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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 #3

Received and published: 1 December 2009

The authors are clearly aware of the limitations and advances of the PTRMS instrument in the analysis of emissions and ambient air, both complex samples with changing compositions. They have interpreted the ambient composition BVOCs based on their local emissions and simulation of oxidation in laboratory and have done an excellent job in it using combining several measurement techniques. The experimental setup is clearly described, unfortunately the results are not as clearly written. Perhaps due to the many different measurement setups and results obtained the results were at times impossible to follow. The technical aspects of the interpretation outshine the important

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Discussion Paper



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Comment

results that 93% of the emissions were identified and that 73% of the ambient sample were identified. In addition I feel that some information is missing e.g. some of the tables were missing units and more consistences with the nomenclature (especially in section 3.2. from which emission measurement are the emission results from and in tables and text terpenoids/terpenes/MT/OMT/other MT) would help the reader from getting confused. Below are specific comments to further improve the manuscript.

The abstract does not reflect the title, include results on how much of the emissions were identified and how much of the emissions were identified. The results should be written out more clearly e.g. in table 4: Are the MS75, MS5, MS101 and MS109 included in the identified or unidentified compounds?

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

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

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

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

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.

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

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

P20826 line 13- : Is p-cymene an important species? Has it been observed? Why is

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Tani et al., 2004 not referenced here?

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

P20828 line 12: compare to toluene emissions 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.

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.

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

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.

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

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

P20832 line 14-: Consider adding a new chapter 3.4 on the oxidation study. Were the

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Comment

experiments done in dry or humid air?

P20832 line 17-: 'OH- and ozone-initiated oxidation products and their yields from -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.

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

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?

P20835 line 4: a-pinene miss spelled 'atpinene'.

Summary: please include MBO and total MT and SQT emission rates.

P 20836 line 21: 'The identified species comprise most of the signals (~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.

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.

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.

Table 3. please check the units.

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

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

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