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Interactive comment on "Measurement report: Exploring the NH_3 behaviours at urban and suburban Beijing: Comparison and implications" *by* Ziru Lan et al.

Anonymous Referee #1

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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 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

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Discussion paper

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.

Section 2.2 It is clear that the authors have taken care to calibrate the 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.

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?

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 OA-ICOS 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.

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.

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 it s own graphs so that the reader can easily look at the NH3 data which is the primary focus of the paper.

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.

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.

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 – specifically it is exponential with equilibrium concentrations doubling for $\sim$ 5oC 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). Another concern was that the relationship was been studied over very small concentration ranges (<2 ppb 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.

Minor point: Some language checking would be useful.

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