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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 #2**

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The study describes measurements of HONO and associated atmospheric constituents in Seoul during KORUS-AQ. The authors find that elevated nocturnal HONO mixing ratios are detected on certain nights and that ground-level ozone mixing ratios are elevated during the following daytime period – a relationship that has been shown in the present study on several different days. The authors use a zero-dimensional box model to simulate this chemistry and show the effects of morning HONO photolysis on daytime O3 by jump-starting the HOx-NOx cycles with exogenous OH.

Overall, this paper leaves me thinking that I am unsurprised by the observation. The reason that HONO has received intense focus over the past number of years has been to elucidate this type of mechanism – that elevated HONO in the morning would jump-start the HOx-NOx cycle, resulting in more rapid production of O3 during the day. In the end, I am still asking myself about what I have learned from this paper – and I am struggling to find very much. If the authors seek to provide a report of the atmospheric chemistry that is occurring in Seoul and contributing to high O3 days, this may be a worthy goal. I do not think that the present study provides new fundamental insight into HONO chemistry. It is recommended that the authors either more thoroughly utilize the data to extract useful quantitative information about HONO formation and provide insights that are more useful to the research community or back away from the HONO formation mechanism aspect of the study and focus more singularly on the impact that HONO can have on O3 chemistry in Seoul.

In its current state, this reviewer cannot recommend that this paper be published in Atmospheric Chemistry and Physics. If the paper were to be heavily revised (beyond what I would call a 'major revision'), the manuscript could be re-considered.

It is also recommended that the authors revisit their use of English language, perhaps hiring help to edit the manuscript if needed. Clearer language will only help the paper communicate the most important points.

Line 87: "The introduction of spectroscopy technique [sic] has facilitated measurement through instrumentation such as Chemical Ionization Mass Spectrometry (CIMS)..." CIMS is not an optical spectroscopy technique like the others listed. In addition, it is not discussed later in the paragraph when the positives and negatives are described.

Section 2.2.2 is difficult to understand. Parameters are weakly defined and technical terminology that is not typical for the atmospheric sciences makes the section challenging to understand for a likely ACP audience (including this reviewer). It is recommended that the authors include a description of how the choices made by the authors impact the outcomes of the ANN approach.

Lines 263-267: The average concentrations cited are not necessarily useful numbers because the diel variations in mixing ratios are so large. The nocturnal HONO and daytime O3 mixing ratios are the most important, respectively. Do the 'average' values for the high-O3 and non-episode days reflect the day-long averages? If so, the authors should consider changing the presentation of data to be more applicable to the chemistry at hand.

Lines 280-282: The reason for the anti-correlation of O3 and HONO is due to the source and sink processes for these two gases. While the paper is suggesting that a relationship between these two important reactive trace gases exists, the sources of variation in the diel profile of HONO and O3 are actually *distantly* related. I do not understand why it is appropriate to discuss the data in such a simplistic way.

Figures 3 and 4: There is an important discrepancy between the HONO, NO, and NO2 data in Figs 3 and 4. It appears from inspection of many day-long periods in Figure 3 that NO and HONO are almost positively correlated. . . the peaks in NO and HONO occur at very similar times, but the data in Fig 4 show that these peaks occur at different times (NO is increasing as HONO is decreasing in the morning). Would it be better to plot the diel mixing ratios after splitting the cases into 'high-O3' and the 'non-episode' periods? The data, as plotted, are not necessarily consistent.

Line 301: Why does the 80% RH threshold only mean "mist" vs "haze" in Korea? This seems arbitrary. Perhaps consider the RH dependence of water uptake to urban aerosol particles (yes, a mixed and perhaps uncharacterized composition for sure, but there are typical particle types to consider qualitatively).

Figure 5: It may be clearer, or at least less arbitrary, to colorize the markers in Figure 5 by the NO mixing ratio. If a global relationship truly does exist, it will be borne out in the FULL dataset, rather than the arbitrarily chosen >90th percentile of NOx.

Line 309 and others: As presented throughout this paper, the HONO mixing ratios are said to be high during high-O3 episodes. Please alter these descriptions to be specific about how HONO is higher *at night* and is associated with elevated daytime ozone.

Eq 10: To what do the t1 and t2 subscripts refer?

