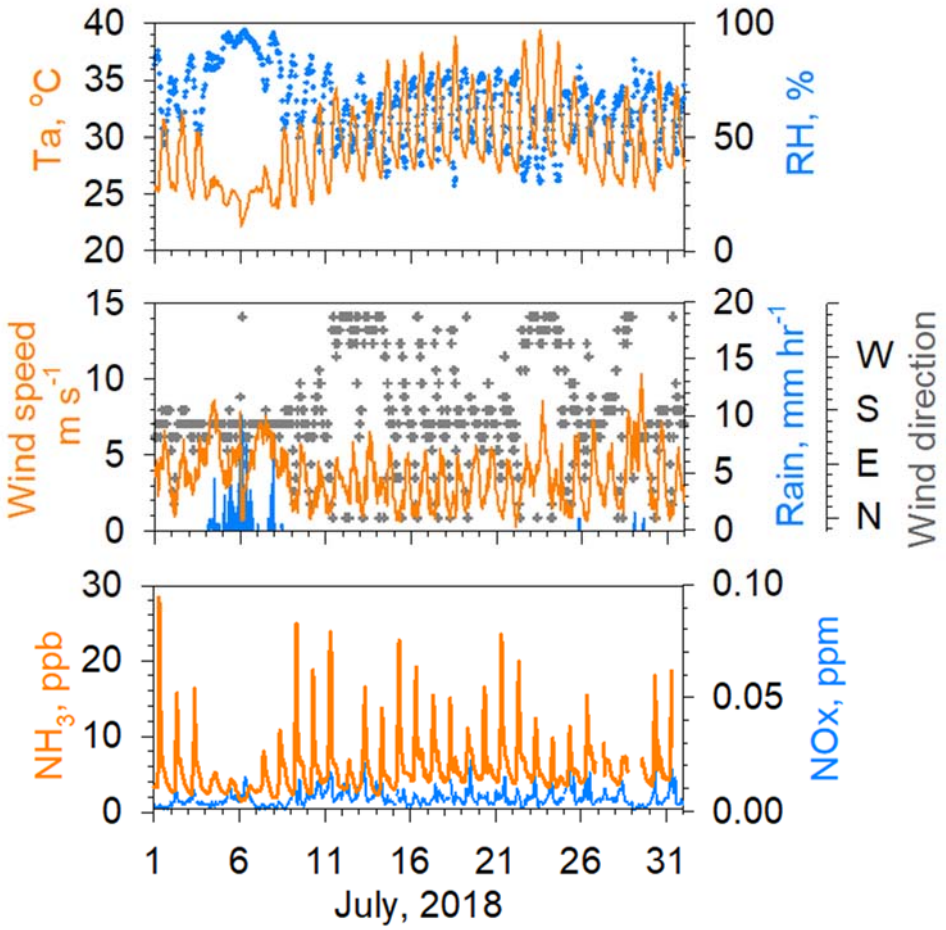


Figure 2 NH_3 and NOx concentrations with meteorol~~ogical~~ ogical data in Nagoya during July~~,~~ 2018.

