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Interactive comment on "Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere" *by* P. Rantala et al.

Anonymous Referee #1

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This paper by Rantala et al presents a 4-year dataset of PTRMS VOC measurements and calculated fluxes based on profiles of VOCs at different heights. The technique used for flux calculation (in lieu of eddy covariance) is justified by the low VOC flux magnitudes of these type of pine forests in Finland. This manuscript is a good contribution to the VOC knowledge in boreal forests and can be accepted for publication after addressing the points raised below.

General comments.

It would be valuable for the reader to see the typical diurnal cycle of monoterpenes at this forest site. For example, having a figure for monoterpenes similar to figure 7.

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Specific comments.

Section 2.4. Please clarify the "pool" algorithm for the reader. Throughout the manuscript, authors talk about the "pool" algorithm, however this algorithm is not explicitly described in the text (e.g. does not even have an Equation number). Also, in Table 4 the "storage" name is used, which I guess is the same as the "pool" algorithm, but such a variety in names only confuses the reader.

p9550 ln15-17. Please clarify what the authors meant with this sentence.

P9555 ln8-11. It is possible to roughly estimate the influence of humidity on formaldehyde sensitivity, because the proton transfer to formaldehyde and the backwards reaction with water have known reaction rates. Together with information about the ambient humidity level, this influence and the formaldehyde mixing ratios can be estimated. Have the authors tried this approach?

P9555 ln22-23. Do the authors mean hexanol or hexenol? m/z 85 has been attributed to hexanol in other works (e.g. the Buhr et al 2002 cited in the manuscript), while hexenol has been attributed to m/z 83, and Hakola et al 2001 also reported hexanol emissions from birch in addition to hexenols. Please clarify and, even better, provide some additional references to support the assumption of the identity of m/z 85.

P9557 ln8-13. What is the purpose and value of this "first step" of analysis of m/z 69? It is expected that isoprene and/or MBO fluxes follow light and temperature variations, as has been shown e.g. for MBO at the leaf (Harley et al 1998) and canopy (Kaser et al 2013) levels from Pinus ponderosa. This known relationships explain the good correlations with the algorithms. Anyway, given that authors talk all the time about having correlations with $p < 0.0027$, they should show the values of p in the corresponding tables (e.g. Table 3 in this case).

P9561 ln1. Maybe change "material" to "dataset"?

Table 2. This reviewer has always seen the statistically significant results marked with

an asterisk. The authors, however, chose to mark the non-significant results. Unless there is a very good reason for it, I suggest marking the significant results with an asterisk, otherwise the reader may be confused.

Tables 3-5. Please show the p values for the correlations and whether the authors considered the correlation significant or not.

Table 4. This table shows the "E0,hybrid" parameter. If this reviewer interprets correctly, the lower part of the table corresponds to the "pool" algorithm (please unify the name of this algorithm throughout the manuscript, and explicitly show the pool algorithm formula). If that is the case, I think that the relevant parameter should be in the caption of the column of this lower part, because the pool algorithm does not use the "E0,hybrid" parameter, but the "E0,pool" instead.

Figure 4. The "E0,pool" and the fsynth symbols are easily confused when used with error bars in the graph. Please change the symbols to avoid confusion.

References

Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A., and Vasconcellos, P.: Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere, J. Geophys. Res., 103, 25479–25486, 1998

Kaser, L., Karl, T., Guenther, A., Graus, M., Schnitzhofer, R., Turnipseed, A., Fischer, L., Harley, P., Madronich, M., Gochis, D., Keutsch, F. N., and Hansel, A.: Undisturbed and disturbed above canopy ponderosa pine emissions: PTR-TOF-MS measurements and MEGAN 2.1 model results. Atmos. Chem. Phys., 13, 11935–11947, 2013. doi:10.5194/acp-13-11935-2013

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