

We thank the reviewers for their insights and helpful suggestions. We feel that their feedback has led to changes that have strengthened the quality of the revised manuscript. Please find below the original reviewer comments in black, our responses in blue, and changes to the manuscript in red.

Reviewer 1

This study focuses on the comparison between measured OH, HO₂ and the sum of HO₂ and RO₂ (XO₂) radicals and results from 2 different chemical mechanisms, one the RACM (lumped) and the other the MCM (semi-explicit). Measurements were conducted in an isoprene dominated forest in Michigan where a lot of ancillary species as well as ISOPOOH were detected.

This study seems to suggest that quite a large loss rate (termination reaction) for both HO₂ and XO₂ is needed for both chemical mechanisms investigated to agree with the measurements. Several hypotheses are made such as fast deposition of the radicals on surfaces, faster than used RO₂+RO₂ reactions for isoprene RO₂, RO₂ radicals reaction with alkenes and/or segregation could play a role. The authors suggest that most probably a combination of all the above could explain the discrepancy although a rather large loss rate of about 60% during daytime is needed.

The paper is well written and structured, and the arguments are presented in a clear manner. The study is interesting but as it is not possible to give a clear conclusion on what is causing the discrepancies, I would recommend adding a bit of analysis to try and see if something more can be understood and after that I would recommend the publication.

My first suggestion would be to try and perform an experimental budget with the available data. I understand that it might not be possible for the HO₂ and RO₂ but it would be possible to perform it for the OH radical. In this way it should be clear if the very low OH observed in the morning hours is an instrument artefact as it is quite dubious. The OH budget would also help (possibly) to clarify if indeed there doesn't seem to be the need for additional sources of OH radicals as the comparison with the model seems to show. I have to say that isomerization reactions for isoprene-RO₂ are more or less a given now so I am also wondering why there seems to be such a large overestimate of the OH radical when the most up to date mechs are used.

As suggested, we have added an experimental budget for OH to the supplement of the revised manuscript. As expected, the experimental budget is not balanced in the morning hours which suggests either a missing OH sink or an error with the measurement at this time. This is consistent with the discussion of the discrepancy between measured and modeled OH concentrations which was attributed to participant activity near the detection cell in the morning or a potential systematic measurement error.

An experimental OH budget based on measured concentrations of OH, HO₂, and other species, is also shown in Fig. S3. The imbalance between 7:00 and 12:00 suggests either a missing OH sink or errors with the OH measurement during this time.

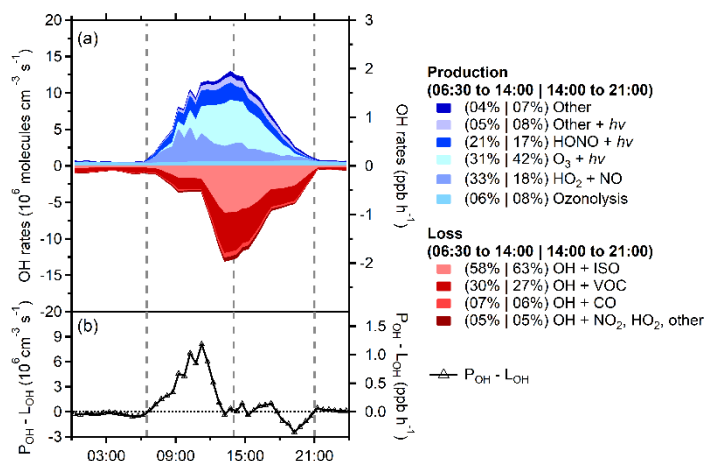


Figure S3: Experimental OH radical budget. In panel (a), shades of blue represent reactions that produce OH, and shades of red represent loss rates, including reactions that propagate to RO_2 or HO_2 . Percentages indicate the relative contribution of each respective process in the morning (06:30: to 14:00) and during the evening (14:00 to 21:00) time periods which are indicated by the vertical dashed lines. The net rate of production or loss is shown in panel (b).

