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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.

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Response to Review 2

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.

Line87 : "The introduction of spectroscopy technique [sic] has facilitated measurement through instrumentation such as Chemical Ionization Mass Spectrometry (CIMS). . .

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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. Yes, CIMS was discussed after spectroscopic techniques. Section 2.2.2 : 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. We should have been more cautious when introducing new method and terminology. In the revised manuscript, the method section regarding the ANN was shortened and instead, a full explanation is given in supplementary information including the structure of ANN and the detailed procedure of calculation. 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 Yes, the daily averaged concentration is not useful for O3 in urban areas because of a big difference between the daytime and nighttime. In comparison, the daily average of HONO concentrations reflect the nighttime level well and thus, can be compared from region to region and from time to time. The daily averaged concentrations are to compare the HONO level of Seoul with those of other cities from previous studies. In this study, HONO was discussed in relation with O3 and for this reason, the O3 average concentration was given in pairs with HONO. The various types of concentrations are discussed and compared in the text. For clarity, they are summarized in Table 2 in the revised manuscript. 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

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way. The inverse relationship between O3 and HONO stems from their inherent photochemical property. Nonetheless, their daily maximum concentrations were linearly correlated in this study. These relationships are shown in Figure 5 that was added to the revised manuscript. The relevant part was modified in the revised manuscript as follow: In general, HONO and O3 showed an inverse correlation and the overall correlation between the two species was good (r2 = 0.41) (Figure 4). It is mainly derived from their inherent photochemical property. If the daily maximum concentrations are correlated, O3 concentrations are proportionally increased with HONO (Figure 5). 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. Figure 3 shows time-series variations of measured species. Of these NOx levels were noticeably high at night in the beginning of the experiment. It may give an impression of the positive correlation between NO and HONO. The diurnal variations shown in Figure 4 are pretty typical in the study region. NO concentrations used to reach the maximum around 7∼8 h in the morning, followed by NO2 peak. But, NO2 concentrations are higher during the night, when HONO shows a clear peak. The actual relationship between the species is shown in Figure RC 1 below, where the correlation with HONO is better for NO2 than NO. The diurnal variation of HONO and other species are compared for high-O3 episodes and non-episode in Figure 7. 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). The Korea Meteorological Administration (KMA) provides the guideline for meteorological observation, where the 80 % relative humidity is a criterion that distinguishes hydrome-

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teors from haze particles. If RH is below 70 % and visibility is between 1 km and 10 km, it is classified as haze condition. All weather phenomena are coded for sharing through WMO (World Meteorological Organization). In the revised manuscript, the relationship between RH and aerosol surface was more clearly stated. The HONO concentration and conversion ratio of NO2 was found to be the highest in the RH range of 70 $\sim$ 80 %, which is the upper and lower margin for haze particles and hydrometeors, respectively. At RH > 80 %, PM2.5 concentration was noticeably high (Figure 6). 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 (Figure 10). During this experiment, the deliquescence RH of NH4NO3 and (NH4)2SO4 was in the range of 70 $\sim$ 80 %, over which their concentration dramatically increased with the increase in PM2.5 mass. When comparing the surface area of Aitken mode (30-120 nm) with condensation mode (120-300 nm) 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: The surface area of Aitken mode particles decreased, but that of condensation mode particles increased, leading to the greatest difference at RH range of 70$\sim$80% (Figure 10). 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]. We added this discussion about RH dependence to section 3.3 in the revised manuscript. 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. Figure 5 was modified in the revised manuscript. Color was coded by NO2 concentrations. In this plot, the relationship is not explicit but useful to under-

