

# ***Interactive comment on “OH reactivity from different tree species: Investigating the missing reactivity in a boreal forest” by Arnaud P. Praplan et al.***

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We would like to first thank the referee for acknowledging the importance of our study. We are grateful for their comments, which help us clarify the way we presented and discussed our results. We believe that the revised manuscript can address the referee's concerns and has improved due to the referee's input. In the following, the referee's comments are marked in italics and our answers are written with the regular font.

*The manuscript “OH reactivity from different tree species: Investigating the missing reactivity in a boreal forest” by Praplan et al. presents results of emission measurements of VOC and the total OH reactivity from three typical boreal tree species over*

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*a time period from May to September. The variations in the total OH reactivity emissions (TOHRE) between tree species, seasons, temperature and light are discussed. A comparison to individually detected VOC emissions, by multiplying the measured concentrations with their reaction rates with OH and summing up, revealed a highly variable missing gap. This gap shows that the direct tree emissions were not fully determined by the typically applied methods such as gas chromatography.*

*The general topic further fuels the discussion of where the missing OH reactivity in forests originates from and is of high interest for understanding the processes of both biogenic emissions and atmospheric chemistry. The dataset seems of high quality, is presented thoroughly and discussed in many aspects. I find that especially an extended discussion about uncertainties and detection limits could improve the current state of the manuscript significantly. Therefore, I recommend this manuscript for publication after addressing the following specific comments:*

*Specific comments:*

*This manuscript has a focus on measurements of total OH reactivity emissions from three different boreal tree species. I wonder why the key-word “emissions” is not part of the title.*

It is indeed only implicit in the original title of the manuscript that we are investigating emissions. The revised manuscript's title now states it explicitly: “OH reactivity from the emissions of three different tree species: Investigating the missing reactivity in a boreal forest”.

*p.2, l.29-35: In this paragraph the concept of total OH reactivity is introduced from a historical point of view. It is described that the motivation to determine the total OH reactivity is the inaccessibility of “OH sinks in the model”. For the reader to understand the following paragraphs, an accurate definition of the total OH reactivity would be needed here.*

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We edited this paragraph to define total OH reactivity as the “total OH loss rate”. We also state that it can be seen as the inverse of OH lifetime, meaning that high OH reactivity values translate into short atmospheric OH lifetimes (see also comment from Anonymous Referee 2).

*p.2, l. 47: This paragraph introduces previous results of measurements of the total OH reactivity to the reader. It is said that the studies of Sinha et al. (2010) and Nölscher et al. (2012) find missing reactivity in the boreal forest. Then you refer to Praplan et al. (2019) who “recently demonstrated that including modelled oxidation products of VOCs that are not measured is not sufficient to explain the missing reactivity at the site”. Please, make clear what site you are talking about here.*

We have clarified in the revised manuscript that all these studies have been performed at the SMEAR II boreal forest station in Hyytiälä, Finland.

*p.2, l.53/54: The study of Nölscher et al. (2013) examined TOHRE of Norway Spruce, not Scots Pine.*

We regret to have let this mistake in the introduction. It has been corrected in the revised manuscript. We, however, discussed correctly the results of Nölscher et al. (2013) for Norway spruce in the discussion section and cited it in the appropriate context in the abstract.

*p.3, l.73: In the section 2.2 the studied tree species are described. Seedlings of three boreal tree species were chosen for enclosing branches and detecting the branch emissions. How representative are the emissions of seedling? How comparable are the emissions of a “young” tree with an “old-grown” one?*

We perfectly understand the concerns of the referee. However, we do not claim that our study yields results that can be upscaled immediately. It is a part of a more global conversation regarding BVOCs emissions in the boreal forest.

While emissions vary with the seasons, the environmental conditions and even from

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tree to tree of the same species (chemotypes; Bäck et al., 2012), often studies made of various trees (e.g. age, location) of the same species yield similar results. Also in our study we cite earlier work where similar emission patterns were measured in the discussion section.

The choice of using seedlings was mostly practical as it allowed to bring the trees close to the container with the instrumentation, which can be an advantage over building long sampling line (or move the container, which might prove difficult).

