

We wish to thank Referees for valuable comments that improved our manuscript in many ways.

## RESPONSE TO REFEREE 1

- There is no concise conclusion. The authors state that the emissions were low in spring and early summer but increased during late summer and the maximums were located somewhere in July-August. I think that this is a rather abstract and un-quantitative conclusion.

*The conclusions have been rewritten.*

- There are too less figures and to my opinion poor analysis. This makes the manuscript rather difficult to follow and drive conclusions.

*We have added a new figure (Fig. 2 in revised MS) in to the main text and a graph describing the measurement system as supplement.*

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- In the same context lies the fact that the authors chose to report results and discussion together. Since an overview on the existing studies is just discussed and not depicted in a table or figure, it's easy for the reader to get lost on the findings of other studies and deviate from the scope of the specific one.

*The chapter has been restructured*

- There is a mixture of trees, years and VOC species presented in a rather confusing way. I had to carefully note down all the details provided so I can follow the text which was not always easy. In addition, the different trees were of different age. I believe that greater attention shall be given in this "detail".

*We have clarified this and for example removed tree 2 from the chemodiversity study.*

- The emission potentials. The authors derived the emission potential and the temperature dependency according to Guenther et al. (1993). Even if the core of current models is the same exponential algorithm, further improvements have been made. In addition, the  $R^2 < 0.1$  is which is extremely low to be taken seriously. It would be very interesting to see how the all data lay on a graph together with temperature simulations. I'm afraid that it's dangerous from modeling point of view to report such strong temperature dependencies with such poor quality on the fit. You should at least discuss extensively.

I would have expected the authors to thoroughly analyze such an interesting dataset. I would therefore suggest major revisions addressing the greater picture. Is this temperature dependency and algorithm sufficient to describe the emissions from Norway spruce? How do current models compare with the measured emissions? What is the abundance of these species and how important are the emissions in case of extrapolation? Is the age of the tree important or we can assume

similar emissions for all of them? Do you see any evidence of additional emission drivers apart from light and temperature? How important are Norway spruce emissions to the total reactivity of the boreal forests?

$R^2$  is an inadequate measure for estimating the goodness of nonlinear regression fits and it should not be used for this purpose (e.g. Spiess and Neumeyer 2010). However, many scientists and reviewers want it supplied with the nonlinear data analysis results, and this is why it is also given here. And all  $R^2$  are not  $<0.1$ . Also, the measurements were carried in a natural forest environment, introducing many environmental factors which might affect the plants and their emissions. We have also found in earlier measurements that in Finland the temperature and light conditions are closely connected in summer, often leading to the saturation of the light algorithm, which limits the use of outdoor measurement results for testing or developing emission models (Hakola et al. 2006).

In this work the fits were made for the whole data set, i.e. three years of measurement periods. This will affect the fits, because the conditions in different years and the response on the plants may vary a lot. If just testing different modeling approaches would have been the purpose of this exercise, it would have been better to carry out the measurements in a carefully controlled (laboratory) environment. Maybe also fitting all the outdoor measurement periods separately would have brought better correspondence, but this would have yielded several sets of emission potentials, serving no purpose for getting an average estimate of the emission behavior during the growing period. The measurements were classified as spring, early summer and late summer data groups, because this was the only way to characterize them during the season.

Emission measurements and the model fits for some of the compounds are presented in Figures 1 - 7. The years are shown in separate panels, even though the analysis covered them together. From the results it can be seen, that the simple temperature controlled pool emission algorithm adequately covers all measurement periods, yielding the general levels of emission potentials for the spring, early summer and late summer classification. The emissions represent averages over all the years, so the observed emission strengths may be over or under predicted, and several emission peaks may be missed. But this is to be expected in this type of scattered measurement campaigns, when all conditions are not controlled or even measured, and where the plants are freely growing in their own natural environment. See also the discussion below, concerning the parameterization of the emission modeling.

