

Interactive comment on “Measurement report: Exploring the NH₃ behaviours at urban and suburban Beijing: Comparison and implications” by Ziru Lan et al.

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—We thank both referees for their very constructive comments and suggestions. We revised our manuscript according to their comments and suggestions.

Response to comments by referee 1

Anonymous Referee #1

Overview: The paper is well written and presents a very important dataset which adds to the rather sparse number of long term ambient ammonia datasets. The information provided gives a detailed insight to the ammonia variation at the two sites and the

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influence of meteorological conditions. However the context of the measurement and the emissions environment driving the concentrations would make for a more powerful paper. In addition there needs to be greater detail in the analytical methodology and presentation of quantitative calibration, relevant uncertainties and the analytical method for interpretation of the measurement which hopefully the authors can provide which would strength the paper.

Detailed comments: Section 2.1: It would be very useful if there is an emissions or land use map for each of the sites, for the surrounding area in addition to the large scale map.

Response: The resolution of current NH₃ emission data is insufficient to display the difference of the two sites. We add a land use map (Fig. R1) in the revised version.

Section 2.2 It is clear that the authors have taken care to calibrate they ammonia monitor. However unfortunately no calibration data is presented which it should be. Firstly it is stated that “obtained concentration was normalized with respect to a reference concentration”. The normalisation factor should be reported. The detection limit of the instrument is noted as 0.2 however given that the authors discuss the issue of ammonia stickiness, the baseline would need to be checked for drift regularly in order to identify any baseline drift particularly as the internal surfaces of the instrument become coated. Was this done through out the deployments? Was there any evidence of baseline drift? It is quite important to show this data so that the reader can have confidence in the reported concentrations. Presenting the calibration data and blanks (ammonia free air) would be very useful for the reader to have confidence in the accuracy of the data presented.

Response: The word of normalization is not propriate here. We mean that we use a same calibration standard source to calibrate the instruments. The detection limit of the instrument is 0.2 and the maximum drift of 0.2 ppb/24hrs, which provided by the manufacturer, and we don't check it during the measurement. Due to ammonia

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stickiness, zero check needs more time to stabilize, we only did it during the multiple-points calibrations. Figure R2 is a typical multiple-points calibration of NH₃ analyzer with a cylinder standard gas.

The set up of the instrument is described but key parameters including the flow rates are not reported. What was the sampling flow? Was an external pump used, and did the inlet lines sample directly from the air or pass through a manifold? It is noted that filters are used, but are the filters changed regularly or cleaned to remove particulate (which can revolatilise NH₃ if warmed). Are the filters temperature stabilised?

Response: The inlet lines sampled the air through a manifold and the lengths of the line from manifolds to the analyzers are less than 2.0 m. The flow rates of the analyzers are over 0.4 L/min. The filters are changed every 2–3 weeks. The filters and the instruments are deployed in an air-conditioning room, so the filters temperature is relatively stabilized. Inlet heated is often suggested by people to reduce NH₃ “sticks” to surfaces. According our test (Fig. R3), when heating (70°C) was on, there did have a peak lasting several minutes (5–6 min) and then decreasing to the normal levels in ambient air, which means a new balancing process has been established. Heated filters are not suggested here because it will promote the thermal decomposition of ammonium salt in the particulate matter accumulated at the filter.

Also it would be interesting to know how the calibration was done with a standard gas cylinder. The experience of the reviewer has been that the addition of a dry calibrated reference NH₃ gas leads to a complete loss of the NH₃ signal in some of these OAICOS types of instruments (as the instrument uses the water line for holding the NH₃ signal). Did the authors observe this? Was a humidified calibration done. The details of this would be useful information for the readers.

Response: We use a zero-gas supplier, in which the water in humid air is condensed mostly by the air compressor, to dilute the standard NH₃ gas from a cylinder. The water content in the zero gas is still abundant for holding the NH₃ signal. We com-

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pared the calibration results from a standard gas cylinder (Beifen, Beijing, China) and from a permeation tube (Fine metrology S.r.l.s., Spadafora, Italy) and there showed a comparable result (Fig. R4). As a relatively fixed dilution flow, which is close to the flow demand of the analyzer, can be set using a cylinder gas with a broader range of calibration curve, we prefer to use the cylinder gas instead of NH₃ permeation tube to calibrate the analyzer. While, if the NH₃ permeation tube used, the expected span concentrations only obtained by changing the flow of the dilution flow.

