

Interactive comment on “Volatile Organic Compound fluxes in a subarctic peatland and lake” by Roger Seco et al.

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Received and published: 14 August 2020

Seco et al. provide high-quality measurement data representing very relevant study object, VOC emissions from subarctic peatland and lake. Given how rare such datasets are, the results are obviously worth reporting, though the shortness and temporal limitedness of the data set apparent limitations concerning the data analysis and conclusions. These limitations should not be considered as weaknesses of the manuscript – they are more common features that should be taken into account, than any reason for rejection.

Overall, the manuscript fulfills the review criteria of ACP. The scientific question is well within the scope of ACP, both the data and conclusions are mainly valid, as well as

C1

the measurement and data analysis methods. The manuscript itself is mostly well structured and clearly expressed. There are some minor issues in the manuscript that may need to be reconsidered; those issues will be listed in my detailed comments.

Within the following section, I'll go through my main concerns regarding the data analysis and conclusions. Please note that many of my comments are more suggestions and questions aiming to clarify the results, than sound challenging based on solid scientific evidence. Chances are that many of the aspects pointed out by me have already been taken into consideration during the data analysis and manuscript compilation. In that case, I'd like you to once more consider each aspect, in order to ensure that the data analysis and conclusions are balanced and comprehensive.

The obvious scientific highlight of the manuscript is the high temperature sensitivity of isoprene emissions from subarctic fen. The finding is rather exceptional and has potentially important implications, in so far as it requires and deserves extra careful consideration and special scrutiny. Regarding the analysis and conclusions reported in the manuscript, most of my concerns are either directly or indirectly related to this temperature sensitivity finding.

Conducting any scientific measurements is always by nature imperfect. To analyze something like temperature response of VOC flux, one has to take into consideration at least five aspects: 1) VOC flux per se, as a natural phenomenon, 2) Temperature per se, 3) Assumed relationship between T per se and VOC flux per se, 4) Measured estimate of VOC flux, and how complete or incomplete view that gives for VOC flux or emission per se, and finally, 5) Measured T, and its' ability to describe the thermal conditions relevant for VOC flux or emission. Failing with any of these aspects causes the risk that the analysis and conclusions on temperature response will be partly or fully misleading or incomplete.

I find no special need to believe that there would be any major shortcomings in the VOC flux measurement results of the manuscript. They also likely represent reality with

C2

reasonable accuracy, so aspects #1 and #4 should be in order. Also, it can be quite safely assumed that T response follows some exponential form – that is so common feature in this field – so also the aspect #3 can be left above suspicion. That leaves us with aspects #2 and #5, T per se and measured T as an estimate of that.

The obvious merit of the manuscript is that it includes both air T and surface T as estimates for thermal conditions relevant for VOC flux. However, I suggest that a little bit more attention would be paid on discussing, how completely or incompletely these estimates are able to reflect the true thermal conditions controlling VOC (isoprene) sources. How sensitive these T measurements are to fail in producing accurate and precise description on relevant thermal conditions? Please note, that for example figure 5 gives the impression that if there is rather minor tendency to underestimate high surface temperatures and overestimate low surface temperatures, that would likely have a major impact on detected T response. I have no specific reason to believe that there would be such tendencies for under-/overestimation, but it's especially important to take even the slightest chance for those into account when exceptional T sensitivity is proposed.

In the manuscript, G93 emission model is applied for analyzing the isoprene fluxes. The core assumption is fairly expressed: it is assumed that the fen vegetation is a single big leaf. This assumption is of course inevitable, because there is lack of any other proper way to conduct model analysis on such flux data. However, it includes also significant limitations, mainly because of the inability of unshaded PAR measurement and single T measurement to reflect the true thermal and light conditions controlling VOC sources. Again, these limitations doesn't mean that one shouldn't use the model approach; one should just keep in mind that these limitations may complicate drawing the conclusions.

Although the fen surface vegetation is structurally very simple when compared to for example forest canopy, it still includes self-shading, causing full continuum from full light to totally shaded parts within the shallow layer of vegetation. This degree of self-shading

C3

varies significantly depending on the angle of incoming radiation and/or proportion of diffuse radiation on total radiation. Therefore, any above-surface PAR measurement is judged to fail in fully describing the light conditions within the surface vegetation layer. Similarly, there is T gradient within the vegetation layer, which can't be properly described by air T measurement or even surface T measurement. Again, I have no specific reason to believe that your results would be untypically imprecise or inaccurate in this sense. Based on results presented in the manuscript, it's more and more obvious that models like G93-approach, especially CLxCT as such but also any form of T dependency, works best with simple structures, such as tree leaves. However, when they are applied for more complex structures such as surface vegetation layer, they struggle if the gradients in light and T environment are not described in detail. It's not that G93 or any other model or dependency description would be useless when used with 'single big leaf assumption' in case of complex structures, it's just that special caution is required when relevant findings are tried to distinguish among the features of model, assumptions and incompleteness of recorded environmental drivers. This is not stated as a challenge for the manuscript, but it's more to encourage you to once more consider, which of the conclusions based on findings and features presented for example in figures 5 and S5 are well-founded, given the limitations of 'single big leaf assumption' with complex vegetation structure.