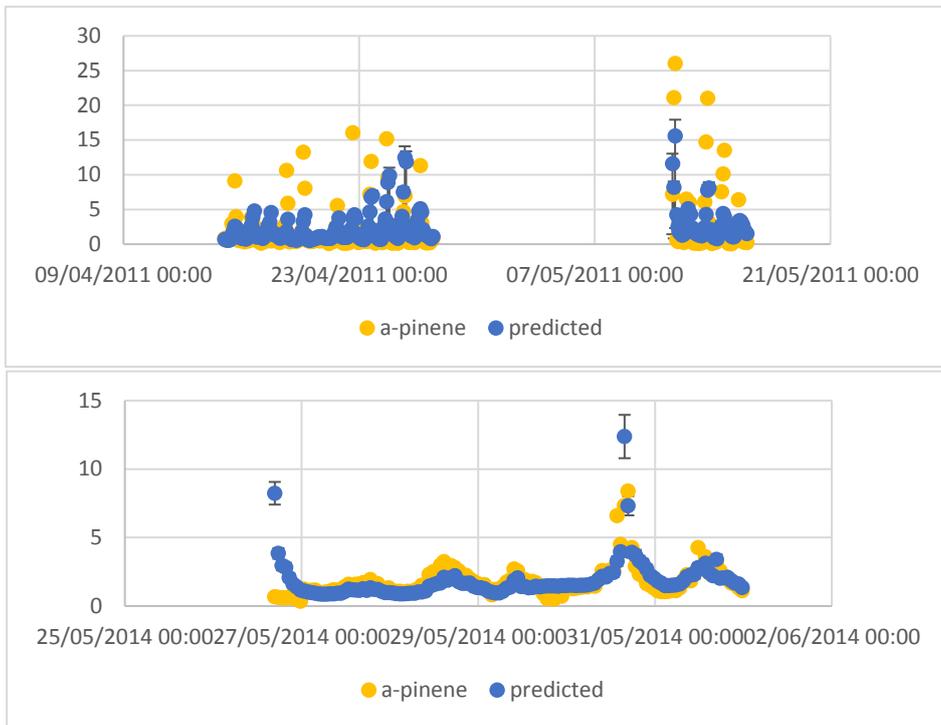


Figure 1.  $\alpha$ -pinene emissions measured and predicted using the temperature dependent emission algorithm in the spring period.

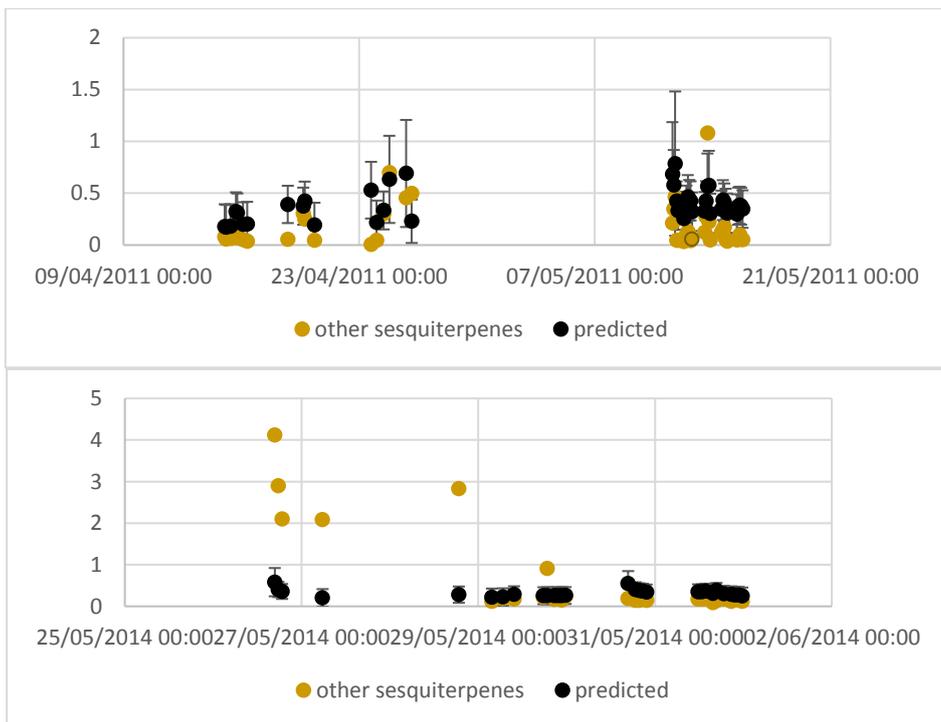


Figure 2. Other sesquiterpenes emissions measured and predicted using the temperature dependent emission algorithm in the spring period.

