

## ***Interactive comment on “Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a Ponderosa pine ecosystem: interpretation of PTR-MS mass spectra” by S. Kim et al.***

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We thank the three anonymous referees for their constructive comments. As indicated below, Most of suggestions have been addressed in the revised manuscript, and our response to all comments are outlined below

Anonymous Referee #1

Although the calculation scheme for the composite spectrum is rather simple, it can clearly show that the oxidation products of MBO and MT cannot explain the ambient

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spectrum from MFO. We limited discussion in the text only to this point.

p. 20824, line 19: filled “with” Tenax and Carbotrap

Corrected

p. 20825, lines 21-25: This is not well formulated. What is probably meant here is: the smaller the difference in proton affinity between the analyte molecule M and B, the conjugated base of the Brønsted acid reactant ion  $BH^+$ , the less energy is available for fragmentation of the resulting protonated analyte molecule  $MH^+$ .

Corrected as the referee suggested

p. 20826, line 2: “number density” instead of “number of molecules”.

Corrected

p. 20826, line 20: The PTR-MS parent ion abundance of linalool has recently been determined as a function of  $E/N$  and relative humidity (M. Demarcke et al., Int. J. Mass Spectrometry, doi:10.1016/j-ijms.2009.11.005) and was found to be around 4% (rather than < 1%) and rather independent of  $E/N$ .

corrected

p. 20826, line 26-27: When looking at Table 1, I don't get the impression that most aldehyde and epoxide species have main common fragment ions. Do the authors mean that elimination of a water molecule following protonation is the major ion/molecule reaction mechanism for all these species ? Table 1: It would be good to add the molecular weight of the mentioned species. “Nopinone” instead of “norpinone”.

We corrected the sentence as “The protonated ions of most aldehyde and epoxide species tend to lose  $H_2O$  in the drift tube as summarized in Table 1.”

p. 20827, line 23-26 and Table 2: It should be made more clear that the abundances of the different neutral species (column 3) are obtained by summing up the transmission-

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corrected count rates of the product ions associated to these species. What about the fragmentation of protonated acetic acid at 120 Td ? Is it negligible or was this taken into account when calculating the abundance of acetic acid ? It should be mentioned in what units the rate constants are expressed, and that the m/z values of the product ions are mentioned in column 2. Concerning the O-MT, what is meant by t-carveol, what is "2-hydroxy methyl ester", is camphor the dominant compound in the list of detected species ? If so, the use of the H<sub>3</sub>O<sup>+</sup>/camphor rate constant for correcting the O-MT relative abundance would be justified. Because of this lack of information the reader is not able to assess the accuracy of the O-MT emission rates in Table 3 as well. Take care: in the table oxygenated MT are abbreviated as OH-MT.

- As noted in the table caption the abundances are summation of the all product ions of each species. We think that acetic acid is detected on m/z = 61+ without significant fragmentation (de Gouw and Warneke, 2007) - The units of proton transfer reaction rate and ion charge are noted - We meant that camphor dominates of the O-MT species associated with m/z 153+. We corrected accordingly.

p. 20828, lines 22-24: The authors state that they might miss some high mass compounds due to the bad transmission of the PTR-MS at masses above 150 u. It might be interesting to take spectra in this mass range at a very bad mass resolution to find out whether additional peaks appear, even if they cannot be well resolved.

This is an excellent idea and we will definitely try this at the same field site in our upcoming field campaigns.

p. 20829, line5-7: SQT/MT ratios of branch enclosure measurements compare rather well with ambient flux measurements. Since SQT are generally considered to be extremely reactive and because no oxidants should be present in the enclosure (in contrast to the ambient atmosphere), could the authors provide some argumentation for this good agreement ?

Our GC-MS analysis indicates that the most abundant SQT species from the enclosure

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was isolongifolene, which has comparable OH reactivity ( $4.8e-11$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) to MTs. This fact can explain the comparable ratio of SQT/MT in the ambient and the enclosure measurement. However, as we noted in the text, the detailed analysis of canopy scale chemical processes will be discussed in following publications.

p. 20832, line 16: some more information about the laboratory oxidation experiments would be welcome, f.i. where they performed in NO<sub>x</sub> conditions similar to those in the forest ? In how far is the distribution of the oxidation products (and therefore the kind of spectra shown in Fig. 4 for OH + MBO) obtained in the chamber studies representative for forest conditions ?

