

Interactive comment on “The role of HONO in O₃ formation and insight into its formation mechanism during the KORUS-AQ Campaign” by Junsu Gil et al.

Junsu Gil et al.

meehye@korea.ac.kr

Received and published: 8 June 2020

Referee Comment 3

Thank you very much for your constructive comments. The point-by-point responses to your comments are given below. Your comments were all considered, and the manuscript was revised accordingly. In the revised manuscript, all changes are marked in blue.

<Major comments> 1. Nocturnal HONO formation chemical mechanisms are not correct. There is clear confusion in the presentation of what HONO production processes

C1

are relevant to exploring its nocturnal formation. The literature has not been sufficiently reviewed and puts the results of this study into question. In the introduction, the Authors present reactions 2 through 4 which have never been demonstrated in many prior reports to be important under nocturnal conditions. Further to this, reaction 4 is for the photolysis of ortho-nitrophenols, not from reaction of NO₂. The Authors seem confused on this mechanism and it generates much skepticism regarding the quality of their model results if established HONO chemistry is presented erroneously here. Since release of HONO from ortho- and para-nitrophenols requires light, it is also invalid to explore for HONO production chemistry at night. This reaction has not been shown to be important in polluted daytime atmospheres for HONO production. How could it possible be important to nocturnal chemistry? Given the focus of this manuscript on nocturnal HONO production, the Authors need to revisit the state of knowledge for relevant nocturnal reactions to consider (e.g. has NO₂ + NO + H₂O ever made a significant amount of HONO in any prior report?) and rerun their ANN from a relevant starting point. Lines 119-123 in the Introduction are irrelevant to this work as this is all daytime HONO chemistry. Direct emissions from soils have not been quantified for diurnal roles (Lines 127-129) so are of limited utility. Seminal works for such investigations are also not cited correctly, a small selection includes: (Maljanen et al., 2013; Mushinski et al., 2019; Oswald et al., 2013; Scharko et al., 2015). The Authors then proceed to describe heterogenous reactions as being universally catalytic, which simply is not true. Again, chemical mechanisms relevant to the day time (photoexcited humic substances) are conflated with marginally relevant nocturnal sources (fresh soot emissions (Aubin and Abbatt, 2007)) raising major questions as to how the quality of the subsequent data analysis can be trusted. Further to this, there is a major oversight on at least 15 years of research reporting on the role of ground and aerosol surfaces in producing nocturnal HONO and the resultant vertical structure of HONO in the nocturnal atmosphere. A small selection of this body of research includes: (Kleffmann et al., 2003; Stutz et al., 2004; VandenBoer et al., 2013; Villena et al., 2011; Wong et al., 2011; Young et al., 2012). Nocturnal HONO production, in short, is a complex func-

C2

tion of chemistry and mixing, often resulting in a complex vertical structure, which has shown in many polluted environments to be highly linked to ground surface conversion of NO₂ with a water dependence. The Authors need to be clear in their understanding of the relevant chemical and physical processes governing nocturnal HONO production prior to exploring which is most important to O₃ production via the ANN. Linking this understanding to the set up of the ANN is critical to validating the approach used in Section 2.2.2, for example. As this currently stands, this particular section is not possible to evaluate with a sound basis in HONO nocturnal chemistry and requires revision. First of all, the reaction 4 was corrected. It is right that some reactions on the list are not important at nighttime. Especially, the reactions 3~5 were from theoretical and lab experiments but used in modelling studies. The reactions 2~9 indicate all possibilities of HONO formation including daytime as well as nighttime. The main objectives of this study are to demonstrate the impact of HONO on O₃ formation and to understand the HONO formation mechanism. To achieve these goals, we used two different models. Unfortunately, the effect of ground surface was not incorporated into the ANN model because there was no measurement to represent its effect. The loss due to deposition to the ground surface cannot be ignored, when being estimated based on previous studies. Since the recent studies suggest various sources of HONO even during the day, the source of HONO from ground surface will have to be investigated in a separate study with a different approach such as chamber or vertical structure measurement. Upon your suggestion, we delved into the aerosol surface areas and refined the result of ANN model, which demonstrates the feature importance of physicochemical factors to HONO formation. As a results, the manuscript was thoroughly revised. 2. Given the focus of this work on the use of ANN to model nocturnal HONO chemistry, the Introduction and results should do a much better review and contrast to the existing capabilities of other models such as CMAQ (Czader et al., 2012; Diao et al., 2016; Gonçalves et al., 2012) or custom models (Kleffmann et al., 2003; Tsai et al., 2018; Vogel et al., 2003; Wong et al., 2012). The Authors should review this literature to aid in preparations for the re-running of their ANN. A. We really appreciated your de-

