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Interactive comment on "Seasonal variation of mono- and sesquiterpene emission rates of Scots pine" *by* H. Hakola et al.

Anonymous Referee #1

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This study reports on seasonal observations of biogenic volatile organic compound (BVOC) emissions in a Boreal Forest. The authors seek to improve on the descriptions that determine the emission rates of monoterpenes and sesquiterpenes from Scots pine trees. Daily measurements throughout the growing season reemphasize a few earlier reports on the strong seasonal changes of basal BVOC emission rates. Their comparison of data series from two branches yielded further insight in the intra-species variation and variability in emission rates. Increases in sesquiterpene emissions occurred during an event when airborne pathogen concentrations were enhanced. Sesquiterpene, linalool, 1,8-cineole and monoterpene emissions were all strongly correlated with temperature, but may also depend on light conditions. A debudding experiment suggested that new needles contribute significantly to the overall monoterpene emissions.

This research is in general well conducted and presented. The quality of this manuscript could be further improved by providing additional details on the somewhat unique experimental procedures, statistical significance of presented data and by correcting a few inconsistencies in the presentation.

The experimental procedures appear to follow an earlier published protocol [1], which unfortunately also lacks some details and references to allow the reader to reproduce these measurements. Providing additional information would be valuable to other researchers in their monoterpenes and sesquiterpene emission studies. It is stated that branches were enclosed in Teflon cuevettes. The cuevettes probably had a glass or other transparent cover, but this is not clear. It is stated that it was equipped with an end that remained open between experiments (I assume to minimize prolonged changes in the microclimate of the enclosed branch). This latter point is also an important experimental detail that is vague. A recent investigation of cuevette sampling strategies found that at room temperature, several hours of equilibration are required to reach steady-state conditions so that adsorption losses of sesquiterpenes to cuevette materials are minimized [2]. The authors do not elaborate on how long their equilibration times were, or when and for how long the cuevettes were closed during the reported measurements. Probably, some of the experiments were conducted at temperatures below typical room temperature (20–25°C) which could have potentially caused increased adsorption losses? Was the cuevette purge flow maintained throughout the experiment or just during the sampling period? What sample volumes were collected? How many samples were collected each day per cuevette? Can the authors provide information on the variance of replicate/duplicate samples that were taken on the same day? BVOC, in particular sesquiterpenes have been shown to rapidly react with ozone. It has been pointed out previously [3,4] that careful attention has to be given to ozone removal in the enclosure purge air and sampling stream. Ozone scrubbers typically loose efficiency at higher flow rates, may degrade over time and may also be effected by high VOC loading [5]. It would be important to mention if/when/how residual ozone was monitored in the enclosure and sampling air streams.

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Interactive Comment

Throughout the text, figures and tables there is some inconsistency in the use of the terms “emission rate” (meaning what is measured) and “basal emission rate” (meaning a value that a branch would emit at a standard set of conditions). The authors sometimes scale their emissions to 20°C and sometimes to 30°C. It would be beneficial to the audience to be consistent and scale to 30°C which is more typical of what land-atmosphere modelers use. Two observed SQT compounds are called “sesquiterpene1” and “sesquiterpene2”. Could possibly retention time, retention index, or mass fragmentation data be provided? This would be more useful for comparison of these observations with other data and to ultimately determine the reactivity of these compounds. Is one of these compounds α-farnesene, which is later referred to in the text?

I assume that the data in Figure 1 are the actual emission rates, measured at the temperature and light conditions encountered during the experiment (please specify if ambient air temperature or cuevette temperature (which possibly was somewhat higher?)) was used. Could emission potentials possibly be included in the plots in Figure 1 to show the seasonality in normalized emission rates?

The data in Figure 2 is used to infer a causal relationship between the occurrence of pathogen spores and emission rates of sesquiterpenes, linalool and 1,8-cineol. Are there any measurements that would illustrate that the spore data (which are ambient measurements) are representative for the air that the branches were exposed to (purged with), as this air probably was pulled through tubing, pumps, mass flow controller (?), ozone scrubber, etc. which may have significantly altered the spore counts? Were correlations with other environmental parameters (temperature, ozone) investigated that may have caused an increase in BVOC concentrations? While there appears to be a correlation between these two time series, further experiments (e.g. by exposure to spores to test if emissions can be induced (in comparison to blank/filtered air experiments)) would be needed to strengthen the argument that the observed sesquiterpene emissions indeed have a defensive role against spores.

Figures 3 and 4 could probably be combined to one plot, since Figure 3 only has one

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other trace that is not included in Figure 4. The right side y-axis title of Figure 4 should mention that this is the sesquiterpene emission potential scale.

Figure 5 is somewhat deceiving as the spacing and title of the x-axis infers that these are time series data. However, upon closer inspection it becomes obvious that the measurement dates are quite irregular (though it is stated earlier that measurements were performed daily (except weekends)). How do model and observations compare during the days that are not shown? I suggest spacing the presented data according to their occurrence, e.g. leaving blank spaces for missing data/weekend days.

Since a number of conclusions are drawn from the comparison of emissions from undisturbed versus debudded branches, it would be important to evaluate the statistical significance of these data. I suggest developing error estimates of the emission rate calculations and performing statistical tests to determine if observed differences are statistically significant.

I am surprised to see that a β-value of 0.09 was applied to all temperature-only dependant compounds, including sesquiterpenes, listed in Table 1. Table 2 shows significantly higher β-factors of 0.18–0.20 for the sesquiterpene β-caryophyllene. Similarly higher β-factors (ranging from 0.12–0.19) were also reported by the same researchers in their earlier study [1]? Applying this higher (more representative?) β-factor to the sesquiterpene data would probably cause a notable increase in their reported emission potentials.

Is the term “EO”, as used in Table 2, defined earlier?

References

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Interactive comment on Biogeosciences Discussions, 2, 1697, 2005.