Atmos. Chem. Phys. Discuss., 4, S2997–S3000, 2004
www.atmos-chem-phys.org/acpd/4/S2997/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

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

C. Spirig (Referee)

christoph.spirig@fal.admin.ch

Received and published: 15 December 2004

General comments

The authors present a comparison of above canopy flux measurements by GC-FID in combination with relaxed eddy accumulation (REA) and by PTR-MS with direct eddy covariance (EC). Considering the still limited number of above canopy VOC flux measurements and the growing number of flux studies involving PTR-MS and EC techniques, such a comparison in reference to a GC-REA is certainly of interest for the readers of this journal and a new contribution. The manuscript is well written and comprehensibly structured. The paper is recommended for publication, but I suggest that some of the interpretations and conclusions about the observed differences are revised to more careful statements, since the agreement between the two methods is actually rather good, in particular when considering the difficult nature and uncertainties of VOC flux measurements.

Specific comments

Page 7822. In the sampling of unsaturated organic trace gases onto solid adsorbents, substantial losses may occur due to reactions with ozone of these analytes. (eg. Helmig, 1997). Given the later finding of detecting lower monoterpene concentrations with the GC system as compared to the PTR-MS, it would be helpful to add some arguments that such an artefact is not responsible for the lower concentrations in the GC measurements.

Page 7825, lines 16f. The REA monoterpene fluxes other than that of β-pinene were determined as a fixed fraction of the β-pinene flux, whereas this fraction corresponds to the mean concentration ratio of the respective compound to β-pinene. As the authors state that this procedure did not affect the mean flux of speciated monoterpenes, the fluxes were apparently calculated for each of the monoterpenes. Since this effort was made anyway, and since speciated monoterpene fluxes are advertised in the title, this information should also be considered in the discussion of the differences between the PTRMS-EC and GC-REA fluxes.

Page 7826: Gaussian error propagation was used for determining the uncertainty of the REA flux measurements. The authors present the details about the terms for calculating the uncertainty of concentrations, but it should also be described how the uncertainty of the b factor was considered.

Page 7827: I agree that a high frequency correction can be omitted after carefully demonstrating that the potential losses are below the overall measurement uncertainty.

But, as already requested by T. Karl, a clarification of the data processing would be helpful for understanding the high frequency losses. It seems that the fluxes were calculated from the data acquired by the PTR-MS. If the sonic raw data (10 Hz, presumably) were simply logged at 2 Hz, the signals of the masses 81 and 137 will be correlated with the same wind data, although the measurement of the two masses is separated by 0.2 seconds, resulting in an overall time resolution of 2 Hz, in fact. Or, was the wind signal averaged over the length of a measurement cycle? Please clarify. Figure 1: Plotting the cospectra on a semi-log scale makes sense in this context, but an analysis of the inertial subrange slopes would be more appropriate on a log-log scale.

Page 7828, line 24f: The interpretation that the GC-FID is not able to detect these very reactive compounds (on p. 7830 it is concluded that these are monoterpenes) should be complemented by some thoughts why the GC is not able to capture them. Since the authors mention numerous interferences on the masses 81 and 137 by compounds other than monoterpenes, one might also argue that the difference is due to such interferences in the PTR-MS measurement, e.g. from sesquiterpenes. In the current version of the manuscript, there is more information on possible interferences in the total monoterpene measurements by PTR-MS as compared to potential problems with the GC-FID measurement. It is thus not obvious, why the total monoterpene measurement by PTR-MS is considered as the reference, and the GC-FID measurement is interpreted to miss certain monoterpenes.

Page 7829, comparison of REA and EC fluxes. A discussion of the differences solely based on the standardised mean of the fluxes is difficult. A direct comparison of simultaneous measurements would provide more insight. It was demonstrated that the “unidentified monoterpene peaks” can account for the daytime difference between GC and PTR-MS concentration measurements. It is thus consistent, that the GC-REA fluxes of the 8 identified monoterpenes are lower than the total monoterpene fluxes measured by PTR-MS-EC. From Figure 2 it is not evident, that the underestimate of the GC-REA fluxes is systematically larger at night than during the day. As this is stated in the abstract, the comparison of fluxes should be extended so that this trend can be recognised. The largest differences seem to occur either early morning or late afternoon (concurring with the reversal of the heat flux direction?). Were these points excluded in the comparison?

Since one of the strengths of this manuscript is the measurement of speciated monoterpene fluxes, it would be of high interest to also hear about the composition (and its variation?) of the monoterpene emissions.

Page 7830, Conclusions. In light of the uncertainties in both flux measurement methods, the agreement of the fluxes is good (and indicates that the measurements were performed skilfully). Therefore, it is suggested to limit the last conclusion to the results of the mixing ratios. As the chromatograms showed no more signals at the typical retention times of monoterpenes during the occurrences of differences, the obvious conclusion would be that the missing components are likely to be other compounds than monoterpenes.

Technical corrections

Figure 1: Uniform scales should be used in both parts of the figure. The 2Hz spectra in a) and b) seem to differ.

Reference

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

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

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU