

Interactive comment on “A comparison of new measurements of total monoterpene flux with improved measurements of speciated monoterpene flux” by A. Lee et al.

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General comments:

Reactive volatile organic compounds i.e. terpenoids play an important role in the chemistry of the lower troposphere. Therefore, understanding of component composition (mixing ratio), dynamic of canopy fluxes as well as quantification of these fluxes are prerequisites for a better understanding of chemical processes occurring inside and above canopies. To date less information on canopy fluxes in particular on terpenoid fluxes is available. This lack is due to a certain extent to methodological difficulties as-

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sociated with the accurate analysis of volatile terpenoids. Considering the still limiting number of flux data the present comparison of canopy flux measurements using two different approaches (i) GC-FID in combination with REA (relaxed eddy accumulation) and (ii) the new PTR-MS technique combined with direct EC (eddy covariance) is very helpful to point out the strength and weakness of both analytical techniques. Since generally field sites are equipped with only one analytical technique, the present data may help colleges to weight and interpret their own data with respect to weaknesses in the experimental approach.

The set up of the experimental systems had been performed and described quite well. In particular the experimental description of calibration and routine controls reflect the great experience of the authors. For publication, however, the manuscript needs minor revision and careful implementation of reviewer comments and suggestions.

Specific comments:

In the Introduction I miss a description of the emission potential of the ponderosa pines and the field site in general. Which compounds can be emitted by this species. Where do emissions come from: resin ducts in needles and sapwood, light-dependent emission from, soil emission? In the context of the described discrepancy between mixing ratios and fluxes determined by GC-FID / REA and PTR-PS / EC, respectively, this might help to get an idea on the chemical nature of the unknown terpenes as well as on the 'missing' compounds.

In the 'Experimental' section the authors made strong efforts to describe the set up and the calibration of both systems. I miss, however, a figure showing the correlation between terpene fluxes measured by both techniques. Beside the description of the accuracy of monoterpene analysis and the quality of REA and EC this will give the reader a direct view on the data.

In the 'Results and Discussion' section main point of is the discrepancy between mixing ratios and flux rates quantified by both approaches: For my feeling the strongest

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percent difference between GC-FID and PTR-MS measurements occurred not in principal during night as mentioned by the authors. Fig. 2b shows that at least at two days (one and two) highest deviation was present during the morning hours with increasing light intensities. In the manuscript no information is given if the GC spectrum changes from day to night. In addition, It is not mentioned if the authors have performed 'mass scans' with the PTR-MS during night and day time to get an impression of additional or missing ion masses.

All over the text and also in the 'Conclusions' I miss a more explicit discussion of this result.

What are possible explanations? (a) Experimental /technical: How influenced the ambient ozone concentrations monoterpene accumulation on sampling traps (Use of ozone scrubbers)? Are 30 min means generated from the 2 Hz PTR-MS / EC data and by the GC-REA technique really comparable? (b) Biological: Does the emission pattern of needles /plants change from light to dark; in relation to different potential monoterpenes sources (data from literature)? Are changes in the mixing ratio visible? If not, might this be related to the detection limit of 8 pptv? (c) How will the authors proceed with their work to solve the open question?

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 7819, 2004.

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