

# ***Interactive comment on “Sesquiterpenes identified as key species for atmospheric chemistry in boreal forest by terpenoid and OVOC measurements” by Heidi Hellén et al.***

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Anonymous Referee #1

Thank you for the very good comments. We have considered them and we have improved our manuscript based on them as explained in more detail here:

1. A more detailed comparison with measurements already performed at the site should be included. During the HUMPPA-COPEC 2010 campaign, for example, measurements and fluxes of VOCs were performed with GC and enclosed to the trees branches and the results have been published (Eerdekens et al., 2009; Yassaa et al.,

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2012; Hens et al., 2014). Putting the measurements from this study in the context of what was previously observed at the same site would strengthen the conclusion of the manuscript. In addition, the results of the reactivity of the different VOC classes should be compared with a modelling study investigating the reactivity of VOC towards OH radicals in the specific site (Mogensen et al., 2011). A more structured comparison with previous measurements would be very interesting and could be included as a separate section (instead of scattered around the different compounds as it is at the moment) by possibly reducing the intercomparison of all species with temperature which occupies a large fraction of the discussion and could be partly moved to the supplementary information.

-There are only very few earlier measurements at SMEARII of the compounds we have measured. Earlier measurements include PTR-MS monoterpene sum and some isoprene measurements (Eerdekens et al. 2009, Ruuskanen et al., 2009, Kontkanen et al. 2016 and Lappalainen et al. 2008). Hens et al., presented time series of monoterpene measurements, but there were no means or medians calculated to compare with. Yassaa et al. (2012) presented median values and diurnal cycles of isoprene, carene and  $\alpha$ - and  $\beta$ -pinene in mid July to mid August. We added a supplement Table (S3) on these earlier measurements and more discussion on monoterpenes to the second paragraph of the section 3.1.1 and on isoprene to the section 3.1.3.

-We also added discussion on the study of Mogensen et al. (2011) to the manuscript into section 3.3.1

2. For the OH radical concentration determination, the authors refer to a publication by Petäjä et al. (2009). Unfortunately, this publication is not listed in the references but assuming they refer to the ACP paper, in that work there is no proxy described for the OH radical concentration. Proxies are given to determine the H<sub>2</sub>SO<sub>4</sub> concentration. Therefore an explanation on how the OH radical concentration is calculated is needed. In addition, although it is true that there is a direct correlation between OH radical concentration and photolysis of O<sub>3</sub>, a previous study which evaluated the OH radical

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budget at the same site (Hens et al., 2014) highlighted how the production from photolysis of ozone was actually marginal compared to other production paths. An error analysis study on the determination of the OH radical should be included. For the NO<sub>3</sub> radical concentration, a description of the formula is given (could be explicitly written as formula) but there is confusion regarding the value plotted in Fig. 3. The units for both OH and NO<sub>3</sub> radical concentrations are cm<sup>-3</sup> s<sup>-1</sup> which is the unit for a production rate. Assuming the plots is showing concentrations (and if this is the case, please fix the unit on the axis), is the NO<sub>3</sub> concentration in the order of 0.5 pptv? How does it compare with measurement of NO<sub>3</sub> radicals performed at the same site (Liebmann et al., 2018)?

-Description on how OH radical concentration was calculated was added as well as reference to Rohrer and Berresheim (2006)

-Reference Petäjä et al. (2009) was added to the reference list

-Incorrect units of OH and NO<sub>3</sub> mixing ratios were corrected in Fig 3.

-Measured NO<sub>3</sub> in Liebmann et al (2018) was below the detection limit (1.3 pptv) all the time during their measurements in September 2016. Mean of calculated NO<sub>3</sub> in September during our measurements was 0.12 pptv, which is also well-below their detection limit. We observed our 30 minute averages exceeding their detection limit only three times (N=220) during September.

- We think that error analysis of OH calculations should have been conducted for example in the publication of Petäjä et al. (2009), and is beyond the scope of our study. However, we added to the manuscript a comment on measured OH radical concentrations being clearly lower than estimated by this method as shown by Petäjä et al. (2009).

3. All the plots would be easier to follow if the x and y axis would be at the bottom and on the left of the figure, respectively (as for example figure 7b). Right now they

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are most of the time somehow in the figure making the reading of the numbers on the axis a bit difficult. The notation logarithm should also been added to the axis when necessary. Do the fit performed take into account the errors on both concentrations and temperatures (York fit, (York et al., 2004))? As temperature measurements are relative accurate, the error on the x-axis could be ignored but the error on the concentration of the different species should be taken into account for a proper analysis.

