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.

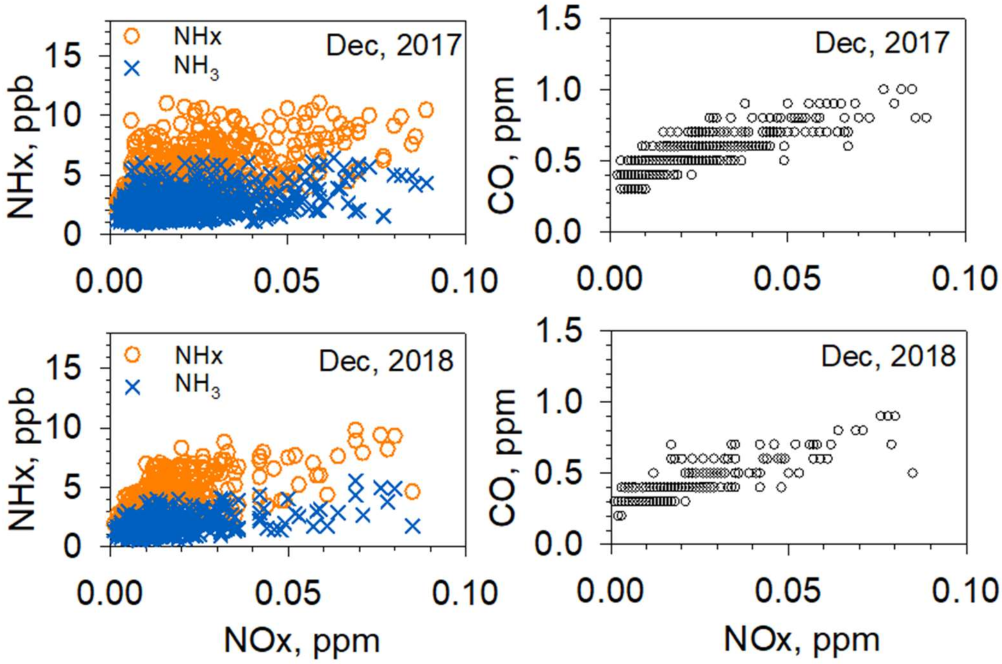
Minor suggested edits #2:
Include dates in Figure captions: Figure 5. Impact of the rain–mist event on the ambient NH_3 concentrations from 14 to 17 November 2017.

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.