Response to interactive comments on

"High resolution vertical distribution and sources of HONO and NO_2 in the nocturnal boundary layer in urban Beijing, China"

by Anonymous Referee #1

Fanhao Meng and Min Qin

General comments:

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 NO_2 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 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.

Response: We thank the Anonymous Referee #1 for pointing out the shortcomings in our analysis and presentation of the measurement data. We have significantly revised the manuscript to address the referee's comments and concerns. Below we give point-to-point response to address the referee's specific comments.

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, NO_2, 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.

Response: As the referee suggested, we have analyzed the correlations of HONO with CO, NO, and BC, which are considered to be the primary pollutants emitted from combustion processes like vehicle emissions (Sun et al., 2014; Zhang et al., 2018). Good correlations of HONO with CO (R^2=0.85), NO (R^2=0.76), and BC (R^2=0.84) at ground level were observed (Figure S5). This indicated the potential impact of direct emissions on the ambient HONO concentrations at night. Following the suggestion by Jörg Kleffmann, we have re-estimated the emission factor based on the field data. Five criteria were applied to ensure as much of freshly emitted air masses as possible: (a) only nighttime data (from 18:00 LT to next 6:00 LT) were included to avoid the fast photolysis of HONO; (b) only sharp peaks during nighttime and the elevations of HONO and NO_x over the background levels were estimated; (c) $\Delta NO/\Delta NO_x > 0.80$; (d) good correlation between HONO and NO_x; (e) short duration of the plume (< 30 min). The typical nocturnal wind speed at measurement site was 1.2 m s^{-1} and the distance to the roads was less than 1 km. So the duration of fresh air masses should have been less 30 min during transport processes. Criteria (b) and (c) were used as indicators for identifying fresh vehicular emissions. Criteria (d) and (e) further confirmed that the increase in HONO was primarily caused by direct emissions instead of heterogeneous reactions of NO_2.

Two examples of emission plumes based on the preceding selection criteria were showed in

Figure 6 in the manuscript. The slopes of HONO to NO_x can be considered as the emission ratios (Rappenglück et al., 2013). For a month field observations, 11 fresh emission plumes satisfied criteria (Table 1). The derived emission factors ranged between 0.78% and 1.73%, with an average value of 1.28% ± 0.36%, which was larger than the 0.53%–0.8% measured in the tunnel in Wuppertal (Kurtenbach et al., 2001) but within the range of previously published results (0.19%–2.1%) (Kirchstetter et al., 1996; Kurtenbach et al., 2001; Su et al., 2008; Rappengluck et al., 2013; Yang et al., 2014; Xu et al., 2015; Liang et al., 2017; Zhang et al., 2018; Li et al., 2018). The minimum ratio of 0.78% approximated the value (0.8%) measured in Wuppertal. The maximum ratio of 1.73% in our study was comparable to the value of 1.7% in Houston, Texas by Rappenglück et al. (2013). Comparisons of the derived HONO/NO_x ratios with the previously reported results are summarized in Table S2 in the supplementary information, as the referee suggested.

The minimum HONO/NO_x ratio of 0.78% was used to minimize the risk of overestimating direct emissions (Su et al., 2008). In this case the risk of overestimating vehicular emissions was minimized, but still could be the potential secondary HONO formation during the transport from emission to the measurement site. The direct emissions contributed an average of 29.3% ± 12.4% to the ambient HONO levels at night, with an average $HONO_{emis}$/HONO value of 35.9% ± 11.8% during the clean episode and an average $HONO_{emis}$/HONO value of 26% ± 11.3% during the haze episode. The lower vehicular emission contributions during haze episode could be caused by an odd-even car ban.

As pointed out by the referee, we have already considered the influence of direct emissions in the aerosol conversion analysis, which has been stated in detailed in section 3.4.2. The discussion in "3.3 Direct emissions" have been significantly revised to address the referee's comments and concerns.

2. Aerosol conversion of NO_2 to HONO: A simple calculation is made to conclude that aerosol surface conversion of NO_2 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 $PM_{1.0}$ 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 NO_2 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 NO_2 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 NO_2 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.

