

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

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Received and published: 7 June 2013

We thank referee 2 for valuable and thorough comments, which improved the manuscript substantially. Below we give our detailed answers.

1-P.4640, lines 17-19: “The measurements were conducted during three campaigns in the summer of 2009: 3–24 June, 8–26 July, and 14–30 August.”

Could the authors justify the decision of publishing these results after one season of measurements? My concern here is the representative character of the dataset for modeling studies. A dataset of at least two growing seasons would have been more robust, although I am aware that these kinds of measurements

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done in the subarctic zone of Russia needs a substantial amount of human and material resources.

As the referee points out, the practical arrangements for such measurement campaign in Russia is a demanding task. Purely on a scientific basis, it would have been beneficial to reproduce the measurements during several growing seasons and this would have allowed us a more in-depth scientific analysis of e.g. the inter-annual and tree-to-tree variability. However, this was not possible within this study due to limited time and resources available. In our opinion, this work already is a substantial contribution and increases the scientific knowledge of the emissions of the biogenic volatile organic compounds from the Siberian Larch forests that are representative for a vast land area in Siberia.

For the three measurement campaigns: We see a range of days for each campaign but how many actual days of measurements each campaign has? This information should appear in a following sentence. This would describe better the amount of samples used to build the dataset.

We added to the chapter 2.2 the sentence: “73 samples on 7 days, 62 samples on 6 days and 84 samples on 7 days were collected during the first, second and third campaign respectively.” Also we added to the table 2 the amount of data points used for calculating each emission potential value.

2-P.4641, line 10: “Teflon chambers” What was the proportion of light blocked by the Teflon film?

According to Pape et al. (2009) less than 10

3-P.4641, line 11: “VOC-free air” How VOCs were filtered out, was it with a char-

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coal filter?

We had two different ways of removing the VOCs from the air: charcoal filter and zero air generator. We added to the text: "...VOC-free air, which was generated either by charcoal filter or catalytic zero air generator (Parker Balston, model 75-83-220, USA)" Also, in order to know the background VOC concentration, one to three samples were taken from the zero air on every measurement day. This information was also added to the section 2.2: "In order to determine the background concentration of the VOC free air, one to three adsorbent samples were taken from the zero air on each measurement day." 4-P.4641, lines 12-13: "the chambers were put in place at least one day before the measurements started." How far is this from natural conditions? There is probably no stress from the manipulations but a chamber put one day prior is not that natural for the shoots. Were the chamber flushed/purged from the moment they were put on the shoots, i.e. one day prior to measurements or was this done like in Hakola et al 2006, purged only during the measurements?

The chambers were only flushed during the measurements and during other times they were kept open to the ambient air. Thus, when the measurements were not being performed, shoots were kept in ambient conditions. We changed the text to: "During the measurements, the chambers were flushed with constant flow (5 l min⁻¹) of VOC-free air, which was generated either by charcoal filter or catalytic zero air generator (Parker Balston, model 75-83-220, USA). When the BVOCs were not measured, the chambers were open to the ambient air from the other end of the cylinder.

5-P.4641, lines 16-17: "For more detailed description of the technique see Hakola et al. (2006)." I suggest putting this sentence before "The measured shoots were enclosed in Teflon chambers that were flushed with constant flow (5 l min⁻¹) of VOC-free air", to state clearly the method from the start.

The reference was moved as was suggested by the referee.

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6-P.4641, line 27: "filled with Tenax-TA and Carbopack-B" Would it be possible to specify how many mg of Tenax-TA and Carbopack-B there were in the cartridges?

The adsorbents were not weighed, but the sampling tubes were filled according to the manufacturer's instructions. They were filled so that there was about 1 cm of free space at both ends of the tube and in the middle equal volumes of the two adsorbents, Tenax first and then Carbopack. The two adsorbents were separated with a little glass wool.

7-P.4642, lines 2-3: "The PAR was measured with a Li190 quantum sensor (Li-Cor Inc., USA)." Was the PAR measured under the Teflon film? I ask the question because it was not mention how much PAR was blocked by the Teflon film (see comment 2).

