

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.

Anonymous Referee #2

Received and published: 27 November 2009

This paper describes measurements done by PTR-MS in a Ponderosa Pine forest at the Manitou Forest Observatory. The main focus of the paper is the interpretation of the mass spectra taken by PTR-MS and the authors show that the majority of the signal, especially from the BVOC emissions, can be explained by a surprisingly small number of compounds and their respective oxidation products. The emissions were determined using branch enclosure measurements and the oxidation products using laboratory kinetics experiments for MBO and β -pinene. The paper is generally well written and very interesting, particularly for the PTR-MS community, because it clearly furthers our un-

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derstanding of the BVOC emissions and their oxidation that have been discussed in the literature lately as potential ozone sinks and SOA precursors. The only issue that I have with the paper is that it is rather qualitative in various places, but I would recommend publication after the issues that are described below are addressed.

Specific comments:

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.

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.

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.

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?

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.

Page 20831 line 3: It looks to me that the spectrum is dominated by formic acid and

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not MBO. Please reformulate this and the next sentence.

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

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.

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

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.

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

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.

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.

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

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?

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

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error due to missing calibrations for many compounds.

Table 5: The HMP_r yield is missing. Also give the units for the yields.

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

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