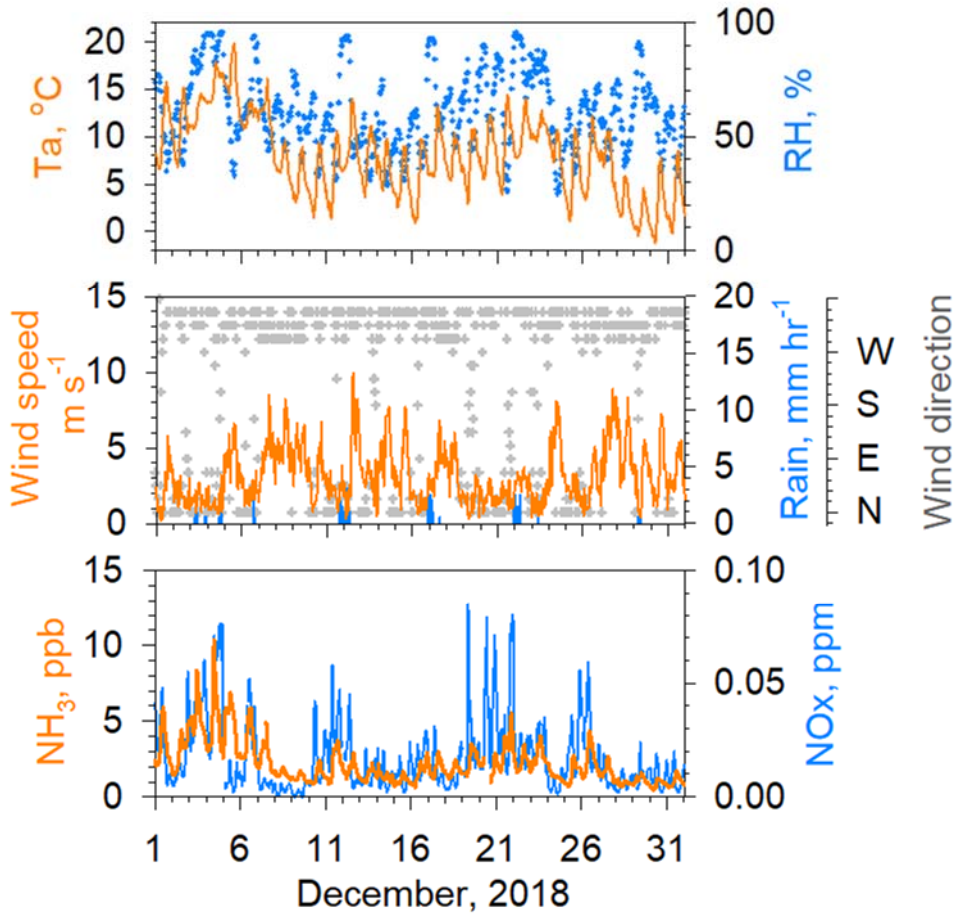


Figure 3 Same as Fig. 2, but for results obtained during December, 2018. The maximum of the vertical axis for NH_3 is reduced to 15 ppb.

