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Interactive comment on "Terpenoid emissions from fully grown East Siberian *Larix cajanderi* trees" *by* M. K. Kajos et al.

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We thank referee 1 for the valuable comments. Below we give our detailed answers to each comment.

GENERAL COMMENTS:

Kajos et al. measured emission rates of biogenic volatile organic compounds (BVOC) from shoots of two mature larch trees in three campaigns during summer 2009. In contrast to many other studies on boreal forest species, Kajos et al. for the first time investigated emissions from Larix cajanderi in their natural habitat near Yakutsk in Eastern Siberia. As the Arctic warms, BVOC emissions in the Arctic will likely increase and this could have important feedbacks with

the climate. Monoterpenes accounted for the vast majority of emissions from Larix cajanderi, with Δ^3-carene being the most important. Emission potential and reaction rate constants for oxidation with ozone and hydroxyl radicals were calculated. Concentrations of hydroxyl radicals and ozone were derived from previous studies in Finland. The results were compared to other boreal tree species. This study addresses existing information gaps on Arctic and Subarctic BVOC emissions. Also, among all the studies on Boreal emissions, Siberia remains underrepresented. The study therefore contributes to eliminate white spots on the map. It demonstrates that a lot more information is needed to improve emission models for the boreal forest.

Overall, the manuscript is comprehensibly written but appears to be based on only a very small dataset. The authors should more clearly explain if their presented data are representative and if they recommend their use in BVOC model development for Siberian forests.

As the referee points out, we have analysed the emissions from the Larix Cajanderi and provided the first estimates of the biogenic volatile organic compounds from the Siberian taiga. These observations are a result of a relatively short field study and thus they should be considered as the first results that need to be verified with additional measurements. Taking the data of one tree at face value and utilizing it in a model would lead to a substantial increase in monoterpene emissions from the Larix Cajanderi, whereas the results from the other examined tree would lead to a more moderate increase in the emissions. These data illustrate variability of the emissions from real trees and provide scientific basis for the model experiments with variable emission rates. We address these issues at the end of the conclusions section.

The boundary layer VOC oxidation calculations should be based on ambient concentrations/flux measurements. The scale up procedure from measurements of just a few leaves to the canopy likely has very large errors which should be

discussed. In the methods part, all the equations are carefully deduced and explained.

As the referee points out, the implications of the emissions of the ambient mixing ratios of BVOCs depend on e.g. the oxidative potential and boundary layer mixing. In this study our aim was not to quantify exactly the ambient mixing rations by up-scaling the emission rates. We merely wanted to have an estimate of the relative roles of various BVOC compounds in atmospheric chemistry and secondary aerosol formation. Also, as we utilized typical oxidant concentrations observed in the Finnish boreal forest, our estimates do not reflect the absolute concentrations of the oxidation products, but only their relative amount from the observed precursors.

SPECIFIC COMMENTS:

My specific comments are mostly focused on detail information for general understanding and less on chosen methods, since these concerns largely have been addressed by reviewer 2.

Do you really need the sorbent material used in the abstract?

The adsorbent material was removed from the abstract.

l-106: you are not avoiding stress BVOCs by simply waiting one day before measurments. Perhaps you should say to minimize stress-induced BVOCs

The text was modified so that we are now talking about minimizing the stress-induced BVOC emissions instead of avoiding them. Furthermore, we added to the text that the chamber was closed and flushed with the zero free air only during the measurements and it was always kept open to the ambient air when we were not sampling.

The authors should remember that the total BVOC emissions is likely much

greater and include compound not easily measured including oxygenated VOCs, aromatics, and fatty acid oxidation products. Thus, the use of relative emission rates is useful, but the absolute emission rates should be included, especially in the abstract.

We agree that there are many other compounds emitted by the trees than those reported in this paper. We added more information about the measured compounds and total emissions to the abstract by adding the following: "Seven different monoterpenes, six different sesquiterpenes, linalool isoprene, and 2-methyl-3-buten-2-ol (MBO) were identified. The monthly median total emissions varied between 0.006 and 10.6 μg $g_{dw}{}^{-1}$ h^{-1}."

