Interactive comment on “Terpenoid, acetone and aldehyde emissions from Norway spruce” by Hannele Hakola et al.

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We wish to thank Referee 2 for many valuable comments. We have now corrected our manuscript accordingly.

Abstract Please state objectives and conclusions
They have been added

Introduction
It is missing an overview on the boreal forest. Norway spruce has only been mentioned once. Please rewrite the introduction taking into account a better explanation of the boreal ecosystem and the role that VOC emissions have in such ecosystems

We have written more about boreal forest and the BVOC emissions in the boreal
ecosystem.
What is the objective? Very few data on emissions? I suppose there is another rationale, please state.

More text about knowledge gaps in BVOC emissions from boreal area is added to the introduction.

Page 1, Line 14: please insert references that show forested boreal emissions of mt, sqt and OVOCs.
The references have been added.

Page 1, Line 16: contribute to the increase of methane lifetime? How? Please explain.
Oxidation of VOCs consume hydroxyl radicals and hence affect the lifetime of methane. This has been added to the text.

Page 1, Line 26: You say in addition to isoprene, but is the first time you mention isoprene. Please expand.
We added isoprene also earlier in text, line 13.

Page 1, Line 28: please give an example of saturated aldehydes.
C4-C10 saturated aldehydes are given

Methods The methods sections needs considerable attention. The measurement times and tress are expressed in a confusing manner, and better explanation of sampling must be given.

We clarified the measurement protocol.

Another important issue is the comparison among trees. The tree measured in 2011 was different from the tree measured in 2014 and 2015, therefore I think they are not comparable as different processes such as age or different climatic conditions may come into play. This different tree should be removed from the comparison. Not nec-
The tree measured in 2011 is not included in the chemodiversity study. Only measurements conducted during the same day are included. All the trees were different in chemodiversity study, because the idea was to show the diversity during the same day between individuals.

To begin with, a table with the different measured trees, years and techniques shall be stated.

Only two trees were measured (tree 1 in 2011 and tree 2 in 2014 and 2015) and only one technique was used (in-situ gas-chromatographic measurements), so we do not think this needs a table. Additionally chemodiversity study was conducted during one day and then also trees 3-8 were measured, not with in-situ measurements but by taking adsorbent tube samples as shown in Fig 2.

We clarified this by adding more text.

Furthermore, a better explanation of the cuvette used is needed, a picture of the setting will help the reader considerably. Is there a blank cuvette? How do you take into the possible effects of the cuvette on the branch used?

We have added a picture of the set-up in supplementary material. There is no separate blank enclosure, but a blank can be measured by using empty enclosure. Branches can be harmed when they are enclosed in chambers and this can be seen in increased emissions. Therefore, we did not use the data until the emissions seemed settled. We also let the branch remain in the frame during the whole growing season, only the Teflon film was removed when the measurements were not conducted. This can be done without disturbing the plant.

Page 2, line 50: You say here the samples were collected. What do you mean by that? We mean that the sample flow to the GC was directed from the branch located at about two meters height. The word 'collected' has now been changed to word 'taken'.
Which samples? GC cartridges? You take samples from the outlet of the cuvette?
We mean the sample flow to the GC from the enclosure outlet port. The sampling system was described in more detail in the text.

Please specify. Page 2 line 55: you mention you have a thermometer inside the enclosure. What brand? Is this thermometer having a possible artefact effect?

Thermometer conductor was covered with Teflon tubing and it is not supposed to cause any disturbance. The brand has been added to the text.

Page 2 line 56: how did you measure PPFD? Please include brand.
The brand has been added to the text.

Page 2 line 66: Please explain how the quantification of sabinene can be done using the calibration curve of b-pinene.

This is not an accurate method for quantification, but at least by using b-pinene calibration curve we can see how sabinene concentrations vary diurnally and seasonally. Sabinene, α-pinene and β-pinene have quite similar mass spectra and the ion 93 response of b-pinene is about 10% larger than the response of α-pinene. Sabinene elutes very close to b-pinene in our system and therefore we used b-pinene response factor. Surely the error of sabinene measurements is higher. This has been added to the text.

Page 2 line 70: please include the manufacturer of the calibration solutions.
They have been added.

