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Interactive Comment

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 #1

Received and published: 22 May 2012

General Comments:

This article reports on emission and ambient air measurements of monoterpenes and sesquiterpenes at the Hyytiälä research site. The uniqueness of this research lies in the determination of monoterpene enantromers in emission samples and ambient air, as well as comparing the signatures that were observed in these two sample groups. The remainder of the described work does not present much that has not been published in quite a number of previous publications.

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There are three rather substantial weaknesses in this manuscript:

- 1. The comparison of emission rates (from enclosure measurements) and ambient air sampling is one of the major objectives of this paper. Those two measurements were conducted using two different analytical techniques. SPME was used for the enclosure sample collection, and enrichment of BVOC on solid adsorbents was used for the ambient measurements. Unfortunately this work does not provide any insight into what the comparability and error margins of both of these measurements are. Ideally, both measurements should be conducted side by side for the same sample matrix on a subset of samples (i.e. emission samples) and data obtained from these parallel measurements be compared and evaluated. Without this information the reader has no way of judging if the differences seen in the two sample sets are due to analytical biases or to real differences in the sample composition.
- 2. The vast majority of BVOC emission studies either normalize measured emission to standardized emission rates (i.e. at 30 deg C and 1000 micromol m-2s-1), or to the least, show under which concrete conditions reported data points were obtained (Ortega and Helmig 2008) (Niinemets et al. 2011). Unfortunately, this paper does not follow any of these recommendations. Consequently, the presented data can not readily be compared with other previous related work. Without normalization of the data these measurements are also of comparatively low value for BVOC emissions modeling.
- 3. The experimental description does not specify if any steps for mitigating interferences from ozone in the BVOC enrichment for the GC/MS analysis were considered in the ambient air measurements. Unfortunately, experimental details provided in this section are somewhat slim. Similarly, none of the three listed references (Song et al. 2011), (Eerdekens et al. 2009), and (Williams et al. 2007) provide any of these details. This solidifies the impression that no measures for selective ozone removal were used. By now there is a rather rich body of literature that has shown the importance of addressing this important issue and it is worrisome that apparently these authors did not

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follow those recommendations ((Arnts 2008); (Pollmann et al. 2005); and references therein). Due to this omission this reviewer believes that presented ambient air BVOC determinations can not be considered publishable data.

Other Specific Comments:

It should be clearly stated in the abstract if emission rates are actually observed (need to give temperature range) emission rates or temperature and light normalized data.

Page 10432/line 11: 9.6 cm i.d. sampling line? Probably, the unit here should be mm?

10432/1: Using helium for simulating blanks is not a very convincing method. Typically, researchers use 'zero air' containing realistic levels of moisture. This is particularly important when working with solid adsorbent focusing systems as artifacts can be produced from interaction of oxygen and water with solid adsorbent polymers.

10432/1: Did the standard contain the particular compounds that were analyzed? The stability of monterpenes in compressed gas cylinders is quite a debated issue (Rhoderick 2010). How old was the standard when it was used? Is there evidence that the standard had been stable since its preparation? How were SQT quantified? This reviewer is not aware of compressed gas cylinder calibration standards for this compound class.

10432/12: Please give the specific temperature for the 'cold' enrichment trap.

10432/23: Please give specific regression results instead of using the rather subjective term "good linear dependency".

10432/16: Should Song et al., 2012, be Song et al., 2011?

10437/22: The sentence "..our data shows the first evidence of induced sesquiterpene emissions from Scots pine at field conditions due to high temperature" is quite an overstatement. There have been a number of other previous studies that, in much more detail, have shown the steep response of SQT emissions to temperature ((Staudt and

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Lhoutellier 2011) and references therein).

10440: The discussion on the diel cycles does not present or touch anything that has not been published in previous literature.

10451: The term 'terpenoid' may be a better choice than 'isoprenoid'?

10453: Fonts used in figures 2, 3, 4, 5, 6, 7, 8 for legends and titles are so small and blurry that I could not read and evaluate these figures.

References

Arnts, R.R. 2008. Reduction of Biogenic VOC Sampling Losses from Ozone via trans-2-Butene Addition. Environmental Science & Technology. 42:7663-7669.

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Niinemets, U., U. Kuhn, P.C. Harley, M. Staudt, A. Arneth, A. Cescatti, P. Ciccioli, L. Copolovici, C. Geron, A. Guenther, J. Kesselmeier, M.T. Lerdau, R.K. Monson and J. Penuelas 2011. Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols. Biogeosciences. 8:2209-2246.

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Song, W., J. Williams, N. Yassaa, M. Martinez, J.A.A. Carnero, P.J. Hidalgo, H. Bozem and J. Lelieveld 2011. Winter and summer characterization of biogenic enantiomeric monoterpenes and anthropogenic BTEX compounds at a Mediterranean Stone Pine forest site. Journal of Atmospheric Chemistry. 68:233-250.

Staudt, M. and L. Lhoutellier 2011. Monoterpene and sesquiterpene emissions from Quercus coccifera exhibit interacting responses to light and temperature. Biogeosciences, 8:2757-2771.

Williams, J., N. Yassaa, S. Bartenbach and J. Lelieveld 2007. Mirror image hydrocarbons from Tropical and Boreal forests. Atmospheric Chemistry and Physics. 7:973-980.

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