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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 3 very much for the suggestions, they will make the manuscript much clearer. The comments are re-written in bold, and our responses are given in normal text.

**GENERAL COMMENTS**



**Section 4.1 It is not clear what value the new measurements add to their knowledge of 'Control over emissions'. The two data sets of BVOC mixing ratios were collected at two different elevations – one at ground level and the other above the canopy. Since they were collected over non-overlapping periods (days 232-255 and days 255-281), these measurements can be viewed as concentration gradients only if one assumes that meteorology and emissions are identical. Hence the statement that "The combination of these factors (climactic variability, height within the canopy, reactivity of each species) causes the lower average mixing ratios measured above the canopy at 9.3 m (Fig 1, Table 1)" while probably true is not supported by any data or analysis presented. There is discussion of the impact of reactivity on the gradients without any supporting ozone data. Yes mixing ratios are probably lower at lower temperatures but how much is due to proximity to emission surfaces, more mixing, greater inlet losses or more ozone? In addition there is no attempt to interpret mixing ratios versus the three primary vegetations present. How does canopy structure impact observed distribution of monoterpenes and sesquiterpenes? How do ambient measurements compare with enclosure-based emissions measurements of local vegetation? Do the basal emission rates change with season? Section needs to be re-written or deleted.** The first paragraph in section 4.1 was merely trying to explain why we detect lower mixing ratios at the 9.3 m inlet than the 1.5 m inlet. As you correctly point out, we cannot use the data collected at the two different levels as if they were two points within a vertical gradient because they were not collected during overlapping periods. Because there are too many variables changing simultaneously, we deleted this first paragraph in section 4.1. The rest of the discussion isolates the analysis to either the earlier time period (the emission mechanisms: section 4.1 and mass emitted: section 4.2) or to the later time period (impact on ozone reactivity: section 4.3) but not comparing the data collected during the two different time periods.

You are correct that we did not interpret the ambient mixing ratios in light of the branch enclosure measurements and emission rates of the three dominant species at Blod-

gett Forest (experiment detailed in Bouvier-Brown et al., 2009a) or canopy structure. The present study is focused on providing the first measurements of sesquiterpenes at BEARPEX and putting them in context of the monoterpenes and methylchavicol observations. This is not a flux study, and again, we cannot interpret a gradient from this dataset. 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.

**Section 4.1.1 "The monoterpene average diurnal patterns indicate that their emissions are driven by temperature because elevated mixing ratios occur when high temperatures induce emissions in a shallow boundary layer with low oxidant mixing ratios (Fig 3A)" Figure 3A shows lowest mixing ratios of monoterpenes occurs during mid-day when temperatures and at a maximum. No boundary layer depth or oxidant levels data are presented to support this statement.** We have inserted a panel into Figure 3 showing the average diurnal profile of ozone and carbon dioxide (Fig 3F). The ozone profile shows the morning dip at 7-8:00 PST (as explained at this site by Bauer et al., 2000 and Kurpius et al., 2002) which coincides with the morning peaks of most BVOCs. The carbon dioxide profile is used as a proxy for the timing of vertical mixing. The nocturnal boundary layer breaks and vertical mixing begins during the same 7-8:00 time frame. The boundary layer re-forms $\sim$19-21:00, which coincides with the evening peaks of most BVOC profiles. The sentence is now re-written to provide clarification. "The monoterpene average diurnal patterns indicate that their emissions are driven by temperature because elevated mixing ratios occur at night and in the morning (7:00-8:00 PST) (Fig.3A). These times occur when temperatures are warm enough to induce emissions and both oxidation and vertical mixing are slow (Fig. 3F)."

**SPECIFIC COMMENTS**

**Page 10240, line 15. What it the internal diameter or wall thickness of the inlet**



**line?** This information was added to the text (4.57 mm ID).

**Page 120240, lines 16-20. Was a single ply of filter membrane used to fabricate the ozone filter? How was filter scaled from Pollman et al. design? Pollman et al. used a 25 mm diameter filter tested at a flow rate of 255 ml min-1. This works out to a face velocity (a rough measure of contact time) of 0.87 cm s-1 . Your system is passing 4 lpm through your filter. Have you altered your filter diameter or number of layers to scale to Pollman? If not, what measurements do you have showing ozone removal efficiency for your configuration?** Downstream of the ozone filter before the 20 mL/min subsamples, the ozone concentration was qualitatively monitored using a 2B Technologies Model 202 Ozone Monitor. This instrument indicated that no significant amount of ozone was getting through the single ply thiosulfate-coated filter (within the stated 3.0 ppb detection limit). In addition, we carefully looked at the chromatograms just before and after each filter change to ensure that there was no difference in the sample quality. The use of the Ozone Monitor was added to section 2.2.