In order to understand the response of the instrument, it would be good to have a figure with some of the measured data before averaging is done, particularly during the case study of the precipitation event perhaps or during Spring when the ammonia concentrations are highest. What was the estimated response time of the instrument? It is true that the response time is faster than when going from low to high concentrations, but it would be useful for the authors to characterise that for this setup – it is the response of the sample lines as well as the instrument. From the long term dataset a precision and accuracy and LOD should be presented.

Response: We have a test in summer, 2018. The sample air was switched between room air and outside air. The room air was with less humidity because air condition was on. And the outside air was with high humidity. NH₃ levels in room and outside air also show a great difference. The result is showed in Fig. R5, which is plotted with 1-min average data. Under these extreme changes of H₂O, NH₃ exhibited a response less than 1 hour. The response time is faster when going from low to high concentrations than from high to low one. The test tells us that it's sound to present the NH₃ in hourly mean, although minute-average data might have a limitation.

Results and Discussion: Figure 2: Please move baseline to zero as it is hard to interpret the NH₃ concentrations at the low end. I would prefer the NH₃ to be on its own graphs so that the reader can easily look at the NH₃ data which is the primary focus of the paper.

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Response: We modified the figure (Fig. R6).

P6-7: Soil: There is some discussion around soil emissions of ammonia. I think it would be useful for the authors to make clear that soil itself does not emit ammonia per se, ammonia emissions from soils or vegetation are due to either fertiliser applied to the soil or ammonia deposition and re-emission. It would also be good to frame the discussion on the acidic soils with the aqueous acid-base chemistry, of which there is quite a big literature.

Response: Agree the opinion.

Section 3.2 and Section 3.3 and Supplementary material: The discussion of the differences in the seasonal and diurnal variability of NH₃ and H₂O is really interesting and highlights the importance of understanding the boundary layer height and dilution/dispersion processes driving ambient ammonia concentrations – which are very high for an altitude of 70-100m! Though outside of the scope of this paper, a detailed modelling study of the datasets could be very insightful. However because of the complexities and rather small concentration changes I think that both of these sections need to be more conservative about the changes/trends/drivers of changes in concentrations. I would suggest through out that they authors should highlight uncertainties in the analysis.

Response: Agreed. In this paper, we report and compare the measurement results of NH₃ at urban and suburban Beijing. We are surprised by their difference in diurnal changes because the distance between the two sites is only 32 km away, which difference indicates a difference in source and sink. Section 3.2 and Section 3.3 are mainly the statistical results.

In particular the use of linear correlations is difficult to justify. In the supplementary material the linear correlation between T and RH of the NH₃ are plotted and the correlations summarised in Section 3.3. I am a bit concerned about this simple approach. There is much evidence that the ammonia equilibrium in the environment is non-linear

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– specifically it is exponential with equilibrium concentrations doubling for a 5°C in thermodynamic equilibrium. So rather than start with linear correlations the exponential model should be tested first (as the best theoretical relationship which has basis in physical chemistry).

Response: The linear correlations are for the average diurnal changes, not for all the hourly data (see fig. R7). In Fig. 2, scattering points are divergent, and the exponential model are not the best fitting. Similar result can be found in Chang et al. (2016). Your suggestion will be considered in further analysis on selected data. Chang, Y., Zou, Z., Deng, C., Huang, K., Collett, J. L., Lin, J. and Zhuang, G.: The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai, *Atmospheric Chemistry and Physics*, 16(5), <https://doi.org/10.5194/acp-16-3577-2016>, 2016.

Another concern was that the relationship was been studied over very small concentration ranges (<2ppb in some cases). Once the authors have assessed the precision and accuracy of their dataset, then error bars can be applied to these plots and then in some cases no line should be plotted, or a larger data group analysed. A non-linear relationship can be seen in some of the graphs. The opposite relationship is seen in a couple of plots, therefore it would be useful for the authors to look at those in a bit more detail. I would suggest a review of this section to make more clearly justifiable statistical analyses between ammonia concentration, relative humidity and temperature.

Response: Yes, for seasonal data, the error bars show a similar pattern with the average data (Fig. R8). In the section, we statistically analyze the relationships between the average diurnal ammonia concentration with relative humidity and temperature. Yes, there showed small concentration ranges in the diurnal variation in a seasonal average, but for the hourly data, they exhibit more fluctuate (Fig. 1).

Minor point: Some language checking would be useful.

Response: The paper has been edited in language by Wallace Academic Editing. We

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try the best to check the language again.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1047>, 2020.

