Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-399-RC1, 2018

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 12 June 2018

This study focuses on the measurement of VOCs (speciated monoterpenes and sequiterpenes and oxygenated species) performed for a period of two years in a Boreal forest. The measured data are compared with temperature to highlights trends and derive simple proxies to estimate the VOC concentrations. In addition, by using O3 data and proxies to estimate OH and NO3 radical concentrations, the reactivity of each class of compounds is calculated together with production rate of oxidation products.

This work contains a large amount of data and measurements of speciated sesquiterpens which are extremely sparse and limited. The manuscript is suitable for publication in ACP after the authors have considered the following points:

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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., 2012; Hens et al., 2014). Putting the measurements from this study in the contest 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.

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 proxie described for the OH radical concentration. Proxies are given to determine the H2SO4 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 O3, a previous study which evaluated the OH radical 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 NO3 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 NO3 radical concentrations are cm-3 s-1 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 NO3 concentration in the order of 0.5 pptv? How does it

compare with measurement of NO3 radicals performed at the same site (Liebmann et al., 2018)?

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 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.

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.

Technical comments:

Title. Suggest "Long-term measurements of VOCs highlight the importance of sesquiterpenes for the atmospheric chemistry of a boreal forest".

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

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

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

Page 2, Line 14. "...Therefore a better characterization of..."

Page 2, Line 17. "...Once emitted, BVOCs readily..."

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

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

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

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

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

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

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

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

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.

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

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

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

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

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

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

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

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

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.

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.

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

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).

Page 10, Line 9. "...α-pinene showed the highest concentration of the measured MT..."

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.

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.

Page 11, Line 5. "...β-caryophyllene showed the highest concentrations among the measured SQTs followed by longicylene, β-farnesene and 4 unidentified SQTs detected only in the summer months (List of months)..."

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

Page 11, Line 10. "...β-farnesene, which was also detected in local..."

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

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?

Page 12, Line 9. "...but monthly averages of MACR..."

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?

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

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

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?

Page 17, Line 21. "...BVOCs correlates exponentially with temperature...".

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

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

Page 19, Line 2. As most of the measured sesquiterpenes consists of β-caryophillene, 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 β-farnesene and β-caryophyllene in the figures.

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

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.

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.

Page 23, Line 20. Please use α instead of a.

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.

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, O3 and NO3 radicals would be beneficial for this section. The authors explain that SQTs have the largest contributions to the O3 reactivity despite the fact their concentration is $\sim$ 50 times lower than the concentratrion of MTs. This is not surprising as the rate coefficient of β-caryophyllene with O3 ($\sim$ 1e-14 cm3 s-1) is up to 3 order of magnitude faster than the rate with the main MTs measured at the site (α-pinene, 9.4e-17 cm3 s-1, β-pinene, 1.9e-17 cm3 s-1, and carene, 4.8e-17 cm3 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,

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it is not much surprising, that the SQTs dominates the O3 reactivity but rather it is important to underline the large absolute concentration of SQTs observed.

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 O3 therefore, despite lower concentrations, they can have a large impact in the formation of secondary products.

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 O3 with SQTs, a relatively (compared for example to monoterpenes) small concentration of SQTs can have a large impact on O3 deposition.

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