Page 3 line 72-75: here you say that in 2015 you were able to measure acetone and C4-C10 aldehydes. Then you say acetone was coeluted with propanal. Either you give a proof that you were able to properly calibrate acetone or you do not report acetone. In addition, please specify which C4-C10 aldehydes were you analysing.
The aldehydes measured are mentioned in the section 2.1. Calibration can be satisfactory although it is not linear.

Page 3 line 93: there are more recent studies (Guenther et al., 2012) that suggest the slope value should be 0.1.


Page 4 line 102: you say that you have used a temperature dependence for monoterpenes and a light and temperature dependence for isoprene. Please calculate also the temperature only dependence for isoprene and the light and temperature dependence for monoterpenes to conclude which is the best choice.

Several modeling approaches were tested on all compounds, including the traditional temperature only monoterpenel-type pool emission dependence, the isoprene-type light and temperature instant emission dependence, and a hybrid algorithm with both pool and instant emissions. However, the results were not conclusive, and the temperature only relationship, which has also previously been found to correspond with the emission behavior of monoterpenes, covered the observed emissions well. For isoprene, the standard approach has generally been using the light and temperature dependent instant emission algorithm, and applying the other algorithms did not provide a better fit.

Page 5 line 128-133: This part is confusing. You need to properly explain how the sampling was performed in the different years. So for this day on the 24th of June of 2014, you analysed 6 different spruces which then you compare to the 7th tree which is the one continuously measured in 2014. I don’t understand how can they be comparable if the sampling is different (tree number 7 uses the Teflon cuvette via the dynamic flow through, whereas the other 6 trees were sampled with a Teflon bag. Did you have a blank? For how long were you sampling? I also noticed that for the cuvette tree the adsorbents are different than for the Teflon bag, and disturbances can be different, therefore I would not compare them together. You need to give tree numbers from the beginning of the methodology, so it is clearer to the reader. Furthermore, a more detailed information about sampling and how this is different to the main sampling
is provided. I supposed these samples are analysed with the same instrument that is measuring cuvette air. Please state.

When taking samples only for qualitative purposes, as in this case, the sampling procedure is simpler. You do not need to know flow rates accurately and just few minutes sampling on tubes or on-line GC gives a monoterpene pattern that we were interested in. We have numbered the trees and described the sampling procedure better to make this clearer. The adsorbent in the tubes and in the GC cold trap was the same all the time. There is an error in the manuscript and this has now been corrected.

Page 5 line 139: you say that when experimental data was not available you use this software. Then use it to estimate the reaction coefficient for b-farnense and nitrate, as you mention its importance (linked to page 9 line 288).

There is no estimate available for nitrate+b-farnesene reaction

Results and discussion

3.1. Weather patterns during the measurements. Here you need a graph showing the year to year variability. In the table you cant really see what are the changes. Furthermore, in table 2 you say that those are mean values, therefore is needed to use standard deviations. For the rain you must state the mm, is it mm per month? A better explanation of how do you consider the seasons is needed, therefore perhaps pointing in the new meteorological figure when it is spring, early summer, late summer, etc, can help and then you express in the text why.

See response below. The section has been rewritten.

Page 5 line 145: you say temperatures are exceptionally high and precipitation is extremely low. what is high, what is low. This must be stated!

See response below. The section has been rewritten.

Page 5 line 151: you mention a warm spell in June and a cold spell in July. Please
show on new meteorological graph and explain what is a warm/cold spell. A clear and
“based on meteorological data” election of the seasons must be stated. This can be
added into the measurements table (i.e. year, tree, measurement technique (Cuvette,
Teflon bag)

Section 3.1 Weather patterns during the measurements has been rewritten, with the
purpose to only characterize the conditions in Finland during the growing season pe-
riods when the measurements were carried out, and say that they were in no way
exceptional compared with the long-term averages. The weather patterns or meteoro-
logical data are not used to specify the seasonality for the measurements. The tem-
poral distinction is only based on calendar months, spring months (March, April, May)
and summer months (June, July, August). The summer months period was divided
in early and late summer, because it has been observed in our earlier measurement
campaigns that the emission speciation and emission rates may be different in early
and late summer. (Tarvainen et al, 2005).

3.2. Variability of VOC emissions

Page 6 line 157: what do you mean by early season?