From results and discussion as well as from figure S5 one gets the impression that light is not the primary control of fen isoprene fluxes. However, based on figures 2 and 3 there is remarkable similarity between PAR and fen isoprene flux. Or to be exact, at first glance there is similarity, but with a closer look there is also distinctive differences. First, before noon there is little variation in isoprene flux whereas during afternoon hours there is more variation. There is no similar bimodality in PAR recordings, but in air T there is some bimodality (figure 2), so it's obvious that thermal conditions have some effect on this difference between the different degree of variation in isoprene flux during morning hours and afternoons. Also, during morning hours PAR typically reaches value of $400 \mu\text{mol m}^{-2} \text{s}^{-1}$ soon after 6 o'clock in morning (which I believe should correspond

C4

to $CL=0.8$, after which the isoprene fluxes tend to differ from zero, figure S5), but the detected isoprene fluxes in figure 3 differ from zero only some hours later. Overall, it would be very interesting to understand why the dynamics in fen isoprene fluxes differ between morning hours and afternoons. Would there be any chance to deepen the analysis in this sense? Also, do you have any guess why $PAR=400 \mu\text{mol m}^{-2} \text{s}^{-1}$ looks like a threshold value for fen isoprene flux? What does that value for detected PAR would mean in regard to light conditions within the surface vegetation layer?

Detailed comments:

L34-56: This paragraph has all the right ingredients, but I felt that it's somehow difficult to follow. Please consider at least dividing it to two or more paragraphs (for example cut it from L45); or any other way to make this paragraph just a bit more easier to follow.

L126: Use of the term 'teflon' here and elsewhere in the manuscript. Please consider if the term could be removed. Originally, it's commercial brand-name. It's scientifically inexact, because nowadays it can refer to practically any fluoropolymer. And the exact name of your tube material is already mentioned in the same sentence.

L126: Please mention inner diameter instead of outer diameter, because the inner diameter is more relevant for the context.

L168: Was the T/RH probe equipped with radiation shield? Was it passively or actively ventilated? These details matter when one tries to judge how well the recorded T represents air T per se.

L230: This sentence is missing context. Emission from where? Please rephrase to clarify the context.

L254-255: Would there be difference in these Q10 values between morning hours and afternoon hours? Based on figure 3, there may be different type of response to environmental conditions between morning hours and afternoon hours. I understand that the lack of data points having high PAR somewhat limits partitioning this dataset

C5

between morning hours and afternoon, but what if you include also data with PAR just below $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, let's say starting from 900 or $800 \mu\text{mol m}^{-2} \text{s}^{-1}$? Using $PAR=800 \dots 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ shouldn't be a problem, because at $800 \mu\text{mol m}^{-2} \text{s}^{-1}$ the CL is already > 0.96 . These are suggestions that not necessarily lead to any reasonable result, but in case you haven't considered them earlier, they would potentially be interesting. Or what do you think, wouldn't it be even more unexpected if there is difference in T sensitivity between morning hours and afternoon?

L256-273: In this paragraph some very interesting points are raised. Could you consider to give recommendations for the community considering this issue? Maybe underline in the conclusions how important it is to measure T accurately, precisely and with such methods that it represents the true thermal conditions controlling the VOC production and release processes? The results and findings of the manuscript clearly support this kind of remark. Or should this be a topic for a follow-up article?

L294: I have nothing to contest; it's clear that biomass growth is a classical source of methanol. However, according to the figure S1, leaf expansion period has already ended before the mid-July measurement period. This methanol flux after the leaf expansion period is not surprising, because based on my own experience with boreal forest methanol emission continues throughout growing season (for example Aalto et al., 2014). I'd like to see more observations about cases when methanol emission is not clearly linked with biomass growth; here you would have chance to present one such case. Otherwise the community will keep repeating this Hüve et al. (2007) finding as the only relevant source for methanol emissions for another 13 years. I believe it's true finding but I also believe that it's not the whole truth.

L330-340: Were the deposition rates tested against relative humidity? At least in case of acetaldehyde it could be interesting. It's very likely that the potential effect of RH on these deposition rates returns to T (due to autocorrelation of T and RH), but there are chances that it could be vice versa: high humidity could be the main driver, instead of T itself. I don't ask you to add anything regarding RH, but just to consider by yourselves,

C6

would accounting RH make sense for the analysis.

References: Hüve, K., Christ, M. M., Kleist, E., Uerlings, R., Niinemets, Ü., Walter, A. and Wildt, J.: Simultaneous growth and emission measurements demonstrate an interactive control of methanol release by leaf expansion and stomata, *J. Exp. Bot.*, 58(7), 1783– 1793, doi:10.1093/jxb/erm038, 2007.

Aalto, J., Kolari, P., Hari, P., Kerminen, V.-M., 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, doi:10.5194/bg-11-1331-2014, 2014.

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