Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2020-37-AC2, 2020

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

Arnaud P. Praplan et al.

arnaud.praplan@gmail.com

Received and published: 29 May 2020

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.

This manuscript is an important contribution to our knowledge about the emission of BVOCs from vegetation, particularly from boreal forest, and its implication for OH reactivity, considering current gaps in our knowledge in this research area. In particular, this work highlights some important aspects related to difficulties in OH reactivity evaluation, and its dependence on both environmental conditions and methodological limitations. My comments are mostly about the way the results are presented and discussed. While the methodological aspects are generally described in detail, in few cases important aspects should be clarified. There are a number of language flaws that should be corrected. Specific comments are listed below.

We thank the referee for his comments and for pointing out the sentences in which we were not able to express clearly what we wanted to tell. The revised manuscript underwent a professional language check (see also answer to Anonymous Referee 1).

Specific comments:

Line 11: why “even though”?

We reformulated this entire sentence.

Introduction: While you emphasize the importance of accounting for OH reactivity by its effects on the lifetime of VOCs oxidants in the atmosphere, there are additional central reasons why OH reactivity and BVOCs composition are important. Among these you can mention photochemical air-pollution and secondary aerosol formation.

We agree with the referee that we arbitrarily limited ourselves to a subset of reasons about the important aspects of OH reactivity and BVOCs. This has been addressed in the revised manuscript with the suggestions of the referee: “Moreover, the oxidation of VOCs in the atmosphere can lead to the formation of secondary aerosol formation and may play a role in photochemical air pollution by affecting levels of oxidants and pollutants.”

Line 29-35: This paragraph use extensively “OH reactivity” which you define on line 111. It will be good to provide a brief explanation/definition before you discuss it here.

This paragraph has been rewritten taking into account both referee's comments. The revised manuscript contains additional definition in this paragraph about OH reactivity (inverse of OH lifetime, also named "total OH loss rate").

Line 31: Can you provide reference/s to support this statement?

We rephrased this sentence in the revised manuscript to reflect its intended original meaning. It is now: "To estimate the magnitude of missing OH chemical sinks, Kovacs and Brune (2001) started measuring total OH loss rates to compare with model results."

Line 42: remove extra ")".

Done.

Line 50: "contradictory" – the use of this word seems inappropriate taking into account the rest of the paragraph.

We replaced the word "contradictory" with the word "inconclusive".

Line 57: What do you mean by "important" trees? Can you make this point clearer?

We replaced "important" by "common" in the revised manuscript, as this is what was originally meant.

Line 83: It's not a comparison between the "changes in biomass" and other uncertainties; you probably refer to the effect emanating from the former on OH reactivity. While this assumption seems reasonable can you indicate to what extent (e.g., in percentage) this effect could affect your results?

Based on the work by Aalto et al. (2014), it was estimated that pine needles did not experience much growth during the measurement periods. It was also estimated that spruce needles were fully grown by 30 May and that the biomass difference is at most 20 % for the periods before (Branch S1). For birch, all the growth happen rapidly from no laves to the full measured dry weight of the biomass during the first period (Branch B1), so that the uncertainty due to the normalization of the biomass is very large at the beginning of that period and only the last five days the difference of the biomass is within 20 % of the measured dry weight. We therefore indicate this period with a

dashed line and added a note in the figure caption.

Lines 141-142: Can you explain why you didn't use C3H8 for the calibration as described by Parplan et al. (2019) and Shina et al. (2008)?

While a C_3H_8 calibration is described in Praplan et al. (2019), only the reactivity calibration for α-pinene (as a proxy) was used, based of the input from a referee. In the present study, we also consider α-pinene to have an average reactivity for the emissions, considering that some compounds will be more reactive (e.g. sesquiterpenes) and other compounds less reactive (e.g. alcohols). We estimated for the revised manuscript that the uncertainty of using α-pinene as a proxy for the reactivity of the emissions is about 50 %. See also the answer to the comment from Anonymous Referee 1 about this.

Line 147: Are the values in Eq. 3 referring to the calibration factors? Please indicate their meaning in the text.

We included more information regarding the calibration factors in the text. We also streamlined this paragraph as Eq. 3 and 8 were redundant.

Line 148: To what extent humidity can affect your results in addition to (/relative to) the dilution effect?

We moved our description of the correction needed for RH difference between C2 and C3 measurements right after the sentence about dilution to address this referee's comment.

Line 152: "Other correction factors need to be applied..." – Do you mean other than the presence of NOX and O3? If so, why did you write "However" in the next sentence?

Our formulation was indeed misleading. In the revised manuscript we simply state why these corrections are not required.