See the answer to question 2.

8-P.4642, lines 8-9: "The sample cartridges were stored in a refrigerator before they were shipped to Finland, and were later analysed in the laboratory of the Finnish Meteorological Institute." What kinds of caps were used to seal the cartridges? It should be mentioned here. How long was the period (in average) between the sampling on the field and the analyses at the GC-MS in Helsinki? It should be mentioned here. Have you tested if this period could cause the loss of some compounds or a decrease in the concentration before the analyses at the GC-MS? It should be mentioned here.

We used Swagelok caps made from brass to seal the cartridges. After each campaign the samples were analysed as fast as possible, within a month from the sampling. It has been tested, in the same laboratory as these samples were analysed, that this type of cartridges keep the sample stable for more than a month under proper storing conditions. The text was modified to: "The sample cartridges were sealed with brass

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Swagelok (USA) caps and stored in a refrigerator before they were shipped to Finland. The cartridges were analysed within a month after sampling in the laboratory of the Finnish Meteorological institute. The same laboratory has tested that when this type of sample cartridges, sealed with the same kind of caps, are stored properly in the cold, the samples remain stable for at least a month."

9-P.4642, section 2.3: The algorithms described in Guenther et al. publications were built in conditions that were totally different than from those observed in the Eurasian boreal and subarctic forests. Moreover the species used to build these algorithms were different than those growing in the boreal and subarctic forests. How the authors could justify the use of the algorithms built in conditions that were different from those observed in the present study?

Did the authors consider using a standard temperature of 20 C instead of 30 C as it was done in Ekberg et al. (2009. Biogeosciences 6: 601-613. www.biogeosciences.net/6/601/2009/) for isoprene emission)? A standard temperature of 20 C is more representative of the one observed in the present study as described in line 2-4 of page 4641:"The annual mean air temperature at the site is +10.4 C, with mean temperature of the coldest month, January, being -39.5 C and that of the warmest month, July, 18.6 C (Dolman et al., 2004)." However, I see in table 2 that the authors calculated variable β coefficients, which can account for the different conditions observed in the present study compared with those in which the algorithms were built.

Please, could the authors address these questions in one or two sentences in section 2.3?

The algorithms by Guenther et al. have been used to standardize the emissions of boreal tree species in several studies (see eg. Rinne et al., 2009 and references therein). Using the same algorithms that have been extensively used in previous studies en-

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ables us to better compare our results to existing emission potentials of different tree species.

The study done by Ekberg et al. (2009) was done in the arctic area in northern Sweden, where summertime mean daytime temperature is lower than in Yakutsk. The mean daytime temperature during our measurement campaigns was 26.8 °C for the first, 26.0 °C for the second and 19.0°C the third campaign. Thus we think that using standard temperature of 30 °C is well justified. We added the mean daytime temperatures to the text. Now it is clear why we can use the generally applied standard temperature of 30 °C also in this study.

10-P.4646, section 3.1: In this section, the total emission rates are used to make some comparisons while figures 2 to 4 show median and percentiles that are not used here. Thus I recommend showing the mean and total emission rates below the pie charts of figures 2 to 4 instead of the median and percentiles.

In the chapter 3.1 we are comparing the fractions of different compounds to the total emissions. This does not depend on the absolute values of the total emissions. In figures 2-4 we show the monthly medians and percentiles of the total emission rates.

11-P.4646, lines 5-7: "The emission rates determined from the data are thus representative for L. cajanderi trees during the growing season, excluding the potentially important and different VOC emission spectra and rates during the burst of the needles or the initial growth of the needles." Please, could the authors add a reference supporting this fact?

We added to the text: "Hakola et al. (1998) found substantial monoterpene emissions from the Populus tremula, Salix Phylicifolia and Betula pendula species at the time when leaves werestill young and emerging. The current measurements did not cover this season."

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12-P.4646, line 15: “significant” As pointed out earlier by referee 1, it is preferable not to use the word “significant” in this context as no statistical analyses were done to compare the measured emission rates between trees A and B. The term “important” or another term describing the fact that linalool has a high proportion in the relative emissions could be used.