The MCM v3.3.1 and RACM2-LIM1 models likely overestimate the OH concentrations due to a lack of adequate peroxy radical sinks that are relevant in this forested environment. This is illustrated by the green line in Figure 4, which represents a RACM-ACC model that features additional loss terms for HO_2 and isoprene- RO_2 . The additional loss terms were discussed in terms of the necessary loss rate required to match the HO_2 and XO_2 measurements, but the impact of these loss terms on the modeled OH concentrations was only briefly mentioned – the following sentence has been added to page 23 of the revised manuscript to clarify.

The addition of these peroxy radical loss mechanisms reduces the predicted daytime maximum OH concentration by 25% to $1.65 \times 10^6 \text{ cm}^{-3}$, which is within the combined uncertainties of the measurement and the model (Fig. 4a).

My second suggestion concerns the XRO_2 . I am wondering if it would not make sense to remove the HO_2 fraction from it from the LIF measurement and then have a more or less RO_2 measurement. I understand it does not make much of a difference since the measurement is compared with the some of HO_2 and RO_2 but to be able to compare with previous studies it would make it easier if it was RO_2 instead of XO_2 .

We focused on comparing the direct measurements to their modeled counterparts (i.e. comparing XO_2 measurement to the modeled sum of HO_2 and RO_2) but do understand that this makes comparison to previous studies more complicated. As suggested by the reviewer we have added a plot that compares the average modeled RO_2 to the average measured RO_2 (HO_2 measured by LIF subtracted from XO_2 measured by ECHAMP) to the supplement of the revised manuscript.

In addition, measured RO_2 mixing ratios (HO_2 measured by LIF subtracted from XO_2 measured by ECHAMP) are compared with modeled RO_2 mixing ratios in Fig. S4.

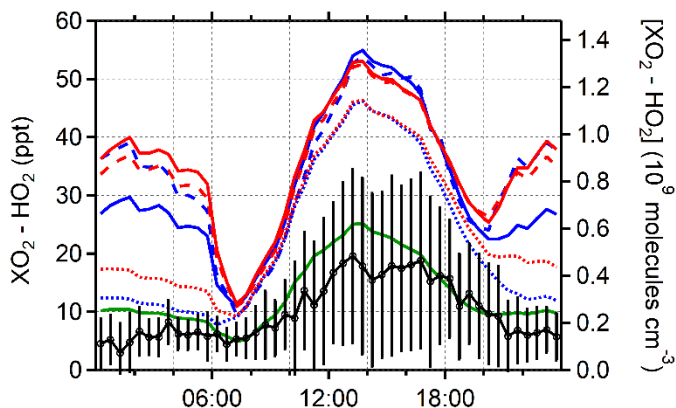


Figure S4: Diurnal average measured (black) and modeled concentrations of RO₂. MCM models are shown in red and RACM2 in blue. The green line represents an additional version of the RACM-ACC model with added sinks for HO₂ and isoprene peroxy radicals. The measured RO₂ mixing ratios were determined by subtracting the measured HO₂ (LIF) from the measured XO₂ (ECHAMP).

My third suggestion is about the ISOPOOH. I am not aware of many ISOPOOH ambient measurements and although I could imagine a different publication focusing on that, it would be good to extend the discussion about it in this study. One thing that I find a bit odd is that the measured concentration of ISOPOOH is more or less zero (within the uncertainty) for the all time? I can see a bit of an increase but it is rather small. Even the model results after constraining HO₂ and RO₂ would expect quite a bit more. Could this be an instrument artefact? Is this consistent with previous measurements?

The reviewer is correct that there are not many measurements of ambient ISOPOOH available. The data in this manuscript were first presented in Vasquez et al. (2018). The measured mixing ratios for the sum of ISOPOOH isomers were between approximately 10-250 ppt, with an average maximum of approximately 100 ppt. We have added an inset in Figure 7a for better visibility. The measured mixing ratios of ISOPOOH were similar to that measured during the SOAS campaign (Kaiser et al., 2016). This has been clarified on pages 21 and 22 of the revised manuscript.