The details on the chamber experiments were added in the experimental section. Since we observed relatively high NO concentrations (> 100 pptv) at MFO during the field campaign period, chamber experiment conditions (high NO<sub>x</sub>) were in the same regime in terms of peroxy radical chemistry.

Anonymous Referee #2

Page 20825: I would like to see a few more experimental details on the environmental chamber measurements: a short description of the FTIR, wall losses and the OH and ozone generation.

The details on the chamber experiments such as the FT-IR model and OH and ozone generation methods were added in the experimental section. Since we measuring oxidation product distributions relatively short time periods (10-20 minutes), we don't expect significant wall losses. Our empirical estimation is that wall losses should not be exceeding around 10%.

Page 20827: Figure 1b is the only mass spectrum that is normalized to m69 from MBO. All other figures are normalized to m59 from acetone. Please be consistent throughout the manuscript.

We corrected the spectrum in Figure 1b to be normalized with the signal of m/z 59+.

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The text was changed accordingly.

Page 20828: line 13 and page 20833 line2 and conclusions: The authors say that in ambient air mass 61 is acetic acid and in the chamber study it is glycolaldehyde, but no explanation is provided on the identification of this mass in both experiments. Please add the identification methods for this mass in both places.

In the revised text, we justified why we concluded the signals of  $m/z$  61+ as either acetic acid or glycolaldehyde or combined signals. Basically, in the chamber experiments we could confirm that  $m/z$  61+ signals were solely from glycolaldehyde from FT-IR measurement results, but in the ambient conditions we could not separate it. Finally, in the branch enclosure measurements, only acetic acid was confirmed by GC-MS.

Page 20828 line 22-24: The mass spectrum shown in Figure 1b is a three day averaged spectrum. This means that the detection limit of an averaged spectrum like this must be very low and even very small signals should be clearly detectable. It seems to me rather unlikely that large quantities of heavier compounds are missing in this spectrum. What is the detection limit of such a long average and what is the upper limit for the missing mass from heavier compounds?

Since we averaged four hours of each day (11am to 3pm), each mass ( $m/z$  40+ to 210+) in the spectrum is the result of  $\sim 3$  minute averaged signals with exclusion of the background check time span. In a given time average, detection limits in the high mass range ( $>150$  amu) will be close to several hundred pptv (Kim et al., AMT 2009) which could be a significant ambient mixing ratio.

Page 20830 line 20: The authors claim that the change in boundary layer height is the main driver for the diurnal variation in many compounds. What about chemistry? For very short-lived compounds this has to be equally important. Please add that to the discussion.

We added the point

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Page 20831 line 3: It looks to me that the spectrum is dominated by formic acid and not MBO. Please reformulate this and the next sentence.

What we meant by a MBO or a MT dominated spectrum was that MBO or MT was the dominant BVOC emission rather than BVOC with highest mixing ratio. We added a clause to make our intention clear.

Page 20831 line 9: please add: not "significantly" influenced by pollution

We corrected this

Page 20832 line 4: The exclusion of the even masses not only removes the nitrogen containing compounds, but also the isotopes and I think those should be included in the total mass.

The purpose of our analysis is to quantify the known and unknown signals from the spectra rather than to quantify concentrations of compounds. Therefore, we think that exclusion of even masses does not affect our analysis.

Page 20832 line 14: I suggest starting a new paragraph here: 3.4: Lab kinetics experiments.

We separated the section

Page 20833 line 22: b-pinene experiments are in reasonable agreement with previous studies. Here no references are given to those previous studies, please add them.

We added references

Page 20834 line 5: Here again I would start a new chapter 3.5 Composite mass spectra.

We would rather leave this as one section because the composite mass spectrum was directly calculated from the product distribution spectra, obtained from the kinetic experiments.

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Page 20834 line 3: The oxidation products can explain 75% of the total counts in the spectrum. Is this only for the b-pinene OH oxidation? If so, please give the values for the other oxidation experiments as well.

