

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

Anonymous Referee #2

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General Comments: This paper describes measurements of urban plume export from Sacramento. Specifically the researchers measured 3 classes of NO_y with a thermal dissociation-LIF instrument developed in-house. Along with the sum of peroxyacetyl nitrates (SumPN), they describe data on NO₂, O₃ and some aldehyde precursors. They test the hypothesis that the PAN compounds are in steady state with aldehydes in this outflow from the urban source about 30 km away (assuming that that aldehydes are the dominant precursors) against an analytical kinetic solution. They then use their data to estimate OH concentrations. The measurement of SumPN is still very unique to this group and the data are always interesting. The agreement between the steady state treatment of PAN and the time dependent treatment is strong and a

little surprising. In general the paper is well organized and well written, although the last section describing OH estimates was somewhat cumbersome with explanations of different model scenarios and conditions. In general, this is an interesting paper that is clearly appropriate for this publication and attempts to reason out relationships of photochemical processes from a limited set of ambient data.

Specific Comments: 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.

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.

The estimation of [OH] is a clever idea, but I am concerned that the robustness/ accuracy of the steady state analysis that worked well 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 stated 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.

I was surprised to read the last line of the conclusions paragraph suggesting a different way to look at relationships between NO_y 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.

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Technical Corrections:

Abstract line 8: subject verb agreement “calculations”

Abstract line 9: “of are be” ?

If reactions are listed as “Rx”, can the equations be listed as “Ex” to make it unambiguous what is being called?

Section 4 line 11: “. . . steady state with their ALDEHYDE sources . . . ”

The caption for Fig. 5 can be clarified. I think it would be clearer if it read “Model inputs used to compare time dependent and steady state models.”

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.

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

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