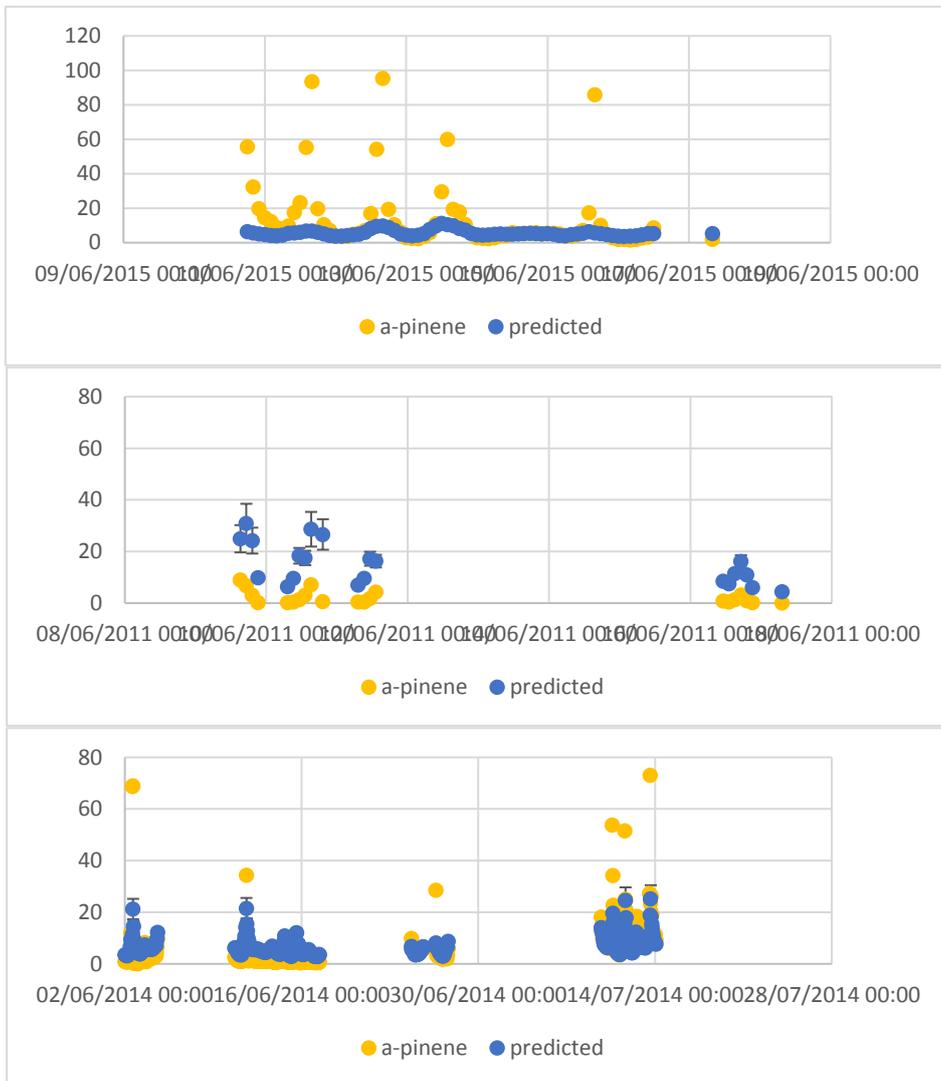


Figure 3.  $\alpha$ -pinene emissions measured and predicted using the temperature dependent emission algorithm in the early summer period.

