Response to the Interactive comment by Anonymous Referee #2 on "Tropospheric HONO Distribution and Chemistry in the Southeast U.S."

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General Comments

This manuscript explores the generation and fate of HONO above and within the planetary boundary layer over the southeastern United States during NOMADSS 2013 from several research flights aboard the NCAR C-130 aircraft. The vertical distribution of HONO throughout this layer is clearly demonstrated to be derived from volume sources, with a robust testing of the known mechanisms of HONO formation against parameterizations of particulate nitrate photolysis, which is emerging as an important source of tropospheric HONO. The Author's find that previously established volume-based mechanisms of HONO formation cannot account for the observed quantities and that the photolysis nitrate in the condensed phase can possibly explain the majority of the observed quantities. The Authors demonstrate that HONO is a minor OH source at these altitudes when its production is driven solely from volume production and also that it is an important intermediate in the renoxification pathways of tropospheric trans- port of nitrogen oxides. Overall, this manuscript is well written with a solid analysis of the dataset. There are minor modifications necessary to make the manuscript more clear and concise in its purpose and findings. The removal of some figures and text by the production of a supporting information document would easily facilitate this.

Response: We thank Anonymous Referee #2 for the positive and encouraging comments. The detailed and insightful comments and suggestions have greatly helped us in revising and improving the manuscript. A supplement document has been generated to include supporting content as suggested.

Specific Comments

Page 2, Lines 7-10: The detailed analysis of the isoprene transport and subsequent lifetime calculations for HONO are a quantitative assessment of the decoupling of surface emissions from the observed HONO. The Authors should consider using their quantitative assessment as the basis for their statement here instead of the more qualitative observation of no vertical gradient.

Response: The abstract has been revised and reorganized, as the referee suggested.

Page 2, Lines 14-15: Please provide the average +/- SD of the actual fraction of the observed HONO that was generated by pNO3 photolysis from the presented calculations instead of 'appeared to be the major daytime HONO source'.

Response: The abstract has been revised and reorganized, as the referee suggested.

Page 2, Lines 20-25: Provide the quantitative findings from each section of the detailed analysis here over the general statements of relative importance. This will generate greater impact for this work.

Response: The abstract has been revised and reorganized, as the referee suggested.

Page 3, Line 39: Remove ', as an important OH precursor,' as it is redundant.

Response: The phrase has been removed as suggested.

Page 3, Lines 51-57: I would suggest removing this length section and replacing it with a single sentence following the statements on combustion HONO sources (Line 48). This level of detail in the introduction is not really relevant to the tropospheric chemistry discussed in this work.

Response: Revision has made as the referee suggested.

Page 4, Lines 75-84: The last two sentences demonstrate that R4 is unnecessary and it should likely be removed from here and from the presented data analysis, since it has been show to be a two-photon process. It should be removed here and the section on the hydroperoxyl-water complex mechanisms should be replaced with one sentence on its existence and low yield of HONO.

Response: As the referee pointed out, both reactions (R4) and (R5) are not important as HONO sources. Since we intend to conduct HONO budget analyses in the later sections, to include all NOx-related reactions. We feel that a brief discussion of reactions (R4) and (R5) here is justified.

Page 5, Lines 104-107: It would be useful to guide the readers through the major explorations of this dataset here. Consider listing the major sections of this work here in the order that they are presented in the abstract, manuscript, and conclusions, to improve clarity.

Response: We did provide some field campaign and measurement information in the first paragraph in section "2 Experimental", right after the paragraph.

Page 5, Line 108: The experimental section could use subsections to improve clarity.

Response: Revision has made as the referee suggested.

Page 5, Line 126: The baseline subtraction of interferences from particulate nitrite here does not acknowledge that there is a size-dependent collection efficiency in these style of instruments. For example, fog droplets would be effectively captured in the primary channel to appear as HONO and not be corrected for in the secondary channel. This has been demonstrated in other works with this analytical approach (e.g. (Sörgel et al., 2011) and references therein). Is there any potential for droplet nitrite interferences in these measurements where clouds may have been encountered?

Response: As pointed out by the referee, cloud droplets may be collected at significant efficiency and be an interference in our measurement. We have excluded the in-cloud measurement data from our data analysis, due to lack of valid way to correct the data. The following sentences have been added in the revised manuscript (lines 163-166): "Noisy baselines were observed when the C-130 was flying in the clouds, due to the sampling of cloud droplets by our sampling systems. Because of the lack of a valid way to correct for this interference, all in-cloud measurement data of HONO and pNO_3 have been excluded from the data analysis."