The word season is now replaced with the word summer, which is defined later in the
sentence.

Page 6 line: 159-161: you cant compare the measurements of year 2011 to the mea-
surements on 2014 and 2015 as they are different tree, so please only use 2014 and
2015 data for comparison. Furthermore, you present seasonal means and do no report
of standard deviation. Please report standard deviations.

We are not comparing the trees, we want to give as representative value of the amount
of compounds emitting to the atmosphere. Therefore, we think it is important to use all
the data we have. The standard deviations are now included in the table.

Page 6 line 162: what is a low and a moderate emitter? Please report about values.
Furthermore, this kind of information suits much better in the introduction. It would also be good to have a comparison among other high emitting species from the boreal region.

We have added the emission rates we have cited. However, we decided to keep them here since it is easier to compare to our results. We do not really have high emitters in boreal region. Some birches emit monoterpenes in quite high amounts (Hakola et al., 2001), but seasonality of deciduous and coniferous trees is very different and comparison would not give very useful information.

Page 6 line 164: you say that you studies confirmed the low isoprene and moderate monoterpene emitters but the seasonal patterns were clearly different. Different to what? I have no indication of the seasonality of low isoprene and moderate monoterpene emitters, please mention and discuss.

The sentence “low isoprene and moderate monoterpene emitters” has been deleted” and the text concerning isoprene has been re-written.

Page 6 line166: this is the only mention of MBO (apart from the methodology). I would skip it or expand the explanation on MBO.

MBO sentence has been deleted.

Page 6 line 162-170: you report several emission rates but no uncertainty, please report.

We think that the text would be not nice to read if lots of numbers were included. Instead we wrote there Table 3, so readers were suggested to have a look at the Table and find the standard deviations there.

Page 6 line 171-172: you are still talking about monoterpenes and sesquiterpenes from your data, so this should go in the above paragraph.

The paragraphs have been combined
Table 3: In order to have an easier visibility of the data I prefer to see a bar graph of table 3, with uncertainties!

We have added standard deviations to the Table 3 as requested by the reviewer earlier and we think that numbers are more useful to most readers since then our figures can be compared with other results easier and they can be used by modellers. We have also added a new Figure 2 that describes the data statistics.

Page 6 line 171-184: here you do a comparison with Bourtsoukidis et al., 2014b. This is a nice comparison. But I prefer that first you mention the why of your found seasonality in the boreal forest to then start stating the difference to the German forests and thus differences in emissions. Furthermore, you mention only a difference between 0-84 ng g(dw)-1h-1 for SQT in your study, and this is a big part of your results. Please expand your SQT results and then compare to other studies.

The text has been restructured

Page 6 line 186: you say that the main sqt is b-farnense, can you comment about the other SQT measured?

\(\beta\)-caryophyllene and \(\alpha\)-humulene were also identified and this was added to the text. However, we observed several other SQT as mentioned, but since we did not have standards for them we cannot identify them conclusively. According to the mass spectra library there are usually many potential candidates for each of them and therefore we decided not to speculate what they could be.

Page 6 line 189: this is an important result and statement, therefore please show a graph showing the Linalool and sqt increase together. Furthermore this can be another conclusion from you study.

We have included a figure (Figure 2) showing monthly means of linalool, MT, SQT and aldehyde sum. Aldehydes and MT peak in July whereas SQT and linalool later in August. This was also added to the conclusions.
Page 7 line 193-207: This role should also be mentioned in the introduction. Furthermore, there has to be a better integration between the results from this study and the literature research.

The role has been added to the introduction.

Page 7 line 209: If you can't measure most volatile aldehydes then it does not make sense to say that the amount of measured carbonyl compounds was comparable to the monoterpenes, as it is misleading.

In this sentence we are not talking about aldehydes generally, but referring to the measured compounds. We do not think it is misleading. This just shows that also these emissions are significant.

Page 7 line 212: Could you provide with mean values for the percentages? Was this percentage calculated from both early and late summer, or they were calculated separately?

The percentages were for the whole summer. This has been added to the text. The mean values are shown in the Table and this has also been added to the text.

Page 7 line 213: you mention the possibility of bidirectional exchange when moist vegetation. Why? What is the link to your study? Please state.