Measurements of isoprene hydroxy hydroperoxides (ISOPOOH) produced from the reaction of isoprene-based RO₂ radicals with HO₂ can provide an additional test of the model chemistry at this site. Figure 7 shows the average ISOPOOH mixing ratio measured during PROPHET-AMOS between July 22 and July 27 by the Caltech low-pressure GC-CIMS instrument (Vasquez et al., 2018). The measured mixing ratios were similar to that observed during the SOAS campaign (Kaiser et al., 2016).

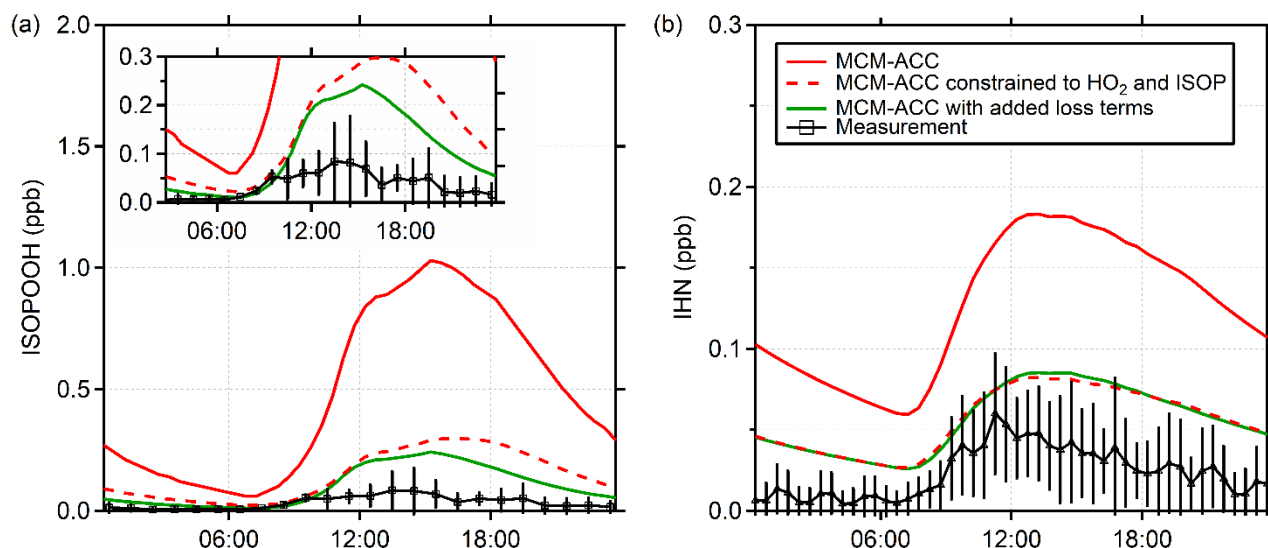


Figure 7: Measured and modelled mixing ratios of (a) isoprene hydroxy hydroperoxides (ISOPOOH) and (b) isoprene hydroxy nitrates (IHN). Measurements of ISOPOOH are an average from July 23-27 (Vasquez et al., 2018) and measurements of IHN are an average of July 6-31. The solid lines represent modeled mixing ratios from MCM-ACC models, the dashed line represents predictions of the same model constrained to measured values of HO₂ and measurements of XO₂ scaled to the modeled isoprene RO₂ composition.

