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

Anonymous Referee #1

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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 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.

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.

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.

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

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?

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?

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?

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.

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

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?

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.

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

p.9, l.218/219: The “deviation from pseudo first-order kinetics applied to the CRM data is based on calibration with a-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 ka-pin with a reaction rate that represents the measured VOCs.

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.

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?

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).

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?

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…

Figures 2, 3 and 4:

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.

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.

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°.

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

Reference:

Dillon et al. (2012): Terry J. Dillon, Maria E. Tucceri, Katrin Dulitz, Abraham Horowitz, Luc Vereecken, and John N. Crowley: Reaction of Hydroxyl Radicals with C4H5N (Pyrrole): Temperature and Pressure Dependent Rate Coefficients, The Journal of Physical Chemistry A 2012 116 (24), 6051-6058, DOI: 10.1021/jp211241x.

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