Response to interactive comments on

"High resolution vertical distribution and sources of HONO and NO₂ in the nocturnal boundary layer in urban Beijing, China"

by Anonymous Referee #3

Fanhao Meng and Min Qin

<u>**General comments:**</u>

Manuscript acp-2019-613 reports results of a nighttime vertical gradient study aimed at determining the sources and sinks of nitrous acid (HONO) in Beijing, China. Measurements were made from an instrumented container capable of ascending and then descending a 325 m tower over an hour, enabling measurements at ground level and up to a height of 240 m. The maximum height achieved means that measurements covered the surface layer, nocturnal boundary layer, and residual layer. Furthermore, the measurement campaign covered three periods of time marked by clean or hazy air masses. The results are then used to draw conclusions about the relative importance of direct (automobile), ground, and aerosol sources of HONO to the airshed.

The analytical measurements appear to be of high quality. The tower experiments are ideal for elucidating HONO sources and sinks, and it was a good idea to operate simultaneous ground-based and vertically transported IBBCEAS systems. It is not the first time that gradient measurements of HONO and related physical/chemical have been made using a tower/elevator and much of the approach to data analysis and interpretation closely follows previous studies (especially, VandenBoer, et al. J. Geophys. Res. 2013, 118, 10,155–10,171, doi:10.1002/jgrd.50721 and Stutz et al. J. Geophys. Res. 2002, 107, doi:10.1029/2001JD000390). Despite the lack of novelty, the data has the potential to provide insights into myriad processes affecting HONO production and loss in Beijing, an area where frequent high aerosol concentrations mean that multiphase chemistry has a large influence on atmospheric composition. However, I do not feel that sufficient analysis of the data was carried out to support the authors' conclusions. Therefore, I feel that the manuscript is not ready for publication; additional work must be carried out to properly analyze the data and extract the information it holds.

Response: We thank Anonymous Referee #3 for the valuable comments. The detailed and insightful comments and suggestions have greatly helped us to revise and improve the manuscript. We would like to point out that the measurement container in our study is lifted on the side wiring of the tower,

far away from the steel structure of the tower, thus minimizing potential wall effects, which is different from previous studies (Kleffmann et al., 2003; VandenBoer et al., 2013). To the best of our knowledge, this study is the first high-resolution vertical measurements conducted in China, which has suffered from heavy air pollution for several years. We have significantly revised the manuscript accordingly to address the referee's comments and concerns. Below are a point-to-point response to address the referee's specific comments.

Specific comments:

One of the most important aims of the manuscript is to determine the relative contribution of direct sources vs. ground and aerosol surfaces to overall HONO production at the site. The conclusions are: (1) direct sources are a major source (~51% of total ambient HONO is from combustion); (2) vertical profiles of HONO concentration do not support heterogeneous NO_2-to-HONO conversion on aerosol surfaces; (3) heterogeneous NO_2-to-HONO conversion on ground surfaces followed by vertical convection dominate HONO production at night. These conclusions are based on interpretation and discussion of results on p. 11-15, which I found to be unclear and not necessarily supportive of the final conclusions. To be suitable for publication I feel the relative contribution of the various HONO processes need to be quantified in more detail for the full data set and the derivations of those calculations more clearly explained in the text.

There was some ambiguity regarding how the contribution of direct emissions to ambient HONO was determined. It seems to be derived from the $HONO/NO_x$ ratio measured on days dominated by fresh vehicle emissions, which were identified when $NO > 80$ ppb and $NO/NO_x > 80\%$. The ratio was then used to devise a linear relationship between ambient NO_x and direct HONO emissions that is applied over the whole campaign. How this relationship was used to derive the contribution of direct emissions to ambient HONO is not clear. Also, the statement that direct sources constitute 51% of total ambient HONO is generalized for the entire campaign. However, it is clear that the relative contribution of HONO sources will change with time of day, traffic intensity and type of traffic, meteorology. Indeed, it is expected that the HONO mass balance for each nocturnal profile will be different, with each source/sink having a different relative contribution depending on time and meteorology.

Response: Thanks for the comment and suggestion. Considering the differences in the type of

vehicles, fuel compositions, etc., the reported emission factors of HONO might not be representative for the Beijing region. The local emission factors of HONO were derived from the field data. Following the suggestions by Jörg Kleffmann, five criteria were applied to ensure as much of the 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). 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 freshly emitted plumes instead of heterogeneous reactions of NO_2.

