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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007 – implications for gas- and particle-phase chemistry" *by* N. C. Bouvier-Brown et al.

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We thank Referee 2 for the suggestions. The comments are re-written below in bold followed by our our responses in normal text.

This manuscript presents ambient measurements of MT (monoterpenes), SQT (sesquiterpenes), linalool, and methyl chavicol using a modified GC-MS system. The dataset is valuable because ambient concentrations of SQT and oxygenated

monoterpenoid have been rarely measured and reported. As significances of their roles in SOA (Secondary Organic Aerosol) formation have been speculated, the authors estimated their contributions in photochemical reactivity (OH and ozone) and SOA within the Blodgett Forest canopy, a ponderosa pine ecosystem. The results and discussion of this manuscript is pertained to aims of Atmospheric Chemistry and Physics. Therefore, I recommend the manuscript to be accepted with minor revisions, based on following points.

1. Some of the measured compounds such as linalool and bergamotene in the ambient air have been known as "herbivore-induced plat volatile emissions" (e.g. Kessler and Baldwin 2001 Science). Is there any indication that biotic or abiotic stresses were triggered at the ecosystem? There was no indication of biotic or abiotic stresses triggered at the ecosystem. We would also like to note that α -bergamotene was also the dominant emission from the ponderosa pine trees in the branch enclosures conducted two years prior in the summer of 2005 (Bouvier-Brown et al., 2007; Bouvier-Brown et al., 2009a).

2. How different was the ratio of SQT/MT that you observed from branch enclosures and the ambient air? Authors' argument that reactive SQT were quickly removed from the ambient air can be quantitatively discussed by comparing the ratios and fractions of reactive SQT emissions from enclosure measurements. Especially, the discussion about SOA formation potential from newly measured BVOC in section 4.4 can be supported by the discussion. In the section, the assumption for the amount of SQT contributing SOA formation is simplified although it can be more quantitative by comparing the speciation information between branch enclosure (Bouvier-Brown et al., 2009a) and ambient measurements. The SQT/MT ratio was substantially different. It was 0.74 in the branch enclosures, but much less in the ambient air (Day, warm, 1.5 m: 0.061, Night, warm, 1.5 m: 0.20, Day, cool, 9.3 m: 0.14, Night, cool, 9.3 m: 0.08). In order to assess how much sesquiterpene mass would have reacted away in the canopy, we assumed the SQT/MT ratio was consistent throughout the canopy at the same emission rate observed in the branch enclosure (0.74), just as you suggested. In order to quantitatively compare the speciation of terpenes between the branch enclosures and ambient measurements, we would need to scale by leaf area and foliar density, and this type of calculation not only introduces a lot more uncertainty and error, but it also is not appropriate for these highly reactive compounds.

3. Although ambient concentrations of SQT and other oxygenated compounds have not been reported, number of publications has reported the emission rates of SQT using various GC methods (Duhl et al., 2008). Is there any possibility of underestimation of emission rates by previous studies due to different GC configurations from this study? In the method section, authors described the modifications, added to Millet et al. (2005) but it is not sure that the modifications have not been tried by other research groups or authors adapted from other groups. Most studies that have reported sesquiterpene emissions (like those mentioned in Duhl et al., 2008) quantified sesquiterpene concentrations using adsorbent-packed cartridges placed in branch enclosures that are subsequently thermally-desorbed into a GC system. These methods limit the exposure of the reactive sesquiterpene compounds to surfaces (e.g. inside tubing) onto which these low-volatility compounds can condense. When a sample containing low-volatility compounds must travel down a long span of tubing (as it does in the present study), the tubing must be inert, internally passivated, and heated to prevent condensation. To the best of our knowledge, these modifications have not been done before to measure sesquiterpene compounds in ambient air of forested environments.

More specific comments and questions on the manuscript are listed below.

Page 10237 Line 18-23 Many other SQT other than β-caryophyllene and α-humulene are described in this study. Therefore, SOA yields from the chamber studies other than β-caryophyllene and α-humulene could be explained if they are available. If they are not, the fact should be also pointed out

so that other researchers can conduct studies on SOA yields of other SQT. We added a note in section 4.4 about the lack of SOA yields for α-farnesene and α-bergamotene. We refer you to Lee et al. (2006a,b) for SOA yields of longifolene (as well as the monoterpenes and methyl chavicol also measured in this study). We are also aware that I. Kourtchev is working on SOA yields of β-farnesene; his abstract from the Goldschmidt 2009 conference can be found at: http://www.goldschmidt2009.org/abstracts/originalPDFs/455.pdf.

Page 10240 Line 15 Please specify the sample residence time in the sampling line so that readers can get a clear idea about wall loss. Done

Page 10241 Line 9 How was the temperature of the sample pathway ($50\,^{\circ}\mathrm{C}$) decided? Have you tested various temperatures and ended up the temperature? Please provide more information. A sentence was added in section 2.2 explaining this choice. $50\,^{\circ}\mathrm{C}$ was chosen because it was a sufficient temperature to heat the valves and tubing for SQT recovery by Helmig et al. (2004). Limited by the current GC-MS system used in this study, we could not achieve a higher temperature.