The sentence has been deleted.

Figure 1: please include light as well to see the effect that light can have. Please remove/separate the graph from 2011 as it is not comparable to the other years as you were measuring a different tree. Please report as well standard deviations, name the compounds in the sum of C4-C10 aldehydes. If you were not able to give a proper explanation of the calibration for acetone, please remove from graph. In addition just a as help for the reader indicate which months comprehend the different selected seasons.

Light shows similar variation as temperature and we have shown in the modelling part
that has no effect on the SQT and MT emissions. It would not give any useful information and would make figures more unclear. Early spring (April) measurements were only conducted in 2011 and in this Figure we want to show variability of all the compounds/compound groups that were the most meaningful each season. Therefore we would like to keep also April measurements in the Figure. Standard deviations cannot be reported since these are not averages. The names of the aldehydes have been added. We mentioned earlier that the calibration was satisfactory. It is not linear, but still it is satisfactory. The seasons are mentioned.

3.3. Tree to tree variability in emission pattern. It is expected to have different emission patterns in threes that have a considerable difference in age. Furthermore, the climatic variability among years makes it harder for comparison. The comparison is ok for the trees measured in 2014 so I would stick only to it.

The tree 2 has been removed from the study.

Page 8 line 232: variability of what, please state.

Variability in the monoterpene emission pattern. This has been added to the text.

Page 8 line 234: if the tree number 2 has a different sampling technique than the other trees, can this be really comparable?

The tree 2 has been removed from the study.

Have you check the differences among sampling? Please make sure tree 2 and 3-8 are comparable to each other.

See above.

Page 8 line 236: the values for monoterpenes were not statistically significant different from 0? Please state what you mean by significant.

This has been added to the text.
Page 8 line 242-244: please expand in how this study shows the importance of species specific measurements.

We have added more clarifying text.

3.4 Standard emission potential. As commented in the methodology, make a comparison between the temperature only and the temperature and light dependency, to see why the choosing of the algorithms makes sense.

Several modeling approaches were tested on all compounds, including the traditional temperature only monoterpene-type dependence, the isoprene-type light and temperature dependence, and a hybrid algorithm with both pool and instant light-dependent emissions. However, the results were not conclusive, and the temperature only relationship, which has also previously been found to correspond with the emission behavior of monoterpenes, covered the observed emissions well. For isoprene, the standard approach has generally been using the light and temperature dependent emission algorithm, and applying the other algorithms did not provide a better fit.

Table 5: please change to bar graphs to see the comparison among species and seasons.

We think that numbers are more useful to most readers since then our figures can be compared with other results easier and they can be used by modellers.

Page 9 line 266: please insert similar behaviour to monoterpene emission potentials.

