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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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Author Comments in response to reviews on "A comparison of new measurements of total monoterpene flux with improved measurements of speciated monoterpene flux".

The authors thank T. Karl, C. Spirig, and J. Schnitzler for their constructive reviews and suggestions. We will respond here to the comments from all three referees individually.

Response to referee comments by T. Karl:

Introduction

The introduction will be updated as suggested, and the review paper by (Kesselmeier

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and Staudt, 1999), will be included in the reference list, as well as the recent work by (Spirig et al., 2004), and (Karl et al., 2004).

Experimental

1. While the reported detection limit may seem high compared to mixing ratios reported by (Holzinger et al., 2005), those measurements were from 2003, when the sensitivity of the PTR-MS was better. Additionally, the very low mixing ratios (down to 15 ppt) reported by (Holzinger et al., 2005), were not monoterpenes, but other compounds with different background signals, and different sensitivities in the PTR-MS.

The PTR-MS detection limit for total monoterpene mixing ratios, based on 1 x sigma (background counts) / sensitivity was 0.09 ppb, or 90 ppt, which is relatively high due to poor counting statistics from the 0.2 s dwell times on m/z 81 and 137. The background counts do not change the result that larger differences between the PTR-MS and GC-FID were observed at night than during the day. In the revised manuscript, we will clarify the description of background and detection limit issues.

2. The total monoterpene signal used to calculate mixing ratios and fluxes came from the sum of the PTR-MS signals for m/z 81 and 137, each with a dwell time of 0.2 s, over a 0.5 s measurement interval. We thank Dr. Karl for pointing out that our sampling frequency, based on disjunct sampling, should be 5 Hz, with a time resolution of 2 Hz. This will be corrected in the manuscript, and the corresponding discussion of the high frequency corrections will be revised accordingly.

3. The differences between mixing ratios and fluxes measured by GC-FID-REA and PTR-MS-EC reported in the manuscript were indeed calculated from correlation regressions between the data directly, but a plot of this was not shown in the original manuscript. A correlation plot will be added to the revised manuscript, so that the day versus night difference in monoterpene mixing ratios will be more visible.

Emission of the dominant monoterpenes from Ponderosa pine exhibit temperature

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dependences, but a light dependence has not yet been observed for the dominant monoterpenes from this field site. (Schade et al., 1999) reported that monoterpene emissions from this site were also affected by humidity, but for the measurement period described in this manuscript, no rain was observed and the humidity levels were characteristically low.

Comment on Figure 2

Dr. Karl suggests that the difference between PTR-MS and GC-FID measurements at night may be a result of nighttime advection of reactive terpenes from further upwind. Gradient measurements within and above the canopy by PTR-MS of total monoterpenes, described by (Holzinger et al., 2005), show that the mixing ratios of total monoterpenes are highest at the ground, and lowest above the canopy, which seems indicative of a local source, rather than advective transport.

Conclusions

The photochemically reactive terpenes may be more difficult to measure by GC-FID if they are compounds that are easily lost on the trapping material, such as sesquiterpenes, or other large terpenoid compounds.

Minor comments

1. The manuscript will be revised to state from where the terpene standards were obtained.

2. The manuscript will be revised to clarify this statement. Noise was not added to the signal; rather, the “added noise” refers to the noisier cospectra resulting from low frequency sampling, compared to the cospectra of samples taken at a higher frequency.

Response to referee comments by C. Spirig

1. A KI-scrubber to remove ozone was used to prevent terpene loss on the solid adsorbents, thus, lower concentrations measured by GC-FID should not be an artifact. This

information will be added to the experimental portion of the manuscript.

2. A plot showing mixing ratios of the speciated monoterpenes will be included in the manuscript.

3. Uncertainty in the b factor was not considered in the uncertainty calculation for the flux of the sum of speciated monoterpenes by GC-FID-REA; however, since the standard deviation of the b factor was $<$ 5% of the mean, the uncertainty in b should represent a minor contribution to the REA flux uncertainty.