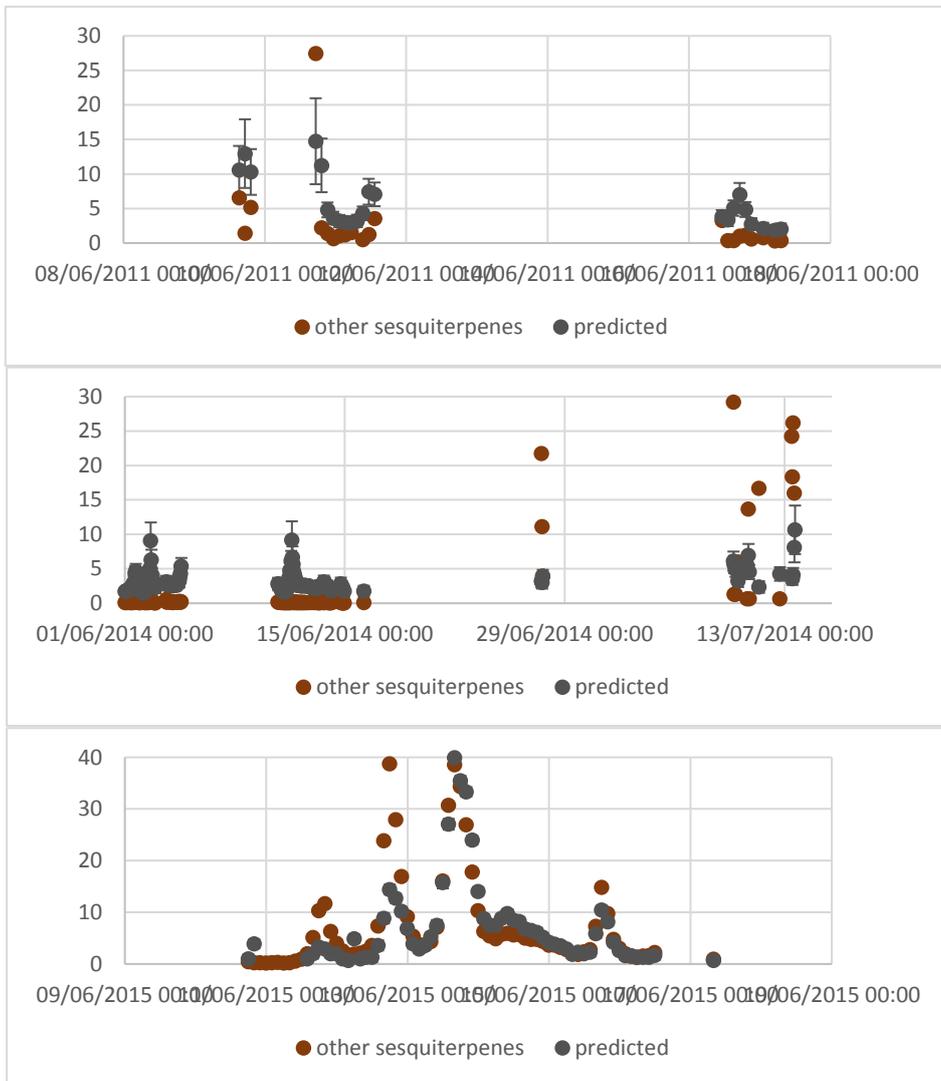


Figure 4. Other sesquiterpenes emissions measured and predicted using the temperature dependent emission algorithm in the early summer period.

