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Discussions

Interactive comment on “Speciation of OH reactivity above the canopy of an isoprene-dominated forest” *by* J. Kaiser et al.

Anonymous Referee #2

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This paper presents measurements of total OH reactivity with measurements of many OH radical sinks, including several isoprene oxidation products during the SOAS campaign. In contrast to many previous studies, the authors find that the modeled OH reactivity agrees well with the measured total OH reactivity when the model is constrained to the measured OH, VOCs, and OVOCs. However, when the OVOCs are unconstrained, the model tends to overestimate the mixing ratios of OVOCs, including isoprene oxidation products MVK+MACR, ISOPOOH, IEPOX and HPALD. Because the model tends to overpredict OVOCs, the authors conclude that the observed missing reactivity in the morning at this site is not due to unmeasured oxidation products, but due to unmeasured primary emissions and their oxidation products.

The paper demonstrates the importance in measuring these isoprene oxidation products in order to constrain models and understand OH reactivity. It also appears to demonstrate the inability of current models to accurately model these OVOCs. Unfortunately, the paper treats the modeling of the OH reactivity and the modeling of the OVOCs separately. However, it appears that if the OVOCs were not measured, the model would overestimate the observed OH reactivity, bringing into question the ability of models to fully reproduce the observed OH reactivity and therefore RO_2 and O_3 production.

Overall, this is an interesting paper that does provide some new information regarding the nature of missing OH reactivity in forest environments. The main thrust of the paper is that the modeled reactivity agrees well with the measured reactivity when constrained to measured OVOCs and that primary emissions dominate the OH reactivity at this site, in contrast to previous studies in similar environments. However this conclusion is not highlighted clearly enough in the paper and the authors attempt to extend this conclusion to our understanding of RO_2 production and O_3 production without providing sufficient modeling studies to support this conclusion. The fact that the model significantly overestimates the measured OVOCs suggests that our understanding of RO_2 chemistry and O_3 production is still incomplete. Unfortunately, there is little discussion as to potential reasons why the model significantly overestimates the observed OVOCs, although the paper mentions that uncertainties associated with modeled dilution rates of these species may be responsible. The paper would benefit from an expanded discussion of potential reasons for the model overprediction of OVOCs and their implications.

Specific comments:

1) As discussed above, a main conclusion of the paper appears to be that because the modeled OH reactivity (constrained to the OVOCs) agrees well with the measured OH reactivity that the total RO_2 production rate and therefore O_3 production is well understood (page 9 lines 10-11). However, the fact that the model overestimates isoprene oxidation products and other OVOCs suggests that when the model is not constrained to measurements of these compounds that the model may not be able to reproduce

total RO_2 production, as many of these OVOCs are produced from RO_2/HO_2 chemistry, such as ISOPOOH and HPALD. The authors need to provide more information to justify this conclusion.

2) One test of the ability of the model to reproduce the observed OH reactivity would be to unconstrain the model to the measured OH and the measured OVOCs. It's not clear from the information given in the paper whether unconstraining the model to the measured OH impacts the modeled OH reactivity as the paper does not state how well the model is able to reproduce the measured OH when constrained to the measured species, or how sensitive the modeled OH reactivity is to the OH concentration. The paper would be stronger if the authors provided several model scenarios to compare to the measured OH reactivity, such as i) a base scenario where the model is constrained only by the traditional measured VOCs, NOx, etc., ii) a scenario where the model is further constrained by the measured OH but not constrained by the measured OVOCs, and iii) the scenario where the model is constrained by all measured species.

3) It is surprising that the authors chose to constrain the model to the measured OH but not to the measured HO_2, given the importance of peroxy radical chemistry to the formation of OVOCs such as ISOPOOH and HPALD. Were HO_2 measurements not available? Does constraining the model to the measured OH reproduce the measured HO_2? Or does this model scenario overestimate HO_2 leading to the overestimation of the observed OVOCs? If the model is constrained to both measured OH and HO_2, are the modeled OVOCs in better agreement with the measurements? These and other tests of the model would provide important information regarding the reasons for the model's inability to reproduce the observed OVOCs.

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