**Page 10241, lines 3-4. Are you using retention time/index along with single ion response to identify compounds?** We are relying on the mass spectra library matches for the average $\sim$15 ions monitored for compound identification.

**Page 10242, lines 12-13. This needs more elaborations concerning what assumptions you are making about the 'average response of the sesquiterpene standards' relative to a compound for which you have no standard. How do you decide which ion to monitor and how do you know what percent of the total fragmentation this represents? How do you arrive at a calibration factor from this based on monitoring a single ion? This would seem to introduce a huge amount of uncertainty concerning your bergamotene and farnesene isomer concentrations.** Since the ambient concentrations of sesquiterpenes are so low, we had to use the single ion mode (SIM) detection; we realize this is not ideal. We chose to monitor 15 ions (m/z 41, 55, 69, 77, 79, 80, 81, 91, 93, 205, 107, 119,133, 161, and 204)

within the window where sesquiterpenes would elute because of the known ion spectra found in the NIST database and from our experience with SPME fibers. Bouvier-Brown et al. (2007) described the use of solid phase microextraction (SPME) fibers to detect sesquiterpenes in branch enclosures using a GC-MS system. This SPME method allowed for MS detection using full scan mode. The ions used for quantification (in standards (see Table 2) and samples (see Table 1)) were the dominant ions for each compound, with the exception of $\beta$-farnesene and aromadendrene, which were 3rd and 2nd most abundant, respectively. Each of these dominant ions averaged 8$\pm$3$\%$ of the total fragmentation abundance. With this consistency, the uncertainty due to this calibration procedure is minor.

**Page 10242 last paragraph. In Table 2 you show only 19$\%$ recovery of methyl chavicol from the 1.5 m line while the 9.3 m line transmits 108$\pm$64$\%$! This does not the reader much confidence in your ability to make an accurate measurement of methyl chavicol.** We did not find any reason to exclude the test on the recovery from the lower inlet line, but the one data point that gave us the 19$\%$ value is not statistically reliable. As discussed in the response to reviewer 2, we consider the recovery tests on the higher inlet more reliable since we had 10 repetitions.

**Page 10242, last paragraph. Your transit time from the inlets to the ozone filter are short (420 ms for the 11 m line and 687 ms for the 18 m line). This is too short for much gas phase loss to occur with the caryophyllene and humulene. This would suggest that you still have considerable ozone entering your Tenax trap or the transmission of these compounds through Silicosteel at $50\,^{\circ}$C is poor. For discussion of the effect of residual ozone on BVOC on Tenax see Arnts 2008, EST 42:7663-7669.** Yes, some residual ozone in the system (perhaps in the Tenax adsorbent) would help account for the loss of caryophyllene and humulene, but again, we have no direct evidence of this. As stated above, the sample air was monitored with a 2B Technologies Ozone Monitor. We acknowledge that we did not transmit $\beta$-caryophyllene and $\alpha$-humulene through the system, but we do not have evidence of



the location of this loss.

**Page 10247, section 4.1.1. "The monoterpene average diurnal patterns indicate that their emissions are driven by temperature because elevated mixing ratios occur when high temperatures induce emissions into a shallow boundary layer with low oxidant mixing ratios (Fig. 3A)." This statement is unsupported by Figure 3. There are no coincident oxidant data presented. Secondly, there are no data presented to indicate changes in mixing or changes in boundary layer depth.** As stated above, we have inserted a panel to show the diurnal profiles of ozone and carbon dioxide, as a proxy for the timing of the vertical mixing, into Figure 3.

**Page 10249. Discussion of Figure 4a. I assume this plot attempts to capture canopy and understory emissions. Is this weighted by the average biomass composition in the immediate area?** Figure 4a shows the data collected from the chamber measurements weighted by the percent leaf area contribution to the ecosystem for each major plant species.

