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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds" *by* R. Holzinger et al.

R. Holzinger et al.

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We thank Hal Westberg for his insightful review in which he requested us to address two specific issues:

1) "better evidence needs to be provided to show that the OX products are really terpene oxidation products and that they are not direct emissions and/or derived from some independent process such as oxidation of cuticle wax, etc."

In this regard we summarize:

–> The vertical profiles of the OXx are not consistent with the profiles observed for primary emissions such as MBO and monoterpenes: the spatial separation of the region of highest concentrations (e.g. 5-9m for m113/OX02) from primary emission sources

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(average tree height <4.9m, 80% of the trees below 6.4m) is a significant piece of evidence that needs to be explained when considering their source. We do not think it is possible to explain the observed profile without assuming the OXx being oxidation products even when considering a balance between soil deposition and direct biogenic emission.

–> In summer 2003 we also performed experiments with dynamic branch enclosures. We did not see direct emission of the OXx in these experiments and we refer to our previous replies to referee #1.

–> Our hypothesis is that the precursors of the OXx are terpenoid compounds for following reasons: (i) previous work (Kurpius and Goldstein, 2003) shows that the chemical ozone flux (due to ozone+VOC reactions in the canopy) and the monoterpene emission exhibit the same temperature dependence but are opposite in sign. (ii) The lifetime of precursor compounds must be in the range of few minutes or less. Many terpenoid compounds have such short lifetimes with respect to ozone mixing ratio that are typically observed at our site.

–> If the OXx concentrations were due to independent processes such as oxidation of cuticle wax, we would expect a vertical profile that more closely resembles the profile of primary emissions such as monoterpenes or MBO. Such processes would occur at the plant surface and our experimental setup would provide no means to distinguish them from primary emissions.

2) How good is a surface renewal model for predicting biogenic fluxes?

–> The surface renewal method, specifically based on the coherent structure/ramp repetition duration and amplitude of the ramp patterns, has been tested numerous times, but for the sake of brevity we cited only two major publications in our manuscript (Paw U et al., 1995, Snyder et al., 1996). Other publications on this topic, comparing the surface renewal method and other related discussion, mostly based on structure function-derived ramp repetition durations and ramp ampltitudes, can be found in Spano et al.

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(2000; 1997a; 1997b), Snyder et al. (1997), and Zapata et al. (2001; 2002). While it remains disputable whether the accuracy is +/- 30% (our estimate) or slightly higher or lower, our adapted surface renewal approach yields reliable results. We have shown this by comparing the surface-renewal fluxes with eddy-covariance fluxes of monoterpenes. Surface renewal fluxes of methanol and MBO are in good agreement with GC-REA fluxes measured in previous years at the site. We are aware that our approach was not the most accurate one. But this method allowed for the broadest monitoring of unknown species. Now that these compounds have been detected and production rates inferred, we are planning future research to refine our understanding of both the production of the OXx compounds and the emission of the underlying very reactive compounds. We intend to include EC flux measurements of the OXx compounds in this future research as suggested by Dr. Westberg.

Reply to other comments/issues:

–> We appreciate the information on long chain aldehydes measured during the ROSE campaign and we'd be happy to compare their findings with ours. Unfortunately we were not able to find a published reference which included these data. We agree that this is an interesting theory that deserves further investigation as other studies are launched to determine the structure/identity of the observed OXx. However, as indicated above we don't think the vertical profiles we observed are consistent with oxidation of cuticle wax at the plant surface.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5345, 2004.