Lines 152-153: Is this because NOX and O3 are assumed to be effectively removed by *the HPZA-7000?*

Yes. This is now stated in the revised manuscript.

Line 164: "OH levels" – do you mean the effect on RH levels?

In the CRM instrument, RH levels in the reactor are directly associated with the production of OH in the reactor. This sentence has been reformulated to clarify is meaning to tell and the whole section about the Comparative Reactivity Method has been streamlined for further clarity.

Line 168: "t o" should be "to".

Fixed.

Line 180: Eq. 8, please indicate clearly what is the meaning of the (calibration?) values.

We have rewritten parts of this section and streamlined it in order to improve its clarity. It includes now a clearer explanation of how the calibration values have been derived.

Lines 187-188: Please provide a reference to support this estimation.

Using a similar setup, Owen et al. (1997) mention that the enclosure temperature can be used as a close estimate for the leaf temperature as it is 2 °C lower at most. We included this reference in the revised manuscript.

Results and discussion: In this section you present 4 figures and 2 tables, but you only once refer to Fig. 5 and Table 1 and 2. Please try to refer the reader to each of these from the text.

We have edited the results and discussion section(see also comments from Anonymous Referee 1). Proper references to figures and tables have been incorporated in the revised manuscript.

Lines 209-2013: I suggest making this paragraph shorter and generally avoid summa-

rizing or discussing the results prior presenting the results themselves.

This paragraph is indeed summarizing results before they are presented. We moved this paragraph towards the end of the section (see also answer to comment from Anonymous Referee 1).

Table 1 caption: Acronyms - "Te" is not consistent with RH if the latter refers to measurements in the enclosure.

We replaced "RH" with "RHe" as we always meant "RH in the enclosure". The table caption has been updated as well in the revised manuscript to clarify this.

Line 214: Can you support it by statistical analysis?

Our statement ("In general the missing OHRE fraction was higher in spring and decreased as the seasons proceeded.") is meant to describe qualitatively the observed trend of the missing OHRE fraction in Table 1. We are unsure what statistical analysis the referee wants to see.

Line 235: GLVs was already defined before.

We use only the abbreviation in this sentence in the revised manuscript.

Line 236: "as well" appears twice.

We have rewritten this unfortunately formulated sentence in the revised manuscript.

Lines 245-247: Can you elaborate on why the fact that stress in your case was not driven by elevated temperature indicates that some of these (missing OHRE) are not terpenoids or oxidized volatile organic compounds?

We have reformulated these sentences to clarify what it meant to tell: "In our study, these stress periods for pine, identified with GLVs emissions, are not related to elevated temperature (see section 3.5). Missing OHRE was generally higher during these periods, but as terpenoids were monitored, they cannot explain the stress-related emissions of reactivity. Some oxidised volatile organic compounds were also measured, but not methanol, formaldehyde, and acetaldehyde, for instance, which could contribute âĂŤ at least in part âĂŤ to the missing OHRE."

Line 249: What do you mean by "follows qualitatively"? If you imply for correlation, can you calculate the Pearson correlation coefficient and present it to support this notion?

Our statement meant to tell that even though the absolute values of TOHRE and COHRE differ, they follow a similar time evolution (e.g. maxima). This was an arbitrary statement based on visual examination, but thanks to the referee's input we now use the Pearson correlation coefficient in the revised manuscript to support our claim. While for spruce and pine a correlation could be established, it was not the case for birch data. The Pearson's correlation coefficient r is 0.88 and 0.78 pine and spruce, respectively (both with a p-value <0.01), for the periods when both COHRE and TOHRE are available. However, the Pearson's correlation coefficient r is much lower birch when both TOHRE and COHRE are available (0.02 with a p-value of 0.4). The text in the revised manuscript reflect these newly introduced statistics.

Lines 253-255: What about aldehydes? How it compares with the findings by Hakola et al. (2017) about aldehyde emissions from Spruce?

Hakola et al. (2017) found relatively high emissions of higher aldehydes, especially nonanal and decanal. In our study, these high emissions could not be observed, and their contribution to OHRE remained small.

Lines 255-257: Does the higher emission of sesquiterpenes at the expense of GLVs under the different conditions can be supported by statistical analysis? Can you use regression to identify which of the parameters (temperature, radiation, precipitation) shows higher association with the emissions rate of the various VOCs?

Sesquiterpenes are emitted from spruces in normal conditions while GLVs are induced by the stress. Sesquiterpene emission were not higher when GLVs were lower, but their

relative share on COHRE was higher. In our opinion, detailed studies on dependences of various VOCs on different parameters are out of scope of this manuscript and will be studied in separate manuscripts in future.

Line 259: Why "However?

We removed the transition word "However", when we edited this section for the revised manuscript.