Response: We made a deeper analysis in aerosol conversion of NO_2 to HONO, as the referee suggested. The newly obtained aerosol surface areas at ground and at 260 m, which was corrected to ambient aerosol surface area (S_{aw}) for particle hygroscopicity via a growth factor (Liu et al., 2013;

Wang et al., 2018), were used to estimate the nocturnal HONO production from heterogeneous reaction of NO_2 on aerosol surface. The time series of S_{aw} at ground level and at 260 m is shown in Figure. S2 in the supplementary information. The surface area information for particles larger than 0.5 μm were not valid at ground level and at 260 m during the measurement periods. Hence, this is a lower limit estimate of the total surface area for the heterogeneous reaction. The vertical profiles of HONO and NO_2, and the aerosol surface area measured at 260 m allowed us to estimate the nocturnal HONO production by heterogeneous uptake of NO_2 on aerosol surface.

As the referee pointed out, the influence of direct HONO emissions have been considered in the aerosol conversion analysis. The CO and BC measured at ground level were independent of the CO and BC observed at 260 m during the haze period (Fig. S10), since it can be expected that air masses in the residual layer were decoupled from the ground-level processes and largely free of NO_2 emissions (Brown et al., 2012; VandenBoer et al., 2013). An estimate of the nocturnal HONO production on aerosol surface was made using the RH corrected aerosol surface area (S_{aw}) and NO_2 observations from the residual layer during E3. The yield of hydrolysis reaction assumes that HONO and HNO_3 are formed by equimolar disproportionation of two NO_2 molecules and immediately release HONO (Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009). The reactive uptake of NO_2 by the aerosols was assumed to occur on all measured aerosol surface area, regardless of chemical composition. An NO_2 uptake coefficients in the dark of 1×10^{-5} to 1×10^{-6} from the literature, an average S_{aw} of 2314 μm^2 cm^{-3} observed in the residual layer between 22 and 01 h (the vertical measurement periods on December 11th), and the upper limit of the observed NO_2 of 54 ppb from the residual layer were used during E3. The HONO production of 30-300 ppt in an interval of 1.5 h could account for HONO increases of 15-368 ppt between profile measurements. Thus, the production of HONO solely on aerosol surface explained HONO observations during E3. In addition, the data presented in Figure 10 (the original Figure 11) were divided into the clean episode and the haze episodes for re-analysis. The column average concentration of HONO was independent of the HONO mixing ratio observed from the ground level to 10 m in height (R^2 = 0.27) during E3 (Figure 10a), suggesting that the aerosols presumably dominates the production of HONO aloft by heterogeneous conversion of NO_2 during the haze episode.

The same analysis for HONO production on aerosol surface were also made to the other vertical measurements during C2, as the referee suggested. A high correlations (R^2 = 0.83) between the

measured CO and BC at ground level and the CO and BC at 260 m were observed (Figure. S10), which indicated that vehicle emissions affected air masses in the residual layer. The lack of NO vertical profile cannot directly correct the contribution of direct HONO emissions. So we assumed that the contribution of direct emissions was consistent at ground level and in the residual layer, and the relative importance of aerosol and ground surfaces in nocturnal HONO production could be roughly estimated. The average $HONO_{emis}$/HONO ratio of 35.9% ± 11.8% during the clean episode was used as the contribution of direct emissions to ambient HONO levels during C2. This is a higher limit estimate of the contribution of direct emissions to the HONO levels in the residual layer. The average S_{aw} of 791 and 894 μm^2 cm^{-3} from 17 to 24 h (the vertical measurement periods on December 9th and 10th), and the upper limit of NO_2 observations of 36 and 44 ppb from the residual layer were used to estimate HONO production on aerosols on December 9th and 10th. The HONO production of 26–259 ppt in an interval of 5.5 h was lower than the direct emissions corrected HONO increases of 305–608 ppt between the vertical profile measurements on December 9th. The formation of HONO solely on aerosol surface cannot explain the observed HONO increases in the residual layer. The HONO observed in the residual layer was primarily derived from heterogeneous conversion of NO_2 on the ground surface followed by vertical transport throughout the column. The column average concentration of HONO was related to the amounts of HONO observed between the ground level and 10 m (Figure 10b, R^2 = 0.93), which also suggested that the surface source of HONO affected HONO observed throughout the depth of boundary layer. However, the HONO production on aerosols in an interval of 5.35 h is 33–332 ppt on December 10th, which was comparable to the direct emissions corrected HONO increases of 114–369 ppt between the two vertical profile measurements. This could have been due to the formed shallow inversion layer near the surface (Figure 4), which inhibited the vertical transport of nighttime HONO at ground level. Besides the contribution of direct HONO emissions could be even more overestimated, which might also affect the estimated result. All of these may result in the aerosols dominated the heterogeneous production of HONO from NO_2 in the residual layer on December 10th.