For a month measurements, 11 fresh plumes satisfied selection criteria (Table 1). Two examples of fresh plumes observed on December 9th to 10th, 2016 based on the preceding selection criteria were shown in Figure 6 in the manuscript. The derived emission factors varied from 0.78% to 1.73%, with an average value of 1.28% ± 0.36%, which was in 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). Comparisons of derived HONO/NO_x ratios with the previously reported results were summarized in Table S2 in the supplementary information. To minimize the risk of overestimating direct emissions, the minimum HONO/NO_x ratio was used as an upper limit for the emission factor (Su et al., 2008). The HONO/NOx ratio of 0.78% was used to estimate the direct HONO emissions ($[HONO]_{emis} = 0.0078 \times [NO_x]$). The average HONO$_{emis}$/HONO ratio was used to evaluate the contribution of direct emissions to ambient HONO levels at night. The vehicle emissions contributed 29.3% ± 12.4% to the ambient HONO concentrations at night. As the referee pointed out, we have considered the difference in direct HONO emissions at different pollution levels, the contribution of direct emissions during the clean and haze episodes were estimated respectively. The contributions of direct emissions to ambient HONO levels were estimated to be 35.9% ± 11.8% and 26% ± 11.3% during the clean and the haze episodes, respectively. The lower vehicle emissions contribution during the haze episode could have been caused by an odd-even car ban, which required alternate driving days for cars with even- and odd-numbered license plates.

The measurement site as a typical residential area is surrounded by several main roads, and the

nocturnal traffic emission is relatively stable. Because NO was not measured at ground level after 14:00 on December 10th, the direct HONO emissions during the third episode (E3, December 11th to 12th) cannot be directly estimated. The contribution of direct emissions to ambient HONO during the first episode (E1, from December 7th to 10:00 on December 8th) and the second episode (C2, from 10:00 on December 8th to December 11th) were estimated to be 26% ± 5.9% and 32.8% ± 11.8%, respectively, which were comparable to the preceding results. Therefore, we used an average $HONO_{emis}/HONO$ ratio to evaluate the relative contribution of direct HONO emissions during E3, which was used to correct observed HONO concentration in the subsequent analysis.

As the referee suggested, the budget analysis of nighttime HONO has been utilized to estimate the sources/sinks of HONO for the nocturnal profiles at different pollution periods. The nocturnal production of HONO on aerosol and ground surfaces have different relative contribution at different pollution periods, as the referee expected. We have significantly revised the discussion in the manuscript in "3.3 Direct emissions", "3.4.2 Relative important of aerosol and ground surfaces in nocturnal HONO production" and "3.4.3 Nocturnal HONO production and loss at ground level" to address the referee's concerns and to make our argument more clearly.

When determining the relative contribution of aerosol surfaces to the HONO budget, the authors attempt to quantify HONO production using an assumed uptake coefficient (for NO$_2$-to-HONO conversion) and an aerosol surface area-to-volume ratio from a completely different study, which is supposed to be a typical of winter in Beijing. I don't see how one can justify using a single aerosol surface area-to-volume ratio for the entire campaign, especially since this will vary with time, meteorology, and day (see Table 1). Further, it is not clear why a single value was used since a suite of aerosol measurements were made during the current study; measurements of black carbon, non-refractory PM, and AMS measurements at ground and 260 m height are reported. This data should be used to refine the analysis and make it more specific for each ascent/descent period. I encourage the authors to provide a more in-depth analysis of the contribution of aerosol surface area to HONO processes. I believe there may indeed be evidence for an important role for aerosol here under hazy conditions. For example, clear gradients, denoted by decreasing HONO/NO$_2$ ratio with elevation, were only observed on a few occasions, whereas it was more often the case that the HONO/NO$_2$ ratio was quite constant over the vertical range. Thus, it is possible that aerosol

chemistry may influence this profile, but only a detailed quantitative analysis can tell you this.

Response: As the referee suggested, the newly obtained aerosol surface areas (S_a) at ground level and at 260 m were used to estimate the nocturnal production of HONO by heterogeneous conversion of NO_2 on aerosol surface. A hygroscopic factor was applied to correct S_a to ambient (wet) aerosol surface area (S_{aw}) for particle hygroscopicity (Liu et al., 2013; Wang et al., 2018). The time series of S_{aw} at ground level and at 260 m was 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 260 m during the measurement period. Hence, this is a lower limit estimate of the total surface area for the heterogeneous reaction.