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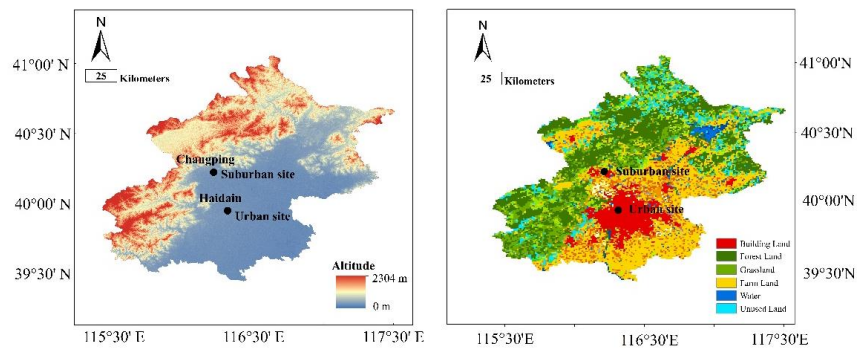


Figure R1. Observation sites and the topography and land use in Beijing

Fig. 1.

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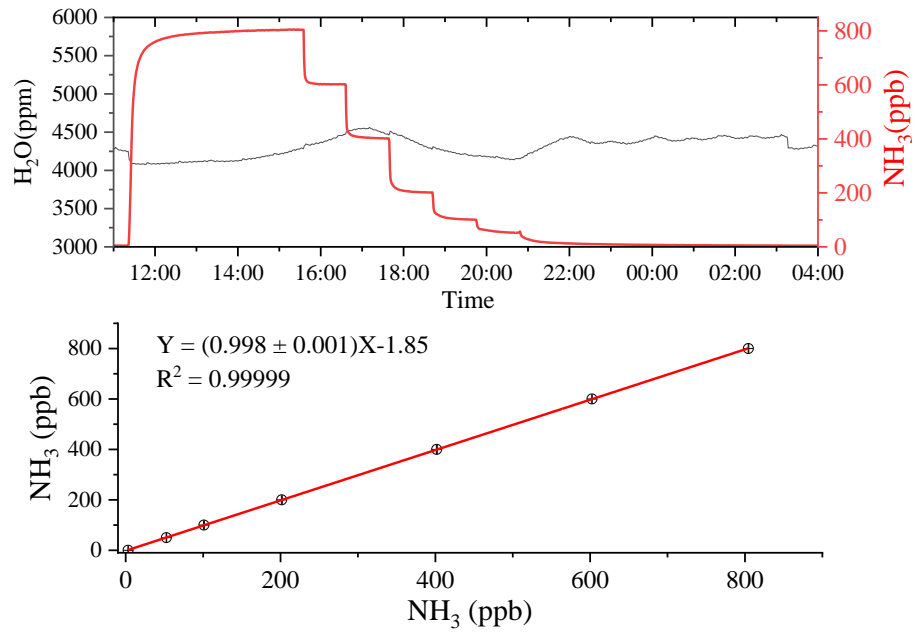


Figure R2. A typical multiple-points calibration of NH₃ analyzer with a cylinder standard gas

Fig. 2.

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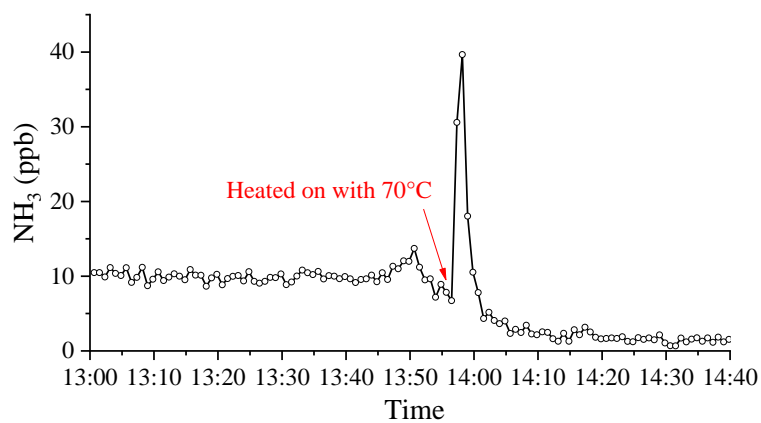


Figure R3. New balance established in 5–6 min after inlet heated.

Fig. 3.

