

Review of “Observations and modelling of HOx radicals in a boreal forest,” K. Hens et al., ACP 2013

Summary

This paper presents a multi-faceted analysis of HOx observations within and above a boreal coniferous forest in Finland. Comparison of OH observed via 2 different techniques lends credibility to later observations by the LIF above the canopy, though it is unfortunate that a similar comparison could not be performed for HO₂. Analyses, including both steady-state and 0-D box model calculations, suggest that missing OH reactivity in the model may explain a concurrent missing HO₂ source. The presentation of results and calculations is almost too thorough in some places and can dilute the key message. Nonetheless, the data is new, and the paper adds to a growing subset of studies outside of isoprene-dominated areas. The paper is appropriate for publication in ACP after consideration of the following.

General Comments

Section 3.1.2 and Table 3: The reviewer found this section and the accompanying table to be very dense and, at times, confusing. Much of the information in the table is repeated in the text, and it is difficult to discern the key points of the discussion when inundated with so many numbers. Furthermore, this breaks the momentum that was built up in the previous section. The following changes are recommended:

- 1) Keep one of the radical cycles in the manuscript, perhaps as a figure instead of a table. The daylight, high-reactivity diagram would be fine. Move the rest to a supplement. Alternatively, perhaps combine the daylight, high and low-reactivity diagrams into a single diagram, using rate-scaled arrows, to facilitate comparison.
- 2) Most of the production rate information can be removed from the text. Try to focus on the key points, such as a subset of those bulleted in Table 3.

Regarding the missing HO₂ source: Can a number or range be assigned to the missing HO₂ production rate, based on model results? This would facilitate comparison with other studies, more so than just the ratio of modeled-to-measured HO₂. This number could be included in both the abstract and conclusions.

Also, a key conclusion of this paper is that missing OH reactivity in the model may explain the missing source of HO₂. Is there sufficient data to make a scatter plot of, e.g., [HO₂]_{mod}/[HO₂]_{meas} versus missing reactivity, or something similar? A clear relationship between these two would help solidify this conclusion.

Specific Comments

P.28565: The authors might also cite (Wolfe et al., 2013), which was published after this paper but deals with a similar topic in a different forest.

P.28565, L.14: These observations are presented in (Edwards et al., 2013).

P.28574, L.8: What is the reason for choosing 4 cm/s? If it is because it provides the best agreement with measured H₂O₂, the authors should state so. Alternatively, Figure 3 could include additional lines for H₂O₂ calculated using 1 and 5 cm/s.

P. 28576, L.24: The description of what is included in the MTM is somewhat confusing. Does this include fast isoprene isomerization chemistry as in MIM3? Perhaps a table summarizing key differences would help.

P.28581, L.19: Why is a direct comparison of observed and steady-state OH concentrations not included?

P.28583, L.8: the branching ratio and rate constant for reaction with NO is very dependent on the type of RO₂. What values were chosen for this calculation and why?

P. 28584, L.9: Alternatively, one could interpret the reasonable agreement of SS and observed OH, along with the fact that HO₂ is a major source, as evidence that there is not a significant interference in observed HO₂.

P. 28587: Why do the authors only mention the 1,5 H-shift, even though the 1,6 H-shift is believed to be the dominant isomerization pathway for isoprene hydroxyperoxyl radicals? Also, several other studies should also be cited (Crouse et al., 2011;da Silva et al., 2010), as these suggest lower isomerization rates than those calculated by the Leuven group.

Section 3.2: While it is not fully clear to the reviewer what the differences are between MIM3 and MTM, the over-prediction of OH with MIM3 is consistent with isomerization chemistry being slower than the theoretical rates used in that mechanism. The disagreement would be further exacerbated if HO₂ were increased to match observations.

P. 28589, L. 19: What is the HO₂ yield from α -pinene? Also, how does modeled RO₂ compare with that calculated from steady state (Eq. 10)?

P. 28594, L. 7: HNO₄ is not really a reservoir in this case because it is short-lived. The two equilibrium reactions in Fig. 16 should be added together to show the net effect of these reactions on HO₂.

P. 28595, Conclusions: The literature review in the first paragraph seems out of place. Recommend moving this to the introduction or discussion.

Technical Comments

P.28565, L.29: concluded

P. 28566, L.11-16: This sentence is long and fragmented. Please re-write.

P. 28567: Please provide a reference for HORUS and/or FAGE.

P. 28569, L.6: on the ground

P.28570, L.5: Is “calibration air” the same as “zero air”? The latter is a more common term.

P. 28577, L.2: recommend removing footnote and defining MCM in the text. This goes for other footnotes appearing later as well.

P. 28582, L.1: Please add a topic sentence as the discussion shifts from OH to HO₂ here.

P. 28586, L.26: Thornton et al. (2002), while perhaps an appropriate reference for this topic, was not a laboratory study.

P. 28587, L.24-28: This is not a sentence. Please revise.

P. 28588, L.2: delete comma

P. 28591, L.26: this phrase implies that MBO is a monoterpene, which is not the case. Perhaps it is meant that the MBO emission rate (per molecule?) is 1-3% of the monoterpene emission rate.

Table 1: There is no uncertainty in VOC observations?

All Figures: remove the word “in” from the axes unit labels

Figures 9-13, 14, 16: Axes and tick labels are quite small. Please enlarge.

References

- Crouse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Physical Chemistry Chemical Physics*, 13, 13607-13613, 2011.
- da Silva, G., Graham, C., and Wang, Z. F.: Unimolecular beta-Hydroxyperoxy Radical Decomposition with OH Recycling in the Photochemical Oxidation of Isoprene, *Environmental Science & Technology*, 44, 250-256, 2010.
- Edwards, P. M., Evans, M. J., Furneaux, K. L., Hopkins, J., Ingham, T., Jones, C., Lee, J. D., Lewis, A. C., Moller, S. J., Stone, D., Whalley, L. K., and Heard, D. E.: OH reactivity in a South East Asian tropical rainforest during the Oxidant and Particle Photochemical Processes (OP3) project, *Atmospheric Chemistry and Physics*, 13, 9497-9514, 10.5194/acp-13-9497-2013, 2013.
- Wolfe, G. M., Cantrell, C., Kim, S., Mauldin III, R. L., Karl, T., Harley, P., Turnipseed, A., Zheng, W., Flocke, F., Apel, E. C., Hornbrook, R. S., Hall, S. R., Ullmann, K., Henrey, S. B., DiGangi, J. P., Boyle, E. S., Kaser, L., Schnitzhofer, R., Hansel, A., Graus, M., Nakashima, Y., Kajii, Y., Guenther, A., and Keutsch, F. N.: Missing Peroxy Radical Sources within a Rural Forest Canopy, *Atmospheric Chemistry and Physics Discussions*, 13, 31713-31759, 2013.