Page 10241 Line 22 Typo (I guess) Marin → Marrin Page 10241 Line 25 to Page 10242 Line 5 Corrected

What was the concentration range of liquid injection calibrations of SQT and other compounds? A sentence was added in section 2.2 clarifying this point. Concentrations ranged from 2-63 ppt for SQTs and 3-94 ppt for linalool and methyl chavicol.

Page 10242 Line 23-29 Kim et al (2009 AMT) reported that wall loss of SQT is a function of temperatures and concentrations. Please, therefore, describe the concentration range of each compound and the temperature range during the tests. The concentration ranges are the same as stated above (2-63 ppt). Kim et al. (2009) describe losses due to the different temperatures of the Teflon sample tubing. Our inlets were always kept at $50\,^{\circ}\mathrm{C}$.

Page 10247 Line 23 Please specify "oxidant mixing ratios" in the text rather than referring from the previous study such as average daily variations of ambient OH and ozone if they are available. We have added the average diurnal profile of ozone measured at BEARPEX to Figure 3.

Page 10248 Line 10 Please put more discussion on "ample evidences". It is an important part of this study so readers may want to see extended discussion We added: "For example, Bouvier-Brown et al. (2009b) showed a strong correlation between methyl chavicol and MBO in terms of diurnal profile and atmospheric lifetime, thus suggesting that the two compounds have a similar light- and temperature-dependent emission mechanism." We refer to Bouvier-Brown et al. (2009b) for detailed information.

10249 Line 1 The title is not clear enough. Authors need to specify what exactly "mass" means. In my perspective, it could be understood either the total organic compound mass in the air or detected masses by the GC-MS system. We changed it to: Newly measured BVOC mass

10249 Line 19 Please provide more quantitative information on the importance of manzanita emission to the total BVOC emission of the ecosystem. Especially, the relative importance, compared with the ponderosa pine emission of the ecosystem will be helpful because most of readers including me probably regard Blodgett Forest as a ponderosa pine dominant ecosystem. Yes, Blodgett Forest is primarily a ponderosa pine plantation, but over the years, the relative importance of trees and shrubs has changed as the forest has grown. The percent leaf area contribution of each species to the ecosystem was 52% ponderosa pine, 29% manzanita, and 19% ceanothus in 2003. This information was added to the text in section 4.2.

10250 Line 1 The title also could be more specific. Most of discussion is about OH and ozone reactivity in the ambient air of the ecosystem, so please specify it. The title was changed to: Impact of BVOC on ecosystem oxidant loss rates

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10251 Line 1-4 In the discussion of OH and ozone reactivity calculations above, authors pointed out that the estimate rate constants using US EPA AOPWIN could cause large uncertainty. In the context, it would be desirable to specify the portion of OH and ozone reactivity that calculated with the EPA software suite. Table 3 shows the reaction rate constants used in the calculations and where each constant came from. 50% of the SQT kO3 and 75% of the SQT kOHs as well as both kO3 and kOH for methyl chavicol were calculated using the EPA software.

Table 2 The recovery of methyl chavicol looks too low by considerations of its chemical lifetimes with respect to OH and ozone. Please explain. Aromadendrene in the table has a very short ozone lifetime but indicates high recovery rates. Is this suggesting that the rate constants could have large uncertainty? Yes, methyl chavicol is reported as having low recovery in the shorter inlet (used to measure 1.5 m from the ground), but unfortunately that calibration was only attempted once for this inlet. Since we have no specific reason to throw out that data point we decided to report it, but it is not statistically reliable. The recovery reported for the longer inlet is more appropriate because we had 10 repetitions. As mentioned in the text, yes, the rate constants (particularly those estimated using EPA AOPWIN) have very large uncertainties. If a small amount of ozone were present in the Tenax traps, although there was no evidence of this, spacial separation of the different compounds within the Tenax adsorbent bed could influence the amount of reaction. Arnts (2009) showed how the apparent ozone reactivity was not consistent with the reported rate constants, and he suggested that the ozone will contact (and thus react with) more sesquiterpenes before it contacts monoterpenes adsorbed deeper in the bed. More work will have to be done to tease out the different factors affecting loss of low-volatility compounds in sample lines.

Table 3 Please edit superscriptions properly for notations of OH, ozone, and NO3 concentrations. Corrected.

Table 4 Please specify how many data points were averaged. This information was added to the table caption. We have also added this information to Table 1.

Figure 3 Please specify how many data points were averaged. This information was added to the figure caption.

References:

Arnts, Environ. Sci. Technol., 42, 7663-7669, 2009.

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Lee et al., J. Geophys. Res.,111, D07302, doi:10.1029/2005JD006437, 2006a.

Lee et al., J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006b.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10235, 2009.