We expanded the rationale for the use of seedlings in section 2.2, while acknowledging that they cannot be considered representative without a broader context of emission measurements. We added the following: “The use of seedlings in pots was mostly practical as it was easier to bring them close to the instruments that characterise the emissions; moving the instruments’ container closer to the trees of interest is not possible. Additionally, extremely long sampling lines and wall losses could be avoided. Emissions from the seedlings might not be representative per se. Nevertheless, put in perspective with results from other studies, they provide valuable information for any potential upscaling effort.”

*p.4, l.91: The study was conducted with three branch enclosures, which were placed on three different trees. As I understand, after some time the enclosures had to be moved and another branch of the tree was enclosed. Over the studied period, each tree was subsequently sampled on three branches. Do you have evidence, that this method provides comparable results? I wonder, did you (or another study) test to measure the emission of various tree branches simultaneously and found that they provide the same results?*

While we had three branch enclosures available, we had two GC instrument measuring each different compounds and only one instrument to measure total OH reactivity. Simultaneous measurements were therefore not possible in this study. Bertin et al. (1997) showed that branch-to-branch variability (for sun-exposed branches exposed to

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sunlight) is similar to tree-to-tree variability for the evergreen oak. However, a large difference (190%) was observed between sun-exposed branches and shade-adapted branch. In our study, the branches are both exposed to sunlight and in the shadow, depending on the time of the day. Also, as stated previously, emissions from this study (and others) show similar emissions patterns for a given tree species. Taken all together these studies contribute to identify the potential causes of variations.

*p.4, l.98: How were the data treated when the temperature differences were high? Was a threshold value defined to filter out high-temperature, hence unrealistic, data?*

It is a known issue of branch enclosures that the temperature in the enclosure exceeds ambient temperature. By removing data above 30 °C, changes for  $\beta$  factors when the coefficient of correlation R is larger than 0.5 are within 15%, except for spruce data in July (highest temperatures), where the  $\beta$  factor (0.1853 without filtering data) decrease to 0.0931. We included this information in the revised manuscript.

*p.4, l.100: In the section 2.4 the VOC-measurements via gas chromatography are described. These measurements are vital for determining the OH reactivity fraction that can be explained or, when subtracted from the measured TOHRE, the missing OHRE. Therefore, please describe here the calibration method used, the uncertainty of the measurement and the limit of detection.*

The instrument was calibrated for MBO, aldehydes, mono- and sesquiterpenes using liquid standards in methanol solutions. Isoprene was calibrated using a gaseous standard (National Physical Laboratory, 32 VOC mix at 4ppb level). Limits of detections for mono- and sesquiterpenes are comprised between 0.5 and 4.7 pptv and the uncertainty of the measurements lies at 17–20% (Helin et al., 2020). For organic acids, the detection limits are in 1–130 pptv and the uncertainty is 32–76% (Hellén et al., 2017). For other compounds that had no standard available, the uncertainty and the detection limits were estimated based on similar compounds. We included this information in the revised manuscript.

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*p.5, l.138: The reaction rate of pyrrole with OH was determined recently by Dillon et al. (2012).*

We thank the referee for pointing our attention to this more recent measurement of the reaction rate of pyrrole with OH. The reaction rate used in this study ( $1.2 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , Atkinson et al., 1985) is, nevertheless, within the uncertainty of the value determined by Dillon et al., ( $1.28 \pm 0.1 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ). While we did not discuss in detail uncertainty calculations in the original manuscript, we did in our previous publications (Praplan et al., 2017; 2019), where we state that an uncertainty of 15% is used for this reaction rate.

*p.5, l.122: The Comparative Reactivity Method (CRM) is used here for detecting the total OH reactivity with a gas chromatograph equipped with a PID. What is the uncertainty of this instrument and the limit of detection? Do you find interfering compounds in the short time period of the two-minute chromatogram?*

We added here information about the GC-PID. Its uncertainty is about 5% and its limit of detection is 1.7 ppbv ( $2\sigma$ ). The retention time of pyrrole is roughly 65 s and we never observed interfering compounds. When the pyrrole flow to the instrument is switched off under various conditions, no peak is ever observed at the position of the pyrrole peak. This is now also explicitly mentioned in the revised manuscript.

