Atmos. Chem. Phys. Discuss., 12, C4885–C4892, 2012
www.atmos-chem-phys-discuss.net/12/C4885/2012/

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.

N. Yassaa et al.

nyassaa@usthb.dz

Received and published: 20 July 2012

We are delighted with the positive and encouraging reviews by referee 2. The manuscript will be revised according to these comments as described in detail below. For clarity we transcribe each referee comment/suggestion, and then follow this with our answer and action.

Comment: Abstract Lines 7-8: The authors mention 3 chemotypes (high, no, and intermediate), based on 3-carene, but use 4 chemotypes in the text.

Reply: The classification into three main chemotypes was based on the paper by Bäck et al (Biogeosciences, 9, 689–702, doi:10.5194/bg-9-689-2012, 2012), where a large number of trees were classified based on their carene emissions (no-carene, high-carene and intermediate chemotypes). The four trees selected for this study cover all three chemotypes namely 1 high, 1 no and 2 intermediate trees.

Comment: Line 15: "The average 3-careneemission rate" – is this for all trees, or just the high-emitter?

Reply: This means the 3-carene chemotype or chemotype "3". To clarify this we have changed the sentence to read: The average 3-carene emission rate (from chemotype 3).

Comment: Line 21: When mentioning "total ambient monoterpenes" measured, the authors should mention at what height above the canopy these measurements were made.

Reply: The measurements were made at approximately 2–3 m above the canopy. This information has been given in section 2.3.

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

Reply: The text is corrected for greater clarity to: ...present at moderate or low fractions of the total emission.

Comment: 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.

Reply: The text is corrected to: The emission rates were measured hourly over several full diel cycles.

Comment: 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

ACPD

12, C4885–C4892, 2012

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 Bäck et al. only used 3 chemotypes (pinene, carene, and intermediate)? Does the new chiral data delineate more chemotypes?

Reply: The four branches were from four different trees, each showing the specific emission blend. N=20 is number of samples for a given tree. The study by Bäck et al (2012) shows that each tree can have individual emission patterns, however, the main differences are in the relative abundance of d-3-carene which we therefore use to define the three chemotypes. Tree 1 is clearly a no-carene chemotype, there are two intermediate chemotypes (2 and 4), and one high carene chemotype (3). We do not yet go so far as to define a new chemotype based on the enantiomers (although the potential is clearly there). Before defining further chemotypes based on these chiral compounds a larger number of trees should be screened and the changes in enantiomeric emissions as a function of plant age, stress, etc further examined. This information was done prior to the monoterpene classification of chemotypes.

Comment: Section 2.2.2, Line 9-11: What compounds were present in the calibration gas standard? Monoterpenes were calibrated a newly supplied compressed gas cylinder containing 16 VOC certified standard (NPL, UK) which included the separate enantiomers of several species. Were there any sesquiterpenes? Sesquiterpenes are typically difficult to storeas a gas standard. If you didn't have sesquiterpenes in this standard mixture, howwere they calibrated?

Reply: This information was indeed missing from the manuscript as also noted by reviewer 1. Sesquiterpenes have been quantified by introducing known amounts of diluted pure liquid sesquiterpene standard in cyclohexane into the SPME sampling chamber, similarly to N.C. Bouvier-Brown et al., 2007 . This is now clarified in the section 2.2.2. of the manuscript.

ACPD

12, C4885–C4892, 2012

Comment: 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.

Reply: SPME has been calibrated with the same calibration gas used for calibrating cartridges. This has been clarified in the text. New text in section 2.3:.... using the same calibration gas described in the previous section.

Comment: 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?

Reply: Sesquiterpenes have been measured only from branch enclosure chamber using SPME and not in ambient air employing on-line cartridge sampling system. The SPME sampling set-up for sesquiterpenes has been installed as close as possible (less than 2 m) to the branch enclosure chamber using Teflon tubes in order to avoid any wall-loss in the tubing. Furthermore, desorption of collected sesquiterpene on SPME fiber coating is achieved directly in the GC injector.

Comment: 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?