C3

tailed information and suggestion. We added these references to revised manuscript. 3. The quality control for the HONO dataset, as presented in the methods section (and is entirely absent from the results/discussion) is not thorough. The Authors state that optical measurements are free of sampling artifacts, yet all instruments have inlets with surfaces where NO₂ can react with water to produce HONO, a phenomenon described for most field instruments along with an applied correction for such an 'inlet effect'. The best studies also account for non-linearities associated with changing NO₂ and water concentrations. No sampling information for the HONO measurements is given. Were inlets used? How long were they? What were they made out of? What was the sample flow through the inlet? Was any particulate matter exclusion done on the sample flow? Was the NO₂ inlet effect in producing HONO quantified and corrected for? The intercomparison made here is also weak. An r-value of 0.74-0.84 is very bad and a correlation alone is insufficient to describe the comparability of the measurements. Slope, intercept, and their associated uncertainties are also necessary to calculate as part of measurement validation. These plots should be provided in a supporting information document. The Authors then go on to state that they made 1 Hz measurements of HONO and averaged these to 1 hour time points. Why was this done? Lines 168-172 suggest that the instrument was not operated correctly to make very good high time resolution measurements, yet no quality control analysis of the data is presented. How can one trust this HONO measurement? Justification for the approach used to arrive at a reliable final HONO dataset must be explained. Further to this, the Author's state a theoretical detection limit, but do not state what timescale this applies to. Presumably if they are averaging 1 Hz data to an hourly timescale, the detection limit is much better than 0.1 ppb? Or was the instrument operated so poorly that they were worse? Were field blanks performed on the instrument by overflowing the inlet with zero air? If yes, these should have been used to calculate the instrument detection limits that existed for this campaign, not the theoretical detection limits. Please perform these analyses to demonstrate that the HONO measurements are reliable and of high quality (or at least possible to clearly understand the potential limitations in their quality). As it currently

C4

stands, the Authors discuss data below the theoretical detection limit in Section 3.1 and one wonders how or why they would report this? The method section was completely rewritten because it focused on the measurement of QC-TILDAS.

<Detail comments>

Line 30: 'but the. . . Unclear'. This is not part of the manuscript objective. Remove from here. It was removed from the abstract. Lines 32-46: Nearly the entire abstract has disjointed writing that is very difficult to follow the logic of. Revise according to major changes to findings/conclusions based on major revisions, but also for clarity. In particular, the sentence from Lines 39-41 makes no sense to me, even with a thorough understanding of HONO atmospheric chemistry. Also, at Lines 42-43 'surface area' is listed but what it applies to (i.e. aerosols or ground or both) is not clear. Thank you for your advice. It was changed to 'aerosol surface area' for clarity. The abstract was revised, too. Line 60: 'huge' is unnecessary to use here. Sensational modifiers throughout the manuscript should similarly be removed. The data will communicate the exact value and direction of changes, so readers can evaluate this objectively. It was modified as follows: This implies that HONO strongly affects the early morning photochemistry cycle, along with the promotion of VOC oxidation, causing high O₃ concentrations in afternoon. Line 80: 'lowing' should be 'lowering' This part was removed in the revised manuscript. Lines 83-86: If you are going to mention real-time IC techniques for HONO, there are earlier studies with better analytical results from the group of Jennifer Murphy (U Toronto) (VandenBoer et al., 2014). There is also a substantial amount of work from Jack Dibb (U New Hampshire) collecting HONO by mist chamber IC that have demonstrated good analytical capabilities in intercomparisons with DOAS (Pinto et al., 2014; Stutz et al., 2010). Also missing from this section is discussion of a substantial body of measurements made by broadband cavity enhanced absorption spectrometry (BBCEAS). Finally, given the lack of discussion on the performance and quality of the QC-TDLAS HONO measurements in this study, one is left wondering what the purpose of summarizing all of these analytical techniques is? Your helpful comments are very