stand key variables determining HONO concentrations. In Figure RC 3 shown below, the relation between RH and HONO was color-coded with NO, NO2, and NOx. As expected from their diurnal variations, NO is not distinguished in RH-HONO relationship. Figure RC4 and Figure 5 indicate that the level of HONO is dependent on NOx (NO2) concentrations. 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. As you suggested, the numbers are summarized and given in Table 2 for quantitative understanding. Eq 10: To what do the t1 and t2 subscripts refer? They are errors and corrected like this: ãĂŰ[OH]ãĂŮ_t1=J_HONO ([HONO]_t1-[HONO]_t2), where t1 and t2 are consecutive times. 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?? It was corrected. In this study, we tried to calculate the OH produced from HONO photolysis, but not an ambient OH concentrations. 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. Although it is a simple calculation, the model results demonstrate the role of HONO in O3 formation through HOx cycle. It is already presented from measurement data when they were compared between the high-O3 episodes and non-episode. The difference between the two periods is evident in diurnal variations of O3, HONO, and other precursors (Figure 7). From the model simulation, the contribution of HONO to HOx cycle was quantitatively estimated (Figure 9). This part was revised with presenting all model runs in Figure 8. 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. 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). 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, according to your suggestion. 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. We admit that some statements go further than they mean. For example, VOCs are intimately coupled with HOx cycle, producing O3. When discussing the OH produced from HONO and its impact on O3 production, it was inevitable to state VOC, especially in model simulation. According to your comments, the manuscript was revised with caution. In the abstract, VOC was removed from the last sentence. In original submission, the model results were presented for four scenarios to demonstrate the role of HONO (Figure 7) . In the revised manuscript, the results for all scenarios using BTEX, HCHO, CO, and HONO are presented in Figure 8 and summarized in Table 3. While the contribution of BTEX is the most pronounced, the time for maximum O3 was shifted toward the morning without HONO. These results highlight the importance of HONO in O3 chemistry. 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. Absolute humidity (AH) was calculated using the following equation, AH (g mˆ(-3))= (6.112×eˆ((17.67×T)/(243.5+T))×RH×2.1674)/(273.15+T). AH was used for calculation of chemical reactions. For comparison, RH was also tested. The results are presented in Figure S3.1, which indicates that RH is more relevant for the formation of HONO than AH. Figure RC 7 (below) compares the relationship of AH and RH with HONO concentrations color-coded by NOx. The overall patterns are similar but, RH shows more consistent relationship with HONO and NOx then AH. These results imply the involvement of heterogeneous reactions in HONO formation mechanism. It was discussed in section 3.3. 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. 1) The diurnal variation of NOx is presented in Figure RC 6 below. While the mean concentrations show a typical variation with two peaks in the morning and night, the concentrations vary in a wide range. This diel cycle is also different from HONO variation. 2) The work of (Wojtal et al., 2011) is cited here to emphasize that the dependence of HONO concentrations on RH was observed in previous studies. In addition, they reported the negative relationship between HONO and RH in high RH condition, suggesting the possibility of HONO loss on aerosol surfaces or microlayer of the sea surface in marine boundary layer. 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 diameter, 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. 1) You are absolutely right regarding the variety of particles available for heterogeneous reactions. Based on the results from previous studies, we examined PM2.5 mass, and Aitken mode (30∼120 nm) and condensation mode (120∼300 nm) particles as substrates rendering surfaces to HONO heterogeneous reactions. As Aitken mode is similar to the size range of BC (or EC) particles, BC mass was also considered in this analysis. Then, the relation of these variables with RH was examined. Surprisingly, all of them showed a turning point at RH of 70∼80% (Figure 10) but in different ways. Of these, the aerosol surface area of the Aitken mode particles showed a similar tendency to NO2 conversion ratio (CHONO). In this study, the RH of 70∼80% was found to be critical point affecting the behavior of aerosol composition as well as surface. Sure enough, it was related to the hygroscopic property of inorganic salts controlling PM2.5 mass. It is also the transition RH between dry haze particles from wet hydrometeors, which is defined as meteoro-

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logical phenomenon by Korea Meteorological Administration. For clarity, this part was completely revised with more information added to the manuscript. Please see the response 6 above. 2) and 3) The detailed measurement techniques and information can be found elsewhere, including (Kim et al., 2020;Jordan et al., 2020) prepared for the KORUS-AQ special issue in Elementa. 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? We used the ANN model to add quantitative evidence to our findings about heterogeneous HONO formation. At present, there is no firm theory that explains its concentration and formation mechanism, except the conditions constraining HONO concentrations such as high-NOx (urban), high-RH (coastal) or highly particle-polluted sites. With a clue from our measurements about how NOx, surface area, and humidity interplayed in determining HONO concentrations, the ANN model was run. The key contribution of ANN model is what is shown in Figure 12, where the influence of surface area of the Aitken mode particles to HONO concentration was nearly equal to NO2 and greater than RH. Therefore, the results of ANN simulation not only confirm the involvement of heterogeneous conversion of NO2, but also reveals the interplay of the main variables in the process of HONO formation. Consequently, it led to the conclusion of this study that RH constrained the available aerosol surface for HONO formation through intimate coupling with hygroscopic inorganic aerosols and NO2 determined the concentration of HONO as a precursor. 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.) They were all changed to percentile. All errors were corrected as far as we could. The revised manuscript was English proofread.

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Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-1012/acp-2019-1012-AC2-supplement.pdf

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