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. The correlation between CO and BC observed at ground level and the CO and BC at 260 m were analyzed. The CO and BC measured at ground level were independent of CO and BC observed at 260 m during the haze period (Figure. 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). The vertical profiles of HONO and NO_2, and aerosol surface areas measured at 260 m allowed to estimate the nocturnal HONO production by heterogeneous conversion of NO_2 on aerosol surface. The HONO production from the heterogeneous NO_2 conversion ($2NO_{2(g)}+H_2O_{(ads)} \xrightarrow{surface} HONO_{(g)}+HNO_{3(ads)}$) on aerosol surface would then have become the primary HONO source in 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 aerosol was assumed to occur on all measured aerosol surface area, regardless of chemical composition. HONO production was calculated using the equation of Ye et al. (2018) modified to account for the disproportionation. The uptake coefficient of NO_2 ranged between 1×10^{-5} to 1×10^{-6} in the dark, an average S_{aw} of 2314 μm^2 cm^{-3} between 22 and 01 h (the vertical measurement periods on Decemebr 11th) and an upper limit of observed NO_2 of 54 ppb from the residual layer were used to estimate the heterogeneous production of HONO on aerosols during E3. The HONO production of 30–300 ppt in an interval of 1.5 h could account for the observed HONO increases of 15–368 ppt in

the residual layer between profile measurements. The heterogeneous production of HONO solely on aerosol surface explained the HONO observations during E3. As the referee expected, the aerosol surface plays an important role in nocturnal HONO production during the haze episode. The column average concentration of HONO was independent of the mixing ratio of HONO observed from the ground level to 10 m in height ($R^2 = 0.27$) during E3 (Figure 10a), which suggested that aerosols presumably dominated the production of HONO aloft by heterogeneous uptake of NO_2.

The production of HONO on aerosols were also discussed to the other vertical measurements during C2, as the referee #1 suggested. The column average HONO concentration was related to the mixing ratio of HONO observed from the ground level to 10 m (Figure 10b, $R^2 = 0.93$), suggesting that the surface HONO source affected the HONO observed throughout the depth of boundary layer during C2. A high correlations ($R^2 = 0.83$) between 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 influence of direct HONO emissions. If it is assumed that the contribution of direct HONO emissions (35.9% ± 11.8%) was consistent at ground level and in the residual layer, the relative importance of aerosol and ground surface in nocturnal HONO production could be roughly estimated. It is necessary to elaborate that the contribution of direct emissions to HONO levels in the residual layer is a higher limit estimate. The production of HONO on aerosol surface was estimated during vertical measurements on December 9th and 10th. The HONO increases of 305–608 ppt between the vertical profile measurements, which have the contribution from direct HONO emissions subtracted, were higher than the production of HONO (26–259 ppt) on aerosols in an interval of 5.5 h on December 9th. The production of HONO solely on aerosol surface cannot explain the observed HONO increases in the residual layer, suggesting that the observed HONO throughout the depth of boundary layer was primarily derived from the heterogeneous NO_2 conversion on the ground surface followed by vertical transport throughout the column. The HONO production from the aerosol surface in an interval of 5.35 h was 33–332 ppt in the residual layer on December 10th, which was comparable to the corrected HONO increases of 114–369 ppt between profile measurements. This could have been due to a shallow inversion layer formed 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 expected, the aerosol chemistry plays an important role under hazy conditions. The production of HONO solely on aerosol surface explained the HONO observations during the haze episode. However, the ground surface was still the dominant nocturnal surface on which HONO was formed from the heterogeneous conversion of NO_2 during the clean episode. We have significantly revised the discussion in section 3.4.2 as suggested, adding more detailed quantitative analysis to draw broad conclusions.

Finally, the authors state that ground level HONO production has been corrected for the influence of direct emissions from automobiles. Has this correction been carried out for the production on aerosol surfaces as well? I had a difficult time understanding the rationale of going through all the calculations in section 3.4.3 on the topic of ground level HONO production. It was not clear how equation 4 and 5 were derived. The purpose of these equations is to estimate a HONO conversion frequency, which appears to be the pseudo-first order rate constant associated with the conversion of NO_2-to-HONO. These values should then be used to compare to the other HONO sources and sinks to evaluate the relative importance of all the various HONO sources/sinks. However, this comparison is not clearly carried out at the end of the paper as I would expect. Instead, starting with line 410 the text veers off subject by deriving a HONO yield from deposited NO_2. While this may be a useful calculation to carry out, I don't see how it helps the authors reach their research objectives and main conclusions.