Lines 280-281: Can you indicate to what extent the constant blank subtraction could have affected your results?

As we used a constant blank for the all the measurement periods, it cannot be excluded that the blank was underestimated or overestimated at times. Underestimation of the blank value affects in particular periods with low reactive emissions and lead to high relative missing reactivity values, which should be considered with caution as we tried to make clear in the manuscript.

Line 282: "quantitatively" - Qualitatively? Can you calculate the Pearson correlation coefficient for all three species?

Yes, "qualitatively" was meant here and we have now included Pearson correlation coefficients in the discussion for all three species (see also answer to comment above).

Line 300: Please indicate the regression you have used to evaluate R. Did you try exponential regression (as is implied by Fig. 5)?

We regret that we failed to explicitly mention in the text which regression we used to evaluate R. This has now been improved in the revised manuscript (see also answer to the comment from Anonymous Referee 1).

Lines 301-303: Can you provide more information about the nature of the stress and the cause for the low TOHRE?

Based on visual observations, we concluded that the nature of the stress was abiotic, which we now mention in the revised manuscript. The low TOHRE values were due to low emissions in the cited periods, possibly due to cooler and cloudier weather.

Line 305: Why not referring to Table 2?

We refer to Table 2 (and Figure 5) in an earlier paragraph.

Line 312: What do you mean by "good correlation with temperature"?

We meant that in July the coefficient of correlation (R) with the temperature is 0.71. We have added this to the sentence in the revised manuscript.

Line 316: "In a few cases was even slightly reduced." – this seems reasonable to me. I just want to make sure you have used exponential regression type for temperature.

As mentioned previously, we used exponential regression and this is now explicitly mentioned in the revised text.

Lines 321-323: A very general sentence - can you specify which factors ("other factors") and elaborate on that?

We mainly meant abiotic stress factors as we demonstrate how they influence our results. This is now explicitly mentioned in the revised manuscript (see also answer to comment from Anonymous Referee 1).

Line 332: "stress-induced" - Please specify stress type as much as possible.

We rephrased this sentence to indicate that the stress was very likely drought.

Lines 337-338: Can you provide an explanation for that?

We mentioned in section 3.3 the study by Hakola et al. (2017), where similar observations were done regarding higher emissions of sesquiterpenes in the late summer. They speculated on the possible defensive role of sesquiterpenes, but the lack of any visible infestations of feeding herbivores indicated systemic defence mechanism rather than a direct one. We included this information in the discussion of the revised

manuscript, but we mention in the conclusions that this is observation is consistent with a previous study.

Line 341: "highest" - Looks like a contradiction with the rest of the sentence

The meaning of this sentence was indeed difficult to understand in the original formulation. What was meant is that if the CRM has a similar background for all species, normalizing with the biomass (smaller values for birch) will yield higher TOHRE values. The phrasing has been improved in the revised manuscript: "This is partly explained by total OH reactivity values measured close to the experimental background (independent of the tree species measured) and normalised by the smallest dry weight of the leaves or needles of all tree species."

References

Aalto, J., Kolari, P., Hari, P., Kerminen, V.-M., Schiestl-Aalto, P., Aaltonen, H., Levula, J., Siivola, E., Kulmala, M., and Bäck, J.: New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests, Biogeosciences, 11, 1331–1344, 2014. doi:10.5194/bg-11-1331-2014.

Hakola, H., Tarvainen, V., Praplan, A. P., Jaars, K., Hemmilä, M., Kulmala, M.,Bäck, J., and Hellén, H.: Terpenoid and carbonyl emissions from Norway sprucein Finland during the growing season, Atmos.Chem.Phys., 17, 3357–3370, 2017. doi:10.5194/acp-17-3357-2017.

Owen, S., Boissard, C., Street, R. A., Duckham, S. C., Csiky, O., and Hewitt, C. N.: Screening of 18 Mediterranean plant species for volatile organic compound emissions, Atmos. Environ., 31, 101–117, 1997. doi:10.1016/S1352-2310(97)00078-2.

Praplan, A. P., Tykkä, T., Chen, D., Boy, M., Taipale, D., Vakkari, V., Zhou, P., Petäjä, T.,and Hellén, H.: Long-term total OH reactivity measurements in a boreal forest, Atmos.Chem. Phys., 19, 14431–14453, 2019. doi:10.5194/acp-19-14431-2019.

Sinha, V., Williams, J., Crowley, J. N., and Lelieveld, J.: The Comparative Reactivity

Method – a new tool to measure total OH Reactivity in ambient air, Atmos. Chem.Phys., 8, 2213–2227, 2008. doi:10.5194/acp-8-2213-2008.

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2020-37, 2020.