The modeled ISOPOOH is sensitive to the rate of ISOPOOH deposition. As described in the original manuscript, the model runs shown in Figure 7 include a literature-based ISOPOOH deposition term, but this term could vary significantly from forest to forest or with meteorological conditions. Due to this and also to the limited amount of ISOPOOH data Figure 7 is not intended to present a direct comparison between measured and modeled ISOPOOH, but instead to illustrate that the measured ISOPOOH is more consistent with the measured HO₂ and XO₂ radical concentrations, regardless of how ISOPOOH deposition is treated in the model. While the model constrained to the peroxy radical concentrations still overestimates the measurements, the model overestimation of the measured ISOPOOH in this study is similar to that observed during the SOAS campaign (Kaiser et al., 2016), where a large dilution rate was needed to bring the modeled ISOPOOH into agreement with the measurements. This has been clarified on page 21 of the revised manuscript.

Constraining the model to the measured concentrations of HO₂ and isoprene-RO₂ (assuming the same relative distribution of RO₂ radicals predicted by the models) improves the agreement (Fig. 7a), although the model still overestimates the measured concentrations. This overestimate of the measured ISOPOOH is similar to that observed during the SOAS campaign (Kaiser et al., 2016), where a large dilution rate was needed to bring the modeled ISOPOOH into agreement with the measurements.

Are there other products that show up which would compensate the production rate of RO₂ that, as mentioned, was rather high, and the reacted isoprene must go somewhere.

In addition to ISOPOOH, measurements of isoprene hydroxy nitrates (IHN) produced from the reaction of isoprene peroxy radicals with NO were also overpredicted by the model. Constraining the model to the measured peroxy radical concentrations also brought the modeled IHN into

better agreement with the measurements, again suggesting that the measured isoprene hydroxy nitrates is more consistent with the measured peroxy radical concentrations. This result has been added to the revised manuscript (pages 21 and 22), and we have included a plot of the modeled and measured IHN in Figure 7b.

Similarly, the model also overestimates the concentrations of isoprene IHN produced from the reaction of isoprene peroxy radicals with NO and measured using iodine adduct CIMS (Xiong et al., 2015). Constraining the model to the measured peroxy radical concentrations improves the agreement with the measurements (Fig. 7b). It is also worth noting that the model does not account for losses of IHN due to reactive uptake onto aerosol and subsequent hydrolysis in the aerosol phase (Jacobs et al., 2014; Morales et al., 2021; Wang et al., 2021). Knowledge and incorporation of such loss rates in the model could better constrain the modeled IHN concentrations but the effect is expected to be small in comparison to the adjustment in the modeled output when constrained to measured RO₂. (Wei et al., 2021; Mayhew et al., 2022) These results suggest that the measured HO₂ and XO₂ concentrations are consistent with the measured ISOPOOH and IHN concentrations and that the models are overpredicting the concentrations of HO₂ and isoprene-based peroxy radicals, either through an overestimation of their production or an underestimation of their loss.

I noticed that on few occasions the subscripts are not correct so I would recommend checking and fixing that.

Thank you for noticing these mistakes. Subscript formatting errors have been corrected in the revised manuscript.

I also recommend adding the work by J. Medeiros et al. (2022) which is consistent with LIM1.

Thank you for the suggestion. We have added this reference to the introduction section discussing laboratory measurements of isoprene oxidation.

Reviewer 2

This paper presented the measurements of OH, HO₂ and XO₂ at the PROPHET site in July 2016. OH and HO₂ were measured by FAGE with dedicated efforts to minimize the interference. XO₂, the sum of HO₂ and RO₂, were measured by an ethane chemical amplification. The measured radical concentrations were consistent with previous field measurement in 2008 and 2009, considering the meteorological difference. The measurements were compared to box model calculations using RACM2-LIM1 and MCM3.3.1 as a standard test with updated information of isoprene oxidation mechanisms, which enhance the OH concentration by 30% and 20%, respectively, compared to those without LIM1 chemistry, namely RACM2 and MCM3.2. However, this standard models overpredicts OH, HO₂ and XO₂ more than 60%. RO₂+RO₂ accretion reactions were added to reduce the model-measurement discrepancy. Further radical budget analysis and model sensitivity tests indicated the model overprediction was related the missing radical sinks.

