

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.

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The authors wish to thank the reviewer for the comments, suggestions and appreciations. 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: The comparison of emission rates (from enclosure measurements) and ambient air sampling is one of the major objectives of this paper. Those two measure-

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ments 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.

Reply: The comparison of emission rates (from enclosure measurements) and ambient air sampling was not one of the objective of the present paper as this was in fact the major objective of our previous paper published in Atmospheric Measurement Techniques (See Yassaa et al., Atmos. Meas. Techn., 3, 1615-1627, 2010) where the results from SPME measurements in both plant emission and ambient air compared well with cartridge derived measurements. The optimised and validated SPME method used here also allows measurement of sesquiterpenes in direct plant emission which is not straightforward with cartridges. This method has therefore extensively tested prior to field use from plant chamber measurement of mono- and sesquiterpenes and on-line cartridge system for ambient measurement of isoprene and monoterpenes. We will emphasize this point further in the revised manuscript.

Comment: 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.

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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 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 ($\mu\text{g l}^{-1}$) in the outgoing air and in the inlet air, respectively, and F was the flow rate (l s^{-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.

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Comment: 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), (Eerdeken 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 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 cannot be considered publishable data.

Reply: The same ozone scrubbers described by Pollmann et al. (2005) have been used for both plant chamber and ambient air measurements, it was indeed omitted in this and previous papers. We thank the reviewer for pointing out this oversight. We now insert the following text giving details of the procedure used "Ozone was removed from the inlet air using MnO₂-coated glass filter (Pollmann et al., 2005).

Comment: 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.

Reply: The following sentence was added in the abstract: Daily maximum temperatures varied between 20 and 35° C during the measurements.

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

Reply: Correct, the inlet was 3/8 inch (9.6mm), text changed to "9.6mm sampling line"

Comment: 10432/1: Using helium for simulating blanks is not a very convincing method. Typically, researchers use 'zero air' containing realistic levels of moisture.

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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.

Reply: The use of helium did not induce any artefacts for the compounds measured during the campaign.

Comment: 10432/1: Did the standard contain the particular compounds that were analyzed? The stability of monoterpenes 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?

Reply: This is a good point and an issue that we only became aware of following our measurement campaign. Fortunately the compressed gas standard cylinder containing the main monitored monoterpenes was delivered by NPL directly to the field site at the start of the campaign thus minimising any stability issues. Moreover, stability tests carried out by NPL in the development of this standard on a range of monoterpenes revealed generally good stability with only sabinene showing unacceptable variation.

Comment: How were SQT quantified? This reviewer is not aware of compressed gas cylinder calibration standards for this compound class.

Reply: 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, *J. Chromatography A*, 1161, 113-120. This is now clarified in the section 2.2.2. of the manuscript.

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

Reply: The cold enrichment trap was held at 10°C.

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

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Reply: The regression results were close to 0.99 for most of measured monoterpenes. This is now clarified in the manuscript.

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

Reply: This is now corrected.

Comment: 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 Lhoutellier 2011) and references therein).

Reply: This has been reformulated to: "...our data confirms the previously noted strong temperature dependency of sesquiterpene emissions from Scots pine in field conditions (e.g. Staudt and Lhoutellier 2011, Jardine et al 2010).

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

Reply: The diel cycles showed how the composition (in particular the enantiomeric) and the concentrations of emitted terpenoids were affected in the exceptionally warm boreal summer. This is the first time that ambient and cuvette data of enantiomeric terpenoids have been reported together and certainly under such extreme conditions (100 year temperature maximum). The general behaviour of terpenoid emission is indeed consistent with current literature but the referenced explanation of the achiral diel behaviour needs to be made here for completeness and to show that the individual enantiomers exhibit similar pattern (sentence added for this see below). Curiously few groups have explored the behaviour of the terpenoid enantiomers, most preferring to report the lumped sum of the two enantiomeric forms. This we find surprising since the analytical effort and cost is the same and the potential for discovering links to between leaf and atmospheric processes are high. We therefore respectfully disagree with the

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reviewer on this point. New text in section 3.2.2 – “It is noted that the two enantiomers of alpha-pinene appear to show very similar diel cycles, although their ratio changes distinctly as is discussed in the following section 3.2.3”

Comment: 10451: The term ‘terpenoid’ may be a better choice than ‘isoprenoid’?

Reply: Now corrected.

Comment: 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.

Reply: Now improved.

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