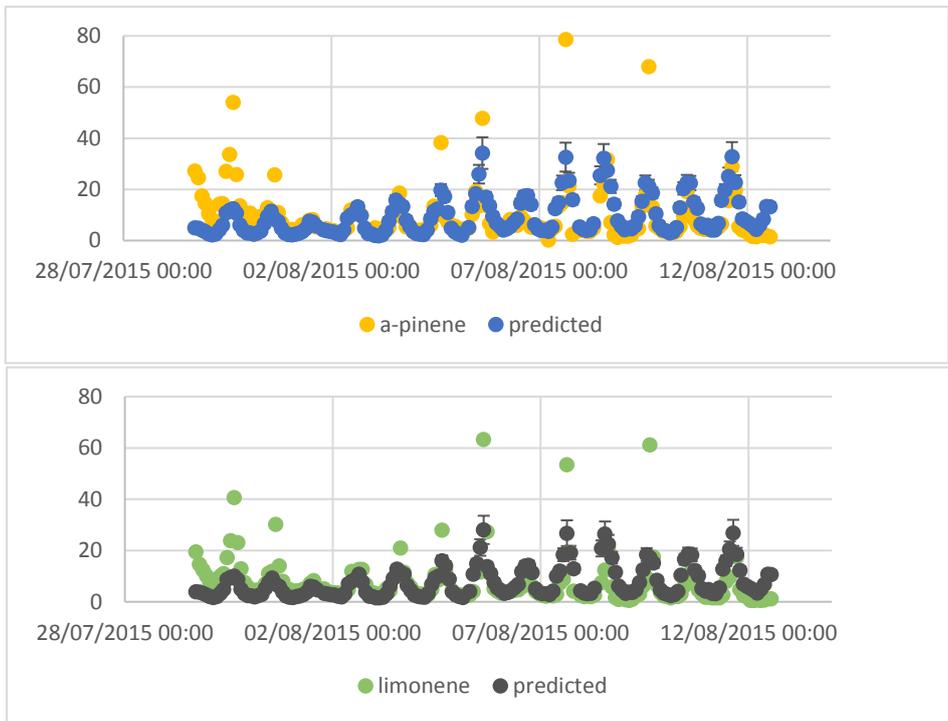


Figure 5.  $\alpha$ -pinene and limonene emissions measured and predicted using the temperature dependent emission algorithm in the late summer period.

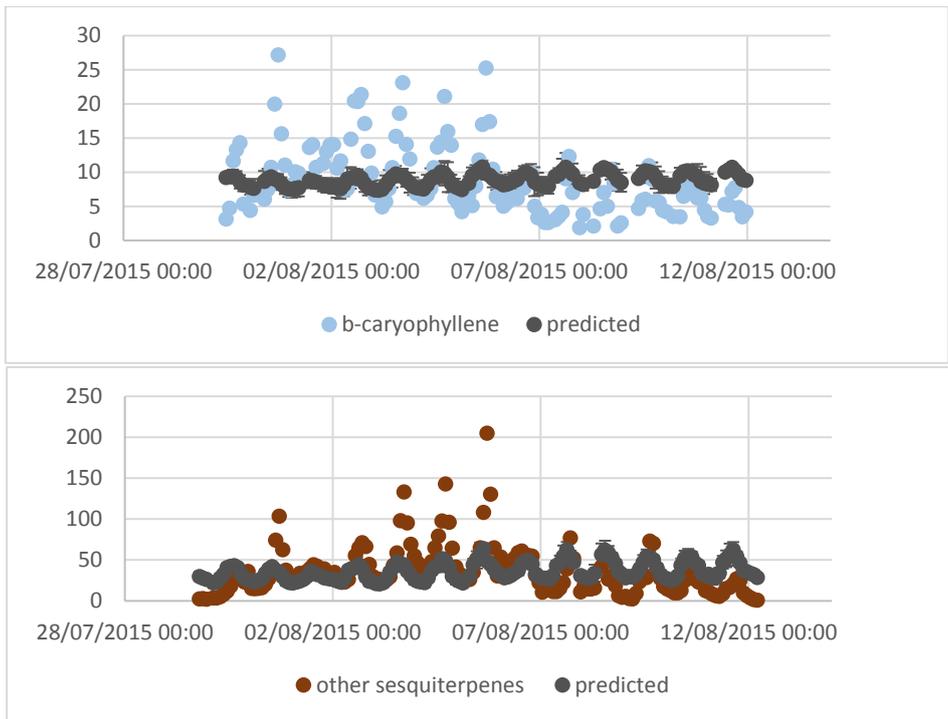


Figure 6.  $\beta$ -caryophyllene and other sesquiterpene emissions measured and predicted using the temperature dependent emission algorithm in the late summer period.