Page 6, Lines 138-139: It is confusing to follow the logic of this estimation. Was the maximum possible interference determined in some sections of the dataset to set the limit at 0.2? If possible, add the quantitative approach used to a section in a Supporting Information document. If not, please improve the clarity here.

Response: We have not determined the collection efficiency for HO_2NO_2 experimentally. The upper limit HO_2NO_2-to-HONO conversion efficiency of 0.2 was estimated from the ratio of the observed [HONO] to the calculated $[HO_2NO_2]_{SS}$ in cold, high altitude air masses under our measurement conditions, assuming ambient HONO concentration approaching zero. We found that the correction was not necessary in the TBL. The discussion has been revised to: "Potential interference from peroxynitric acid (HO_2NO_2) was suppressed by heating the PFA sampling line to 50 °C. The HO_2NO_2 steady state concentration ($[HO_2NO_2]_{SS}$) was estimated to be less than 1 pptv at temperatures of 20 - 30 °C in the background PBL (Gierczak et al., 2005), and thus interference from HO_2NO_2 was negligible. Whereas in power plant and urban plumes in the PBL or biomass burning plumes in the upper free troposphere (FT), HO_2NO_2 interference was not negligible and thus a correction for HONO measurement was made. An upper-limit HO_2NO_2 response efficiency was estimated to be 0.2 for our HONO measurement systems. The estimation was made from the lowest ratio of the measured HONO to the corresponding $[HO_2NO_2]_{SS}$ in cold air masses at high altitude, assuming no HONO existed. HONO concentration were then corrected by subtracting a term of "$0.2 \times [HO_2NO_2]_{SS}$". The correction was below 10% of the measured HONO concentrations in the PBL plumes. However, there may be over-corrections in the cold free troposphere." (lines 13-143)

Page 6, Lines 142-144: Provide the correlation coefficient, slope, and intercept here to improve clarity and validity of analytical approach.

Response: The intercomparison of HONO measurements from the two instruments (the DOAS and the LPAP) was made by overlaying the concentration time-series on each other (Extended Data Fig. S3 in Ye et al., 2016). The measured concentrations closely tracked each other, and the agreements were within the assessed uncertainties. The readers are encouraged to read the paper for more information.

Page 6, Line 149: The order of the used apparatus is not clear. Presumably the denuder followed the filter? Please clarify.

Response: As the referee suggested, the sentence has been revised as suggested to ""Zero-pNO_3" air was generated to establish measurement baselines for pNO_3 by passing the ambient air through a Teflon filter to remove aerosol particles and then a NaCl-coated denuder to remove HNO_3 before reaching the sampling unit of LPAP." (lines 155-158).

Page 6, Line 160: Delete 'NCAR's'

Response: Revision has made as the referee suggested.

Page 7, Line 161: What are 'state parameter measurements'?

Response: The NSF/NCAR C-130 aircraft comes equipped with a package of standard instrumentation that flies on all C-130 research missions. The measurements made by these sensors form the core of any research program and provide the information necessary to place the aircraft in space and time while characterizing the basic "**state**" of the local environment. The parameters include aircraft longitude, latitude, altitude, flight speed, pressure, temperature, dew point, and many more.

Page 7, Lines 183-184: Remove this from here. It is discussed in sufficient detail later and distracts from the results.

Response: Indeed, the vertical HONO distribution is discussed in the following section in more details. However, we feel that in the "General data description" section, this sentence provides some contrast to the horizontal inhomogeneity of HONO distribution, and thus we keep the sentence as it is.

Page 7, Lines 186-188: Remove these statements. The information is already presented in the Table and does not need repeating.

Response: The readers can obtain the information directly from these statements without going the tables and Figures. We feel that some degree of redundancy may be needed. Thus we keep the sentence as it is.

Page 7, Lines 191-192: Delete the sentence on the future paper.

Response: Revision has made as referee #2 suggested.

Page 8, Lines 194-196: Delete these and direct the reader to the relevant section at the end of the preceding sentence by adding '(Section 3.4)'

Response: Revision has made as the referee suggested.

Page 8, Lines 201-203: Remove these statements. The information is already presented in the Table and does not need repeating.

Response: Again, the readers can obtain the information directly from these statements without going the tables and Figures. We feel that some degree of redundancy may be needed. Thus we keep the sentence as it is.

Page 8, Lines 210-212: Remove these statements. The information is already presented in the Table and does not need repeating.