In closing, I feel the interpretation of the vertical profiles relies on highly generalized 'back of the envelope' calculations. Such calculations can be very useful in certain cases; however, the quality and quantity of the data provided by this study should allow for a more elaborate analyses. I recommend the authors revisit their data to devise a mass balance for HONO processes where they quantify the sources and sinks for each vertical profile. I expect this approach will provide valuable insights that are not clear from the current presentation of the data.

Response: Thanks for the comment and suggestion. The influence of direct HONO emissions was taken into account in evaluating the heterogeneous production of HONO on aerosol surface, which has been discussed in section 3.4.2 of the revised manuscript. Equation 4 and 5 were derived by Su et

al. (2008) to correct for the effects of source and diffusion, which was derived from the equation ($[Y]_t^{Xscaled} = \overline{[X]} \frac{[Y]_t}{[X]_t}$), in which the mixing ratio of Y at time t was scaled with species X at the same time (Lammel, 1999). As the referee suggested, the slope determined by linear regression will statistically better describe the efficient first order conversion rate constant of NO_2 to HONO. Thus the conversion frequency was re-estimated following the method by Alicke et al. (2002). The conversion frequencies (k_{HONO}) on 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 (P_{NO_2}) of 0.25 ± 0.03, 0.28 ± 0.02 and 0.60 ± 0.02 ppb h[-1] (i.e. $C_{HONO} \times \overline{[NO_2]}$). 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 surface production rate of HONO was used to compare to the production rate on aerosols based on the assumption that the production of HONO 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 P_{NO_2} could be approximately considered as the net contribution of surface HONO production to the column during C2. The production rate of HONO on the ground surface (0.25 ± 0.03 and 0.28 ± 0.02 ppb h[-1]) was an order of magnitude higher than the maximum production rate on aerosol surface (0.047 and 0.062 ppb h[-1]), which suggested that the HONO observed throughout the column was primarily derived from the heterogeneous conversion of NO_2 on the ground surface followed by vertical transport throughout the column during the clean episode. This result was consistent with the result in section 3.4.2. 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 compare the production of HONO on aerosol and ground surfaces, the production rate of HONO on the ground surface was estimated by equation (Eq. 8) with a deposition velocity (V_{dep,NO_2}) of 0.07 cm s^{-1} (VandenBoer et al., 2013) and a boundary layer height of 140 m. The derived production rate of HONO ($P_{HONO,ground}$) on the ground surface was 0.47 ± 0.02 ppb h[-1] on December 11th (E3), which was comparable to the production rate on aerosol surface of 0.2 ppb h[-1]. This result also suggests that production of HONO on aerosols is an important nocturnal source of HONO during the haze episode.

A budget analysis of nighttime HONO was utilized to evaluate the contributions of various HONO sources/sinks, as the referee suggested. The derived a net HONO yield from the ground surface conversion of NO_2 have been removed in the revised manuscript. The nocturnal HONO budget from 18:00 to 06:00 LT on December 9th (C2) and 10th (E3) were shown in Figure 11 in the revised manuscript. The average production rate of HONO on aerosols (0.04 ± 0.01 ppb h^{-1}) was insignificant compared to the surface production rate of 0.28 ± 0.03 ppb h^{-1} during the clean episode. However, the average $P_{aerosol}$ of 0.19 ± 0.01 ppb h^{-1} was comparable to the surface production rate of HONO (P_{ground}, 0.47 ± 0.03 ppb h^{-1}) during the haze episode. Direct HONO emissions just contributed a small portion of HONO at a rate of 0.06 ± 0.07 and 0.10 ± 0.10 ppb h^{-1} during C2 and E3, respectively. The dry deposition of HONO contributed 0.74 ± 0.31 and 1.55 ± 0.32 ppb h^{-1} to the nocturnal loss of HONO during C2 and E3, respectively, implying that significant quantities of HONO were deposited to the ground surface at night. This had been suggested in another study on the vertical gradient of HONO (VandenBoer et al., 2013).