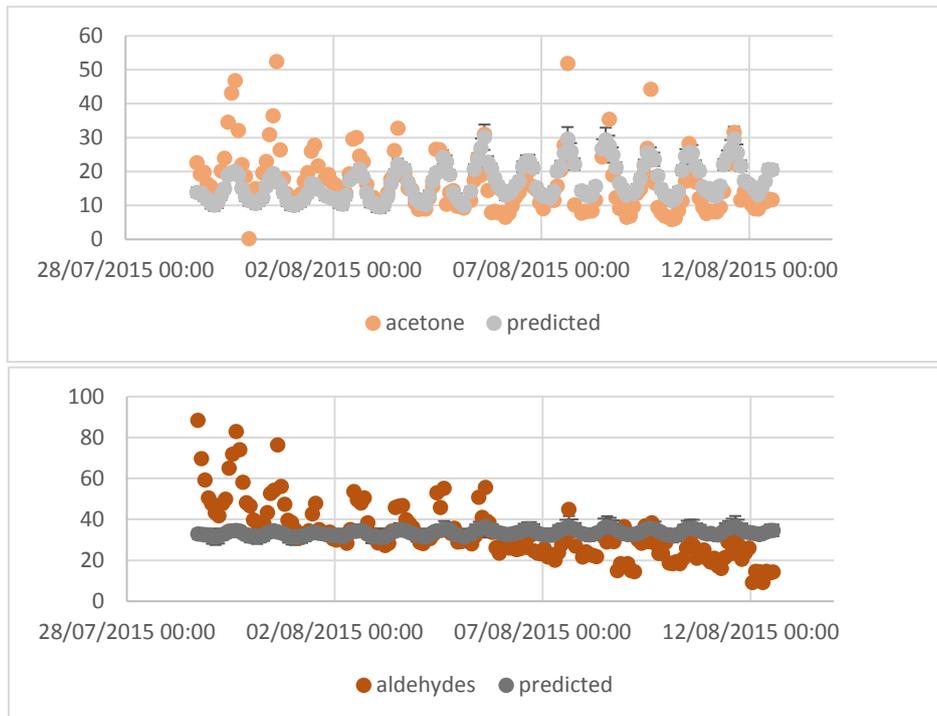


Figure 7. Acetone and aldehydes emissions measured and predicted using the temperature dependent emission algorithm in the late summer period.

Hakola H., Tarvainen V., Bäck J., Ranta H., Bonn B., Rinne J., and Kulmala M., 2006. Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. *Biogeosciences* 3, 93-101.

Spiess, A. and Neumeyer, N., 2010. An evaluation of R<sup>2</sup> as an inadequate measure for nonlinear models in pharmacological and biochemical research: a Monte Carlo approach, *BMC Pharmacology* 10:6. doi:10.1186/1471-2210-10-6.

Specific comments:

L1. Acetone and acetaldehyde are barely reported to have a place in the title. Also “from Norway spruce” is misleading since the authors studied only trees in Finland. I would suggest to change the title into something more specific that would ideally include the main finding.

*The MS has now a new name*

L18-L20. Please provide some standard deviation on the values reported. Emissions from conifers are usually reported per grams of dry weight as you did. However, I would appreciate an attempt to convert such emissions in area, if at all possible.

*Standard deviations are included in the Table 3. A conversion factor from needle dry weight to needle area is now provided in chapter 2.2.*

L24. The reported reactivity value lies on calculations and accounts for only the few measured VOC species. If it was measured, the authors would have probably seen the same contribution reported by (Nölscher et al., 2013). Since the SMEAR station implements a large suite of measurements for over a decade, I would suggest making a complete budget including inorganics before reporting that 70% of the OH reactivity comes from SQT. Please understand that such high value could be easily misinterpreted.

*-Here calculated reactivity is the reactivity of the emissions and not ambient air reactivity. Therefore it is not possible to compare these with the compounds found in the ambient air. However, in summertime in ambient air at this site most of the known OH reactivity (which is ~50 % of total measured reactivity) is coming from the VOCs (Sinha et al. 2010). Other trace gases has lower contribution. In addition, aromatic hydrocarbons have only minor contribution compared to the terpenoids (Hakola et al. 2012). In those ambient air studies contribution of SQTs has been much lower than MTs, but those results are misleading, since lifetimes of the SQTs are so short that most of them are not detected in ambient air measurements and estimation of their contribution to the reactivity is possible only directly from the emissions. In the study of Nölscher et al (2013) measured also reactivity of the emissions and monoterpenes had major contribution to the total measured OH reactivity in the Norway Spruce emissions. However, they did most of their VOC measurements with PTR-MS, which is not the best methods to measure SQTs and we think that they could have missed major fraction of them.*

