

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 greatly appreciate the reviewers effort in reviewing our manuscript, but we honestly disagree with the picture developed in the first paragraphs of the review, and in particular with the conclusion that our “interpretations and conclusions seem preliminary and premature”.

The reviewer claims our results are “in stark contrast to many, many dozens of carefully performed experiments ... that yielded the chemical identification of probably > 99 percent of observed emission”. We think it is highly unlikely that any study including ours has ever identified > 99 percent of the actual biogenic compounds emitted from plants. As new instrumentation has been developed over the past several decades, the field of atmospheric chemistry has continually evolved the ability to detect additional organic

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compounds in the atmosphere, and our knowledge of atmospheric chemistry has similarly evolved. Our observations are another example of this remarkable progress in our field, and push us to revise our understanding of atmospheric chemistry occurring in the forest canopy accordingly.

The results in our manuscript actually imply that total terpene emissions from this system are of a similar scale as methylbutenol or methanol emissions, higher than acetone and acetaldehyde emissions, and a factor of 10 higher than the above canopy monoterpene flux. Nowhere do we state that total biogenic emissions from this system are a factor of 10 higher than previously reported. We are focusing specifically on one class of compounds, terpenes, and claiming that only approximately 10% of the total terpenes actually emitted were previously reported by us as a measured flux above the canopy. We recognize there has been a great deal of research on terpene emissions by groups around the world, but also assert that significant gaps in our knowledge remain, particularly with regard to very reactive compounds such as sesquiterpenes.

We do not claim that “90 percent of the terpene emissions were overlooked by all of these studies” the referee is referring to; in fact we imply that many compounds measured in branch enclosures which excluded oxidants would be missed by above canopy flux studies in similar ecosystems. Enclosure studies using oxidant free air are clearly different from what we are reporting here, and we are engaged in such studies at Blodgett Forest to search for these unidentified compounds. In a separate manuscript, we have discussed some of these observations where very small amounts of literally hundreds of terpenoid type compounds were actually observed and identified by GC/MS analysis (Goldstein et al., GRL in review, GC/MS analysis by R. Rasmussen), many of which have lifetimes that are consistent with those required for oxidation before escaping the forest canopy. Without knowing exactly which studies the referee is referring to, we disagree with the viewpoint our paper would question results of carefully performed experiments. That’s not what our work is about.

Our message focuses on strong new evidence from observations of vertical gradients

of oxidation products that the actual terpene emission is ~10 times the monoterpene flux measured above the forest canopy at our site. We also reference work done in other ecosystems supporting the idea that a significant fraction of biogenic emission is lost by within canopy processes or that significant fractions of the total biogenic VOC (or possibly BVOC oxidation products) above the forest are not typically observed (Ciccioli et al., 1999; Di Carlo et al., 2004; Faloon et al., 2001; O'Dowd et al., 2002). We start the conclusion by referencing that emission of VR-BVOC has been previously reported (e.g. Ciccioli et al., 1999), but we will change the manuscript to be more specific and add that Ciccioli et al. observed VR-BVOC emissions in plant enclosures which were not observable above the forest canopy presumably because of their short lifetime with respect to reaction with ozone. Our results build on this observation published 5 years ago. We understand our results may be considered “provocative” by some, but we consider our new observations and conclusions as an evolution of understanding based on new observational capabilities and well documented and careful research efforts, both our own and consistent with other related published studies.

With regard to the experimental issues raised we can not completely exclude artifacts due to ozone in our inlet system. Therefore we have designed all five gradient inlets identically (same flow rate at all times, same materials, filters, valves and length of tubing). Note that during daytime ozone gradients were small (less than 10 percent) and for our analysis we used relative differences between the concentrations at different height levels. The OXx profiles were not correlated with water or ozone. We can explicitly state that the observed OXx products are not transported anthropogenic pollutants. Anthropogenic pollutants, such as carbon monoxide, oxides of nitrogen, and many volatile organic compounds we measure, are transported to the site from sources that are typically 5-6 hours transport time away; therefore their mixing ratios are lower before noon and rise in the afternoon coinciding with the arrival of polluted air from the Sacramento region. This has been discussed in detail in many papers reporting observations from Blodgett Forest (e.g. Lamanna and Goldstein, JGR 1999; Dillon et al., JGR 2002). Ozone concentrations largely follow the diurnal pattern of

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transported compounds. The features of water concentration were similar to those of primary emissions (e.g. monoterpenes); i.e. highest concentrations at the bottom level and sequentially lower concentrations at higher levels. In addition to our automated standard additions (monoterpenes, MBO, acetone, MVK, MACR etc.) we also measured standards of nopinone, b-carophyllene, and methylchavicol and found our system to be reliable for measuring these sort of compounds. We have also performed branch enclosure measurements using Teflon chambers that indeed revealed emission of very reactive compounds (we refer to these measurements, p5354, lines 22-26), and report some of them in a separate manuscript which is in review (Goldstein et al., submitted to GRL). We have also observed many of these same mass to charge ratios as terpene plus ozone oxidation products in smog chamber experiments at CalTech in collaboration with John Seinfeld and his group, and have data on their yields. We don't include these data here because they will be the subject of a separate manuscript (A. Lee et al., in prep) but they provide clear evidence that we can measure these compounds with the PTR-MS, and they are produced from many terpene plus ozone oxidation reactions. The referee made a couple of other very good suggestions which are actually included in our proposed (pending) future research efforts at the Blodgett forest site (especially those aimed at identifying the OXx products).

With respect to concerns regarding our approach of estimating fluxes and production rates we refer to more that 10 years of cited literature (Paw U et al, 1993 and 1995; Chen and Blackwelder, 1978, Snyder et al., 1996). Our approach yields results in agreement with fluxes from eddy-covariance and previous measurements with a REA-GC-FID system as we have stated in our article (page 5353, lines 5-10) for monoterpenes and MBO.

We want to express our strong disagreement with the referee's judgment on our interpretation and conclusions which he or she considers as preliminary and premature. This certainly is not the case. In fact, we are presenting firm and solid evidence of chemistry occurring inside the forest canopy. However, we appreciate many of the re-

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viewer's comments and acknowledge that we have to add additional information (i.e. ozone diurnal cycle, transport mechanisms, inlet design) to the final version in order to avoid any such misconceptions of our paper.

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

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