We changed the word significant to important.

13-P.4647, lines 1-2: “The relative fraction of sesquiterpenes had a somewhat increasing trend towards the end of the summer.” How the authors judged that a SQT proportion starting from 1% in June and ending to 3% in August was “a somewhat increasing trend”? This was only observed for tree B. To my judgment, the trend is rather constant throughout the summer. In Fig. 3, the authors judge that the MT spectra were similar throughout the summer between trees A and B while differences between compound proportions were within or higher than 1-3%. My concern here is that such sentences relate to a subjective judgment and not objectivity.

In order to remove the subjective statement, we revised the sentence to: “The relative fraction of sesquiterpenes was rather constant throughout the summer, although the fraction increased from 1 to 3% towards the end of the summer for tree B.”

14-P.4647, lines 2-7: “This trend was clearer for tree B. Sesquiterpene emissions can also be related to herbivore attacks or other damages the tree may have experienced. Haapanala et al. (2009) found large α -farnesene emissions from mountain birches in northern Sweden two years after an outbreak of autumnal moth; when the measurements were repeated the following year, α -farnesene was not found any more.” Have the author noticed signs of herbivore attacks during the summer of 2009? It seems so as described later in section 3.2: the

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white “cotton like” spots. However, it is not clear here, in this part of the text, why the authors have the hypothesis of the herbivore attacks. I would recommend transferring the description of the white “cotton like” spots already here.

The discussion about the herbivore attacks was moved to the section 3.2 where we discuss more about the possible effects of the attacks on the sesquiterpene emissions from the *Larix Cajanderi*.

15-P.4647, line 8: “although the total emission rate of the monoterpenes was notably higher for tree B.” The total emission rates are not shown for trees A and B. This refers to comment 10.

We added a reference to figure 2, which shows the total emission rates for both trees.

16-P.4648, line 2: “Generally speaking” For tree species in the boreal or subarctic forests? This sentence is too general, please specify for which trees in which forests β -caryophyllene is the most abundant.

To make the sentence less general we added: “trees of the boreal zone”

17-P.4648, section 3.2: Why the authors did not show the measured emission rates for all campaigns in fig. 5? The results discussed in this section justify showing the MT and SQT emission rates for all the campaigns.

The emission rates during all campaigns followed temperature and light conditions. We decided to show only one example of the data for clarity. We modified the beginning of the chapter 3.2 to: “During all three campaigns, the measured emission rates of *L. cajanderi* had a distinct daily pattern following both temperature and light. Figure 5 shows the mono- and sesquiterpene emission rates, temperature and the PAR radiation during the second campaign in July.”

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18-P.4648, lines 6-7: “Measured emission rates of *L. cajanderi* had a distinct daily pattern following both temperature and light (Fig. 5).” Is this also true for other measurement periods than the one shown in Fig. 5? I recommend softening this affirmation if the data are not planned to be shown or if the authors do not mention that this was also observed in all the measurement periods/campaigns.

See comment above.

19-P.4648, line 28: “However, the measured shoot was not visibly affected by this herbivore.” This is a nice hypothesis that can explain the different emission rates between trees A and B although the authors write later that it could be a within-species variation. Could the author add a reference supporting that the VOC patterns of a branch/shoot of a tree, although not attacked by herbivores, can be affected by herbivore attacks done on another branch/shoot of the same tree? A reference would support better the hypothesis explained here.

This sentence was removed from the text.

20-P.4649, lines 11-19: These sentences would belong to section 2.3. Why the authors put them here?

Thank you for the comment. Generally the methods are described in section 2.3. However, the authors feel that the details of the calculations fit better to the beginning of the section 3.3 as they are then more easily connected with our results.

21-P.4649, lines 18-19: “(ii) β was kept as a free parameter when fitting the algorithm to the observations.” Could the authors justify the reasons for keeping the β value free when fitting the algorithms?