-The axis of the figures were corrected and notes on the logarithmic scales were added. The values in the figure were not logarithms of the concentrations, only the scale in the y-axis was logarithmic. We added a note to the figure captions, whenever logarithmic axes were used.

-We now added uncertainties of the concentration values shown in the plots as error bars. Uncertainties were calculated as combined uncertainty of the measurement points using the propagation method. Measurement uncertainty was calculated as combined uncertainty given by the precision and systematic errors (calibration standard preparation and sampling flow).

4. The manuscript, before publication, requires some careful language check. In particular articles are missing and the structure of the sentences is often confusing. Some examples are listed in the technical comments but they do not cover the entire manuscript.

- A language check was done by a native speaker.

Technical comments: Title. Suggest “Long-term measurements of VOCs highlight the importance of sesquiterpenes for the atmospheric chemistry of a boreal forest”.

-This is a good suggestion. We changed the title accordingly.

Page 2, Line 8. Citation needed at the end of “. . .forest”.

-A reference to Guenther et al. (2012) was added

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Page 2, Line 11. Citations needed at the end of “. . .studies”.

-A reference to Mellouki et al. (2015) was added

Page 2, Line 14. More citations needed as examples of unmeasured BVOC.

-As stated in the review article by Yang et al. (2016) as well as in Sinha et al. (2010), Nölscher et al. (2012), and Praplan et al. (2018), cited in the manuscript, these unmeasured VOCs are not known and unmeasured fraction of BVOCs is based on the studies of total reactivity.

Page 2, Line 14. “. . .Therefore a better characterization of. . .”

-This has been corrected.

Page 2, Line 17. “. . .Once emitted, BVOCs readily. . .”

- This has been corrected.

Page 2, Line 20. Suggest adding the word paths after reactions at the end of the sentence.

- This has been corrected.

Page 2, Line 21. The expression “vary a lot” is for the spoken language. Suggest “. . .terpenoids are very different. . .”

- This has been corrected.

Page 2, Line 22. “. . . essential to understand biosphere-atmosphere interactions. . .”

- This has been corrected.

Page 2, Line 34. “. . .less sensitive instruments. . .”

- This has been corrected.

Page 3, Line 1. “. . .to be emitted by the pine trees. . .”

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- This has been corrected.

Page 3, Line 4. The word lots can be substituted with the word many.

- This has been corrected.

Page 3, Line 16. “. . .and 2016 in a boreal forest at the SMEAR II. . .”

- This has been corrected.

Page 4, Line 16. “. . .in situ thermal-desorption gas. . .”

- This has been corrected.

Page 4, Line 24. A small description of the heated inlet, although already described in details in another publication, would be beneficial to confirm the ability of the system to measure sesquiterpenes.

- A more complete description of ozone removal was added.

Page 4, Line 32. Remove the hooks for internal standard.

- This has been corrected.

Page 5, Line 3. It is specified that an extra flow of 2.2 L min<sup>-1</sup> was used. There is no indication of the flow drawn by the GC-MS2 (probably 1 L min<sup>-1</sup> ?).

- The sampling flow of 30 ml/min is mentioned a couple of sentences earlier in the sampling description

Page 5, Line 14. “. . .This method has been. . .”

- This has been corrected.

Page 5, Line 16. “. . .A similar behavior. . .”

- This has been corrected.

Page 5, Line 17. “. . .isomerization to be reproducible. . .”

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- This has been corrected.

Page 5, Lines 18-20. Sentence starting with “In our tests” and ending with “tube standards” is not clear and needs rephrasing.

- This has been rephrased.

Page 5, Line 20. “. . . Interconversion/degradation was not observed with the two other GC-MS used within this study. . .”.

- This has been corrected.

Page 5, Line 33. “What is identified by the authors as unknown sesquiterpenes? For which known sesquiterpenes was the instrument calibrated? C4

- The sentence ‘Calibration solutions contained all individual studied compounds except for the SQTs there were only longicycene,  $\beta$ -farenese,  $\beta$ -caryphyllene and  $\alpha$ -humulene.’ was added to the method description.

Page 6, Line 19. There are way more recent studies (compared to a study from 1994) on degradation of monoterpenes and products yields which should be considered for the calculation of PR.

