Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-105-RC2, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tropospheric HONO Distribution and Chemistry in the Southeast U.S." *by* Chunxiang Ye et al.

Anonymous Referee #2

Received and published: 9 April 2018

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 transport 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.

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.

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'.

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.

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

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.

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.

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.

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

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?

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.

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

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

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

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

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

and distracts from the results.

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

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

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)'

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

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

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.

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.

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

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).

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.

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

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

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

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

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

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

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.

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.

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.

Page 27, Figure 2: Consider moving this figure to the supporting information or remov-

ing 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.

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.

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.

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.

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.

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

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.

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.

References

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A. and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: Influence of turbulent exchange on mixing ratio differences, Atmos. Chem. Phys., 11(2), 841–855, doi:10.5194/acp-11-841-2011, 2011.

Wu, C. and Zhen Yu, J.: Evaluation of linear regression techniques for atmospheric applications: The importance of appropriate weighting, Atmos. Meas. Tech., 11(2), 1233–1250, doi:10.5194/amt-11-1233-2018, 2018.

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