Response: Again, the readers can obtain the information directly from these statements without going the tables and Figures. We feel that some degree of redundancy may be needed. Thus we keep the sentence as it is.

Page 9, Line 236: Here is the first definition of the altitudes considered to by the PBL versus the FT. The Authors should add their criteria for distinguishing between the PBL and FT to the methods section. If it would be a lengthy addition, then a condensed description with supporting details could be placed in the Supporting Information document.

Response: The discussion in this section was focused on the transport and contribution of HONO from ground level to the overlying PBL, based on the vertical distributions of HONO and other species in the PBL (300 -1200 m). Transport into the FT would be much slower and was not discussed in the section. The PBL height can be estimated by the temperature inversion in the vertical potential temperature profile.

Page 9, Lines 238-250: This is a fantastic analysis of the vertical mixing and transport of surface-emitted species, but it is outside the focus of this work. Consider relocating this detailed analysis to the Supporting Information document.

Response: The main discussion of this manuscript is on HONO daytime budget and chemistry. HONO is a unique species mainly produced by heterogeneous processes on surfaces. Ground surfaces provide the sites for the heterogeneous processes to produce HONO. We feel that it is important to examine the input from ground HONO source to the HONO budget in the PBL. Therefore, we keep the equation (Eq. 1), vertical profiles in Figure 4, and discussion of vertical transport in the main section.

Page 9, Lines 250-254: Distinguish between ground-emitted and volume-produced HONO here to improve clarity.

Response: We have significantly modified the discussion in that paragraph. The two sentences have been changed to "With a photolytic lifetime of ~ 11 min for HONO, about 11% of the HONO originated from the ground level is expected to reach the altitude of 300 m, the lowest flight altitude of the C-130 aircraft between 11:00 – 12:15 LT in RF #4." (lines 266-268).

Page 9, Line 256: 'of its precursors' should be 'of its potential precursors' since this work is yet to demonstrate this quantitatively (although it is shown quite well later).

Response: Revision has made as the referee suggested.

Page 10, Lines 286-287: This was stated in the introduction as insignificant (and potentially invalid), so why have the authors chosen to include this in their analysis? Suggest removing throughout.

Response: We intended to include in our calculation all the NO_x-related reactions reported in literature. While the importance of R4 and R5 are still under debate in literature, our HONO budget analysis does suggest they were insignificant under the conditions we encountered in the Southeast U.S., as stated in the Introduction.

Pages 10-11, Lines 289-291: Consider providing a justification for selecting all upper limits in these calculations to improve clarity.

Response: As suggested by the referee, the following sentence has been added after equation (Eq. 2): "It should be noted that the upper limit values of rate constants were used in the calculation to avoid the underestimation of $[HONO]_{pss}$ value." (line 307-309)

Page 11, Line 302: Remove ', such as pNO3.' As it is redundant for the transition between paragraphs.

Response: The phrase has been removed as suggested.

Page 11, Lines 309-310: Remove 'over the terrestrial areas', 'on Teflon filters. . . summer field study'. This information is already presented in the methods.

Response: The redundant information has been removed as suggested.

Page 12, Lines 326-330: This is a single sentence and is difficult to follow. Consider breaking into 2-3 sentences to improve clarity.

Response: The long sentence has been changed to "However, the r^2 of 0.34 is not as strong as expected from pNO_3 photolysis being the major volume HONO source. It may be in part due to the use of a single median J^N_{pNO3} value of ~ 2.0×10^{-4} s^{-1} in the calculations of the ambient J_{pNO_3} and the production rates of HONO in Figure 5b; the actual J^N_{pNO3} values are highly variable, ranging from 8.3×10^{-5} s^{-1} to 3.1×10^{-4} s^{-1} (Ye et al., 2017)." (line 337-341)

Page 12, Line 331: Delete 'only rough'. Redundant. Also see comments on Figure 6 regarding weighted error analysis.

Response: The redundant phrase has been deleted as suggested.

Page 13, Line 357: What is the error on this ratio of 0.02? Is it statistically different from the fresh power plant emissions?

Response: Standard deviations of the HONO/NO_x ratio have been added in the revised manuscript. The sentence has been revised and expanded to "The observed HONO/NO_x ratio was 0.019 ± 0.004 in the power plant plumes (e.g., P4) and 0.057± 0.0019 in urban plumes, significantly higher than the typical HONO/NO_x emission ratio of ~0.002 in the fresh power plant plumes (Neuman et al., 2016) and ≤0.01 in automobile exhaust (Kurtenbach et al., 2001; Li et al., 2008b)." (lines 380-383)

Page 13, Line 370: Since plume G is the only case study from these labels, consider a uniform label for the urban emissions (A) and the remainder of the power plant plumes (B). The increasing lettered format makes it seem that each instance will be discussed.