- More studies are discussed in the results section and therefore reference to Hakola et al. (1994) was removed. There are several recent studies available on reactions of MTs, but to our knowledge, yields for the compounds we studied (nopinone and 4-AMCH) are not included. Especially for 4-AMCH, very few studies with yields are available.

Page 6, Line 30. It would be beneficial to have a little bit of background information on how the software derives rate coefficients for unknown VOC. Also, a list with all the VOCs species for which a derived rate coefficient was used (and the used rate coefficient) is needed.

- We use the ChemiSpider’s implementation of the software available online

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(www.chemspider.com). Description of this was corrected to the manuscript and the list of the used reaction rate coefficients was added as supplementary table S1. .

Page 7, Line 15. The dependency of OH radical concentrations from UVB radiation was firstly showed by Rohrer and Berresheim (2006).

- More information on the calculation of OH mixing ratios as well as this reference were added to the manuscript.

Page 9, Line 24. Please add the reference to measurements performed during the HUMPPA-COPEC campaign 2010 at the same site where monoterpenes were also measured (see general comment 1).

- Our purpose here was to discuss other long-term measurements and therefore the sentence was rephrased to show this more clearly. However, HUMPPA-COPEC measurements are also referred now in the sections 3.1.1 and 3.1.3.

Page 10, Line 9. “. . .-pinene showed the highest concentration of the measured MT. . .”

-This has been corrected.

Page 10, Line 25. Figure S1a) does not have any correlation plot but the mean diurnal variation and figure S1b) does not show any correlation factor equal to 0.85.

- The reference to Figure S1a) was removed.

Page 11, Line 2. “. . .Concentrations of SQTs did not increased during the sawmill episode in contrast with what observed for MTs. . .”. This is a suggestion of what the meaning of the sentence could be.

-This has been corrected.

Page 11, Line 5. “. . .-caryophyllene showed the highest concentrations among the measured SQTs followed by longicylene, -farnesene and 4 unidentified SQTs

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detected only in the summer months (List of months). . .”

- This has been corrected.

Page 11, Line 8. A new study from the Amazonia forest (Bourtsoukidis et al., 2018) also shows large emissions of SQTs from soil.

- This has been added.

Page 11, Line 10. “. . .\_-farnesene, which was also detected in local. . .”

- This has been corrected.

Page 11, Line 15. Same point as for Page 10, Line 25.

- The reference to Figure S1a) was removed.

Page 11, Lines 16-17. The meaning of this sentence is not very clear. It is normal that sink terms (as much as production terms) will affect the concentration of a certain species. So what is the point the author is trying to make here?

- Based on the modelling study of Zhou et al. (2017), the dilution due to mixing has a much stronger effect on local MT concentrations than the chemical sink. For SQTs, the chemical sink is also important during the day and therefore the relative diurnal variation of SQTs was stronger than for MTs. We clarified this in the manuscript

Page 12, Line 9. “. . .but monthly averages of MACR. . .”

- This has been corrected.

Page 12, Line 10. The possible anthropogenic origin of MACR should be discussed in more details. One paper is cited which, interestingly, suggests that a large source of MVK and MACR comes from car traffic. Would this be a reasonable source for the site? Are there more studies on anthropogenic sources for MACR? Why was MVK not measured?

- MVK was not quantified due to a lack of calibration standard and low concentrations.

Page 12, Line 18. “. . .During the summer month its concentration was. . .”.

- This has been corrected.

Page 12, Line 20. Please add the work by Kaminski et al. (2017).

- This has been added.

Page 12, Lines 20-21. What is the message of the sentence starting with “Further reactions. . .”? Do the authors want to compare the yields and discuss possible differences between different studies?

- This sentence was removed.

Page 17, Line 21. “. . .BVOCs correlates exponentially with temperature. . .”.

- This has been corrected.

Page 18, Line 3. “. . .The high correlation with temperature observed indicates that temperature. . .”

- This has been corrected.

Page 18, Line 22. The linalool is missing from the legend of figure S2b) and/or the data for bornylacetate are missing.

- Linalool was added to the legend.

Page 19, Line 2. As most of the measured sesquiterpenes consists of  $\alpha$ -caryophyllene, it is not surprising that the sum of SQTs shows a high correlation with temperature. . . Please use the greek letter (and not b) to label  $\alpha$ -farnesene and  $\alpha$ -caryophyllene in the figures.

- This sentence and the corresponding figures were corrected.