C5

much appreciated. Following the other reviewer's comment, however, the description of measurement technique was shortened in Introduction. Instead, the details about QC-TILDAS measurement was given in section 2.1. Measurement. Lines 95-96: The Authors have the sensitivity of the LOPAP backwards. It is very good a detecting 'low mixing ratios of HONO'. The detection limits of the LOPAP are often below 1 pptv if integrated over 5 minutes or more. Furthermore, there are many custom built stripping coil instrument references that are missing here (Ren et al., 2011; Ye et al., 2016; Zhang et al., 2009). This information was added to the introduction. Line 102: 'TIDLAS' should be 'TDLAS' It was corrected. Line 103: 'albeit' should be 'despite' It was corrected. Lines 152-154: The TDLAS technique has been described three times up to this point in the manuscript and denoted with three different descriptions and abbreviations. Pick one and use it throughout. It was corrected. Line 187: Reference formatting is incorrect and needs to be revised throughout. It was corrected. Lines 195-197: Why is the dilution factor the only parameter adjusted in the model that is worth mentioning in the methods? This sensitivity test comes out of nowhere and no justification is provided for why this is a sound approach. In the revised manuscript, this part was modified as follows: As a first-order dilution rate constant in the model, the dilution factor (kdil) was adjusted to reduce uncertainties due to the lack of explicit representation of transport processes. As a variable of the model, the dilution factor needs to be adjusted before it was run. It is the inherent property of the F0AM model that we used in this study. The dilution factor is analogous to physical loss lifetime and was introduced to represent transport processes. The result of sensitivity test is given in section 3.2 and shown in Figure 8. Line 197: 'session 3.3' should be 'Section 3.3' It was corrected. Lines 199 – 201: The Authors define Artificial Neural Network (ANN) over and over. Do it once at the first mention and simply use ANN moving forward. The second instance of its use at Line 201 has been written incorrectly. The most part of section 2.3.2 regarding ANN was moved into Supplementary Information. Details of the ANN model and its running procedure is provided there. Lines 205-206: The use of ANN for quantum states of HONO is irrelevant to this work. Remove. It was deleted. Line 208: Revise to '. . .of

C6

each neural network node with a clear chemical or physical process It was modified as you recommended. Line 211: Check citations for correctness of Author names and all other details according to ACP guidelines for Authors Yes, they are correct. Lines 216-218: But what are you doing, and why, with the calculation in Equation 1? This is very unclear. Revise As input variables, the measurement data are in wide range. For example, HONO in $0 \sim 4$ ppbv and MLH in $0 \sim 3000$ m. If these values are not normalized and used in the model, the result will be more dependent on large values, thereby being biased. Therefore, all variables were normalized to have equal weight using (Eq S2.2). Line 260: '%ile' is incorrect. This is 'percentile'. Fix throughout. All of them were corrected as percentile. Line 264: 'average O3 and HONO' What kind of average is this? 24-hour average? Clarify. The presented data does not look like it has any 24-hr period with more than 1 ppbv of HONO. Line 268: 'High' should be 'high' There are various measurement statistics stated in the text. For clarity, they are summarized in Table 2 in the revised manuscript. For example, the average concentrations of HONO and O3 are given for daytime and nighttime during the high-O3 episode and non-episode. For the two episodes, the concentrations are the average for episode days. High was changed to high. Line 277: The dataset for HONO would be expected to be log-normal distributed. Here and above, the authors are discussing the 95th percentile with an implicit meaning of significance, yet if the dataset is not log-transformed, then the 95th percentile would be a biased value to report due to the skewed distribution from a normal distribution. As you said, HONO concentrations show lognormal distribution. The top 10 percentile concentrations are generally used to represent the high concentrations of the measurement. In case of O3, the 90th percentile is considered relevant for comparison in background sites for a long time. In comparison, the 99.9th percentile of 1 hr-O3 represents the maximum concentration in urban areas. This study was conducted as an intensive experiment for a relatively short period, about a month. In this case, the 95th percentile would be appropriate for representing the maximum concentration. Lines 291-294: This is suggestive of strong direct emissions. See many recent papers from Beijing and perform the same analysis for Seoul (Liu et al., 2017; Tong et