As the referee suggested, we have significantly modified the discussion in this section to make our statements more clearly. The representative uptake coefficient of NO_2 in Beijing derived from the chemical speciation of the aerosol will be further studied in other manuscript. In this study, we primarily focused on estimating the relative importance of aerosol and ground surface in nocturnal

HONO production at different pollution levels.

3. Nocturnal surface processes: The Authors evaluate the conversion efficiency of NO_2 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 NO_2 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.

Response: Thanks for the comment and suggestion. Following Jörg Kleffmann's suggestion, the slope determined by linear regression will statistically better describe the efficient first order conversion rate constant of NO_2 to HONO. Thus, we re-estimated the conversion frequency and corresponded HONO production rate by NO_2 (P_{NO_2}). Direct HONO emissions have been considered and removed in evaluating the conversion frequency. The conversion frequency during vertical measurements (December 9th, 10th, and 11th) were 0.0082, 0.0060 and 0.0114 h^{-1}, respectively, corresponding to a HONO production rate by NO_2 of 0.25 ± 0.03, 0.28 ± 0.02, and 0.60 ± 0.02 ppb h^{-1}. It is necessary to elaborate that the derived P_{NO_2} is net HONO production, which means sources and sinks of HONO (aerosol and ground surface source, deposition, etc.) have already been taken into account in P_{NO_2}. As the referee suggested, the net contribution of surface production of HONO to the column could be roughly estimated based on the assumption that HONO production on aerosols was insignificant compared to the ground surface during the clean episode, which has been suggested in other studies of HONO vertical gradient (VandenBoer et al., 2013; Wong et al., 2011; Zhang et al., 2009). The surface production rate of HONO was estimated to be 0.25 ± 0.03 and 0.28 ± 0.02 ppb h^{-1} on December 9th and 10th, respectively, which was an order of magnitude higher than the maximum production rate of HONO on aerosols (0.047 and 0.062 ppb h^{-1}). The agreement supported that ground surface dominated HONO production by heterogeneous conversion of NO_2 during the clean episode.

In contrast, the production of HONO on aerosols as an important nighttime HONO source cannot be ignored during the haze episode, as discussed in section 3.4.2. To estimate the contribution of the surface HONO production, a deposition velocity of NO_2 to the surface in the dark, V_{dep,NO_2} of 0.07 cm s^{-1} (VandenBoer et al., 2013), in a measured boundary layer of height, h of 140 m, were used to estimate the HONO production rate ($P_{HONO,ground}$) by heterogeneous conversion of NO_2 on ground surfaces ($P_{HONO,ground} = \frac{1}{2}\frac{V_{dep,NO_2}}{h}\overline{[NO_2]}$). The $P_{HONO,ground}$ of 0.47 ± 0.02 ppb h^{-1} on December 11th (E3) was comparable to the HONO production rate on aerosol surface of 0.2 ppb h^{-1}. This result also suggested that the production of HONO on aerosols is an important nocturnal HONO source during the haze episode.

The calculation and sensitivity analysis of deposition velocity of HONO have been stated in the revised manuscript, as the referee suggested. The temperature-dependent deposition velocity of HONO ($V(HONO)_T = \exp(23920/T - 91.5)$) (Laufs et al., 2017) was used to estimate the deposition velocity of HONO ($V_{dep,HONO}$). The average $V_{dep,HONO}$ calculated from nocturnal measurements (00:00–06:00 LT) was 1.8 cm s^{-1}, with a range of values spanning 0.9 to 3 cm s^{-1}, which was within the range of previously reported values between 0.077 and 3 cm s^{-1} (Harrison and Kitto, 1994; Harrison et al., 1996; Spindler et al., 1998; Stutz et al., 2002; Coe and Gallagher, 1992; Laufs et al., 2017). A mesured boundary layer mixing height of 140 m was also used for analysis as suggested. Following the referree's suggestion, we also made a budget analysis of nighttime HONO, which was utilized to estimate nocturnal sources/sinks of HONO. The average dry deposition rate (L_{dep}) of HONO was estimated to be 0.74 ± 0.31 and 1.55 ± 0.32 ppb h^{-1} during C2 and E3, respectively, implying that significant amounts of HONO were deposited to the ground surface at night. The budget analysis results also suggested that the production rate of HONO on aerosols (0.19 ± 0.01 ppb h^{-1}) was comparable to the surface production rate (0.47 ± 0.03 ppb h^{-1}) during the haze episode.