Response: We have revised Figures 2 and the text, as the referee suggested, and have labeled the plumes according to their sources.

Page 15, Line 439: The conclusions section of this manuscript is similarly qualitative, as the abstract is, despite the excellent quantitative analysis presented throughout the results and discussion. Suggest revisiting this section with more quantitative information to improve clarity and impact.

Response: We have followed the referee's suggestion, and have revised the conclusions.

Page 25, Table 2: The +/- SD is in brackets in one part of the table and not the other. Please correct this. The terms PBL and FT are not defined anywhere in the manuscript and should be given at least an operational definition somewhere in the methods section. Lastly, the number of data points being used in each of these calculations should be provided in a column or in the caption.

Response: Revision has made as the referee suggested.

Page 27, Figure 2: Consider moving this figure to the supporting information or removing it entirely from the manuscript. The only specific features necessary here are the plumes which are presented again in Figure 7. With respect to the urban and power plant plumes, it could be simpler to assign the urban plumes a single letter (such as A), and similarly assign all the power plant plumes with a single letter excepting the one plume discussed in detail, which could be assigned a third letter. With each plume having a different letter, the figure suggests that there is something different between these, when there is nothing in the discussion that suggests this is the case. It would improve the clarity to simplify this.

Response: The figure has been referred 8 times in the main text. We feel that it is important to keep this figure in the main manuscript so that the reader can get to it quickly. The plumes have been re-labels according to their sources, as the referee suggested.

Page 28, Figure 3: This figure does not seem necessary for inclusion in the main manuscript and should be considered to be moved to the supporting information. Figure 4 and Table 2 provide redundant and better insight into the measurements.

Response: Again we feel that it is important to keep Figure 3 in the main manuscript; it was referred three times in the discussion. Only a few vertical HONO concentration profiles have been reported so far in literature. They provide important information to understand the budget, the chemistry and the transport of HONO in the troposphere. Figure 3 contains far more data points from 5 research flights over different environments in the southeast U.S., while Figure 4 shows many more parameters from only one race-track over one area, and Table 2 only summarizes the statistics of the measurements. Therefore, they are not really redundant, but rather complementary.

Page 29, Figure 4: It could be useful to add the typical PBL to FT height as a shaded area (if it has some variability) or horizontal line in each panel to facilitate clarity between the figure data and the discussion.

Response: As stated in the figure caption, Figure 4 shows the vertical distributions of concentrations of HONO, NO_x, pNO_3, isoprene and potential temperature in **the PBL** during the first race-track of RF#4. According to the potential temperature and isoprene profiles, the PBL height was around 1200 m.

Page 30, Figure 5: The two sentences in the paper communicate all the information contained in this figure. Suggest removing this figure altogether or relocating to the supporting information. Further, the correlation analysis undertaken here is unclear and may be subject to some error if an error-weighted analysis is not being used (Wu and Zhen Yu, 2018). Is the error in both datasets being taken into account when calculating the regression coefficient? Please update the analysis and discussion to reflect the approach and ensure it is robust for the presented data.

Response: The figure has been moved to the supporting information, as the referee suggested. And more robust Deming least-squares regression (Wu and Yu, 2018) has been used in the data analysis, as suggested.

Page 31, Figure 6: The same regression questions from Figure 5 also apply here. Please clarify the approach utilized and ensure that the appropriate regression analysis and statistics have been used when interpreting the data.

Response: As the reviewer suggested, more robust Deming least-squares regression (Wu and Yu, 2018) has been used in the data analysis.

Page 32, Figure 7: Panel (a) here can be move to the supporting information or removed altogether.

Response: We have moved the panel (a) to the supporting information as the referee suggested, and have also added SO_2 as power plant plume tracer and acetonitrile as a biomass burning tracer to the revised Figure S1, as Andy Neuman suggested in his Short Comments.

Page 33, Figure 8: This information in this figure is presented concisely in the discussion and the figure does not add anything further. Consider removing this figure from the manuscript.

Response: The figure has been moved to the supporting information as suggested.

Page 34, Figure 9: The lines are very hard to see on this figure and the green line does not print well. Suggest using two black lines that are thicker than those currently used, with different dashing to distinguish them. The markers are also defined by very thin lines that could be made thicker for clarity.

Response: The figure has been revised as suggested.

References

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