C7

al., 2016; Wang et al., 2017) instead of choosing an estimate for this work. The recent studies were cited in the revised manuscript. In this study, we gave it a try to understand the HONO formation using the ANN model. For this purpose, the estimation of direct emission of HONO was necessary, which is described in [Line 325] of the revised manuscript. Line 304: The Authors conclude here that aerosol surfaces are important, but their lack of awareness of literature reports on the role of the ground surface relative to aerosol surfaces being far more important suggests that they need to reconsider their interpretation of the data after more thoroughly reviewing the literature (see references given in Major Comments above). All vertically-resolved HONO measurements have shown that the ground is a major sink for HONO, as well as dew and available surface water (He et al., 2006; Rubio et al., 2009; Stutz et al., 2004; Tsai et al., 2018; VandenBoer et al., 2015; Wojtal et al., 2011). Based on the study of (VandenBoer et al., 2013), the surface loss of HONO is expressed as $\text{loss} = \frac{1}{4} \gamma_{\text{HONO,ground}} \text{RH}/20$ $C_{\text{HONO}} \approx [\text{HONO}]_{\text{ground}}$. This equation yields $0.007 \sim 0.041$ with the average of 0.025 ($\gamma_{\text{HONO,ground}} = 8.7 \times 10^{-5}$), and $0.005 \sim 0.039$ with the average of 0.022 ($\gamma_{\text{HONO,ground}} = 7.3 \pm 1 \times 10^{-5}$) for this study. The HONO measurement was conducted under 10 m heights, therefore observed ambient HONO can represent $[\text{HONO}]_{\text{ground}}$ (VandenBoer et al., 2013). This result indicates that the surface loss is about $0.5 \sim 4.1\%$ of the ambient HONO concentration. This ground sink is not negligible, but was not considered in this study. In addition to the assumption and simplification stated above, it does not affect the main results of this study and is within the uncertainty of model simulation. Line 319-320: How can the Authors justify ignoring the photolysis of O3 and aldehydes as major sources of OH during KORUS-AQ. This does not seem reasonable. Even in winter atmospheres, this additional chemistry leading to OH production has been shown to be critical to capture (Kim et al., 2014). We admit that it is a wrong expression and corrected in the revised manuscript. Here, we did not estimate the ambient OH concentration, but the OH produced from HONO photolysis. In the early morning around 5 am, when O3 concentration is at its minimum level (< 10 ppbv), it is reasonable to assume that there is no source for OH other

C8

than HONO photolysis. Thus, we calculated the OH produced from HONO photolysis, which was compared for the high-O₃ episodes and non-episode. Lines 336-337: Why is this integral notation being used? The discrete time intervals being used are not given and the explanation here is very unclear. Revise. The integral notation was used to indicate that it was the sum of OH concentrations for several hours of early morning and afternoon, followed by (Alicke et al., 2003), but not an hourly concentration. The time interval is given above: early morning (05:00-11:00 LST) and afternoon (12:00-18:00 LST). In the revised manuscript, the relative % difference was added for clarity. Lines 341-346: Add line colors to the S# references here so they do not get confused with figures in the supplemental information. Or change the identification codes for the model runs to not start with 'S'. Thank you for your insightful suggestion because the supplementary information was added to the revised manuscript. Model scenarios are identified with M instead of S. Lines 357-359: 'physical mechanisms as well as'. This is nonsense. Heterogeneous hydrolysis is a chemical mechanism. Remove. Yes. It was changed to "heterogeneous chemical reactions" in the revised manuscript. Line 360: Exploring the role of NO (and R7), based on all known nocturnal HONO chemistry is useless and should be removed throughout the manuscript. There is no basis for this from the literature. In this experiment, NO concentration showed a big change from period to period (Figure 3). When the aged air mass was encountered (May 24~26), NO came down below the detection limit. In contrast, it was highly elevated particularly at night under stagnant condition (May 17~22). This diurnal pattern of concentration is presented in Figure 4. In recent studies conducted at high NO_x environment, NO was found to contribute to HONO formation (Tong et al., 2015; Zhang et al., 2019). In the ANN model of this study, it turned out that the contribution of NO was the largest among input 8 variables. Thus, it was explained as follows: The largest contribution of NO was primarily due to the chemical coupling with NO₂, but partly reflects the daytime formation of HONO, albeit its low concentrations. You are absolutely right that R7 is slow and negligible in terms of HONO formation. However, the formation mechanism of HONO has not unequivocally understood, yet. Thus, R7

