Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-613-RC1, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "High resolution vertical distribution and sources of HONO and NO_2 in the nocturnal boundary layer in urban Beijing, China" *by* Fanhao Meng et al.

Anonymous Referee #1

Received and published: 29 October 2019

This work by Meng et al. presents some of the first vertical profiles of HONO from China, from a tall tower located in urban Beijing. Using two IBBCEAS instruments, the Authors assess nocturnal HONO production and loss from a limited dataset of 3 case study days of HONO and NO2 observations via established approaches or other measurements for this region. Overall, this manuscript brings very little new information to bear on understanding HONO nocturnal formation in Beijing between clean and haze periods. Much of the analysis is replicated from the literature, but without using those approaches properly to place quantitative constraints on the observations. The presented dataset is frankly too limited to draw very broad conclusions, mainly because the supporting measurements presented in the methods are not being used to clearly

Printer-friendly version

Discussion paper

account for direct HONO emissions or aerosol surface area, nor for ground surface production. The interpretation of this dataset needs to be pushed further with all available measurements in order to be accepted into Atmospheric Chemistry and Physics.

One potentially productive avenue for this work would be to investigate the contribution of vertical transport of HONO produced at the surface into the nocturnal boundary layer, versus that calculated for aerosol formation. The meteorological data collected over the height of the tower is sufficient to carry out this analysis and would bring the necessary new dimension to this work. It is likely that this work can also close the mass balance of nocturnal HONO production for Beijing, but much more work is required. When combined with a thorough re-analysis of the dataset to satisfy the four major comments below, this work should be reviewed again to determine if it is suitable for acceptance.

Major Comments

1. Direct emissions: There are at least two direct emissions analyses for HONO from the Beijing vehicle fleet that have been previously published, which are cited in this work (Zhang et al 2018 and Tong et al 2016), but not used to build a deeper analysis of the observations. The Authors cite one of these and conclude that the majority of their observed nocturnal HONO comes from direct emissions. However, the Authors state they have the necessary measurements from this campaign to thoroughly quantify the HONO primary emissions (HONO, NO2, NO, and CO), but they do not use them. This analysis must be completed in full, with a figure added to this manuscript (or the SI) to show how the value stated was determined along with an assessment of its error. A thorough review and comparison to the literature for this emission ratio must also be made. It will also be valuable if the Authors can comment on the traffic patterns in Beijing that result in so much nocturnal HONO coming from direct emissions, as typically these are reported to peak during morning and evening rush hours. Finally, it is not clear if the Authors have accounted for and removed direct HONO emissions from their aerosol conversion analyses, which should be done, as it may otherwise

confound the interpretation.

2. Aerosol conversion of NO2 to HONO: A simple calculation is made to conclude that aerosol surface conversion of NO2 is not important to the observed HONO in the vertical profiles. The Authors use a single value of aerosol surface area from Beijing to perform this calculation, ignoring that they have a direct proxy for aerosol surface area from their particulate matter measurements (i.e. total PM1.0 mass). While this will also have uncertainty associated with it, the magnitude of potential error will be dramatically reduced. The current analysis is shallow and must be improved. One is left wondering why the aerosol measurements are given in the methods and not used in the data interpretation. The contribution of aerosol surface to HONO nocturnal production as a function of height has been reported infrequently and would be an improved contribution from this dataset. This should, again, include error analysis that spans the range of NO2 uptake coefficients, not only the highest value reported from the literature. The Authors are encouraged to use the chemical speciation of their aerosol to justify a selected NO2 uptake coefficient that is likely to be representative of conversion in Beijing and to propagate error based on the full range of quantified uptake coefficients towards a mass balance for HONO nocturnal production.

Further to this, the Authors make a series of confusing statements in their discussion of the importance of NO2 conversion on aerosols from their calculations. The Authors state that 1.02 ppb of HONO are produced during E3 and that is 'much less' than the measured 3.06 ppb. This is 33 %, which is certainly significant and counter to the conclusion that aerosol conversion is not important. Also here, if direct emissions are not accounted for, then this fraction becomes 1.02/1.53 which is 67 %. These findings need to be clarified as perhaps the time intervals have not been specified, which is leading to the confusion. The same analysis needs to explored and discussed for the other two vertical profiling periods using the measured vertical profile data instead of broad approximations of the necessary species.