Value of the beta illustrates the sensitivity of the emissions to temperature. There-

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fore, the deviation from the commonly used value gives us more information on the temperature dependency of the emission rates with a better fit to the observations.

22-P.4650, line 25: “Several studies have been done on the emissions of other boreal tree species.” Are the authors still referring to MT emissions here? It seems so but it should be clearly written.

We clarified the sentence by adding “monoterpenes” to it: “Several studies have been done on the monoterpene emissions of other boreal tree species.”

23-P.4651, paragraph between lines 8-16. Is it possible to compare this result with other studies or the authors are the firsts to keep the β value free when fitting the algorithms?

This is not the first study to use the pool algorithm with varying β . We decided to show only the β values from our measurements to see how close they are to the fixed value of 0.09 for monoterpenes and 0.143 for sesquiterpenes. Since most of the reported emission potentials of different trees have been calculated using fixed β , we decided to compare only the emission potentials calculated with the fixed β .

24-P.4651 lines 19-28 and P.4652, lines 1-3: These sentences would belong to section 2.4. Why the authors put them here?

Here we report typical oxidant concentrations in a boreal environment. In our opinion they fit nicely here, where they support the discussion in the following sections.

25-P.4651, line 26: “weighted mean reaction rate constants” This is not written in the title of table 1, should it be?

The mean reaction rate used in the analysis is not an arithmetic mean of the individual

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reaction rates. It is weighed based on the compound mixing ratios. Therefore, in our opinion, the title text of Table 1 does not need to be modified.

26-P.4652, lines 11-13: “Sesquiterpene emission rates were increasing as the summer progressed, yielding an increased contribution to the calculated air concentrations, especially in case of tree B.” This refers to comment 13, the judgment on the increasing trend.

We modified the sentence to: “Even though the sesquiterpene emission rates remained rather constant as the summer progressed, their contribution to the calculated air concentrations increased, especially in case of tree B.

27-P.4652, lines 13-15: “For isoprene the atmospheric levels increased somewhat compared to the emission rates for both trees A and B, however isoprene was negligible overall in both emissions and concentrations.” How the authors judge that the atmospheric levels of isoprene can somewhat increase if the emissions and concentrations are negligible? No trend could be judged if it is negligible.

True. The isoprene concentrations were so small that judging any trends from the emissions or predicted concentrations should not be done and thus we modified the text to: “For isoprene both the emission rates and the calculated atmospheric concentrations were negligible for both trees A and B.”

28-P.4652, lines 17-19: “ Δ^3 -carene, which has the highest emission rate, is also dominating the calculated monoterpene air concentrations; however due to its reactivity, its fraction is smaller in air concentrations.” How the author judged that the air concentrations were smaller than the emission rates for Δ^3 -carene? To my eye, it is rather similar. Could the author soften the argument or support

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it by adding the means of the fractions of total in this sentence?

We removed the end of the sentence, thus now it is: “ Δ^3 -carene, which has the highest emission rate, is also dominating the calculated monoterpene air concentrations”

TECHNICAL CORRECTIONS:

1-P.4649, line 16: “value 0.19” Please, correct for “value of”

Corrected.

2-P.4649, line 17: “of value 0.143” Please, correct for “value of”

Corrected.

3-P.4650, line 14: “trend during growing season has” Please, correct for “trends during the growing have”

Corrected.

4-Fig. 7 Please add the tree A or B and the month over each graph as it is done in Fig. 6.

Corrected.

References

Ekberg, A., Arneth, A., Hakola, H., Hayward, S. and Holst, T.: Isoprene emission from wetland sedges, *Biogeosciences*, 6, 601–613, 2009.

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willow (*Salix phylicifolia*), Silver birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmospheric Environment*, 32, 1825-1833, 1998.

Pape, L., Ammann, C., Nyfeler-Brunner, A., Spirig, C., Hens, K. and Meixner, F., X.: An automated dynamic chamber system for surface exchange measurement of non-reactive and reactive trace gases of grassland ecosystems, *Biogeosciences*, 6, 405-429, 2009.

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