**Atmospheric
Chemistry
and Physics
Discussions**

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 #1

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This is an interesting paper dealing with the interpretation of PTR-MS mass spectra of ambient air in a Ponderosa pine ecosystem. In order to interpret the mass spectra the authors take into account PTR-MS mass spectra of BVOC emissions of Ponderosa pine branches using dynamic Teflon enclosures (and complementary GC-measurements), PTR-MS spectra obtained during OH- and O3-initiated oxidation of 2-methyl-3-butene-2-ol and β-pinene (the main emitted BVOCs by Ponderosa pine) in an environmental chamber, and existing literature data on fragmentation patterns of BVOCs resulting from proton transfer reactions using $H_3O^+\cdot(H_2O)_n$ reagent ions. The paper shows

that the potential of PTR-MS for detection of most VOCs in ambient air (at least those with PA(VOC)>PA(H2O)) with roughly the same detection sensitivity (within a factor 2 or so) can provide us with a rough guess of the contribution of unidentified BVOCs. The paper is generally well-written, but sometimes lacks details about the performed experiments (especially the environmental chamber measurements) and one gets the impression that the model calculation of the composite spectrum (based on four PTR-MS spectra obtained in this environmental chamber in non-specified conditions) is a too simple approach. Nevertheless, the presented work remains very interesting to every PTR-MS user dealing with BVOC emissions.

Specific comments:

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

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+.

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

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.

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".

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-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 $H3O+$/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.

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.

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 ?

p. 20832, line 16: some more information about the laboratory oxidation experiments would be welcome, f.i. where they performed in NOx 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 ?

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p. 20835, line 13: "m/z" instead of "amu".

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