Finally, the Authors reproduce the analysis of VandenBoer (2013) to conclude that the

data presented in Figure 11 clearly indicates the ground surface is the major HONO source, without quantifying its contribution with their measurements. Based on the presented vertical profiles in the manuscript and the SI, there is only one very clear observation of a vertical gradient that is clearly consistent with ground production (C2, Figure 7). In particular, the analysis of potential temperature to identify the nocturnal boundary layer height in Figure 8 does not show increasing HONO mixing ratios as the surface is approached, but instead there are uniform vertical profiles in the NBL and the residual layer, which indicates either efficient mixing or significant production in the overlying air (i.e. aerosol conversion). The increasing HONO mixing ratios in the residual layer matching those in the NBL over time strongly support aerosol conversion, since this air is disconnected from surface mixing if the inversion has been properly identified using the Brown et al (2012) approach. This is treated superficially in the analysis and needs to be explored in detail.

3. Nocturnal surface processes: The Authors evaluate the conversion efficiency of NO2 on the ground surface by replicating the approaches used in Zhang et al (2018) and Tong et al (2016), to find values of C-HONO that are comparable to other observations in urban environments. While this is a sound approach to interpret NO2 conversion to HONO, a quantification of the importance of the mechanism is not made. How much of the total column HONO is produced by this mechanism? The Authors have made the measurements, integrated the column HONO quantities, but not performed this analysis. Further to this, the Authors state that they calculated the amount of HONO being deposited on the surface, but do not present any of the values or a sensitivity analysis on the range of deposition velocities reported in the literature. It is concerning that a boundary layer mixing depth of 100 m was used when the mixed layer at the surface was directly measured. This section requires significant revision and expanded analysis to have sufficient quality to be accepted.

4. Figures: All measured and calculated quantities should be presented with the relevant error bars.

Figure 2 regression types are not specified in the caption or in the manuscript. The error in the measurements should be depicted on the panels and the appropriate regression for considering significant error in both measurements used (e.g. orthogonal least-distance regression). The uncertainty in the slopes and intercept should then also be reported.

The purpose of Figure 4 is very unclear. Either expand discussion around it in terms of its importance to nocturnal HONO production or remove it from the manuscript.

Figures 5 and 6 do not seem to have much purpose for this work. Figure 5 can be removed entirely as its contents are described clearly with the first and third sentences from Lines 237-240. Figure 6 could be removed entirely or one panel from parts a) and b) moved to the SI as an example since it, again, shows that the atmosphere is well mixed at sunset, which is expected and does not contribute significantly to the analysis of nocturnal sources.

The Figure 7 vertical profiles do not demonstrate that steady state between HONO production and loss has been reached, as the concentration of HONO at the surface has continued to increase. Typically, this observation has been seen after midnight (e.g. see VandenBoer et al (2013)). It does not mean that HONO deposition is not happening, but it does prevent quantifying the deposition term using the observations, which the Authors should be clear about.

Minor Comments: Line 168: If reported measurements are 15 s, then the associated detection limit should be presented.

Line 171: The measurement error was 'approximately' assessed as 9 %. How was this done and why is it 'approximately'? This should be used to denote error bars on observations presented in the figures. Have any corrections for NO2 to HONO conversion on the instrument inlet and cavity surfaces been characterized and corrected for?

Line 178: The models and detection limits of the supporting gas analyzers need to be

Printer-friendly version

Discussion paper

given. Why is none of this supporting data shown or used in the analysis?

Lines 180-185: Again, supporting measurements are noted as having been made here, but they are not used to interpret the data. These should be used as noted in the major comments above.

Lines 191-194: An NO2 intercept of 750 ppt should be explained. Is it statistically different from zero? See major comment on figure regressions and error analysis above.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-613, 2019.

Printer-friendly version

Discussion paper