

Interactive comment on “Insights into HO_x and RO_x chemistry in the boreal forest via measurement of peroxyacetic acid, peroxyacetic nitric anhydride (PAN) and hydrogen peroxide” by John N. Crowley et al.

Anonymous Referee #2

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This manuscript describes an extensive set of measurements made in the boreal forest in 2010. The data set includes photochemically active molecules, in addition to OH and HO₂ radicals, so that a detailed balance of radical sources and sinks can be assessed. Modifications to a standard model are discussed stepwise, so the reader can follow the logic involved in building the model.

The final agreement between measurements and model is good, with the exception that the HO₂ measurements are impacted by other, BVOC-derived peroxy radicals, RO₂^{*}, that are partially detected by the instrument. Also, additional photolytic sources

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of radicals need to be invoked, e.g., glyoxal, methyl glyoxal and biacetyl, to account for the radical production rates.

Overall, this is a good paper, which is clearly written and explained, and provides a good data set for future comparisons. It can be published after consideration of some minor comments, below. Additionally, there are quite a few grammatical errors (mismatch between subject and verb; misuse of commas) that could be cleaned up by the authors.

Page 1, line 27. “these” peroxy radicals, sounds like it is referring to CH_3O_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$, but I think it refers to RO_2^* ?

Page 2, lines 26 and 30. Inconsistency between the values of k_2 .

Also, in the supplemental table S1, the value of k_2 seems to be a factor of 10 lower yet (A-factor should be $3.14\text{E}-12$).

Page 3, line 4. Mixing ratios and deposition velocities of PAA have also been measured by the CalTech group. See for example Nguyen et al., Proc. Nat. Acad. Sci., 112 (5), E392-E401, 2015. The ambient mixing ratios and fluxes are shown in the Supplemental Appendix, Figure S17.

Page 3, line 26. No need to capitalize “silver”.

Page 3, line 31. Probably need to insert “an” before iodide, or say “mass spectrometry” rather than spectrometer.

Page 5, line 1. Insert space between “gases” and first parenthesis.

Page 6, line 31. Refers to Hall and Claiborn, 1997, and Claiborn and Hall, 1997. Are these the same? Presumably the former is correct, according to the reference list.

Page 7, section 3.1. Please check reaction numbers. So on line 13, the decomposition of PAN should be reaction (R-1) not R(2).

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Page 7, line 14. (R4) does not involve acetyl peroxy loss.

Page 8, line 6. How important is advection? PAN is fairly long lived, and it is well known that it can be transported over long distances. Would you expect it always to be in a photochemical steady state?

Page 8, last line. Should these PAN loss rates be switched? The maximum value is lower than the night time value.

Page 16. Photolysis rate of biacetyl. Klotz et al. (Int. J. Chem. Kinet., 2001) give $j(\text{biacetyl})/j(\text{NO}_2) = 0.036$, measured in the Euphore chamber, roughly a factor of 6 lower than that given here. I realize that the carbonyls introduced here are mostly proxies, but it would be better to use realistic photolysis rates, so that the inferred mixing ratios are also realistic if other people want to reproduce them.

Page 17, line 25. Figure S4 should be Figure S3.

Page 17, last line, has an odd number of parentheses.

Page 18, line 5. Maybe state explicitly that as a result of the internal RO₂ isomerizations, the HOM molecules contain –OOH groups, rather than just “highly oxygenated”. Also, I am not sure that the two references given are appropriate for HOM formation and loss.

Page 20, top. Again, you should include a comparison with the loss rates for H₂O₂ and PAA measured by Nguyen et al.

Page 21, line 17. Sentence begins “This which. . .” Not sure what that refers to.

Page 30, last line. “cantered” should be “centered”.

Page 35, Figure 7. States that open, red circles are HO₂. Should be violet? Also, I maybe missed the section of the text where it talks about adjusting the OH to match levels at the canopy height. Maybe include the section number here, so that it is easier to find.

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Supplemental Figure S2. I like this figure. Could maybe include it in the main text?

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