

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

**T. Karl (Referee)**

tomkarl@ucar.edu

Received and published: 2 December 2004

General comment:

The authors present new insights on monoterpene emission fluxes at Blodgett Forest. A better understanding and quantification of processes leading to terpene emissions adds to our knowledge on reactive organic carbon compounds entering the atmosphere and expands current datasets which are needed for modeling atmospheric chemistry more accurately. The paper is well presented and recommended for publication after addressing comments listed below:

## Introduction:

In their introduction the authors give a partial review on monoterpene emission measurements over the past few years: p 7820, line 23ff: A more recent review on physiological and ecological controls on monoterpene emissions can be found in Kesselmeier and Staudt (J. Atmos. Chem, 23-88, 1999), which should be added as reference. For completeness the authors might also be interested in reading work published during LBA-Eustach (e.g. see references in Andreae et al., 2001) and various other references listed in this review. For example the authors state that their measurements represent the first PTRMS eddy covariance flux measurements for monoterpenes. Is this really true? They might not be aware of two papers that have recently reported fluxes of total monoterpenes measured by eddy covariance using the PTRMS instrument: Spirig et al. 2004 and Karl et al., 2004. Monoterpene flux measurements using PTRMS technology were also conducted during the BEMA study as summarized by Steinbrecher et al. 2004.

## Experimental:

Detection limit: The authors invest considerable effort in constraining systematic and random errors, but don't describe if any background signal was subtracted from m/z81 and m/z 137 and how this would impact the detection limit. Could the difference between the observed PTRMS and FID monoterpene measurements be explained by the fact that the background signal was not subtracted from the PTRMS signal? A detection limit of 60 pptv is reported. For the general reader this might seem high, considering that a recent paper published by Holzinger et al. (APCD) reports mixing ratios of several terpenoid compounds + oxidation products well below this limit (e.g. down to 15 pptv). I suggest that the authors include the equation used to calculate the detection limit which should also illustrate how the DL depends on the averaging period. (note: some groups define the detection limit as  $1 \times \sigma(\text{Cbg})/\text{sensitivity}$ , others as  $2 \times \sigma(\text{Cbg})/\text{sensitivity}$  or even  $3 \times \sigma(\text{Cbg})/\text{sensitivity}$ )

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Flux methodology: The authors might want to read the paper by Spirig et al., 2004 (ACPD) including the corresponding discussion thread, which summarizes implications for disjunct sampling strategies and also partly applies to analysis presented in the present paper: If the dwell time was chosen to be 0.2 s, the actual sampling frequency was 5 Hz and not 2 Hz as stated, unless the authors averaged the PTRMS signal over 0.5 s. Some clarification is needed. In any case it is generally recommended to calculate the covariance from the directly recorded PTRMS signal avoiding any averaging. A dwell time of 0.2 s also implies that the time constant for correcting high frequency loss would be even smaller than the one used. For disjunct sampling (and this is what the authors have actually done in the present manuscript) the Cospectra are not defined at the Nyquist frequency. Since the author's do not apply any correction in the end and considering that there is an ongoing debate on how accurate high frequency corrections can really be, I suggest that the corresponding paragraph could be shortened. However it should be clarified if and how the PTR-MS signal was processed/averaged.

Figure 3: A better way to compare the flux data is to plot the fluxes measured by the PTRMS system vs fluxes measured by the GC-FID system and perform a regression on the flux data directly. The flux comparison then won't rely on any assumptions or depend on any statistical errors due to the assumed temperature dependence. Considering that there could also be light dependent monoterpene emissions this would be a more robust comparison. In general it is noted that there seems to be a shift in the paradigm of light - vs temperature dependent terpene (including monoterpene) emissions, which has also recently been pointed out in an interactive comment by Kesselmeier (see <http://www.cosis.net/copernicus/EGU/acpd/4/S528/acpd-4-S528.pdf>). Numerous emission studies now suggest that temperature dependent monoterpene emissions are rather a special case and that light dependent emissions are probably much more common. In their recent manuscript (see: Holzinger et al., APCD, 2004) the authors point out that this could be the case even at Blodgett Forest and speculated that light dependent terpene emissions could be a factor of 10-30 higher than the temperature dependent monoterpene emissions! This represents an

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extremely large estimate. Considering that some of these terpenes (e.g. terpinolene) have a molecular weight of 136, the temperature dependent regression shown in figure 3 does not reflect differences due to light-dependent monoterpene emissions.

Comment on Figure 2: From figure 2 it appears that while the concentrations measured with the PTRMS system were higher during some events at night, the eddy covariance fluxes were more negative than measurements conducted with the GC-FID system during many of these periods. While nighttime eddy covariance measurements are poorly constrained due to large advection and storage terms at night, a possible explanation for the observed concentration difference at night could be that reactive terpenes could have been transported to the site (e.g. corresponding to a windshift that also changed the observed ozone concentrations) and origin from somewhere further upwind where there was enough time to oxidize a significant portion. Advection in particular might be important if the measurements were performed above the nighttime canopy inversion layer, which can decouple the canopy layer from the nocturnal surface layer for long periods.

Conclusions:

Page 7830 Line 10ff: 'The good agreement between ... during day but not at night suggests that these compounds are reactive enough that they are oxidized during day-time...': It is not clear why photochemically reactive terpenes would not be sampled by the GC FID system unless the GC system was not capable of measuring these terpenes. If the authors believe this is happening the sentence should be clarified.

Minor comments:

Cite if the monoterpene standards were homemade or purchased (if purchased, what vendor?).

Page 7827 line16: '...because of lower sampling frequency and added noise...'. This statement is somewhat confusing. It implies that some noise was added to the sig-

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nal. (??) Does noise (white noise) really bias the total averaged flux? I would argue that white noise only increases the flux detection limit, but that it should not bias the averaged (e.g. 30min) flux above the flux detection limit.

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