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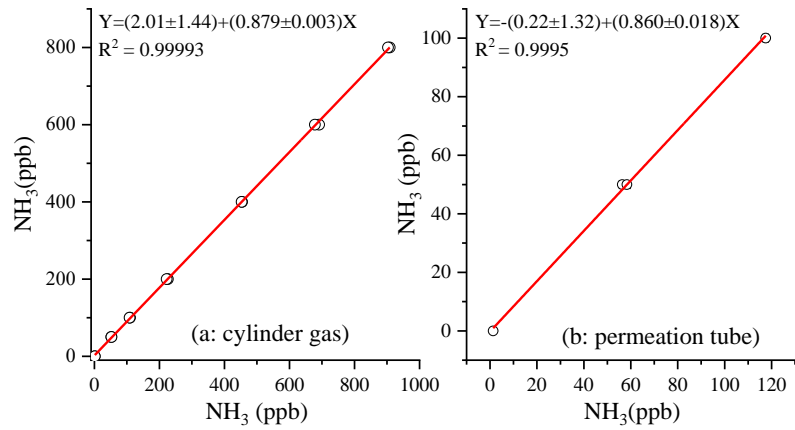


Figure R4. A comparable calibration result from a standard gas cylinder and from a permeation tube

Fig. 4.

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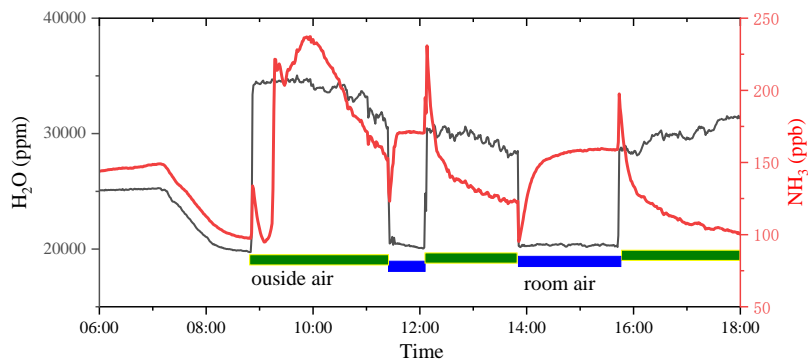


Figure R5. The response of NH₃ and H₂O as the sample air was switched between room air and outside air.

Fig. 5.

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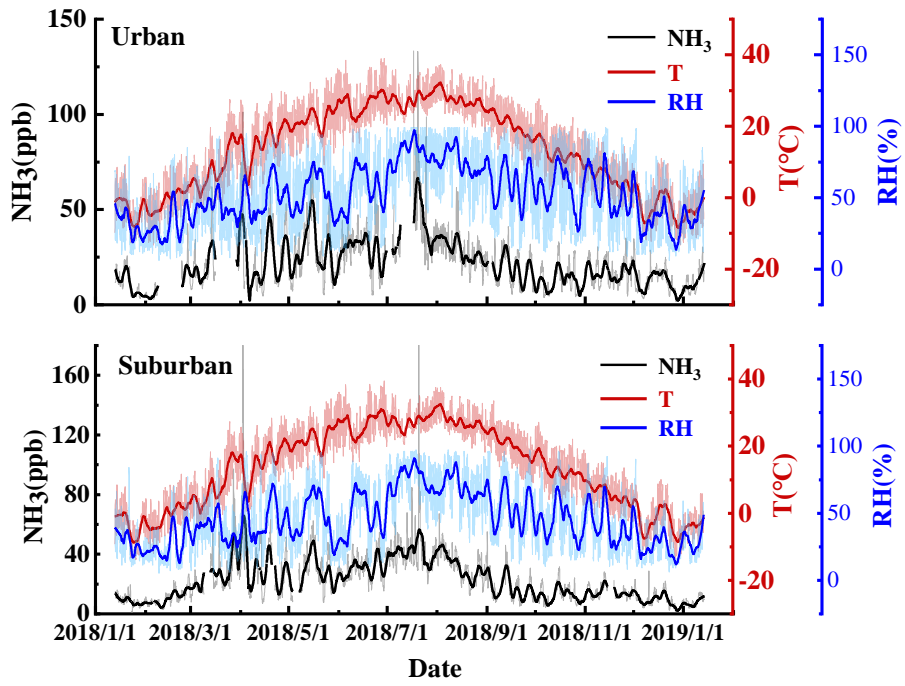


Figure R6. Temporal variations in the hourly average NH_3 mixing ratios, temperatures (T) and relative humidity (RH) at the urban and suburban stations in Beijing. Continuous thick lines were smoothed with 168 points (7 days) by using the Savitzky–Golay method.