Reply: The referee is correct in that monoterpene emissions are indeed many times normalized to air temperature at 30°C with the well known temperature algorithm originating from Tingey et al. (1980) and Guenther et al. (2003). Normalization makes comparisons between measurements easier. However, this approach has evoked some rather important critics (e.g. Niinemets et al., 2011), one of the main questions being that the basal emission factor used for normalizing seems to be very variable in time

ACPD

12, C4885–C4892, 2012

and between species, and dependent on e.g. plant developmental stage. It was shown by Tarvainen et al. (2005) with Scots pine data from the same SMEAR II site, that both the basal emissions and the temperature coefficient can be defined separately for different seasons and also for different compounds, instead of using seasonally aggregated emission parameterizations. As was written in the introduction, the main aim in this study was to compare the mono- and sesquiterpene emissions from four Scots pine trees and one Norway spruce tree under field conditions during a mid-summer period. We feel that the important, qualitative differences in emissions between trees and their diel cycles are more clearly distinguishable with the emission rate data presented, without normalizing the values. Further, as the measurement period was exceptionally hot (see Williams et al., 2011), the daily maximum emissions actually are representing the T=30°C normalized values rather well (see e.g. Fig 2) and if necessary, these values can therefore be applied to models with rather good confidence. The referee also points out that conditions of measurements should be reported. We have reported both PAR and temperature variations in figures 2-3, and the overall conditions during the campaign are reported in a companion paper by Williams et al. (2011).

To clarify this, we have added a sentence in chapter 2.2. as follows: '....where C2 and C1 were the concentrations (μg l$-$1) in the outgoing air and in the inlet air, respectively, and F was the flow rate (ls$-$1) into the enclosure. The dry weight (g) of 5 the biomass (m) was determined by drying the needles at 75 °C until consistent weight was achieved. The results are presented as true emission rates without temperature normalization, however the temperatures during measurements are given in the figures to enable the comparison with literature values.

Comment: 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 sesquiter-

ACPD

12, C4885–C4892, 2012

penes 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.

Reply: We thank the reviewer for this constructive comment and incorporate it into the revised manuscript. "It has been noted previously that the temperature dependence factor for sesquiterpenes (beta in the Guenther emission algorithm) is higher than that of monoterpenes for many pine trees (Helmig et al. 2007). Thus as temperatures increase the sesquiterpene emissions would increase at a faster rate. The change in composition noted at high temperature may well reflect this response.

Comment: 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?

Reply: We thank the reviewer for drawing our attention closer to this phenomena. We now note that multiple isoprene peaks have been noted in the literature and that they could be caused by transport or post illumination bursts. Appropriate citations are now added to the text. New text: Close inspection of the median isoprene diel profiles shows the presence of three peaks. In addition to the peak centred around 12:00 there are two peaks (07:00 and 19:00) for the temperature- and light-dependant compound isoprene. Double peaks for isoprene have been seen at other sites and usually the second peak occurs late in the afternoon (e.g. Dreyfus et al. JGR 2002). In some cases such peaks have been attributed to transport from upwind isoprene emitting regions. Another possible explanation is that isoprene is produced in a post-illumination pulse as small reservoirs of the compound or precursors are vented or processed (e.g. Monson

ACPD
12, C4885–C4892, 2012

et al. 1991 Plant, Cell and Environment (1991) 14, 517-523, Li et al. (2011).Plant Physiology February 2011 vol. 155 no. 2 1037-1046). However, this latter process would not explain the early morning peak. In this study we suggest that the multiple peaks are caused by variation in the boundary layer height and the unusually long daylight time in the boreal summer. Illumination of the tree by the early morning sun (sunrise 04:00) may instigate isoprene emission before the rise of the boundary layer. Likewise under these conditions the sunlight may persist after the boundary layer has formed in the evening. In both cases emissions would occur into a shallow boundary layer and give rise to a peak in concentration. The larger size of the late afternoon peak would then be explained by the larger average temperature at this time compared to the early morning.

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

Reply: The text is corrected to the enrichment of the (-)-enantiomer.

Comment: 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.

Reply: Revised text in conclusions: ‘The unusual high boreal summer temperatures were accompanied by relatively high fluxes of terpenes and greater diversity in the emitted chemical compositions. Since insects and plants discriminate and respond to chiral compounds (e.g. Tumlinson, 1988), changing the emission composition may influence the effectiveness of insect/plant or plant/plant communication in a future warmer climate conditions.

Comment: 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”

ACPD

12, C4885–C4892, 2012

in “Biogenic” capitalized?

Reply: All noted minor typos are corrected in the new version of the manuscript.

Comment: 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.

Reply: All figures and their captions are improved in the new version of the manuscript as requested.

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