1-4638, line 1: "Volatile compounds" Since only BVOCs are measured in this study, the term "biogenic volatile organic compounds" should be used instead

We changed volatile compounds to biogenic volatile organic compounds.

2-4638, lines 5-6: "In this study the shoot scale terpenoid emission rates from mature Larix cajanderi trees growing in their natural habitat in Eastern Siberia were measured." It should be specified how many trees have been sampled, where exactly, and how long. At least the station name and maybe coordinates and the location close to the Lena river should be mentioned. Also, the number and time of campaigns and the year should be indicated, since in line 12 it is referred to the campaign in June. This would help a lot to assess the scope of this study. In comment 1, reviewer 2 is concerned about the representative character of this study for modeling. The authors do not appear claim that they provide representative data for this purpose, as pointed out in the conclusion. If this is the case, it would limit the impact this paper will have on BVOC model improvements from Siberian forests. It would help to clarify this from the beginning, to

avoid any misconceptions about transferability of the results.

We added to the abstract more detailed description of the measurement site. Also we now explain in the abstract when the measurement campaigns were done and how many samples were taken during each campaign.

Our results are from a short field study and provide the first estimate on the BVOC emissions from the Larix Cajanderi. As the referee points out, we address the transferability at the end of the conclusions section. We feel that this is enough.

3-4638, lines 11-12: "Linalool emissions were also substantial, especially in June." Please give the exact values here

In our opinion reporting the exact values is not relevant, as the emission depends on the environmental conditions and values vary during the summer. We now tell in the abstract, which compounds were identified in this study and we feel that it is better to report the fraction of the total emission than the exact numerical value. We added the fraction of linalool to the abstract.

4-4639, lines 2-3: "growing the initially formed nanoparticles to climatically relevant particle sizes". Could you give one example of how these particles are climatically relevant? It would help to show the general importance of these measurements.

To address how the particles affect climate, we added sentence: "These are the particles that can act as cloud condensation nuclei (CCN) and scatter sunlight (Kerminen et al., 2005; Sihto et al., 2011, Kerminen et al. 2012, Paasonen et al. 2013). Paasonen et al. (2013) observed a direct connection between ambient monoterpene concentrations and CCN sized particle concentrations."

5-4641, lines 8-9: "two fully sunlit shoots of two different trees" Could you give more detail about the two trees? Why were they chosen, how old are they, how tall are they, how big are the measured shoots? I ask that because the trees are denoted as "mature" in the introduction, and on page 4646, lines 21-25, emissions are compared to a "young, 5-yr-old L.sibirica".

As mentioned in the chapter 2.2 "The measurements were done at the upper canopy of L. cajanderi forest from trees that could be accessed from a 15 m high scaffolding tower." The choice of the trees was primarily based on their accessibility from the tower. The measurement height was from the highest level of the tower, inside the forest canopy, approximately 2 meters below the tree tops. We don't know the exact age of the trees, but they are several tens of years old. The size of the measured shoots was such that they fitted easily to the 15 litre chamber.

The reason we compared our results to the emissions of 5-yr-old L. sibirica is that to our knowledge that is, so far, the only study reporting emissions from larch. The young age of the L. sibirica was mentioned, because it could have an effect on the emissions.

6-4641, line 10: "Teflon chamber" What is the volume of the chambers?

The volume of the chambers was 15 litres. This information was also added to chapter 2.2.

7-4642, lines 4-5: "After each of the measurement campaigns, the measured shoots were cut" Did you somehow monitor the effects of cutting on VOC emission? Since cutting itself is a stress factor, how did you make sure that cutting shoots after the first campaign hat no influence on the later campaigns?

Since the measured trees were big mature trees, losing one shoot should not have a notable effect on the VOC emissions of the whole tree. It is also not unusual for trees

to lose shoots and branches due to e.g. wind. This is a stress factor that we did not have control over. During the field study we did not cut any extra branches or shoots precisely to minimize the stress effects induced by the measurement campaign.