We added the corresponding MBO experimental results

Page 20834 line 11: Here a maximum value of 2.5e6 for OH was picked without a reference or rationale. I would suggest looking at the parameterization by Ehhalt and Rohrer [2000]. If all the parameters are available, as it might, OH can be calculated somewhat more accurate. At least an explanation for the chosen value should be given.

Very limited OH measurements during the field campaign indicated that the daytime maximum OH concentration was around 2.5e6. However, we calculated ratios of oxidation products with precursors rather than mixing ratios of the oxidation products in our analysis. The absolute OH mixing ratios, therefore, are not important but the value that we choose is not unrealistic. We include this point in the text.

Tables: Table 1: Please add the molecular mass of the compounds and the relative abundances of each fragment.

We added the molecular masses of the listed compounds in the table. We would like to refer the exact relative abundance information to the listed references to prevent the table from looking too busy.

Table 2: Please add units. Are those normalized to m69 or m59? The branch enclosure mass spectrum was normalized to m69, so why is the relative abundance not 100% of m69?

We added units and we replace the term "relative abundance" to "abundance in %".

Table 4: The table in transmission corrected counts is not much meaningful for a non PTR-MS person. The mixing ratios should be given in ppb, even if they have a large error due to missing calibrations for many compounds.

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The daily variations of mixing ratios of major compounds are shown in Figure 2. Therefore, we would like to deliver the quantitative information of relative strengths of each mass rather than mixing ratios in this table. In this perspective, we think the table can be meaningful as it is.

Table 5: The HMP<sub>r</sub> yield is missing. Also give the units for the yields.

We added calculated yields of HMP<sub>r</sub>. We have now defined the yields as 'fractional molar yields' in the table caption. These are by definition unitless.

Typos: Page 20832 line27: in the figure "shows the" product distribution. Page 20833line 2: m/z=71 Page 20833 line19: reported the same results Page 20833 last paragraph: nopinone not norpinone Page 20835 line 4: a-pinene

We addressed the typos

Anonymous Referee #3 We addressed the major issues that the referee raised and clarified abstract as listed below.

P20820 Lines 1-7: Please consider splitting the first sentence.

We split the sentence

P20820 Line 16: What is meant by 'total signal'? PTRMS/GC-MS? Emission/Air?

We clarified the point

P20820 Line 17: what is meant by 'known' compounds, consider replacing with 'identified'.

We changed the word

P20820 Lines 23-25: consider removing 'due to their impact: : : : : cycle', this is repeated in detail with references in the following sentences.

We removed the clause

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P20824 Lines7-9: Background (BG) was defined as measuring scrubbed air. Call the night time measurement reflecting the effect of the chamber something else than BG. Table 1. Include the relative abundances (at 120 Td) of the measured fragments. Although fragmentation depends on the instrument, it would be very usefulness for PTRMS users to see how they have fragmented in this experiment.

The accounted background signals are the scrubbed air but the nighttime measurements can show any interference signal from the enclosure bag. We would rather refer to other literature references that provide quantitative fragmentation information because the inclusion of all quantitative fragment abundances makes the table appear very busy (e.g. several different MT species and SQT species). We direct the readers to several different references that contain the desired quantitative information.

P20824: why call samples sorbent and not adsorbent? Do you suspect that the sampled compound is absorbed (and not only adsorbed) to the substrate.?

Both words, Tenax sorbent and adsorbent are commonly used. We are using commercially manufactured sampling tubes that are referred to as "Tenax sorbent" by the manufacturer.

P20826 line 3. ': : two of the major BVOC species: : .' in the air or emitted? Clarify.

We clarified it.

P20826 line 13- : Is p-cymene an important species? Has it been observed? Why is Tani et al., 2004 not referenced here?

There have been some reports of p-cymene emissions, although p-cymene has not been observed as commonly as -pinene or -pinene (Hewitt et al, 1995). The reason, however, that we discussed p-cymene in the text is that its fragment can be a significant interference for toluene measurement. We think we are clear about the point. We also added the reference (Tani et al) in the text.

P20827: why are the SIFT results described in detail? Consider revising this para-  
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graph, at the moment it is missing the linking to the results in the manuscript.