Specific comments by line number:

Lines 45-133: I feel that the introduction lacks an explicit statement of the study's research objective(s). The authors provide a [somewhat long] background section reviewing aspects of HONO chemistry that ends with a summary of what they did in their study. The introduction would be far stronger if the authors include a focused discussion of what research objective they hope to achieve. This could be accomplished by stating a hypothesis, following by a plan for how they hoped to test the hypothesis. At the moment, it is only in the second to last sentence of the introduction that one finally learns that a comparison of HONO heterogeneous chemistry on ground vs. aerosol surfaces is the major aim of the work.

Response: We have significantly revised the discussion in the introduction section. The background introduction of HONO chemistry and vertical observations have been revised as suggested, and more explicit statements of research objective have been added to the introduction section.

64-66: The authors state that hydrolysis of NO_2 on humid surfaces via R2 is considered the most likely explanation for observed HONO concentrations. The authors should be aware that this is not a viable mechanism under atmospherically relevant concentrations of NO_2. Reaction R2 is too slow and only

becomes important when the NO_2 concentration is high enough to promote N_2O_4 formation. Initial mechanistic studies of this mechanism had to use high NO_2 concentrations due to high instrument detection limits. More recent laboratory studies of this process using state-of-the-science sensitive field-grade instrumentation do not report this chemistry occurring under lower concentrations (50 ppb or less). One can refer to numerous lab studies over the past 10-15 years aimed at studying NO_2 conversion on surfaces containing humic acid reactive sites to learn more about this. It is notable that these studies often include control experiments aimed at quantifying background levels of HONO derived from NO_2 hydrolysis on their experimental system (i.e., in the absence of redox active substrates). These studies consistently show that NO_2-to-HONO conversion on organic matter and other redox active surfaces produce orders of magnitude more HONO than does R2.

Response: We would like to thank the referee for the constructive suggestion. The introduction has been significantly revised as suggested. This statements have been revised as below,

Line 86–92

"The heterogeneous reduction of NO_2 with organic substrates is proposed to be another effective pathway to generate HONO (Brigante et al., 2008; Stemmler et al., 2006; George et al., 2005). However, extrapolation of lab results to real surfaces remains challenging. The nocturnal production of HONO has been considered to be dominated by the NO_2 heterogeneous reaction (R2). Although the heterogeneous reaction (R2) of HONO formation is first-order in NO_2, the mechanism for the conversion of NO_2 on surfaces remains unclear (Finlayson-Pitts et al., 2003; Finlayson-Pitts, 2009)."

81: The colon after the references should be deleted.

Response: Revision has made as the referee suggested.

349: The authors attribute a decrease in HONO/NO_2 ratio at RH above 70% to enhanced HONO deposition. While RH does impact HONO uptake (see Donaldson et al. Environ. Sci. Technol. 2014, 48, 375), it would affect NO_2-to-HONO conversion as well (by enhancing to a point); so there are competing effects here. The abovementioned Donaldson et al. paper suggests that the uptake coefficient for HONO actually decreases with increasing RH.

Response: Thanks for the comment and suggestion. We have revised the description in this paragraph, as below.

Line 548–558:

"A previous observation at ground level also reported that the HONO/NO$_2$ ratio increased with an increase in RH when the RH was less than 70%. A further increase in RH would lead to a decrease in the HONO/NO$_2$ ratio, which was considered to be caused by the number of water monolayers that formed on the surface leading to an efficient uptake of HONO (Li et al., 2012; Yu et al., 2009; Liu et al., 2019). However, a decreased uptake coefficient of HONO with increasing RH from 0% to 80% was observed in a laboratory study (Donaldson et al., 2014). The NO$_2$ to HONO conversion efficiency depended negatively on RH at an RH above 70%, which was presumably caused by the relative humidity affecting both HONO uptake onto the surface and the NO$_2$-to-HONO conversion."

372: The number listed having unit of h^{-1} is not a formation rate as stated. Those are units of a first-order rate constant. Rather, units of ppb h^{-1} are appropriate for a formation rate.

Response: The unit of the NO$_2$-normalized HONO production over time, $\Delta \frac{[HONO]}{[NO_2]}/\Delta t$, is h^{-1} according to the equation (Eq. 5). The unit of its equivalent HONO production rate at constant NO$_2$ concentration is ppb h^{-1}. We have revised the statements in this paragraph to make it clearer.

405: It would be beneficial to provide a visual comparison of all the production rates (calculated in units of mixing ratio per hour). See for example Fig. 11 from Vandenboer et al. JGR, 2013, 118, 10,155.

