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Atmospheric Chemistry and Physics
Discussions

# *Interactive comment on* “Differences in BVOC oxidation and SOA formation above and below the forest canopy” *by* Benjamin C. Schulze et al.

**Anonymous Referee #1**

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This paper describes a modeling study of chemistry occurring above and within a forest canopy, with a focus on understanding differences that arise between the canopy and above-canopy regions as well as between different NOx levels. The authors construct two 0-D box models using the Master Chemical Mechanism (MCM) to describe the oxidation of isoprene and monoterpenes by OH, O3, and NO3 over the course of an entire day. The authors emphasize the importance of NO3 chemistry, pathways that form organic nitrates, and use an equilibrium partitioning model to predict SOA formation from the oxidation products.

Overall this study has some nice insights and could be suitable for publication in ACP, but only after some fairly major concerns are addressed. These concerns are listed in no particular order.

1. The validity of 2 0D box models. Surely the authors are aware that there is efficient mixing of below canopy air with above canopy air, and vice versa. This fact is apparently not mentioned (or at least not thoroughly discussed), and without some additional discussion and figures of actual data, the modeling results are very difficult to interpret. The canopy layer makes up <10% of the full boundary layer, so are findings of production rates, etc normalized or corrected for this small contribution to the mean boundary layer mass concentration? Presumably the observations used to constrain the model are vertically resolved but no vertical profiles of the observations are shown to evaluate how representative the two boxes used for modeling actually are. Oxidation products formed below the canopy, or above, would cycle many times between the two regions over the course of a day, scrambling the signatures and likely diluting the effect of chemistry occurring within the canopy itself.

2. While the MCM is becoming more useful, it is still rather a dangerous model to use for SOA studies because the mechanisms are not complete at the 5% level of carbon mass, but that 5% might be 90% of carbon capable of forming SOA. For example, the MCM does not include auto-oxidation of monoterpenes (Ehn et al Nature 2014 and others) - thereby missing a likely significant fraction of SOA mass, as well as highly oxygenated nitrates (Lee et al PNAS 2016). How might this affect the conclusions?

3. Lack of deposition. Deposition of oxidation products appears not to be included. This seems rather problematic for interpreting the SOA formation potential. Deposition in the canopy will be much more significant than above the canopy, at least during nighttime, and during daytime deposition from both would significantly impact the available vapors for SOA formation, especially given the equilibrium partitioning assumption used for modeling SOA. With any horizontal wind through the canopy, there will presumably be a significant depositional sink given the proximity to canopy elements. What is the lifetime of a product formed in the canopy against deposition compared to mixing out of the canopy layer or to SOA formation? How was the vertical distribution of the condensation sink constrained?

4. Given 2 and 3 above, the discussion on SOA seems rather limited in its usefulness to actual SOA formation potential. In addition, more interesting would be to incorporate the lapse rate and vertical mixing impacts on SOA formation given the cycling of oxidation products across a 10K temperature gradient.

5. If I understand correctly, RONO2 form ∼45% of the SOA mass in the model. In the SE U.S., it was more like 3-10% (Xu et al PNAS 2015, Lee at al PNAS 2016). The authors cite Fry et al, and note consistency with that study, but, are the distributions of BVOC emissions at all similar between Manitou and UMBS? Presumably the high fraction of particulate RONO2 at Manitou was the dominance of monoterpenes, is that the case at UMBS?

6. Odd model set up choices. The "urban" case, which apparently mixes data from Detroit and Houston is a bit odd. Why not make it purely hypothetical? I don't see why the authors fix the NO/NO2 ratio - that would seem to be a good metric to test the chemistry in the model as it is sensitive to total RO2, not just HO2 and O3. Moreover, as NOx increases the NO/NO2 ratio isn't going to be fixed, there are important feedbacks between O3, HO2, RO2, and NO concentrations that are important and why one would want to use a model in the first place. Fixing the NO/NO2 ratio makes nitrate formation rates a linear extrapolation with increasing NOx when the non-linear couplings of HOx and NOx might lead to a different result than found here.

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