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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.

**Anonymous Referee #3**

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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.

Section 4.1.1 "The monterpene 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.

SPECIFIC COMMENTS

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

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?

Page 10241, lines 3-4. Are you using retention time/index along with single ion response to identify compounds?

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.

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±64%! This does not the reader much confidence in your ability to make an accurate measurement of methyl chavicol.

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°C is poor. For discussion of the effect of residual ozone on BVOC on Tenax see Arnts 2008, ES&T 42:7663-7669.

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.

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?

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Page 10249 last line. Should read: ÎŚ-bergamotne has an estimated longer lifetime. . .

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.

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.

Page 10250 line 11. “methyl chavicol dominated the newly measured ambient BVOC mixing ratios and mass” Table 4 shows $\beta$-pinene>3-carene>methyl chavicol and Figure 4B shows MT>MC.

Page 10250 line 19 refers to “Fig 5B”. There is no Figure 5 included.

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.

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.

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

Page 10258 Table 1. Why are the standard deviations not presented?

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.

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TECHNICAL CORRECTIONS

P. 10238, LINES 7-9. poor sentence structure

p. 10239, line 2.' . . .there must be rapid chemical transformation occurring.. ' chemical transformation of what?

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.

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

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

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