Response: As the referee suggested, the comparison of the production and loss rate of HONO have been added in section 3.4.3. Figure 11 shows the production and loss rate of nighttime HONO on December 9th and 10th.

413: I recommend that the authors choose another symbol to represent the compensation point, which they call the HONO yield from deposited NO$_2$; the greek letter phi is reserved for the photolysis quantum yield. The symbol "H" used for mixing depth is also confusing. Some readers may mistake this for the Henry's law constant without reading further into the text. Consider using "d" (for depth) or lower case "h" or "z", all of which have been used in the past to represent height.

Response: Following the referee's suggestion in the specific comments above, the derived a net

HONO yield from ground surface conversion of NO$_2$ have been removed in the revised manuscript. The symbol "*H*" used for mixing height has been modified to symbol "h" as the referee suggested.

421: Why choose a deposition velocity from the literature, which is derived from completely different studies. Isn't the point here to model the vertical profile to derive a deposition velocity and the uptake coefficients for NO$_2$, HONO, etc. that are specific for the current sampling site?

Response: As the referee suggested, the temperature-dependent deposition velocity of HONO ($V(HONO)_T = \exp(23920/T - 91.5)$), which was adjusted to value of 2 cm s^{-1} at 0 °C decreasing exponentially to non-significant values at 40 °C (Laufs et al., 2017), was used to derive the dry deposition velocity of HONO. The $V_{dep,HONO}$ calculated from nocturnal observations (00:00–06:00 LT) ranged between 0.9 and 3 cm s^{-1}, with an average value of 1.8 cm s^{-1}, which was within the range of previously reported values (0.077–3 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). However, the limited vertical profile data in this study restricted the estimaton of the uptake coefficients for NO$_2$ and HONO. Thus we used the uptake coefficients and the deposition velocity from the literature to estimate the heterogeneous production of HONO on aerosol and ground surfaces, which have also been used in other studies of HONO vertical structure (VandenBoer et al., 2013; Wong et al., 2011; Ye et al., 2018).

More general remarks:

More general remarks: More work should be devoted to providing error analysis. For example, error bars on data and errors in reported values derived from their analyses. This will be especially important when comparing quantitatively the relative contribution of sources/sinks to ambient HONO. I felt there were too many figures in the text. For example, what is the purpose of showing Figure 5, where the information is more useful plotted in the format shown in Fig. 6, etc. The manuscript could benefit from editing by a native English speaker. Grammatical errors start on the first line of the abstract and persist throughout the manuscript. Lastly, I note that the authors are comparing their IBBCEAS results to data collected on an instrument from Cambridge University. Does this contribution need to be acknowledged in some way (e.g., in the acknowledgement section or author list)?

Response: Thanks for the comment and suggestion. The error analysis have been taken into account in data analysis, and error bars have been presented in the revised manuscript. Figures 5 have been removed from the manuscript as suggested, and the panel (a) of Figure 6 has been moved to the supplementary information. As the referee suggested, the revised manuscript was edited by a native English speaker. We also acknowledged Bin Ouyang from Cambridge University for providing HONO comparison data in the acknowledgement section.

References:

Alicke, B., Platt, U., Stutz, J.: Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, J. Geophys. Res., 107, LOP 9-1-LOP 9-17, https://doi.org/10.1029/2000jd000075, 2002.

Brown, S. S., Dubé, W. P., Osthoff, H. D., Wolfe, D. E., Angevine, W. M., and Ravishankara, A. R.: High resolution vertical distributions of NO_3 and N_2O_5 through the nocturnal boundary layer, Atmos. Chem. Phys., 7, 139-149, https://doi.org/10.5194/acp-7-139-2007, 2007.

Coe, H., and Gallagher, M. W.: Measurements of Dry Deposition of NO_2 to A Dutch Heathland Using the Eddy-Correlation Technique, Q. J. Roy. Meteor. Soc., 118, 767-786, https://doi.org/10.1002/qj.49711850608, 1992.

Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D., and Ramazan, K. A.: The heterogeneous hydrolysis of NO_2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, Phys. Chem. Chem. Phys., 5, 223-242, https://doi.org/10.1039/b208564j, 2003.

Finlayson-Pitts, B. J.: Reactions at surfaces in the atmosphere: integration of experiments and theory as necessary (but not necessarily sufficient) for predicting the physical chemistry of aerosols, Phys. Chem. Chem. Phys., 36, 7760-7779, https://doi.org/10.1039/B906540G, 2009.