**Page 10249 last line. Should read: $\alpha$-bergamotene has an estimated longer lifetime. . .** Corrected.

**Page 10250. I do not think the term 'ozone reactivity' is appropriate. What you are discussing is the relative contributions of each biogenic VOC to the total ozone-olefin loss rate.** We appreciate this clarification and have changed the text.

**Page 10250. There is no presentation of the actual results from the NOAA GC-MS speciation. It would be useful to see the mixing ratios of these other compounds.** Mixing ratios of the NOAA GC-MS VOCs have been added to Table 5.

**Page 10250 line 11. "methyl chavicol dominated the newly measured ambient BVOC mixing ratios and mass" Table 4 shows $\alpha$-pinene>3-carene>methyl chavicol and Figure 4B shows MT>MC.** Throughout the manuscript, the "newly measured BVOCs" just include the sesquiterpenes, oxygenated monoterpenes (i.e. linalool), and

methyl chavicol. The quantification of ambient monoterpene mixing ratios is not new to this site.

**Page 10250 line 19 refers to "Fig 5B". There is no Figure 5 included.** Corrected. It should read Fig 4B.

**Page 10250. Given that enclosure emissions show considerable contribution from $\beta$-caryophyllene and $\alpha$-humulene which are not measured in ambient air, Figure 4C only shows distribution after these compounds have already reacted. It is therefore an incomplete picture of ozone-olefin loss.** We acknowledge at the end of section 2.2 that all of the reported measurements are lower limits. We have added emphasis to the discussion of ozone reactivity (section 4.3) that this is a lower limit considering many of the highly reactive compounds (i.e. $\beta$-caryophyllene) is not adequately measured.

**Page 10251 Section 4.4 line 15-17. I re-calculated your numbers to this point. I believe the result you get of 534 ppt is actually 'equivalent monoterpene'. To convert to ppt of sesquiterpene you must multiply this value times the ratio the molecular weights (136/204) which gives you 356 ppt of sesquiterpene. Subtracting 44.5 ppt of sesquiterpene yields 311 ppt of reacted SQT. A 10 to 50 $\%$ SOA yield from 311 ppt gives you the resulting 0.26 to 1.3 micrograms per cubic meter.** Thank you. We have made the appropriate corrections to the calculations.

**Page 10258. Table 1. Caption or table columns should note the two different time periods monitored (day of year).** Corrected.

**Page 10258 Table 1. Why are the standard deviations not presented?** The standard deviations are presented in Table 1. Perhaps the reviewer meant to ask why there are not standard deviations on Figure 3? Each panel of Figure 3 would be extremely difficult to read with added deviation or error bars. We have now specified the number of data points averaged each hour in the caption of Figure 3. With the standard deviations in Table 1 and the average number of data points used to create the figure,



readers have an idea of the error. Perhaps the reviewer meant to ask why there are not standard deviations on Table 4? They have been added to Table 4.

**Page 10269 Table 4C. Does this data set from your measurements only include the same day 267-270 period corresponding to the NOAA data set? Please specify.** Yes, Figure 4C only includes data when the two inlets were co-located (during day 267-270). We have added this clarification to the Figure's caption.

**TECHNICAL CORRECTIONS P. 10238, LINES 7-9. poor sentence structure** The sentence was changed to read: "The vegetation enclosure provides a way to measure emissions of reactive BVOCs because oxidants can be controlled."

**p. 10239, line 2.' . . .there must be rapid chemical transformation occurring.. ' chemical transformation of what?** Changed to "chemical reactions"

**Page 10243. The entire page is verbatim from your previous paper: page 19714 from Bouvier-Brown, et al.,2008. Methyl chavicol: characterization of its biogenic emission rate, abundance etc., Atmos. Chem. Phys. Discuss. 8, 197707-19741. Cite it instead of copying it.** We cited this paper and changed the text so that it summarizes the NOAA GC-MS measurements.

**Page 10261. spelling '3-carnene' should be 3-carene.** Corrected.

References:

Bauer et al., J. Geophys. Res., 105, 22123-22136, 2000.

Bouvier-Brown et al., J. Chromatogr. A, 1161, 113-120, 2007.

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