The previous studies, listed as the references in the text have consistently shown that the fragmentation patterns between SIFT and PTR-MS methods are identical in the semi-quantitative sense. Since no studies about the fragmentation pattern of caronaldehyde from 3-carene oxidation using PTR-MS has been conducted, it is worthwhile to referring to the fragmentation pattern, observed by the SIFT technique for this study which was conducted in a 3-carene rich environment

P20828 line 12: compare to toluene emissions by White et al., 2009.

It is hard to directly compare White et al. (2009) results to ours because they reported with a unit of flux (mass area-1 time-1). We are preparing a manuscript on VOC flux measurement at the site and will try to compare our results with the reported fluxes by White et al. (2009).

P20829 lines 11-16: clarify. Are the emissions estimated based on measurements (gradient?) and compared to (branch) measured emissions? Or are the emissions estimated e.g. from G93 model? Please go carefully through the whole section 3.2 and refer to the different emission measurements consistently.

In all of section 3.2, we discussed branch enclosure emission rates, rather than gradient flux measurements except one occasion, comparing the SQT/MT ratio between enclosure and gradient flux measurements. We separated the discussion about the G93 model results into a separate paragraph to avoid such confusion.

P20830 line 16 ': : :show a clear anti-correlation.' consider replacing with exhibit different diurnal patterns etc, anti-correlation refers to a mathematical relation. Both concentrations are correlated to temperature through their local emissions (one due to enzymatic activity and the other due to evaporating storages), and MBO is in addition correlated with light.

We re-wrote the sentence.

P20830 lines 20-23: please add a reference, this has been observed in many studies.

We added a reference, explaining our observation (Hewitt et al., 1995).

P208360 lines 26: 'The diurnal variation of compounds with sources that include both direct emissions and BVOC oxidation such as acetone, possibly contributed by direct emissions, and acetic acid is more complex due to photochemical production during daytime and variations in boundary layer height throughout the day.' Consider splitting into two or more sentences.

We made it into two sentences

P20831 line21: 'We also observed significant concentrations in ambient air.' Add e.g. the oxygenated-MT

We made it clearer

P20832 lines 3-4: Are the MS75, MS5, MS101 and MS109 included in the identified or unidentified compounds?

Those masses were included. We made the point clear.

P20832 line 14-: Consider adding a new chapter 3.4 on the oxidation study. Were the experiments done in dry or humid air?

We made a new section and we added a description of the experimental conditions (in the experimental section. The experiments were conducted in dry synthetic air.

P20832 line 17-: 'OH- and ozone-initiated oxidation products and their yields from  $\alpha$ -pinene were quantified with PTR-MS by Wisthaler et al. (2001) and Lee et al. (2006), : ' for clarity change to 'have been' to distinguish from what was done in this study.

We explained the difference. Our mass range is much higher than those from the previous study. We have changed the wording to 'have been' for clarity.

P20832 line21: what is meant by 'all chemicals'? Please clarify.

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We listed chemicals in the sentence.

P20832: are blank and background spectra in this case the same? For ozone a background spectra was subtracted to get production. What was done for the OH experiment?

The background spectrum was taken for each experiment. We now describe this point.

P20835 line 4:  $\alpha$ -pinene miss spelled 'atpinene'. Summary: please include MBO and total MT and SQT emission rates.

We corrected it.

P 20836 line 21: 'The identified species comprise most of the signals ( $\sim$ 93%) in the mass spectrum.' Of the PTRMS or GC-MS spectrum? Please clarify. Go carefully through the tables and figure captions, they appear carelessly written.

We corrected it and we went through the captions.

Table1: add relative abundances (%) of the ions. Reconsider classes. Terpenoids could include all isoprene unit based compounds (also oxidized terpenes). Write classes and species names with small capitals.

We directed the readers to a number of references for this information rather than putting it in the table to avoid an overly busy table.

Table 2: what is other MT? Please consider consistence with nomenclature between tables, text and figures. Also write oxidized-MT (like in text) instead of O-MT. Units of abundances and constants are missing. Write 'Mostly Isolongifolene' with small capitals (like other species). Change + to a superscript, like in others.

We addressed the issues

Table 3. please check the units.

We added the temperature unit

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Table 4. Stand alone text: normalized counts per second (for an average of ?)

We corrected the caption

Figures, please change AMU to m/z like in text.

We corrected theseâ

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20819, 2009.

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