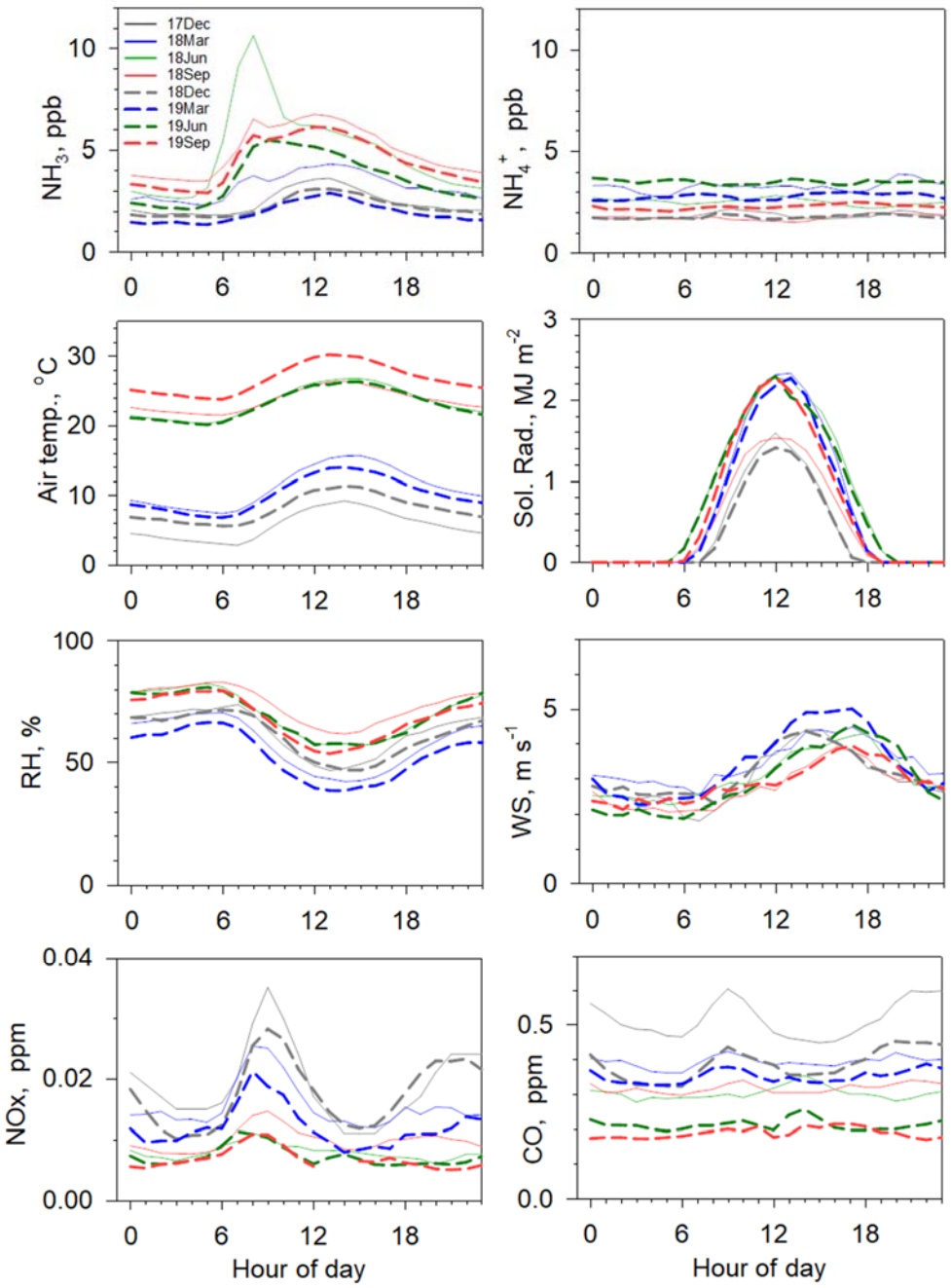


Figure 4 Hourly averages of various concentrations and meteorol~~ogical~~ ogical parameters for several months: December (fine gray), 2017; March (fine blue), June (fine green), September (fine orange), and December (dotted gray), in 2018; March (dotted blue), June (dotted green), September (dotted orange), 2019~~.~~; RH~~:~~, relative humidity; WS~~:~~, wind speed~~.~~

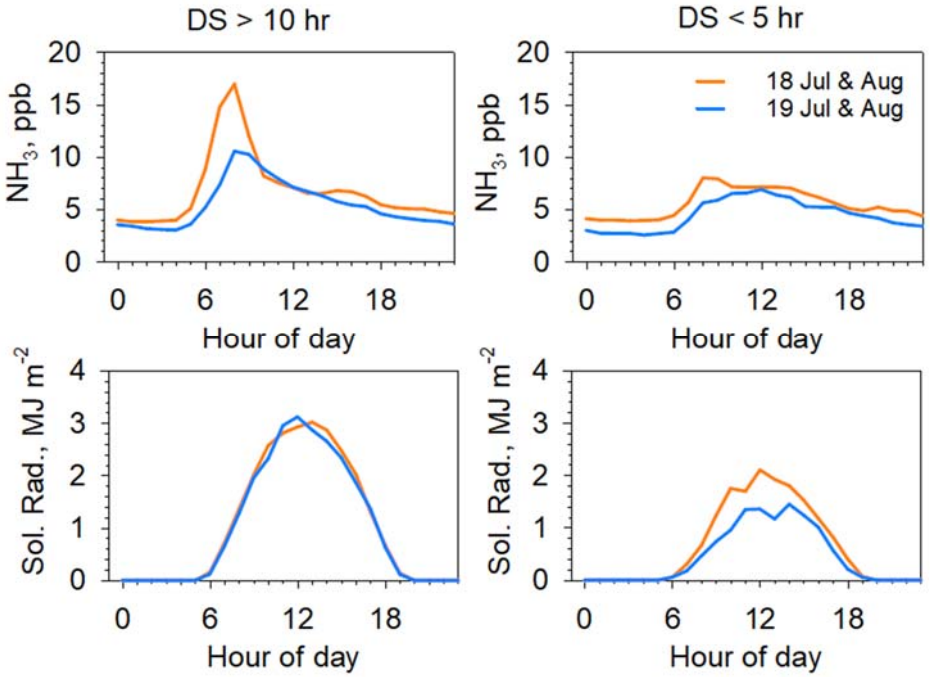


Figure 5 Hourly average of NH_3 concentration and solar radiation during~~from~~ July ~~to~~ August in ~~in~~ 2018 (orange) and 2019 (blue). Left column: averages for ~~the~~ fine ~~the~~ days both ~~fulfilled~~ daily sunshine >10 hr and daily wind speed <3 m s^{-1} (11 days in 2018 ~~and~~, 10 days in 2019~~, respectively~~respectively~~)~~). Right column: averages for ~~the~~ cloudy days all ~~fulfilled~~ daily sunshine <5 hr, daily wind speed <3 m s^{-1}, and daily rain <3 mm (4 days in 2018 ~~and~~. 7 days in 2019).

