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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of HONO in O_3 formation and insight into its formation mechanism during the KORUS-AQ Campaign" *by* Junsu Gil et al.

Anonymous Referee #3

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General Comments

This paper presents an analysis of nighttime sources of nitrous acid (HONO) to the urban atmosphere of Seoul, Korea during the KORUS-AQ campaign through the use of an Artificial Neural Network (ANN) to model ambient concentrations. The manuscript has major flaws in the presented understanding of chemical mechanisms long established for importance to HONO nocturnal chemistry, and therefore, the analysis of the datasets and subsequent modeling are also compromised. The manuscript also suffers from unclear arguments and descriptions that makes many critical details almost impossible to follow for a valid review. This work requires major revisions to meet the

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Discussion paper

standard of publication in Atmospheric Chemistry and Physics, with particular attention paid to correct representation and analysis of nocturnal HONO chemistry, to which the presented dataset is limited. The revised manuscript will need to be further reviewed at that time.

Major Revisions

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

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.

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 stands, the Authors discuss data below the theoretical detection limit in Section 3.1 and one wonders how or why they would report this?

Detailed Comments

Line 30: 'but the.... Unclear'. This is not part of the manuscript objective. Remove from here.

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.

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.

Line 80: 'lowing' should be 'lowering'

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?

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).

Line 102: 'TIDLAS' should be 'TDLAS'

Line 103: ‘albeit’ should be ‘despite’

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.

Line 187: Reference formatting is incorrect and needs to be revised throughout.

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.

Line 197: ‘session 3.3’ should be ‘Section 3.3’

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.

Lines 205-206: The use of ANN for quantum states of HONO is irrelevant to this work. Remove.

Line 208: Revise to ‘. . .of each neural network node with a clear chemical or physical process’

Line 211: Check citations for correctness of Author names and all other details according to ACP guidelines for Authors.

Lines 216-218: But what are you doing, and why, with the calculation in Equation 1? This is very unclear. Revise.

Line 260: ‘%ile’ is incorrect. This is ‘percentile’. Fix throughout.

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’

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.

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 al., 2016; Wang et al., 2017) instead of choosing an estimate for this work.

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).

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).

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.

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'.

Lines 357-359: 'physical mechanisms as well as'. This is nonsense. Heterogeneous hydrolysis is a chemical mechanism. Remove.

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.

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.

Lines 371-373: It is the conversion of NO2 that is typically used for this calculation, not NOx, 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?

Line 381: Figure 9a. Fix notation.

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.

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.

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.

Line 421: Revise in accordance with new contents of the manuscript after addressing all comments from Reviewers.

Figure 2: Aerosol SA and ground SA need to be considered separately in the ANN.

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.

Figure 4: Move this to the SI. Add sensitivity test figures to the manuscript.

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