Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-1080-RC1, 2017

Atmospheric Chemistry and Physics
Discussions
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Interactive comment on "Secondary organic aerosol formation from in situ OH, O_3, and NO_3 oxidation of ambient forest air in an oxidation flow reactor" *by* Brett B. Palm et al.

Anonymous Referee #1

Received and published: 16 March 2017

Summary and Overall Recommendation:

This well-written and impressive manuscript summarizes oxidation flow reactor (OFR) experiments aimed at studying in situ SOA formation from ambient pine forest air during the BEACHON-ROMBAS campaign after oxidation by OH, O3, and NO3 radicals. Since SOA formation was measured semi-continuously during this study, the authors were able to capture diurnal and daily changes. More SOA was formed from precursors present in nighttime air than in the daytime air for all 3 oxidations. Interestingly, OH oxidation produced $\sim$ 4 times more SOA than NO3 and O3 oxidation at all times of day. O:C and H:C ratios of the SOA formed by O3, NO3 and several eq. hours of OH oxidation yielded similar oxidation levels of ambient organic aerosol (OA). The

authors previously demonstrated that ambient VOC concentrations alone could not explain the amount of SOA formed in the OFR by OH oxidation. This behavior was likely due to SOA being formed from semivolatile/intermediate volatility organic compounds (S/IVOCs) that entered the OFR. However, for SOA formed from O3 and NO3 oxidation, the measured VOCs were found in the present study to be sufficient in explaining the amount of SOA formed in the OFR. More specifically, this means that for O3 and NO3 oxidation of ambient S/IVOCs does not yield appreciable SOA amounts. The difference between the OH and O3/NO3 OFR experiments provides some support for their hypothesis that ambient S/IVOCs generally lacking double bonds in their structures (especially since double bonds in VOCs emitted upwind of the site are likely already oxidized before they enter the OFR). Using ambient mixtures in this study provides important insights into SOA formation potential and chemical evolution in the real atmosphere, and thus, this work will be of high interest to the larger atmospheric chemistry community. I only have a few minor comments below that I kindly ask the authors to address before publication. As a result, I recommend that this manuscript be accepted with minor revisions noted below.

1.) My biggest comment is related to timescales in the OFR for multi-phase chemical processes. Since the authors appear to justify that their OFR experiments can produce similar oxidation states (O:C ratios) in OA found in the atmosphere, my question is this a result of the "correct" processes that actually occur in the atmosphere? Besides for heterogeneous oxidation (through OH oxidation), what about aqueous-phase processes such as accretion or decomposition reactions of epoxides and or hydroperoxides? There is a lot of work published now by the Caltech, UNC, Oberlin College, and other groups that have shown epoxides are really important in aqueous-phase chemical processes. Recently, the Harvard (Martin) and UNC groups have shown that multi-phase chemical reactions of hydroperoxides could be important as well (Liu et al., 2016, PCCP; Riva et al., 2017, Atmos. Environ.). There is evidence from this site that even MBO oxidation products can undergo aqueous-phase reactions within aerosol to yield organosulfates (Zhang et al., 2012, ES&T). I'm not sure authors can really address this issue now, but I think some discussion needs to be included that acknowledges that these processes may explain some part of ambient oxidation states, which can't be reflected on the reaction timescales of the OFR.

2.) In section 2.2 of the experimental methods section, can the authors provide more information or clarify on how the ambient might or might not change upon entering the OFR? Specifically, is it drier in the OFR compared to the ambient RH? If the RHs aren't the same, how might this affect the interpretation of the results?

3.) I'm curious if the authors know how hydroperoxides behave in their OFR? Do they photolyze quite easily due to the UV radiation you are using? How might this affect the interpretation of the results?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1080, 2017.