*p.5, l.144: Here it is described how the total OH reactivity background was experimentally derived by measuring from an empty enclosure. In light of the following results and discussion, I think it is necessary to determine a detection limit for the TOHRE measurements. With the noise of the blank enclosure measurement, a 2-sigma value for the total OH reactivity can be calculated and with this a detection limit for TOHRE. Especially, when comparing the measured and calculated OHRE during low emission periods, this value will aid to judge the significance of the results.*

We thank the referee for this helpful suggestion. In addition of subtracting blank values, we plot the  $2\sigma$  value for total OH reactivity from the blank cuvette adjusted for flow

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through the enclosure and dry weight of the needle/leaves and plot it in the top row of Figures 2 to 4 to indicate the limit of detection of the method. In addition the missing fraction is displayed now only for cases when the measured total OH reactivity is higher than the limit of detection (defined as  $2\sigma$  of the total OH reactivity from the blank measurement in an empty enclosure). This did not affect significantly the monthly averages in Table 1.

*p.8, l.205: How do the measured TOHRE values compare to previous studies (e.g. Nölscher et al. 2013)?*

We would have liked to compare our measurements to the previous studies. However, in Nölscher et al. (2013), the “Total OH reactivity emission rates were expressed as emitted total OH reactivity ( $R_{\text{total}}^{\text{ins}^{-1}}$ ) per unit needle dry weight ( $\text{g(dw)}^{-1}$ ) per unit enclosure volume ( $\text{m}^{-3}$ ) per unit time ( $\text{s}^{-1}$ )”, resulting in  $\text{s}^{-2} \text{g(dw)}^{-1} \text{m}^{-3}$  as TOHRE units, while our study uses a similar normalization as for VOC emissions (Eq. 5), resulting in  $\text{s}^{-2} \text{g(dw)}^{-1} \text{m}^3$  units for TOHRE.

This difference seems to stem from the different method used: dynamic branch enclosure in Nölscher et al. (2013) and flow through technique in our study. We failed to see how to reconcile the units and therefore refrained from comparing values and opted for a qualitative comparison only. We added this information to the revised manuscript.

*p.9, l.218/219: The “deviation from pseudo first-order kinetics applied to the CRM data is based on calibration with  $\alpha$ -pinene as a surrogate for biogenic emissions, but monoterpenes do not always represent the largest fraction of the emissions, which result in some uncertainty in TOHRE.” This uncertainty could be quantified by comparing the  $k_{\alpha\text{-pin}}$  with a reaction rate that represents the measured VOCs.*

For reactivity calibrations with propane from our earlier work, the slope of the regression comparing measured reactivity ( $R_{\text{eqn}}$ ) and expected reactivity ( $R_{\text{true}}$ ) is 0.751. We do not have reactivity calibrations for compounds with higher reactivity than monoterpenes (e.g. sesquiterpenes), but based on reaction rate coefficients, the difference

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in reactivity between propane and  $\alpha$ -pinene is larger to the difference in reactivity between  $\alpha$ -pinene and  $\beta$ -caryophyllene. Therefore, considering the uncertainty between the slopes of the regressions for propane and  $\alpha$ -pinene (51 %, lower uncertainty), it is reasonable to assume a lower upper uncertainty. We extended our statement regarding the uncertainty of this correction in the revised manuscript.

*p.9, l.222-226: The authors discuss here the results that will be shown in the following paragraphs. This is difficult to follow by the reader.*

We acknowledge that this was not the right place to discuss the results showed only later. This has been corrected in the revised manuscript by moving the paragraph to the end of this section and rewriting parts of this section (see also Anonymous Referee 2's comment).