We have significantly revised the discussion in the manuscript in "3.3 Direct emissions", "3.4.2 Relative importance of aerosol and ground surfaces in nocturnal HONO production" and "3.4.3 Nocturnal HONO production and loss at ground level" to address referee's concerns and to make our argument more clearly.

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.

Response: Thanks for the comment and suggestion. The relevant error bars have been presented in the revised manuscript as suggested. We have significantly modified Figure 2 and added the regression type to the caption. The orthogonal linear squares regression was utilized to estimate the error of both measurements. The uncertainty of slope and intercept were also added in Figure 2. As the referee pointed out, the measurement uncertainty of IBBCEAS instrument have already been depicted in section 2.2 (line 249–253) of the manuscript. Thus, we did not add the statements of measurement uncertainty of IBBCEAS instrument here.

The purpose of Figure 4 was to identify the variation of wind speed in the overlying air. The vertical profile data were used for analysis when wind speed less than 6 $m \cdot s^{-1}$ throughout the column. The statements in line 334–338 are sufficient to describe its contents, so we removed it from the manuscript as suggested. Figure 5 has also been removed, and the panel (a) of Figure 6 has been moved to the supplement as an example, as the referee suggested.

We agree that a near-steady state between HONO production and loss has not been reached in

Figure 4 (the original Figure 7). A near-steady state plateau in HONO mixing ratio and HONO/NO_2 was observed near midnight during E3 in Figure 5 (the original Figure 8), and the vertical profiles showed an approximate plateau between 23 to 01 h. We have revised the description of Figure 4 and 5 (the original Figure 7 and 8) in section 3.2.2 to make our argument more clearly.

Minor Comments:

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

Response: The detection limits of HONO and NO_2 at time resolution of 15s are 120 ppt and 200 ppt, respectively, which have been added to the revised manuscript (line 247–248) as suggested.

2. 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 NO_2 to HONO conversion on the instrument inlet and cavity surfaces been characterized and corrected for?

Response: The measurement error of 9% is the total relative uncertainty of the IBBCEAS instrument, which is estimated considering the uncertainty in the absorption cross sections (5%), the calibration of mirror reflectivity (5%), spectral fitting (4%), the correction of effective cavity length (3%), the pressure in the cavity (1%), $\Delta I/I_0$ (1%) and sample loss (0.5%). The propagated uncertainties are estimated to be 8.7% which is approximately to be 9%. The relative uncertainty of IBBCEAS instrument and estimated uncertainty of 8.7% have been presented in the revised manuscript.

The inlet and optical cavity made exclusively of PFA Teflon are used to minimize the generation and wall loss of HONO. To investigate any potential secondary HONO formation on the inlet or cavity walls from conversion of NO_2. We measured 80 ppb NO_2 at different RH levels (20% RH, 30% RH, 50% RH and 70% RH) flowing through a 3 m PFA inlet tube into the IBBCEAS instrument for a long time at typical sampling flow rate (6 L min^{-1}). No significant HONO was observed in the cavity, suggesting that the secondary HONO formation is negligible for IBBCEAS instrument under typical operation condition. A more detailed description of our IBBCEAS instrument can be found in our published article Du et al. (2018).

3. Line 178: The models and detection limits of the supporting gas analyzers need to be given. Why is none of this supporting data shown or used in the analysis?

Response: Instrumental section has been revised including adding the models and detection limits of gas analyzers and giving related references. The auxiliary data was also shown in manuscript Figure 3, which was used in the subsequent analysis as the referee suggested.

4. 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.

Response: The auxiliary data have been used to interpret the vertical measurements in the subsequent analysis.

5. Lines 191-194: An NO_2 intercept of 750 ppt should be explained. Is it statistically different from zero? See major comment on figure regressions and error analysis above.

Response: We would first like to apologize for our mistake. The NO_2 intercept of 750 ppt in Figure 2 was caused by the mismatch of the timeline of NO_2 data measured by two IBBCEAS in correlation analysis. We have corrected this error and significantly modified Figure 2 as the referee suggested.

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