Lines 319-320: “assuming that OH is produced only by HONO”. Why do you make this assumption? The modeled diel OH curves shown cannot possibly be dependent only on HONO photolysis – what about the HOx-NOx cycle??

Section 3.2 up to Line 338: I think the problem here is in the way that this modeling experiment is presented. Please re-consider how this is presented and clearly indicate the question that you are asking, reasons for simplifying assumptions, and clear statements of conclusions based on this ‘toy’ experiment with modeling OH from your data. It appears that the authors are trying just to illustrate the impact of HONO on the morning OH mixing ratios, but their descriptions make it seem like their results are broadly accurate, which they are likely not based on their simplifying assumptions.

Lines 336-337: Time integrated values should have some indication of the limits of the integrals, otherwise these numbers lack real meaning. If the authors simply seek a comparison between the two types of events, then summarizing with a relative % difference may be more appropriate and useful.

Line 339-346: The sensitivity tests using F0AM say much more than the conclusion that the authors draw. The authors only comment on the importance of HONO to the O3 profile, but the other members of the HOx cycle also play extremely important roles – clearly shown by the model runs!! The authors are encouraged NOT to cherry-pick the results of their studies for the purported benefits of the story that they wish to tell. If the authors would like to highlight the importance of HONO, it would be beneficial to *quantify* the importance of HONO vs other factors.

Lines 357-364: The role of water in certain HONO production reactions is known. It is recommended that the authors explore RH vs absolute water vapor mixing ratio (or specific humidity). If water participates in the reaction, the kinetics will be related to the absolute concentration of water molecules, rather than a temperature-dependent, saturation-normalized metric like RH. Temperature changes by enough to drive diel variations in RH. This may be masking the importance of water to the chemistry, or it may be over-emphasizing its role due to coincident diel changes in HONO, NO, NO2, and (temperature-driven) RH.

Lines 380-385: Two items: 1. The response of the conversion ratio to high RH is presented as an independent verification of the behavior of HONO under such conditions. The conversion ratio is essentially a ratio between a measure of [HONO] divided by a measure of [NOx]. If [NOx] is stable over time as it is in this study, then the [HONO]_emission metric is stable over time, and then of course the conversion ratio responds only to [HONO]_formation! The authors have simply shown two ways of expressing the same observation.

2. The connection to Wojtal et al is not very clear, because this is the first time that the marine boundary layer is described at all. Please be more thorough in the description of how the cited work helps to explain your observations.

Lines 386-396: Multiple comments: 1. Indeed, soot has been discussed as a reactive surface and laboratory experiments have shown that HONO can be formed upon NO2 reaction with soot. However, HONO can be formed by reaction with many different types of surfaces. Forcing the discussion into black carbon or soot particles reflects a narrow view of the surface catalyzed formation of HONO. In addition, making a broad assumption that all particles between 30-120 nm is FAR oversimplified and arbitrary. Particles in this size range will have a range of compositions, likely with a strong contribution from organic material. Why not simply cut the discussion of black carbon and use the total surface area of particles?

2. PM2.5 is discussed here but the measurement technique and sampling conditions are not described in the paper.

3. Guessing that PM2.5 is measured using a typical type of air quality monitor, PM2.5 could increase due to secondary aqueous phase reactions or simply the growth of particles due to water uptake. Also, particle mass increases as a cube of particle di-

ameter, so PM2.5 measurements may be responding to an entirely different population of particles than the SMPE and MAAP. Also, if the sampling conditions for the SMPS and MAAP measurements are not identical to the PM2.5 measurements, the authors may be ascribing a real effect to a sampling artifact. Please provide sufficient technical information to reassure the reader that this is not the case. Particle measurements require care and nuance, which cannot be assessed by the reviewer or a future reader based on the present manuscript.

Lines 397-419: While the authors have used an interesting ANN tool, it is not clear what the results have taught us. We already know that the NOx, surface area, and humidity are key factors that control HONO production. . . we have known this for more than a decade. What can this information provide that will help advance the detailed understanding of HONO formation?

Minor overall comments: 1. The use of “%ile” is not typical in formal writing. The authors should consider changing this format from “95 %ile” to “95th percentile”. 2. Line 309: “chapter” should be “section” (I stopped making these comments after this point. Substantial English language editing is advised.)

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