Fig. 6. C13

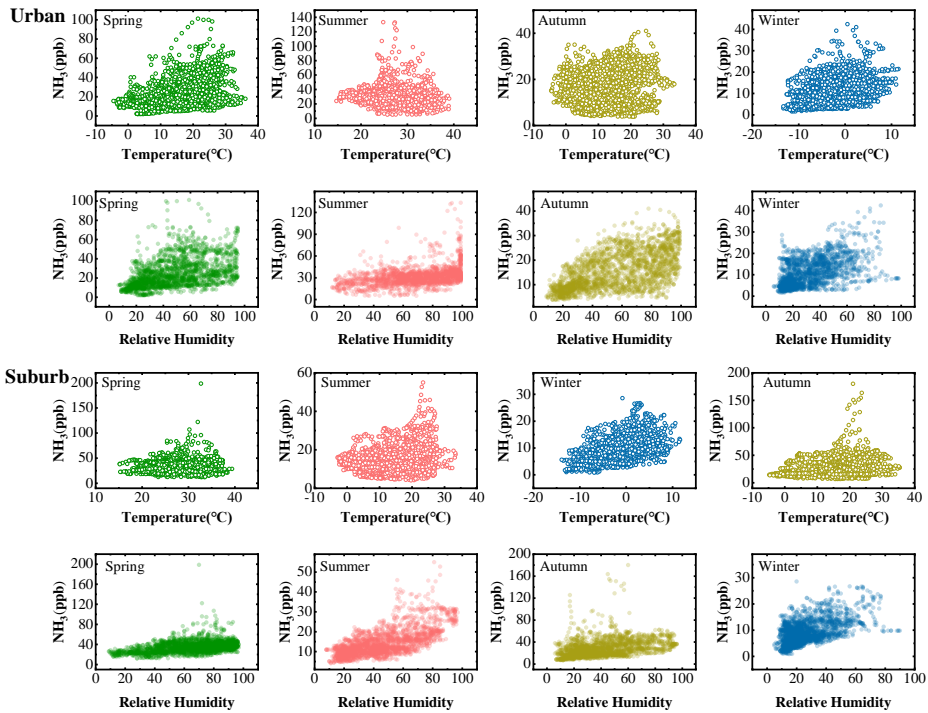


Figure R7. Scatter plots between NH_3 and T/RH in different seasons.

Fig. 7. C14

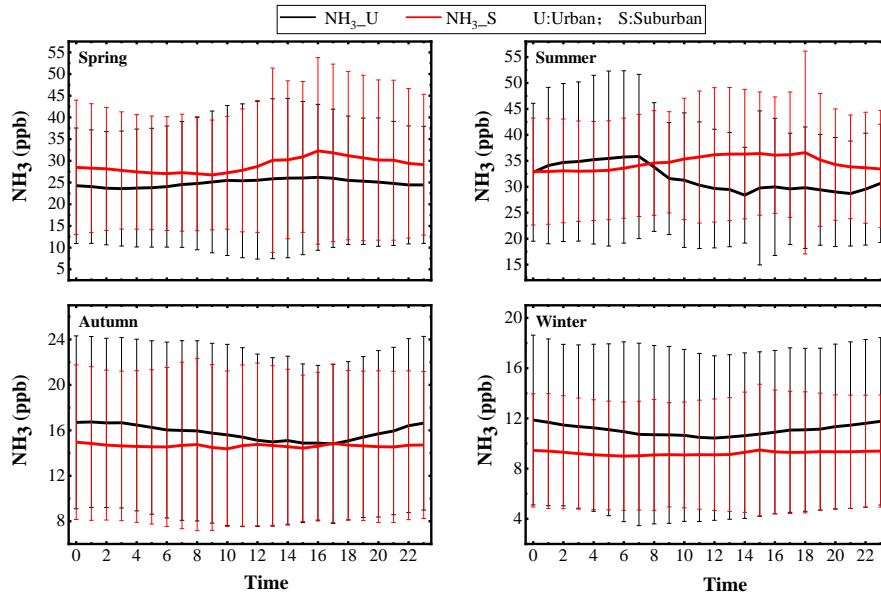


Figure R8. The average diurnal variations in NH_3 in different seasons.

Fig. 8.