*This is now clarified in the text in section 3.5*

L48-L56. An important drawback of the study is the lack of clear objectives. Yes, we need more measurements and in situ GC-MS samples would be the ideal way of doing this. It is absolutely essential to evaluate temperature and light dependency but I have the feeling that this study does not go deep enough to assess these drivers in a boreal environment.

*We have added objectives for the study into the introduction.*

*To assess drivers causing VOC emissions in boreal or any other vegetation area is a huge amount of work. We do not know what we are still missing and we do not know what causes seasonal variation and why it is so different in different places. In situ measurements can provide valuable new data to lead us few steps forward. Using gas-chromatograph has allowed us to determine SQT emission rates and their seasonality together with aldehyde emission rates that has not been measured earlier. These affect greatly local atmospheric chemistry and they should be included in emission modelling.*

L61-63. You have measured five days in May 2011 and three (!) days in June. How can you be sure that from such short periods, you can derive a seasonal profile? Why these days were characteristic for May, June and July respectively? Please provide some statistical evidence if this is the case. L65. What is the age of the 10 meter tree?

*In 2011 we measured only 3 days in June, but in June 2014 two weeks. In 2011 in May measurements covered 5 days and in 2014 in May one week. More measurements would of course be useful, but we are quite confident that these measurements can describe the seasonal variability. Two years show similar results in terms of quantitative emissions although qualitatively monoterpene pattern varies.*

*The age of a 10 m tree is about 40 years. This has been added to the text.*

L67. How many years younger than the 2011 tree? Can you provide evidence that a young tree behaves the same as an older one? Would that mean that if we plant some hectares of Norway spruce, in a couple of years their emission potential and general release of VOC would be similar to an old forest?

*We definitely cannot provide evidence that the young trees behave the same as older ones. They seem to emit much less than big trees. We have highlighted this and concluded that the effect of age should be studied.*

L71. Do you have evidence that PPFD strength is not changing by your enclosure? That would have large implications on the light driven VOC. Laboratory measurements assessing the absorbent strength of your enclosure are needed.

*Photosynthetically active radiation designates the spectral range of solar radiation from 400 to 700 nm. FEP film that is commonly used in reaction and emission chambers transmit solar radiation in the 290-800 nm region (see Finlayson-Pitts & Pitts: Chemistry of the upper and lower atmosphere).*

L72. Why did you choose to remove ozone at the inlet and not at the outlet? It has been shown that ozone can be a strong emission driver upon a given threshold. My objection here lies also on the fact that you are changing the conditions compared with the ambient.

*This is true. We are changing the natural conditions. However, we were especially interested in sesquiterpene emissions and they are so reactive towards ozone that we would have missed a lot of them. Also, ozone scrubber cannot be placed in the outlet port because most of our compounds (all SQTs) would be lost there.*

L76-77. Allowing water vapor to your trap, will decrease the sensitivity of the MSD in a proportion similar to the ambient humidity during sampling. Were the calibrations performed also with wet air and at this trapping temperature? If not, your final values will be probably underestimated.

Please provide a wet and dry calibration with the same setting and trapping temperatures to confirm that your approach was correct.

*We did not allow water to retain in the cold trap. The adsorbent material was hydrophobic and water passed the cold trap. To keep the cold trap dry we needed to keep the cold trap at 20 C temperature. This temperature was not cold enough to retain isoprene completely, so after 2011 we changed the trap material from Tenax-TA to dual trapping, Carbopack-B/Tenax TA. The trapping temperature was the same when analyzing emission and calibration samples.*

L88-89. I would suggest to completely remove acetone from the manuscript.

*We decided to keep acetone in the manuscript. The calibration can be satisfactory although it is not linear. However we marked acetone as acetone/propanal,*

L96. Here is just an aforementioned comment that may make your manuscript more attractive to the modelling community: if it's possible, please convert the emissions to leaf area.