Harrison, R. M., and Kitto, A. M. N.: Evidence for a surface source of atmospheric nitrous acid, Atmos. Environ., 28, 1089-1094, https://doi.org/10.1016/1352-2310(94)90286-0, 1994.

Harrison, R. M., Peak, J. D., and Collins, G. M.: Tropospheric cycle of nitrous acid, J. Geophys. Res., 101, 14429-14439, https://doi.org/10.1029/96JD00341, 1996.

Kleffmann, J., Kurtenbach, R., Lörzer, J., Wiesen, P., Kalthoff, N., Vogel, B., and Vogel, H.: Measured

and simulated vertical profiles of nitrous acid—Part I: Field measurements, Atmos. Environ., 37, 2949-2955, https://doi.org/10.1016/s1352-2310(03)00242-5, 2003.

Kirchstetter, T. W., Harley, R. A., and Littlejohn D.: Measurement of nitrous acid in motor vehicle exhaust, Environ. Sci. Technol., 30, 2843-2849, https://doi.org/10.1021/es960135y, 1996.

Kurtenbach, R., Becker, K. H., Gomes, J. A. G., Kleffmann, J., Lörzer, J., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of emission and heterogeneous formation of HONO in a road traffic tunnel, Atmos. Environ., 35, 3385–3394, https://doi.org/10.1016/S1352-2310(01)00138-8, 2001.

Lammel, G.: Formation of Nitrous acid: Parameterisation and comparison with observatins, Techical Report, MaxPlank-Inst. fuer Meteorol., Hamburg, Germany.

Laufs, S., Cazaunau, M., Stella, P., Kurtenbach, R., Cellier, P., Mellouki, A., Loubet, B., and Kleffmann, J.: Diurnal fluxes of HONO above a crop rotation, Atmos. Chem. Phys., 17, 6907-6923, https://doi.org/10.5194/acp-17-6907-2017, 2017.

Li, D. D., Xue, L. K., Wen, L., Wang, X. F., Chen, T. S., Mellouki, A., Chen, J. M., and Wang, W. X.: Characteristics and sources of nitrous acid in an urban atmosphere of northern China: Results from 1-yr continuous observations, Atmos. Environ., 182, 296-306, https://doi.org/10.1016/j.atmosenv.2018.03.033, 2018.

Li, X., Brauers, T., Häseler, R., Bohn, B., Fuchs, H., Hofzumahaus, A., Holland, F., Lou, S., Lu, K. D., Rohrer, F., Hu, M., Zeng, L. M., Zhang, Y. H., Garland, R. M., Su, H., Nowak, A., Wiedensohler, A., Takegawa, N., Shao, M., and Wahner, A.: Exploring the atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China, Atmos. Chem. Phys., 12, 1497-1513, https://doi.org/10.5194/acp-12-1497-2012, 2012.

Liang, Y. T., Zha, Q. Z., Wang, W. H., Cui, L., Lui, K. H., Ho, K. F., Wang, Z., Lee, S. C., and Wang, T.: Revisiting nitrous acid (HONO) emission from on-road vehicles: A tunnel study with a mixed fleet, J. Air Waste Manag., 67, 797-805, https://doi.org/10.1080/10962247.2017.1293573, 2017.

Liu, X., Cheng, Y., Zhang, Y., Jung, J., Sugimoto, N., Chang, S.Y., Kim, Y. J., Fan, S., and Zeng, L.: Influences of relative humidity and particle chemical composition on aerosol scattering properties during the 2006 PRD campaign, Atmos. Environ., 42, 1525–1536, https://doi.org/10.1016/j.atmosenv.2007.10.077, 2008.

Rappenglück, B., Lubertino, G., Alvarez, S., Golovko, J., Czader, B., and Ackermann, L.: Radical

precursors and related species from traffic as observed and modeled at an urban highway junction, J. Air Waste Manag. Assoc., 63, 1270-1286, https://doi.org/10.1080/10962247.2013.822438, 2013.

Spindler, G., Brüggemann, E., and Herrmann, H.: Nitrous acid (HNO_2) Concentration Measurements and Estimation of Dry Deposition over Grassland in Eastern Germany, Transactions on Ecology and Environment, 28, 223-227, 1999.

