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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of total peroxy nitrates and aldehydes: measurement interpretation and inference of OH radical concentrations" *by* P. A. Cleary et al.

P. A. Cleary et al.

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Response to Referee #2:

We thank referee #2 for his or her comments. We were also initially surprised by the agreement of the steady-state calculation with the time-dependent models and as the reviewer suggests, we hope that this new approach to thinking about PNs will receive continued attention. Our responses (author commnents, AC) to referee comments (RC) are detaild below.

Specific comments:

RC: The fundamental assumption that aldehydes are the primary precursors of PAN

compounds may hold true in urban air, but could be called into question when there are biogenic compounds or larger, branched hydrocarbons in the reactive mix. I think the authors should clearly address this caveat and make it clear why their assumption is justified. It's not clear that it works for the OH estimate, as discussed below.

AC: We agree that there is a need for continued study of the sources and budgets of both PNs and aldehydes. In this study we found the need to speculate on the existence of a large secondary source of PAN that source could just as easily be the other compounds to which the reviewer is referring.

RC: In Section 4, right after equation 4 the authors describe 4 scenarios for the time dependent integration but do not give a rationale for why they look at 4 scenarios. One sentence here would clarify the paragraph

AC: We have added the following text:

"We choose four scenarios which we believe to be either typical or limiting cases for the aldehyde source strength at this site." (page 12940)

RC: The estimate of [OH] is a clever idea, but I am concerned that the robustness/accuracy of the steady state analysis that worked for PAN will not work as well for the other compounds, especially those with biogenic precursors, like MPAN. Fixing the PPN:PAN ratio is potentially problematic. There are many measurements of PPN in the literature other than the one cited from S. America, and the PPN/PAN ratio can vary significantly. Again, the rationale state for the different model conditions are a bit arbitrary., Before this method is used more extensively, the steady state assumption should be tested for different individuals (at the very least PPN) and a more robust selection of conditions for the modeling should be developed.

AC: We apologize for creating some confusion here, the reference listed was in error, it should have been (Grosjean et al., 2002) which describes measurements in southern California. We believe these estimates of PPN/PAN are representative of this site

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based on other measurements in the vicinity and in cities with similar chemistry (e.g. in Nashville (Roberts et al., 2002) where the ratio was 0.137). However our overall conclusions are not particular sensitive to this parameter. Varying the ratio of PPN:PAN over the range 0.05-0.16 affects the OH we calculate by only ś 4%. We do agree with the referee, that further evaluation of our proposed approach be conducted in the field with specific attention to individual PNs and we hope this paper will inspire research groups with capabilities for measuring individual PNs to do so.

RC: I was surprised to read the last line of the conclusions paragraph suggesting a different way to look at relationships between NOy species and O3 in urban air. It appears that the authors have the appropriate data in hand to test this suggestion and it puzzled me that they would make this suggestion out of the blue.

AC: We view this statement as an obvious corollary of PNs being in steady-state. In that sense it says nothing that is not present earlier in the paper. We have added a sentence to the paper at the end of our discussion of the accuracy of the steady-state model that points this out to the reader.

“We note that one implication of our conclusions that PNs are in steady-state with NOx is that they should not be thought of as terminal sinks for NOy but rather as part of the available NOx.” (page 12942)

RC: The last section describing OH estimates was somewhat cumbersome with explanations of different model scenarios and conditions. I found myself thinking that a table with more concise descriptions would make the arguments clearer to follow. Maybe sub-dividing that section between “Model Approach” and “Model Results” or some such thing would help.

AC: In the revised manuscript we take the reviewers suggestion and divide our last section into two parts: Model Approach and Model Results. We also modified Table 3 to show the aldehyde inputs to each model M1, M2 and M3.

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Technical corrections

AC: We have made the technical corrections to the manuscript.

References

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Roberts, J. M., Flocke, F., Stroud, C. A., Hereid, D., Williams, E., Fehsenfeld, F., Brune, W., Martinez, M. and Harder, H.: Ground-based measurements of peroxycarboxylic nitric anhydrides (PANs) during the 1999 Southern Oxidants Study Nashville Intensive, Journal of Geophysical Research-Atmospheres, 107, 2002.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 12929, 2006.