Page 20, Lines 5-7. A little bit more discussion on the observed better correlation observed between temperature only and isoprene compared to temperature and light

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is needed as this is in contrast with what observed previously.

- We expanded the discussion on the significance of this observation. Due to the low concentrations and only small difference in correlations, we cannot still make the conclusions that concentrations would be only temperature driven..

Page 20, Last paragraph. This concept was already discussed previously and, as there is no additional discussion about possible anthropogenic origins or how this is reasonable for such a remote site, it does not add anything from where it was previously discussed.

- The sentence on the anthropogenic origin was deleted.

Page 22, Lines 2-6. The points made in this paragraph would probably not be so strong once a proper error analysis is introduced in the fit results. Though if, for example, a larger than expect concentration of MTs is observed in November and this is tentatively explained by anthropogenic origin of the monoterpenes, a more detailed discussion on which type of anthropogenic sources would produce which monoterpenes is needed.

- The word 'anthropogenic' was changed to 'close-by sawmill' to make the sentence more understandable. These sawmill emissions have been discussed in the manuscript for example in section 3.1.1.

- The sentence 'Then MT sum was correlating (Figure S7) a bit better with soil humus layer temperature ( $R^2=0.87$ ) than with ambient temperature ( $R^2=0.80$ ), which also indicates the soil related sources.' and figure S7 were removed since this small difference is not significant.

- As now shown by the Figure 5b, high values are just within the measurement uncertainty. This is now mentioned in the manuscript.

Page 23, Line 20. Please use `_` instead of `a`.

- This has been corrected.

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Page 23, Line 21. Figure 7 does not seem to depict the results obtained when using equation 10 but more when using equation 11. It would be interesting to see how the proxies developed in this study compare with measurement of VOCs from previous studies at the same site.

- The reference to equation 10 was corrected in Figure 5.

- We think that this kind of comparison would be of interest for a complete different manuscript, where different proxies and data sets could be compared properly. It would need the original datasets to get the 24 hour means from 8:00 to 8:00 and mixing layer height data for diurnal variations. LIDAR measurements have not been available earlier at SMEARII, which increases the difficulty of such comparison. In addition most of the earlier studies are only from short campaigns and would contain only very few 24-hour or monthly points.

Page 24, First 2 paragraphs. The addition of a table which includes the used rate coefficient for the different SQTs and MTs vs OH radicals, O<sub>3</sub> and NO<sub>3</sub> radicals would be beneficial for this section. The authors explain that SQTs have the largest contributions to the O<sub>3</sub> reactivity despite the fact their concentration is ~ 50 times lower than the concentration of MTs. This is not surprising as the rate coefficient of  $\alpha$ -caryophyllene with O<sub>3</sub> ( $\sim 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ ) is up to 3 order of magnitude faster than the rate with the main MTs measured at the site ( $\alpha$ -pinene,  $9.4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ ,  $\beta$ -pinene,  $1.9 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ , and carene,  $4.8 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ ). Similarly, as the rate coefficient with OH for different MTs and SQTs only ranges less than one order of magnitude, it is expected that MTs, as they are present in larger concentrations, dominate the OH reactivity. The point being, it is not much surprising, that the SQTs dominates the O<sub>3</sub> reactivity but rather it is important to underline the large absolute concentration of SQTs observed.

- We added a table of used rate coefficients to the Supplementary Material (Table S1). Our main point here is that we are now able to measure also the concentrations of SQTs, but nevertheless, we think that by using these reactivities, we can show more

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clearly that even these low concentrations of SQTs are very important for the local atmospheric chemistry. This is not directly seen by simply comparing MT and SQT concentration levels.

Page 25, Lines 5-6. Here it is a similar concept as before. Limonene and terpinolene both have relatively fast rate coefficient with OH radicals and O<sub>3</sub> therefore, despite lower concentrations, they can have a large impact in the formation of secondary products.

- We rephrased the sentence.

Page 26, Line 29. Was the concentration of SQTs 30 or 50 times lower than the one of MTs? Anyway, as their reactivity depends on the product of concentration and rate coefficient, the sentence should be rephrase highlighting that due to the very fast rate coefficient of O<sub>3</sub> with SQTs, a relatively (compared for example to monoterpenes) small concentration of SQTs can have a large impact on O<sub>3</sub> deposition.

- SQT concentration was corrected to '50 times lower than MTs'.

- The sentence was rephrased.

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