Stutz, J., Alicke, B., Neftel, A.: Nitrous acid formation in the urban atmosphere: Gradient measurements of NO_2 and HONO over grass in Milan, Italy, J. Geophys. Res., 107, LOP 5-1-LOP 5-15, https://doi.org/10.1029/2001JD000390, 2002.

Su, H., Cheng, Y. F., Cheng, P., Zhang, Y. H., Dong, S. F., Zeng, L. M., Wang, X. S., Slanina, J., Shao, M., and Wiedensohler, A.: Observation of nighttime nitrous acid (HONO) formation at a non-urban site during PRIDE-PRD2004 in China, Atmos. Environ., 42, 6219-6232, https://doi.org/10.1016/j.atmosenv.2008.04.006, 2008.

Tong, S. R., Hou, S. Q., Zhang, Y., Chu, B. W., Liu, Y. C., He, H., Zhao, P. S., and Ge, M. F.: Exploring the nitrous acid (HONO) formation mechanism in winter Beijing: direct emissions and heterogeneous production in urban and suburban areas, Faraday Discuss., 189, 213-230, https://doi.org/10.1039/c5fd00163c, 2016.

VandenBoer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A. A. P., Kim, S., Warneke, C., de Gouw, J. A., Maben, J. R., Wagner, N. L., Riedel, T. P., Thornton, J. A., Wolfe, D. E., Dubé, W. P., Öztürk, F., Brock, C. A., Grossberg, N., Lefer, B., Lerner, B., Middlebrook, A. M., and Roberts, J. M.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT-11, J. Geophy. Res.- Atmos., 118, 10155-110171, https://doi.org/10.1002/jgrd.50721, 2013.

Wang, H. C., Lu, K. D., Chen, X. R., Zhu, Q. D., Wu, Z. J., Wu, Y. S., and Sun, K.: Fast particulate nitrate formation via N_2O_5 uptake aloft in winter in Beijing, Atmos. Chem. Phys., 18, 10483-10495, https://doi.org/10.5194/acp-18-10483-2018, 2018.

Wong, K. W., Oh, H. -J., Lefer, B. L., Rappenglück, B., and Stutz, J.: Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX, Atmos. Chem. Phys., 11, 3595-3609, https://doi.org/10.5194/acp-11-3595-2011, 2011.

Xu, Z., Wang, T., Wu, J. Q., Xue, L. K., Chan, J., Zha, Q., Z., Zhou, S. Z., Louie, P. K. K., and Luk, C. W. Y.: Nitrous acid (HONO) in a polluted subtropical atmosphere: Seasonal variability, direct vehicle

emissions and heterogeneous production at ground surface, Atmos. Environ., 106, 100-109, https://doi.org/10.1016/j.atmosenv.2015.01.061, 2015.

Yang, Q., Su, H., Li, X., Cheng, Y. F., Lu, K. D., Cheng, P., Gu, J. W., Guo, S., Hu, M., Zeng, L. M., Zhu, T., and Zhang, Y. H.: Daytime HONO formation in the suburban area of the megacity Beijing, China, Sci. China Chem., 57, 1032-1042, https://doi.org/10.1007/s11426-013-5044-0, 2014.

Ye, C. X., Zhou, X. L., Pu, D., Stutz, J., Festa, J., Spolaor, M., Tsai, C., Cantrell, C., Mauldin III, R. L., Weinheimer, A., Hornbrook, R. S., Apel, E. C., Guenther, A., Kaser, L., Yuan, B., Karl, T., Haggerty, J., Hall, S., Ullmann, K., Smith, J., and Ortega, J.: Tropospheric HONO distribution and chemistry in the southeastern US, Atmos. Chem. Phys., 18, 9107-9120, https://doi.org/10.5194/acp-18-9107-2018, 2018.

Zhang, N., Zhou, X. L., Shepson, P. B., Gao, H. L., Alaghmand, M., and Stirm, B.: Aircraft measurement of HONO vertical profiles over a forested region, Geophys. Res. Lett., 36, L15820, https://doi.org/10.1029/2009GL038999, 2009.

Zhang, W. Q., Tong, S. R., Ge, M. F., An, J. L., Shi, Z. B., Hou, S. Q., Xia, K. H., Qu, Y., Zhang, H. X., Chu, B. W., Sun, Y. L., and He, H.: Variations and sources of nitrous acid (HONO) during a severe pollution episode in Beijing in winter 2016, Sci. Total Environ., 648, 253-262, https://doi.org/10.1016/j.scitotenv.2018.08.133, 2018.