4. As mentioned above in the response to the comments from T. Karl (#2), we will clarify the description of our data collection and processing. While it is true that a visual analysis of the slopes of the cospectra in the inertial sub-range is more appropriate and customary on a log-log scale, we believe that the plot of the cospectra on a semi-log scale already shows that energy is lost in the inertial sub-range according the -4/3 slope, with noise in the higher frequency ranges, and offers the additional advantage that the area under the curve is proportional to the covariance, showing the contributions of different sized eddies to the monoterpene flux.

5. If the photochemically reactive terpenes are indeed monoterpenes, then we expect that the GC-FID would be able to detect them, as we were able to detect the reactive monoterpene species alpha-terpinene and terpinolene. We had mistakenly used the term “monoterpene” instead of “terpene” on p. 7380 (lines 8 and 17), and will correct this in the revised manuscript.

6. A direct comparison of the GC-FID-REA and PTR-MS-EC measurements will be added to the revised manuscript, as discussed above in the response to referee comments by T. Karl. The points when the largest differences between the PTR-MS and GC-FID tend to occur (˜ 700 PST and ˜ 2000 PST) were not excluded in the comparison. The “daytime” periods used in Figure 3 were defined between 800 PST and 1600 PST, when vertical wind speeds were sufficient to generate reliable flux measurements. Thus, the “nighttime” periods included the times (˜ 700 PST and ˜ 2000 PST) when the

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largest differences tended to occur between the two techniques.

7. We agree with the referee that given the difficulties associated with nighttime vertical flux measurements, it would be wise to limit the discussion to just mixing ratios when stating that the measurements by PTR-MS are higher than by GC-FID. The stability of the ratio of m/z 81 to 137 suggests that the interference from non-monoterpene compounds should be minor. However, because we have little knowledge of the speciated sesquiterpenes or other terpenoid compounds emitted from our site, we also do not definitively know how interference from those compounds might change the ratio of m/z 81 to m/z 137. We expect to be able to detect reactive monoterpene species by GC-FID, thus, we cannot rule out the possibility that the mixing ratio difference between the two instruments may be due to some interference from other terpenoid compounds.

Technical Correction: The y-axes for Figures 1a) and b) will adjusted so that they are uniform.

Response to referee comments by J. Schnitzler

1. A description of previous measurements of monoterpene emission from Ponderosa pines, a brief description of the field site, and references for additional information will be added to the experimental section of the manuscript, e.g. (Goldstein et al., 2000) and (Schade and Goldstein, 2001).

2. A figure showing the correlation between the two techniques will be added to the manuscript (see Response to referee comments by T. Karl #3).

3. While speciated monoterpene mixing ratios were higher at night than during the day, the fraction of the different individual speciated monoterpenes relative to β-pinene generally did not change from day to night. In Summer 2002, full mass scans were not performed routinely by the PTR-MS. However, 32 masses were monitored for four separate week-long periods between July and October, 2002. These masses were chosen to target compounds that we expected to observe, as well as masses that

exhibited significant count rates during a brief mass scan conducted on ambient, above canopy air. Of these 32 masses, besides the very low signal from sesquiterpenes, there were no other ions that exhibited a diurnal cycle similar to the monoterpenes. The brief mass scan, from which the 32 masses were chosen, however, was not preformed at night, so the scan may have missed potentially important compounds that have higher nighttime mixing ratios.

4. KI ozone scrubbers were used in the GC-FID sampling system, and this information will be added to the manuscript (see response to referee comments by C. Spirig, #1). We will include a more comprehensive literature review to discuss emission sources of monoterpenes and the light dependence of monoterpenes from other vegetation types. Additionally, in the conclusions section, we will discuss the open question of photochemically reactive terpenes, and our plans for future work to identify other photochemically reactive terpenes emitted from our field site.

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