

Interactive comment on “In situ measurements of volatile organic compounds in a boreal forest” by H. Hakola et al.

Anonymous Referee #2

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General comments:

Hakola et al. have measured a valuable long term dataset of different alkene classes at the Finnish SMEAR II station in Hyytiälä. This covers the day to day variation for all seasons providing information about the detailed mono- and sesquiterpene composition in an open space within the pine forest. The annual pattern of the individual structures is quite important when investigating atmospheric chemistry effects of biogenic emissions, because the reaction rate constants are essential differing for monoterpenes by order of magnitudes even for specific oxidant. This feeds back in the ambient distribution of specific mono- and sesquiterpenes, i.e. the higher reactive ones are depleted in a rapid way, while less reactive ones can be transported across a

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certain distance. Therefore the relative ratio of contributions to e.g. all monoterpenes changes a lot at different boundary layer mixing situations during a day.

The authors haven't only investigated the individual monoterpene (MT) and sesquiterpene (SQT) mixing ratios but also the enantiomers of selected MTs. Those were proposed to be indicators for the production and release process of e.g. α -pinene. Therefore the study is informative and clearly written. It improved significantly by the addition of reaction rate constants and further information. Some comments and questions I would like to make on the article to allow the highest information possibility to gain by the respectable amount of data for any reader. After clarification of some aspects this study seems worth publishing in Atmos. Chem. Phys.

Specific comments:

* p. 15568: Sampling took place at least during one week every month in order to achieve an annual coverage. Is there any systematic in the selection of the days (good weather, wind etc.) that might have affected the results in a moderate way? Or is the sampling day selection organised in a more random fashion?

* p. 15569: Why did Hakola et al. select exactly α -pinene, camphene and limonene and why not e.g. Δ^3 -carene for enantiomeric studies, which was found by the authors earlier on as a major monoterpene emitted? Because of availability of standards?

* p.15571: It is stated that forest activities certainly affect the measurements as the saw mill in the vicinity does. How are those particular activities taken into account? Are cutting periods or saw mill activity times excluded from the dataset or treated

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separately?

* We have seen effects in emission during bud break. Is there anything apparent in these long term measurements as well?

* There are several mean values of volume mixing ratios provided throughout the manuscript. Please provide the uncertainty (e.g. standard deviation) as well so that the significance of changes can be assessed. With this everyone could clearly see the differences between day and night or between March and August.

* The concentration and volume mixing ratio issue. Please check your manuscript with respect to these two quantities: Concentrations are given in molecules per cm^3 or in g per m^3 , while mixing ratios are stated in ppt, ppb, ppm etc. Correct that in diverse places of the study as well as in Figures and Tables.

* p. 15572: A quite important aspect in my opinion is the biodiversity as shown by Bäck et al. this year. Since different trees of the same kind emit differently at the same time and over one year I would expect e.g. wind pattern characteristics as a consequence of the nearest trees of the measurement location. Is there something like this or is the measurement place sufficiently off? Do the individual contributions average out during the notable transport time to the detection site?

* p. 15572: Please provide the wind direction of Tampere for easier identification of potential anthropogenic sources from urban areas.

* The reactivity part is a very important aspect when measuring not right at the

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emission location by several meters in the open. OH-reactivity and ozone loss rates are provided. Have the authors performed backtrajectory calculations to get an idea about the daily pattern of the transport time from the nearest trees to the online-GC? That would allow a statement about the fractionation of the MT- and SQT-mixture released until arrival at the detection.

* Are there some emission measurements conducted at the very same time for intercomparison? Then one could follow the losses during the mixing and transport process. Probably the long term MTs and SQTs are detected mainly. This is apparent in the statements about longifolene and isolongifolene detected as dominant constituents of SQTs. With a transport time one could deduce certain emission characteristics. Quite interesting is the level of about 2 ppt, a value similar to the rather stable 1.6 ppt we have obtained at temperatures of about -10 to 0°C a couple of meters from the next tree at our site as well.

* The daily pattern are quite substantial and the presentation was nicely reasoned by boundary layer mixing effects. This effect is evident in Fig. 5. The interesting feature was the winter mixing ratio of MTs and SQTs. I would expect small emission as well as a very small sink, especially due to OH. Maybe those effects balance out and a notable boundary layer mixing does not take place.

* Could you include a single mean boundary layer height in Fig. 5a or b? That would provide a simple tool to point at the reason for the daily pattern due to mixing and due to emissions.

* The Hellen et al. (2012) reference is being mentioned adjoined with measurements from Tampere. If the authors would have a guess about source strength and transport

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time, is the contribution to SMEAR II air samples substantial or negligible?

* p. 15573: The limonene drop on the 22nd of June and in September: Is this effect caused by extensive ozone, soil water content or activities in the forest?

* p. 15573: Williams et al. (2007) have suggested the use of enantiomers as indicators for single production and release processes. The uncertainty of the measurements would show more clearly if there is agreement or deviation between both groups, although the Williams et al. (2011; Fig. 8) measurements shows a notable variation over the course of measurements. What about the altitude impact? I suspect Williams et al. (2011) to have measured at the canopy top at the tower site not at the soil level in the open. Therefore emissions from lower tree levels could have accumulated and contributed, which cannot be affected that much by light.

* p. 15577: Finally please check the statements on the sampling location with differ to p. 15568 and homogenize.

Williams et al., Atmos. Chem. Phys., 11, 10599-10618, 2011.

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