Corrected

Page 9 line 268-275: This section needs some reviewing in the sense that past studies have fit a temperature and light dependency emission dependency for carbonyl compounds (SHAO and Wildt, 2002). You mention that the best fit was obtained with the temperature dependent algorithm, please then state how better was as compared to the light and temperature dependency algorithm.
Shao and Wildt refer to Guenther et al. (1993) and Tingey et al. (1991) for their algorithm for acetone emissions. Tingey et al. (1991) present a detailed monoterpene emission rate model which bases monoterpene emission rates on environmental conditions, leaf morphology, and needle resin content, with major emphasis on the effect of needle leaf temperature and the leaf structure. Guenther et al. (1993) discuss this and conclude that the Tingey et al. (1991) detailed model cannot be evaluated with existing field measurement data sets, and that detailed models require variables which are not available on regional scales. Guenther et al. (1993) present the temperature dependent one factor emission model $M = MS_i \exp(\beta(T-TS))$ for monoterpenes, and the multiplicative light factor ($CL$, where $L$ is the photosynthetically active radiation PAR) and temperature factor ($CT$) controlled model $I = IS_i CL_i CT$ for isoprene emissions. Equation (4) in Shuh and Wildt is not a combination of the models in Guenther et al. (1993) and Tingey et al. (1991). It is a hybrid model utilizing the sum of the temperature controlled terpene-type pool emission factor and the temperature and light controlled isoprene biosynthesis-related emission factor in Guenther et al. (1993), with the modification of second power by Schuh et al. (1997). Furthermore, Guenther (1997) has corrected the formulation of the isoprene term to force the factor to be equal to 1 at standard light and temperature conditions (usually set at 30 °C and 1000 µmol photons m-2 s-1, Guenther et al. (1993); Kesselmeier and Staudt (1999); Wiedinmyer et al. (2004)), which is not included in equation (4) of Shao and Wildt (2002). Shao and Wildt (2002) measure pine plants under controlled environmental conditions in a continuously stirred tank glass reactor (CSTR), a 1600 L glass chamber. It is not explained where this reactor/laboratory is, or why Scots pine plants (Pinus sylvestris) are studied. Shao and Wildt (2002) measured acetone and isoprene emissions from pine for about half a year in spring-summer season (April to August). It is not clear how this seasonality is arranged for the measurements carried out in a chamber mounted in a temperature-controlled cell, with light provided by a set of Osram high intensity lamps. Also, it is not clear how the other measurement set covering April to December with a total of 7 measurements, described elsewhere in the article, was carried out.
In Figure 1 (emission rates of acetone and isoprene over the spring-summer period) the authors state that measurements were under leaf temperature of 25 °C and light intensity of 360 \( \mu \text{E m}^{-2} \text{s}^{-1} \). According to Wildt et al. (1997), who utilized a similar CSTR tank reactor and Osram lamps, their high light flux of 1090 \( \mu \text{E m}^{-2} \text{s}^{-1} \) corresponds to 30-40% of full sunlight. Isoprene emissions are not reported for Pinus sylvestris in Kesselmeier and Staudt (1999), a comprehensive overview of biogenic emissions, physiology and ecology. The trees Shao and Wildt (2002) observed, were very young, 2-3 years of age, and not growing in outdoor conditions, which means that their functionalities could be very different from trees growing in the field. Analysis results obtained in a controlled environment cannot be compared with field studies, where the environmental factors may pose conditions completely different to the laboratory surroundings. Also, the measurements we carried out in this manuscript are not involved with pines, we measured the emissions of adult Norway spruce (Picea abies), a different tree, in field environmental conditions. The emissions of different plants comprise different spectra of chemical compounds and there may be variations depending on the stresses or different environmental factors experienced by the plants. Our results yielded for spruce are only used to obtain indicative emission characteristics for the spring and summer period via simple fittings with the most common emission algorithms, not to compare any relative advantages or weaknesses of different emission processes.


Page 9 line 279: how this variability may reflect past temperature history or effects of incident or previous stress events? What is your explanation for saying this?

The past temperature history is a factor incorporated e.g. in the MEGAN modeling framework, similarly water stresses and other factors affecting plants are considered in the modeling work (e.g. Guenther et al. (2012)). In the text of the manuscript, the discussion on the various factors is only descriptive, we are not trying to guess in what ways these factors may affect the emissions.


Page 9 line 280: please state better what shall be taken into account, is past temperature history or effects of incident or previous stress events, or other?

This sentence has been deleted as it is not constructive.

Page 9 line 281: what is reaction potential? Please explain.

Reaction potential means the ability the compounds have to react

3.5 Total reactivity of emissions You mention total reactivity of emissions, but you never
give a total reactivity values, please do so, or else change to relative reactivity of emissions.

We have changed the title to relative reactivity

Page 9 line 292: As you don’t show these compounds in the graph, please state the contributions.

Measured aldehydes do not react with O3 and therefore they are not found in Figure 4. However, they are shown in OH reactivity Figure and their average contribution is also mentioned in the text.

Page 9 line 295: you mention Nölscher et al., 2013 paper, can you please state at what time of the year these measurements were carried out?

This has been added to the text.

Conclusions The first paragraph of the conclusion is just a brief summary of your results. The only actual conclusion I read is that the monoterpene emission pattern varies a lot (what is a lot?) from tree to tree. From your results and discussion I got the following messages, that if expressed as implications for boreal ecosystems can be used as conclusion from your study - What is the seasonality? - There is low isoprene and moderate monoterpene emitters - Sqt emissions - Defence role b-farnense and linalool – OVOC roles, - Diurnal variability - Importance of tree to tree variability - Importance towards reactivity. Please redo the conclusions trying to show what are the take home message from your study.

More text has been added to conclusions

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