*p.9, l.227-p.15, l.295: Sections 3.2 to 3.4 present and discuss the results, however do not refer at any time to the pictured figures. The reader has to guess what to look at. Additionally, the periods indicated in the figures and discussed in the text are not introduced to the reader. How are these periods defined? Why do you not show simultaneous data periods between the three trees?*

We regret that we were not able to present our data in the most intelligible fashion. In the revised manuscript we have partly rewritten sections 3.2 to 3.4 with the proper references to the various figures and with a proper definition of the periods indicated in the figures in the main text and not only in the caption of the figures. As we only have one CRM instrument available, we are unable to measure several trees simultaneously.

*p.16, l.300: "Good correlations with temperature are found for the TOHRE...". Is it really a linear dependency or an exponential dependency? Here the text is rather vague what type of regression was used. Only in the caption of Figure 5 it is stated that an exponential regression is calculated for the temperature dependency of THORE. Please clarify (here and also in the caption of Figure 5 and Table 2).*

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We did reference Eq. (9) in the main text of the original manuscript. We now mention explicitly in the previous paragraph that we use it for exponential regressions in the revised manuscript. The caption of Figure 5 included already twice the expression “exponential regression” in the original manuscript, therefore we did not modify it, but we updated Table 2 to emphasize this important aspect of our study.

*p.16, l.322: The last sentence mentions other factors that can play a major role on the type and amount of reactive emissions. Please, provide examples of that factors. Can you see the effect of these factors in your dataset?*

We referred to abiotic stress factors as we see in particular in the data for pine and to some degree for spruce with high TOHRE values at moderate temperatures. We mention this explicitly as an example in the revised manuscript (see also answer to comment by Anonymous Referee 2).

*Technical comments:*

*While the manuscript overall is well structured and clearly written, it should be checked for the English language. There are a number of language mistakes, that I spotted and probably more than that could be improved in the language.*

*Examples: p.1, l.2: missing s at the end of a verb...a large fraction of total hydroxyl(OH) reactivity remains.... p. 2, l.42: unnecessary closing bracket...during which the forest experienced stressed conditions)...p.5, l.126: missing the...and used for the rest of the measurement periods. p.8, l.212: missing s for plural...in large amounts...p.9, l.226: conjugation of the verb to past tense...cannot be explained only by...p.12,l.252: verb used in singular form when needed in plural...values are observed...*

The mistakes pointed out by the referee (and others) have been corrected and the manuscript has been submitted to a professional language check (see also comments by Anonymous Referee 2).

*Figures 2, 3 and 4:*

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*The main results are presented in the Figures 2, 3 and 4. The upper parts of the figures show the measured TOHRE as well as COHRE (the calculated OH reactivity emissions). This should be indicated in the legend.*

We have replaced the coloured surface depicting COHRE in the upper parts of the figures with a solid red line and indicate COHRE in the legend as well. In addition, the y-axis label has been renamed to “OHRE” instead of “TOHRE”.

*The scatter of TOHRE is especially for periods of low emissions high. Please indicate here the lower detection limit of TOHRE. Which emissions of total OH reactivity can be reliably identified with the method? When are emissions too low? In that case, the missing OHRE should be treated with care.*

We indicate now in Figures 2 to 4 the limit of detection based on  $2\sigma$  of the signal in an empty enclosure (blank, see also answer to earlier comment). Emissions are low usually during the night and the high missing fraction results indeed mostly from these low TOHRE values, close to the detection limit and these results should be treated with caution.

*Can you provide and include the uncertainty of COHRE into the figure? Maybe the figure would be easier to read if pictured across the entire page when turned about 90°.*

COHRE is derived from up to 67 compounds. Considering the uncertainty from the GC-MS measurements and on the reaction rates used to derive COHRE, the uncertainty on COHRE could be up to a factor 4.3. Nevertheless, not all 67 compounds are measured simultaneously for all three trees and all measurement periods. We therefore estimated the uncertainty of COHRE for each measurement point individually according to the compounds contributing to it and display it now in the figure in the revised manuscript. It is mostly comprised between 25 and 50 %. This information has been included in the main text of the revised manuscript.

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*p.16,l.305-310: For consistency with the methods part of this manuscript use Kelvin in the units of the beta-factor.*

Indeed, we should have used Kelvin as a unit for consistency. This has been fixed in the revised manuscript.

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