C9

had better be in the list of reactions, just as a possibility. Line 366: 'considered HONO photolysis, SZA, and MLH' This is nighttime data. Why is photochemistry being considered? The reasoning here is almost impossible to understand. The use of SZA was not to consider photochemical reactions, but to select the times (0~5 am LST) during which HONO is not photolyzed. The nighttime was determined as 7 pm ~ 5 am when SZA was over 90 degrees. Lines 371-373: It is the conversion of NO₂ that is typically used for this calculation, not NO_x, which is consistent with the hydrolysis of NO₂ being the dominant chemical source of HONO to the nocturnal atmosphere. The Authors should use NO₂ conversion efficiency in this work. Given the discussion that follows on Lines 377-380 about NO₂ conversion, perhaps this is a typo? We agree with you and it was done with NO₂ instead of NO_x. Line 381: Figure 9a. Fix notation. It was changed as CHONO,NO₂ Lines 382-385: The work cited here made measurements over open marine water. The dataset in this work is collected over an urban landscape. The uptake of NO₂ to ground surfaces has been described in detail by many other papers that are mentioned above. This reference was cited here to emphasize that the tendency of HONO depending on RH was observed in previous studies, but not to compare the HONO concentrations. Lines 386-396: This needs to be revised to be correctly positioned in the major body of literature regarding the importance of HONO vertical structure and the competing roles of ground and aerosol HONO production. This part was completely revised. The HONO concentration and conversion ratio of NO₂ was found to be the highest in the RH range of 70 ~ 80 %, which is the upper and lower margin for haze particles and hydrometeors, respectively (Figure 10). At RH > 80 %, PM_{2.5} concentration was noticeably high. Initially, the Aiken mode (30-120 nm) particles were considered a suitable substrate for heterogeneous conversion of HONO because the dependence of their surface area on RH was similar to HONO concentration and conversion ratio of NO₂. During this experiment, the deliquescence RH of NH₄NO₃ and (NH₄)₂SO₄ was in the range of 60 ~ 80 %, over which their concentration dramatically increased with the increase in PM_{2.5} mass. When comparing the surface area of Aitken mode (30-120 nm) with condensation mode (120-300 nm)

C10

particles according to RH, it increased with RH until 70 % for both two modes. If RH increased over 70 %, however, the behavior of the two modes split: Aitken mode particles decreased, but condensation mode particles increased, leading to the greatest difference at RH range of 70~80%. From these results, we concluded that RH played a key role in aerosol transformation, by which processes the availability of aerosol surfaces for the conversion of NO₂ was constrained. While Aitken mode particles, which are less susceptible to hygroscopic growth than condensation mode particles, provide surfaces available for HONO formation, HONO concentration was determined by the level of NO₂. It was in good agreement with the results of ANN model. This is explained through section 3.3 (Figure 12). Line 397: The ANN discussion should be presented in a separate section. Given the limited nature of the discussion on the ANN results, this suggests that perhaps the methods section can be reduced and the details of setting up the ANN can be moved to the supporting information. We provide the detailed information and methodology about ANN in supplementary information. Line 421: Revise in accordance with new contents of the manuscript after addressing all comments from Reviewers. The conclusion was rewritten. Figure 2: Aerosol SA and ground SA need to be considered separately in the ANN. It was changed to aerosol surface area (ASA). Figure 3: Is this all hourly data? Not given in the caption. Red and blue traces on every panel is very confusing to interpret. Consider using mainly black lines with solid and different styles of dashing to depict the data or use a wider variety of colors. All data are hourly averaged. This figure looks busy, no matter what colors are used. The red and blue colors are used to distinguish the two plots in one panel. We found that this way of presentation was better than 12 panels of single species. If it is not necessary to show the time series variations of chemical species in the manuscript, it can be moved to supplementary information. Figure 4: Move this to the SI. Add sensitivity test figures to the manuscript. Figures were changed in the revised manuscript

Reference Aliche, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Pätz, H., Schäfer, J., Stutz, J., Volz, Thomas, A., and Platt, U.: OH formation by HONO photolysis during the BERLIOZ experiment, *Journal of Geophysical Research: At-*

C11

mospheres, 108, PHO 3-1-PHO 3-17, 2003. Tong, S., Hou, S., Zhang, Y., Chu, B., Liu, Y., He, H., Zhao, P., and Ge, M.: Comparisons of measured nitrous acid (HONO) concentrations in a pollution period at urban and suburban Beijing, in autumn of 2014, *Science China Chemistry*, 58, 1393-1402, 2015. VandenBoer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A., Kim, S., Warneke, C., de Gouw, J. A., and Maben, J. R.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT, *Journal of Geophysical Research: Atmospheres*, 118, 10,155-110,171, 2013. Zhang, W., Tong, S., Ge, M., An, J., Shi, Z., Hou, S., Xia, K., Qu, Y., Zhang, H., and Chu, B.: Variations and sources of nitrous acid (HONO) during a severe pollution episode in Beijing in winter 2016, *Science of the Total Environment*, 648, 253-262, 2019.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2019-1012/acp-2019-1012-AC3-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2019-1012>, 2019.