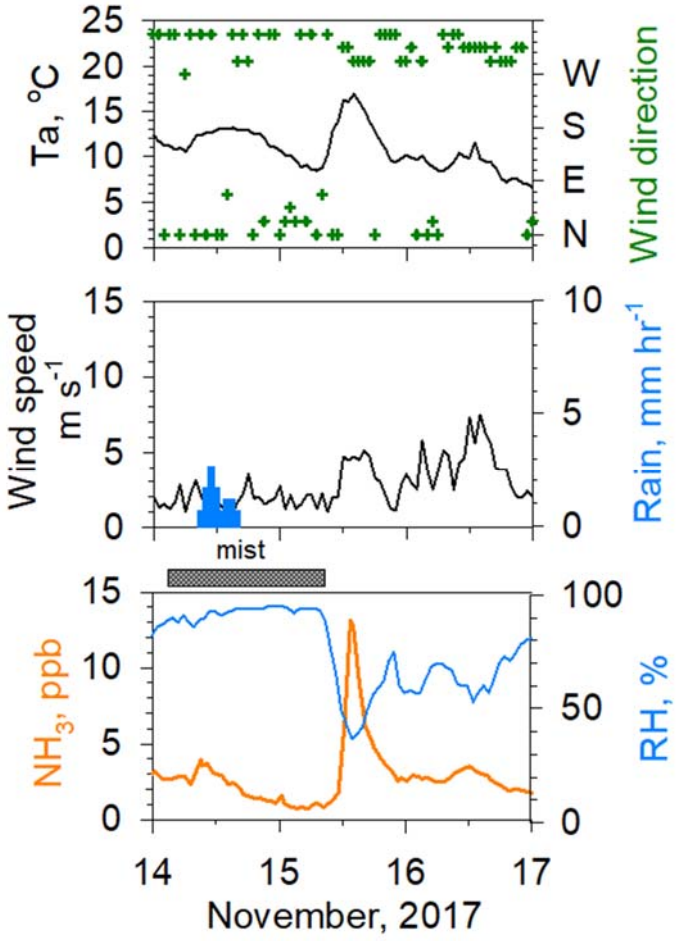
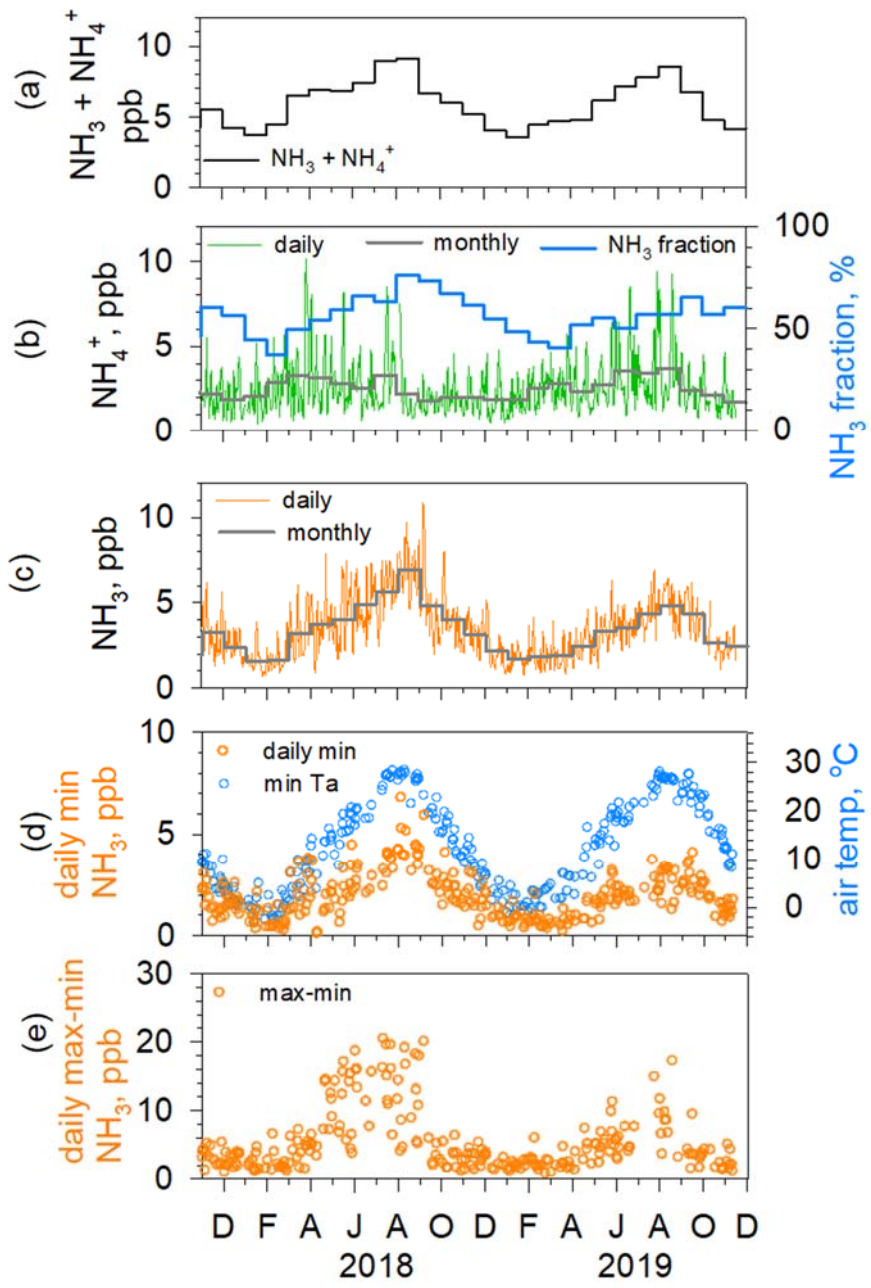
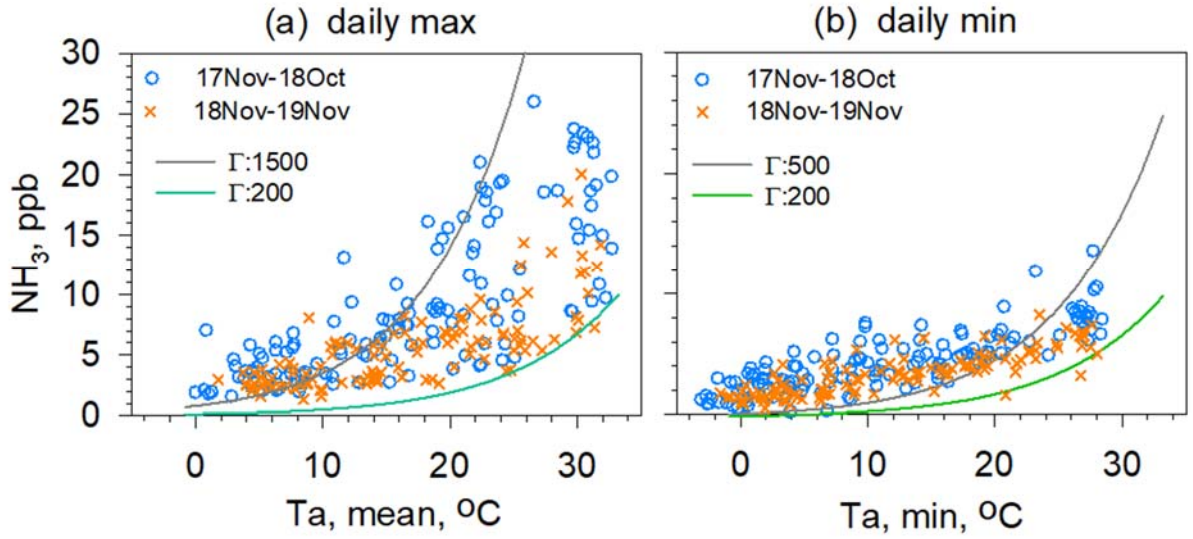


Figure 6 ~~Impact~~ Effects of ~~the~~ rain–mist event~~s~~ on ~~the~~ ambient NH_3 concentrations during~~from~~ 14 ~~to~~ 17 November 2017



~~Figure 7 (a~~Figure 7(a)~~):~~ Monthly NH_3 + NH_4^+ concentrations. (b) ~~daily~~ Daily (thin green) and monthly (thick gray) NH_4^+ concentrations with NH_3 fraction (thick blue) to NH_3 + NH_4^+ concentration. (c) ~~daily~~ Daily (thin orange) and monthly (thick gray) NH_3 concentrations. (d)~~:~~ ~~daily~~ Daily minimum NH_3 concentrations (orange circle) and minimum air temperature (blue circle) for ~~the~~ days of both ~~fulfilled~~ average relative humidity <70% and daily average wind speed <3 m s^{-1}. (e)~~:~~ ~~range~~ Range of diurnal NH_3 concentrations (max-min: orange circle) for ~~the~~ days of both ~~fulfilled~~ average relative humidity <70% and daily average wind speed <3 m s^{-1}.



~~Figure 8 (a~~Figure 8(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.

~~??> in the figure, use a space after the colon in all cases. Use a long dash or —— between days. >~~

(a)

(b)

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