

Interactive
Comment

Interactive comment on “Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest” by S. M. Noe et al.

Anonymous Referee #3

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As both other reviewers already emphasized, the value of this article lies in the seasonal and vertically resolved observations of BVOC in the hemiboreal forest atmosphere. Another finding of particular interest is the observation of a number of sesquiterpene compounds in ambient air, a task that has been accomplished by only few other researchers.

There are a number of shortcomings in the chosen experimental approaches that lead this reviewer to recommend rejection of this manuscript.

The most significant one is the neglect to consider mitigation of interferences from ozone in the sampling of reactive BVOC. The article states (page/line 14612/4) “we

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did not remove ozone from the sample air stream as that would be a change in the chemical composition of air during the sampling". It is unclear what is meant with this explanation. In contrast to the belief of these authors, for many years most researchers have applied ozone scrubbers in BVOC sampling to ascertain quantitative recovery of BVOC in ambient air sampling. As a matter of fact, one of the articles cited by these authors right after their statement (Calogirou et al., 1996) very nicely demonstrates this effect, showing that BVOC loss rates depend on multiple variables, including compound chemical structure, adsorbent age, sampling time, and ozone concentration. The Calogirou et al. article concludes that "The results . . . call into question previous data on terpenes and terpenoids and/or their oxidation products where measurements have been carried out without the prior removal of ozone." The Calogirou study focused around the use of Tenax adsorbent, but also investigated various carbon materials with similar results. Another review of this topic was presented by Helmig (1997). The Pollmann et al. (2005) paper provides further data on SQT losses from concurrent ozone sampling onto Tenax and carbon-type solid adsorbents.

Other shortcomings of this manuscript include:

- There is no information on how many days of sampling were performed and how many samples in total were collected. Without having insight into this information the reader can not evaluate the statistical significance and robustness of the data.
- 14611/5: It would be valuable to provide the distance from the site to major populated areas.
- 14613/17: Explain what is meant by 'LOX' when first mentioned here.
- Information about calibration procedures and quality control for ambient air BVOC quantification is lacking.
- 14615/5: More explanation why there is decreased mixing during the summer month should be provided. Typically one would expect larger mixing from convective transport due to higher surface heating and sensible heat flux during the summer. Larger CO₂ gradients during summer are likely a result of larger respiration activity under the warmer summer conditions.
- 14616/2: The reported 140 microgram m⁻³ (equalling ~25 ppb) are very high ambient concentrations (see also the overview

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of ambient levels cited at 14617/13). Such findings need to be supported with some robust quality control experiments, including sampling of gas phase standards under simulated ambient conditions within this concentration range. - 14616/18: Given the high seasonal variability a display of the seasonal evolution of compound ratios is more meaningful than total annual means. - 14621/6: It is mentioned that logging took place in winter. BVOC in ambient air are expected to be much enhanced during logging operations (Goldstein et al., 2004). Samples that may have been influenced by emissions from logging can not be deemed representative of natural forest emissions. - Overall, the data discussion, interpretation, and conclusions do not go much in depth and report few findings beyond what has already been shown in other previous studies. - Figure 5: Axis titles are too small to be legible. - English writing needs some improvement throughout the manuscript.

References

Calogirou A., Larsen B.R., Brussol C., Duane M., and Kotzias D. (1996) Decomposition of terpenes by ozone during sampling on Tenax. *Anal. Chem.* 68, 1499-1506.

Goldstein A.H., McKay M., Kurpius M.R., Schade G.W., Lee A., Holzinger R., Rasmussen R.A. (2004) Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs. *Geophys. Res. Lett.* 31, Article Number: L22106.

Helmig D. (1997) Review Article: Ozone removal techniques in the sampling of atmospheric volatile organic trace gases. *Atmos. Environ.* 31, 3635-3651.

Pollmann J., Ortega J., and Helmig D. (2005) Analysis of atmospheric sesquiterpenes: sampling losses and mitigation of ozone interferences. *Environ. Sci. Technol.* 39, 9620-9629.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 14607, 2011.

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