This paper is well-written and structured reasonable. The discussion is justified. I recommend the paper published in ACP after minor revision. Here is a few suggestions that might help to improve the paper.

1. There were several radical measurements conducted at the PROPHET site. It would be very useful to show an overview plot to compare different field measurements. In selection 3.2 and 3.3, the measurements from 1998, 2008, 2009, and 2016 are compared in different position. For example, a bar plot summarizing the diurnal maximum OH, HO₂, RO₂ concentrations together with temperature, BVOCs concentrations would help the readers to interpretate the consistency/difference between several campaigns.

We thank the reviewer for this helpful suggestion. We have added Table S3 to concisely summarize the field campaigns conducted at the PROPHET site and added the following sentence to page 11 of the revised manuscript.

These measurements are summarized along with those from previous campaigns at the PROPHET site in Table S3

2. As the authors suggested the radical sink related to surface loss may be relevant to the model overprediction, it would be interesting to have more quantitative analysis. One could calculate the probability of radical loss upon collision on the ground/canopy similar to the aerosol uptake. In this case, the surface area per volume can be derived from the ratio of ground/canopy area to the volume of mixing layer.

We agree with the reviewer that this section should be expanded, though studies investigating radical uptake on canopy surfaces are limited in comparison to studies involving HO₂ uptake to aerosol surfaces. We have added a short paragraph on pages 24 and 25 of the revised manuscript that quantifies the uptake coefficients that are necessary to account for the missing HO₂ and isoprene RO₂ sink given a leaf area index of 3.8 m² m⁻² and assuming a mixing layer height of 1500 m.

Similar to the above discussion, radical loss to surfaces within the forest canopy can be estimated using Eq. 2 where A now represents the ratio of the canopy surface area to the height of the mixing layer. Previous measurements at the PROPHET site reported a leaf area index (LAI) of approximately $3.8 \text{ m}^2 \text{ m}^{-2}$ (Ortega et al., 2007). Assuming a mixing layer height of 1500 m, this suggests that an HO₂ uptake coefficient of $\gamma = 5 \times 10^{-4}$ would result in a first order loss rate of 0.013 s^{-1} , which could account for the proposed missing HO₂ sink. This uptake coefficient is lower than those measured for many atmospheric aerosols, but is similar to measurements of HO₂ uptake on organic aerosols (Lakey et al., 2015). Similarly, an uptake coefficient of $\gamma = 1.7 \times 10^{-3}$ for isoprene peroxy radicals would result in a first order loss rate of 0.024 s^{-1} and could account for the missing radical sink. These results imply that loss to surfaces within the canopy could be a substantial radical loss mechanism in dense forests where low NO_x mixing ratios result in longer peroxy radical lifetimes that are on the order of the transport time through the canopy.

Technical comments.

1. Please check the subscripts for HO₂, RO₂, XO₂ are other chemicals throughout the paper.

Thank you for noticing these mistakes. We have corrected several subscript formatting errors in the revised manuscript.

2. The name of RACM2, RACM2-LIM1, MCM3.2, MCM3.3.1 should be used properly. For example, Line 565, it should be RACM2-LIM1 instead of RACM-LIM1.

As suggested, we have corrected the references to each model mechanism to be more consistent. In the revised manuscript RACM2 models are referred to as RACM2, RACM2-LIM1, or RACM-ACC, and MCM models are referred to as MCM v3.2, MCM v3.3.1, or MCM-ACC.

References

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- Vasquez, K. T., Allen, H. M., Crouse, J. D., Praske, E., Xu, L., Noelscher, A. C., and Wennberg, P. O.: Low-pressure gas chromatography with chemical ionization mass spectrometry for quantification of multifunctional organic compounds in the atmosphere, *Atmos. Meas. Tech.*, 11, 6815-6832, <https://doi.org/10.5194/amt-11-6815-2018>, 2018.