Atmos. Chem. Phys. Discuss., 12, C2926–C2929, 2012
www.atmos-chem-phys-discuss.net/12/C2926/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Diel cycles of isoprenoids in the emissions of Norway spruce, four Scots pine chemotypes, and in Boreal forest ambient air during HUMPPA-COPEC-2010" *by* N. Yassaa et al.

Anonymous Referee #2

Received and published: 24 May 2012

This is an interesting paper, not only looking at diurnal cycles of isoprenoids directly emitted from the trees and in the ambient air, but focusing on the patterns with respect to different chemotypes and the patterns of isoprenoid chirality. This study emphasizes the biological complexity that influences our atmosphere. Not only should we be cautious when scaling branch enclosure emissions to represent ambient emissions, but the synthetic pathways commonly modeled may produce compounds with different chirality. Chirality may not affect gas-phase chemistry, but there is evidence that it affects heterogeneous chemistry in the atmosphere. Chemotypes may even contribute

to the difference between measured and modeled OH reactivity.

I have some comments, mostly clarifications so that this paper better fits with the existing literature.

Abstract Lines 7-8: The authors mention 3 chemotypes (high, no, and intermediate), based on 3-carene, but use 4 chemotypes in the text. Line 15: "The average 3-carene emission rate" – is this for all trees, or just the high-emitter? Line 21: When mentioning "total ambient monoterpenes" measured, the authors should mention at what height above the canopy these measurements were made.

Introduction, Line 14: "present at moderate or low contents" – do the authors mean leaf content (liquid phase), emission rate (gas phase), or concentration?

Section 2.2, Line 25: emission measurements were made over one full diel cycle, but the figures show longer periods (3-5 cycles). Please clarify.

Section 2.2.1: Were the four branches from four different trees? When data in the table indicate N = 20, is that 20 samples on one tree? Chemotypes were only defined after the measurement data was analyzed, correct? If the authors had measured more trees, would they expect more than 4 chemotypes? At what point is it variety within a single chemotype versus two completely different chemotypes? This is also brought up in section 3.1.1. What differentiates chemotype 2 and 4, when Bäch et al. only used 3 chemotypes (pinene, carene, and intermediate)? Does the new chiral data delineate more chemotypes?

Section 2.2.2, Line 9-11: What compounds were present in the calibration gas standard? Were there any sesquiterpenes? Sesquiterpenes are typically difficult to store as a gas standard. If you didn't have sesquiterpenes in this standard mixture, how were they calibrated?

Section 2.3, Line 20: Was this 16-compound VOC standard the same as what was used to calibrate the SPME samples? If so, list the compounds in section 2.2.2 and

refer to that in 2.3.

Section 3.1.1 and 3.2: sesquiterpene emissions were low for most measurements. Is there any way that this due to the sampling protocol? How long was the tubing between the branch enclosure and the SPME static sampling chamber? Could there have been wall-loss in the tubing? The same could be asked for the ambient measurements. Since there are two different analytical methods used, how do they compare?

Section 3.1.1 The typical way of expression emissions is by fitting it to the existing algorithm (i.e. Guenther et al. JGR 1993) where there is a standard emission at 30 degrees Celsius and 1000 umol/m2/s. Why wasn't that used here?

Section 3.1.2 Lines 22-24: Could the authors elaborate on how their data showed a "change in the chemical composition" with increased temperature? Did the temperature change the amounts emitted or the proportion (thus distribution) of the compounds emitted? (For example, more volatile compounds had higher emission rates, but the others did not.) Line 28: Are the authors implying that only sesquiterpenes emission would increase? This may be the first field data showing increased emissions of sesquiterpenes at higher temperatures, but I believe many have predicted this previously. For example, Helmig et al. 2007 (ES&T) showed that the temperature-dependence factor (beta in the Guenther algorithm) is higher than that of monoterpenes for many pine trees. This would imply that as temperatures increase, the sesquiterpene emissions would increase at a faster rate.

Section 3.2.2 Lines 3-4: "as well as in the primary atmospheric oxidant OH by day" is an incomplete thought. Line 16: the "two peaks" of a temperature- and light-dependant compound has been seen many times in the ambient air (for example, Bouvier-Brown et al., 2009 ACP), even without the long boreal summer day. How does your data compliment or disagree with data in the literature?

Page 10444, Line 11: "enrichment" is the enrichment of the (-)-enantiomer, right? Please clarify.

Conclusions Lines 17-18: There is only one sentence for the diversity of chemical compositions, when most of the paper is discussing this issue. Reemphasize the evidence that brought the authors to this conclusion. One additional note for the importance of chirality – insects are stereo-selective, so the emission of specific chiral compounds has ecological impacts as well.

Minor typos: Introduction, Line 22: "BVOCs" instead of "BVOC" Introduction, Line 24: delete comma after "chemotype)" Section 3.2.1, Line 21: why is the "B" in "Biogenic" capitalized?

Figures: Fig 2: Maybe combine (a) and (b) because the same BVOCs are pictured in both. Figs 2-4: what are the units of PAR? Fig 3: Why are the x-axes different if this is a plot of the same branch? Fig 5: There is a lot going on here, but I can't see it very well. Maybe use an x-axis line for each plot to visually divide up the space. It might help to expand the a-pinenes and carene data. In addition, the names all run into each other in the y-axis label, but the authors could cut the "pptv" unit from each, since they are all the same, and put it in the caption. Fig 6: Why are these labeled (a) – (f) when these labels are not mentioned in the caption? Are they even necessary? Why are the x-axes different, when they all stretch from 0 to 24 hr? In addition, the font is very small on these figures. Fig 7: Separate the "/" mark in the legend because it was difficult to read. Fig 8: The "Diel cycle of (-)-enantiomer enrichment" – cut the "s" at the end of "enantiomer. It would also be useful to redefine what "enrichment" means, so the reader does not have to find it in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 10425, 2012.