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Atmospheric
Chemistry
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Discussions

Interactive comment on "Methyl chavicol: characterization of its biogenic emission rate, abundance, and oxidation products in the atmosphere" *by* N. C. Bouvier-Brown et al.

N. C. Bouvier-Brown et al.

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We thank both Anonymous Referees for their constructive feedback and suggestions. We will respond here to the comments from each referee individually. The comments are shown in **bold** and our responses are in normal text.

Specific comments

- Experimental

-Details about how many air samples were analysed and how frequent was the calibration of GC-MS are missing and should be presented.

More specific information was added to address this concern. Once per hour, the Berkeley GC-MS collected and pre-concentrated a sample for 30 minutes. Therefore, we acquired approximately 24 samples per day over the entire campaign. We had added a sentence noting that the instrument was calibrated at least once per day.

-specify the nature of mass spectrometer in the Berkeley GC-MS (quadripole or ion trap).
We specified that it is a quadrupole GC-MS.

-Because the authors used a special way to calibrate methyl chavicol, more details should be provided in the text concerning the mixing, how homogenous was the injected methyl chavicol throughout the line. Since methyl chavicol is a semivolatile compound, how can the authors make sure that it would not condense into the sampling line after injection at 100 C. What was the temperature of the calibration line? It should be similar to the sampling line. -Some details are missing in the following sentence (page 19713, 2nd paragraph, by manually injecting diluted liquid standards (with which solvent?)where the injector port was heated at 100 C. This standard flow was then sub-sampled at 20 mL min-1, it is not clear to me, do you mean into Tenax ?
More details have been inserted into the text. In summary, the liquid standard diluted in cyclohexane was injected directly into a stream of nitrogen gas, where the injector was heated to 100^{c}ircC. This standard flow was then treated exactly as an ambient sample; it was subsampled and collected through the same tubing and at the same flow rate as an ambient sample. To ensure no liquid standard condensed in the sampling lines, subsequent blank nitrogen samples were also collected through the calibration pathway.

-Which kind of ozone scrubbers did the authors use?
The ozone filter was discussed in the text at the end of the first paragraph of section 2.2.1. It was a 1 μm pore size Pall A/E glass fiber filter coated with sodium thiosulfate following Pollmann et al. (2005).

-Results and discussion: Methyl chavicol mixing ratios - Page 19718, line 8-14:

while the emissions of monoterpenes increase immediately following wetting by rain, the emissions of MBO and methyl chavicol do not increase until few days after rain when temperature begins to increase and full light is available. It appears surprising to me since the emission of monoterpene is also light and temperature dependent. The authors should explain that.
The monoterpene emissions at Blodgett Forest are temperature-dependent. This information has been explicitly added to the manuscript introduction. The temperature-driven emission mechanism has been seen at this site many times previously (e.g. Shade et al., 1999; Schade and Goldstein, 2003; Lee et al., 2005; Holzinger et al., 2005, 2006).

- Page 19718, line 15-20: if methyl chavicol represents 15% of total terpene mass measured at 1.5 m during the warm period and 36% at 9.3 m during cool period, what would be the comparison at the same height between warm and cool periods?
We cannot give a quantitative answer to this question because we do not have Berkeley GC-MS measurements at both heights during the two meteorological periods. We also cannot use the PTR-MS data because it was not calibrated for total sesquiterpene measurements, which are also semi-volatile.

-Methyl chavicol emissions - Page 19718, line 27-28: the authors concluded that because ambient methyl chavicol, MBO, and monoterpenes mixing ratios were largest in the lower canopy, their emissions are local and biogenic in origin. This can be true only if the vertical gradient (lower to higher canopy) of emissions has been made during the same warm or cool conditions to draw such conclusion.
This is an excellent point. We have added a plot showing average diurnal profiles of methyl chavicol mixing ratios taken at each level of the vertical gradient measured by PTR-MS (the current Fig. 6). This figure clearly shows that methyl chavicol mixing ratios are largest in the lower canopy. We direct you to Holzinger et al. (2005) for the vertical profiles of monoterpenes and MBO that also show the large mixing ratios low

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in the canopy.

- The authors should discuss the significant difference between night-time mixing ratios of methyl chavicol during warm period (Fig. 6A, around 200 pptv) and cool times (Fig. 6B, close to 0 pptv) and comment how can this be related to the emission from storage pools. Overall the explanations about the night-time emission of MBO and methyl chavicol are presented succinctly and not convincing (e.g., 1st paragraph of page 19719).

The addition of the vertical gradient from PTR-MS data (the current Fig. 6) provides more convincing evidence of the methyl chavicol vertical gradient, even at night. Because daytime methyl chavicol mixing ratios correlate so well with MBO and because these two compounds have very similar reaction rates, daytime methyl chavicol emission is likely emitted as a function of light and temperature, similar to that of MBO. At night, methyl chavicol is present throughout the canopy, but MBO is not. Both the data presented here and by Holzinger et al. (2005) show only a small amount of MBO at night without a vertical gradient. The difference at night alludes to methyl chavicol emission via a temperature-dependent mechanism from storage pools at night, similar to that of monoterpenes at this site.

-Conclusion: Page 19723, 1st paragraph: the estimated methyl chavicol basal emission rates from ponderosa pine trees during cool and wet conditions (i.e., 3-10 μgCg-1 h-1), higher than those during warm and dry conditions (0.7-4.3 μgCg-1 h-1), appear surprising to me assuming that the basal conditions (high temperature and optimum PAR) of emission are much more available during warm and dry periods.

The basal emission estimate for the cool and wet period was based on the correlation in the current Fig. 9 when the two compounds were measured simultaneously. This particular 3-day time period were the warm days following a rain event when large amounts of methyl chavicol was observed (Fig. 5). The MBO basal emission rates to calculate the estimated methyl chavicol emission rates were measured under similar meteorological conditions but many years prior to the BEARPEX campaign. The ratio of methyl chavicol:MBO (or the slope of the correlation plot) is much larger in the cool and wet period (0.34) than in the warm and dry period (0.02-0.12); as noted in the newly-designated section 3.2.1, this is due to a stronger temperature dependence of MBO emissions.

Technical comments

-Abstract - Avoid repetition, a ponderosa pine forest in Sierra Neveda Mountains of California, was reported twice.

Corrected.

- Experimental - if the average height of ponderosa pine is 8 m, how 1.5 m above the forest floor would be within the forest canopy? May be below the forest canopy would be better.

Corrected; 1.5 m above the forest floor is below the main trees of the canopy but near the juvenile saplings.

-Sometimes 9.3 m is reported as the height above the forest floor which I assume correct and in some area of the text it is referred to the height above the forest canopy (e.g., page 19714, line 6; 19715, line 1), it should be consistent throughout the manuscript.

Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19707, 2008.

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