8-4645, lines 9-11: "Hydroxyl radical and ozone concentrations were not measured at the site, therefore typical daytime concentrations in boreal forest environment need to be used for estimating the patterns of above-canopy concentrations of VOCs" The values that have been used here as well as the studies they originate from are mentioned on 4652, lines 1-3. I think it should be mentioned here instead. And could you point out in what way are these values are typical for the entire boreal zone? Could you underpin this statement with a reference?

We think that reporting the values used in our calculations fit better to the results section just before the results as it is more specific to the results than to the general method of the calculation.

We do not claim that the OH and ozone concentrations are the same throughout the boreal zone. However, as we don't have measured concentrations for OH and ozone, we used concentrations that have been measured in as similar as possible conditions to estimate the fractional ambient BVOC concentrations.

9-4647, lines 25-26: "A few other sesquiterpenes were also detected, but due to the lack of suitable laboratory standards these could not be identified" What was their contribution to total sesquiterpene emission? This should be included in the pie charts in fig.4 or at least mentioned here.

The contribution of the unidentified sesquiterpenes was minor. Due to lack of standards, their amount could not be accurately estimated, but we believe that their contribution is less than 10

10-4649, lines 7-8: "It is possible that the difference in the observed emission rates reflects within-species variation of L. cajanderi" Is this a speculation or could you add a reference here to support this hypothesis?

As we measured only two trees it is not possible to conclude, based on these measurements, how much within-species variation L. cajanderi can have. There are reports by e. g. Hakola et al. (2001) and Haapanala et al. (2009) of more than one order of magnitude variation in monoterpene emission potentials due to intra-species variation. We added this also the text.

11-4651, lines 18-19: "In order to assess the role of VOC emissions in the atmospheric chemistry and SOA formation" Throughout section 3.4, results for above-canopy concentrations are shown and discussed, but there is no actual assessment of their role in the atmosphere or even formation of SOA. I suggest to either outline the linkage between discuss it in more detail and ouor to move it ntirely to the introduction

To explain better the role of VOC emissions to the SOA formation, we added sentences: "For the most reactive compounds, the fraction of the relative ambient concentration is smaller than their fraction from the measured emissions. These compounds are oxidized faster by OH and O3 and their SOA formation potential is higher than for less reactive compounds."

12-4652, lines 23-28: This is a summary of a study on Scots pine. Could you discuss how the findings of this study are related to that of Larix cajanderi?

We included this study about Scots pine dominated boreal forest because we wanted to compare our calculated concentration estimates to measured ambient concentrations.

13-4653, lines 2-3: "Also linalool emissions were substantial, especially in June." As in comment 3 for the introduction, please repeat the value, since you refer again to linalool emission in lines 12-13.

See our answer to comment 3. We added the fraction of the total emission to the text.

14-4653, lines 12-13: "its contribution to air chemistry and SOA formation was most significant" Reviewer 2 already made reservations about the use of the term "significant" in comment 12. I agree with that and suggest to include necessary statistics to valide this statement or soften this conclusion.

We modified the sentence to: "In June, when the linalool emission rate was highest, its impact on air chemistry and SOA formation was also the greatest."

15-4654, lines 2-4: "except for the highest emission potential values of the tree B... with the exception of L.sibirica" I suggest to rephrase this sentence to unnecessary confusion.

We rephrased the sentence to: "These results are consistent with previous measurements done for other boreal tree species, except for the highest emission potential values of the tree B. The emission potentials of tree B were higher than those observed for other boreal tree species with the exception of L. sibirica."

16-4654, lines 15-16: "As a result, this would increase the derived SOA and regional radiative forcing due to SOA" Why is this brought up here and not already in the discussion? This should be explained in more detail earlier.

Here we compare our measured emission potentials to those used in two global modelling studies and emphasize the need to have more detailed information on the spatial distribution of the emission potentials in the boreal zone.

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