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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.

H. Westberg (Referee)

westberg@wsu.edu

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Hal Westberg Reference 2

The question of whether or not we are measuring all of the terpene emissions from vegetation has persisted for a long time. The original emissions inventorying work by Zimmerman reported a significant level of unidentified species in enclosure studies. Since then, the ability to measure the polar oxygenated compounds has been achieved and the next challenge appears to be determining whether or not we are able to directly

measure emissions of very reactive terpenes (vr-bvoc). Holzinger et al. clearly feel that we are currently underestimating terpene emissions by as much as a factor of ten. This conclusion is based on measurements at their managed pine plantation in California and is postulated to be the case wherever terpene emissions occur.

The difficulty with this hypothesis is that there is no direct evidence for the vr-bvoc emissions. The authors have identified ions in the ambient atmosphere by PTR-MS that they attributed to oxidation products of the vr-bvoc. However, the identities of the ions are unknown and, consequently, cannot be logically associated with a terpene structure. I feel there are two aspects of the indirect evidence case provided for the missing vr-bvoc that must be addressed: 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. 2) how good is a surface renewal model for predicting biogenic fluxes

Other reviewers have asked for evidence that the OX species are not directly emitted and the authors have promised to provide data to address this issue. I believe the authors need to make sure the fragment ions identified as OX products are not coming from the long chain (C7-C10) aldehydes. These aldehydes have been observed in many forest settings and near lumber processing operations. Table 1 lists possible molecular formulas for the OX ions and the series C7H12OH+, C9H16OH+, C10H18OH+, C11H20OH+ is evident. Are these aldehyde ions? I think it would be wise to rule out the possibility that the OX species are due to oxidation of cuticle wax or some plant product other than terpenes. During the Southern Oxidants Study (ROSE), the NCAR group used real-time measurements with a GC/MS system in a Loblolly Pine forest to measure ambient VOCs. They observed the presence of long chain aldehydes and the diurnal concentration patterns were similar to the OX behavior reported in this manuscript.

The authors base their high vr-bvoc flux estimates on calculations using a surface renewal model. A question that should be addressed is, if fluxes of other species were

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measured by eddy covariance, why weren't OX fluxes determined by EC. Gradient methods are the least desirable approach for determining fluxes in forest environments. More information needs to be presented to convince the reader that the surface renewal model is a valid approach for predicting bvoc fluxes. The statement that median monoterpene fluxes determined by EC and the surface renewal model agree within 30

In summary, I commend the authors for providing us with the results of a very interesting field study. My hope is that this review process leads to a final manuscript that truly reflects the nature and magnitude of bvoc fluxes at the Blodgett forest site.

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