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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

- The introductions is focused on methyl chavicol current knowledge. It should give as well a brief introduction on a-pinene and especially MBO as these compounds are compared to methyl chavicol in the paper (and emission rates of methyl chavicol are scaled by the MBO emission rates).

Good suggestion. We have explicitly noted at the end of the introduction that in order to

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understand methyl chavicol emissions, we will compare its mixing ratios and average diurnal profiles to that of MBO and α-pinene. We now introduce MBO and α-pinene as prominent biogenic emissions at the Blogett Forest site as well as note their emission drivers. MBO is emitted as a function of temperature and light, similar to that of isoprene, while the monoterpenes, such as α-pinene, at Blodgett Forest are temperature dependent.

- measurement section: resolution time of the different measurements should be given. In section, 3.1, the slight differences are attributed to the different sampling times. The sampling timescale has been clarified for the Berkeley GC-MS instrument. Once per hour, the Berkeley GC-MS collected and pre-concentrated a sample for 30 minutes. Sampling times were noted in the original manuscript for all other instruments. In summary, the NOAA GC-MS collected two 5-minute samples concurrently every 30 minutes, the PTR-MS sampled for 6 minutes at each of the 5 gradient heights once per hour, and the TAG samples were collected for 1.5 of every 2 hours.
We note however that PTR-MS measurements are always below GC-MS measurements during the day, which may be surprising as measurements of the GC-MS are more specific and, if any difference, it would be expected that the GC-MS results are lower. Please comment on that. Indeed, one might expect that the PTR-MS signal would be larger than that of the GC-MS at m/z 149. We attribute this difference to the difference in sampling times and inlet types. As noted in the text, the inlet for the Berkeley GC-MS was insulated Silcosteel tubing heated to 50°C, whereas the PTR-MS inlet at each level in the vertical gradient was made of PFA. A semi-volatile compound, such as methyl chavicol, could easily condense in the non-heated plastic tubing, especially under cool conditions (i.e. Fig. 4), thus the tubing used for the PTRMS inlet likely smoothed the temporal changes in methyl chavicol concentration resulting in the apparent but small discrepancy. A comparable figure cannot be made for the early warm period because the Berkeley GC-MS and PTR-MS were not collocated and therefore the PTR-MS m/z 149 cannot be calibrated from the authentic standard injected in the

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Berkeley GC-MS system.

- The first section of the results part is a bit confusing and gives too many information in a too short description. Indeed in three short paragraphs, the following issues are presented: inter-comparison of methyl chavicol measurements by the different instruments, observed mixing ratios, diurnal variation, description of the variability according to meteorological parameters, comparison with other compounds and then in the section 3.2 diurnal variability is again discussed. In the current version, discussion on the consistency of the results obtained by the different techniques is mixed up with discussion of the diurnal variation and the parameters controlling this diurnal variation. This confusion leads to missing information for the different issues. For example, figure 4 is given for the comparison between the different techniques but is it for a specific day? Is it averaged over the whole campaign? Concerning the diurnal variation, different informations are mixed up: what is observed here, what was observed in enclosure experiments, discussion of the vertical mixing in the canopy and of the oxidation in the canopy (but these two last points are closely linked with the discussion which comes in section 3.2) Therefore it is recommended to dedicate the first results section only to methyl chavicol (describing the consistency of the different instruments, its abundance and variability during the campaign) and in a separate section to comment on the comparison with other compounds levels and variability. It is also suggested to gather all information discussing the diurnal variability in a same section.

The results detailing methyl chavicol mixing ratios and emission rates have been reorganized to clarify these issues. First, a paragraph has been inserted explaining how the data is organized in this section. Secondly, we used mixing ratios to evaluate the measurement agreement among the GC-MS, TAG, and PTR-MS instruments and to emphasize methyl chavicolś abundance at Blodgett Forest relative to the total terpene mass. Following that, we focus on methyl chavicol emission drivers. These drivers are revealed through its comparison to MBO and the monoterpene α-pinene. We also cre-

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ated a sub-section to separate our estimation of methyl chavicol basal emission rates from correlation with MBO. This new organization should provide clarity. The data used to make Fig. 4 was averaged over the cool period (12 September - 8 October, day of year 255-281) because this was the time period when all 3 instruments were collocated at 9.3 m. This measurement time period was added to the figure's caption.

- page 19719, line 4-11: this part is not clear. The first sentence notes 'the significant methyl chavicol observed at night' and the sentence just after describes 'low nighttime mixing ratios', and finally a short discussion is made on these levels. Clarify what is discussed here (significant or low levels?)
Thank you for pointing out this inconsistency. 'Significant' was changed to 'presence of'.

- figure 6 A and 6B: represent diurnal variations of the BVOC at different heights (6A1.5m and 6B9.3 m) but also at different periods (6A warm period and 6B cool period). It would be helpful to present at first measurements at heights 1.5m and 9.3 m for the same period (for example the warm period), in order to demonstrate what is said page 19718, line 28 (i.e. 'ambient methyl chavicol were largest in the lower canopy'), that would then be figure 6 and 6 B. And then it could be shown the variations of methyl chavicol (at 1.5 m and or 9.3 m) during the cool period in an additional figure. If data at different heights are not available at the same period, it is suggested to label the second figure 'figure 7' rather than 'figure 6B'.
We agree that it would be more useful to present the data at different levels for the same meteorological period, but unfortunately, we do not have Berkeley GC-MS measurements spanning both heights during the two periods. The inlet was at different heights in these two periods. We do, however, have PTR-MS data showing the vertical gradient within the canopy during the cool period. We have inserted this information as the current Fig. 6. It shows that ambient methyl chavicol mixing ratios were indeed largest in the lower canopy. This new figure also corroborates the GC-MS data showing the presence of nighttime methyl chavicol emissions. To further clarify the different

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measurement time periods at different heights, the former 6A and 6B figures have been separated into the current Figures 7 and 8.

- following the suggestion above about remodeling the sections of the 'results' part, it would then be recommended to separate the section on emission rates (based on some assumptions) from the section on diurnal variation (which is more a description of an observation and the parameters controlling the variations). Eventually the sections concerning 'emission rates calculations', 'atmospheric implications' and 'oxidation products' could be separated in the 'discussion' part.
As noted above, a sub-section was created to separate the section on estimating methyl chavicol basal emission rates from its correlation with MBO.

- emission rates discussion: it is not clear to me to which emission rates estimated in this paper the emission rate range given in the introduction (line 27) should be compared with.
At the end of the new 3.2.1 section, it is noted that the 1.37 μmol m-1 h-1 from the branch enclosure measurements mentioned in the introduction, which is equivalent to 0.491 μgC g-1 h-1, should be compared to the 0.7-4.3 μgC g-1 h-1 estimated methyl chavicol basal emission rate range under similar warm and dry conditions. The phrase 'under similar warm and dry conditions'; has been added to the text to aid in this clarification.

- what is the lifetime of the identified oxidation products?
We do not know the lifetimes of the oxidation products and could not find them in the literature.

Technical comments
- Table 1: what is primary/secondary references? (Sometimes only secondary references are given)
The primary reference describes the measurement and analytical technique; the sec-

ondary reference provides numerical data without detailed analytical information. This information was added to the table caption.

- use consistently ’day of the year’ or the ’date’ (see for example section 3.1, in the text dates are given, in the figure ’day of the year’ are given which makes difficult to follow the discussion)
Corrected; both data and day of year are given throughout the manuscript.

- be more precise in the figure captions (for example figures 6 -according to the text represent mean diurnal variations over specific days, give this information in the figure caption).
Corrected.

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

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