*We have measured leaf area of spruce needles at a site and weighted them. The conversion factor is added to the text in chapter 2.2.*

L104. Actually the parameterization in the models includes more variables, ecosystem characteristic. A detailed description can be found eg. in (Guenther et al., 2012). In general, I would suggest discussing over the current model algorithms assessing and evaluating all parameters.

*The MEGAN model (Guenther et al. 2006; Sakulyanontvittaya et al. 2008; Guenther et al. 2012) for isoprene, monoterpene and sesquiterpene emissions has been developed with the goal of replacing regional emission inventories used to predict biogenic VOC emissions in the U.S.A. and globally. The model incorporates the leaf and branch-scale emission measurements, extrapolating them to canopy scale using a canopy environment model. The canopy model includes a leaf area index (LAI) which is estimated as 5, with 80% mature, 10% growing and 10% old foliage. The canopy is further divided into sun prone and shaded leaves which receive different solar radiation. The emissions are calculated based on plant functional types, and the process takes into account e.g. the canopy environment, the age of the leaves, and the soil moisture. The basic equations, are still the exponential temperature dependent mechanism and the light and temperature dependent formulation, where the light response is based on that of the photosynthesis, and the temperature term is based on the activity of isoprene synthase enzyme*

(Guenther et al. 1993). For monoterpene and sesquiterpenes emissions in MEGAN, Sakulyanontvittaya et al (2008) have described the temperature dependent emissions using the exponential equation. Additionally, they have assumed that 50% of sesquiterpenes and approximately 5-10% (with a few exceptions) of monoterpene species are emitted via the light and temperature dependent route. Guenther et al. 2006, 2012 also extend the light and temperature controlled emission to cover the average leaf temperature over the past 24 and 240 hours. Our measurements deal with fully sunlit branches, placed in Teflon enclosures for measurements in short periods during the growing season. Thus the modeling is carried out only to find any relation of the plant emissions with the direct emission processes. No modeling of sunlit or shaded leaves, effect of leaf age or temperature history, canopy environment, plant functional types and soil properties is carried out. No regional emission estimates that would benefit of a more broad approach are done. Modeling of the temperature controlled pool emissions of monoterpenes and sesquiterpenes, and the light and temperature controlled isoprene emission are straightforward. In addition we also tested a hybrid algorithm which has both the temperature-dependent pool emissions and the instant light and temperature-dependent emissions combined. The hybrid algorithm did not produce more conclusive results when compared with the simple emission algorithms.

Guenther A. B., Zimmerman P. R., Harley P. C., Monson R. K., and Fall R., 1993. Isoprene and monoterpene emission rate variability: Model evaluation and sensitivity analyses, *Journal of Geophysical Research* 98(D7), 12,609-12,627.

Guenther A., Karl T., Harley P., Wiedinmyer C., Palmer P. I., and Geron C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmospheric Chemistry and Physics* 6, 3181-3210.

Guenther A. B., Jiang X., Heald C. L., Sakulyanontvittaya T., Duhl T., Emmons L. K., and Wang X., 2012. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471-1492, doi:10.5194/gmd-5-1471-2012.

Sakulyanontvittaya T., Duhl T., Wiedinmyer C., Helmig D., Matsunaga S., Potosnak M., Milford J., and Guenther A., 2008. Monoterpene and sesquiterpene emission estimates for the United States, *Environ. Sci. Technol.*, 42, 1623–1629.

L109. As you have shown in (Bourtsoukidis et al., 2012), environmental drivers such as high O<sub>3</sub> abundance can also impact SQT emissions. Actually I'm a bit surprised to see that you have kept this study outside of your discussion.

*In our set-up we had to remove ozone before the emission enclosure, therefore we were not able to study effects of ozone on emissions.*

*However, 82 % of the measured O<sub>3</sub> mixing ratios (N=21391) at the height of 4.2 m at SMEAR II in June-August 2015 were below the critical threshold (36.6 ppb) for correlation with ozone suggested by Bourtsoukidis et al. (2012).*

*We have added this reference into the introduction.*

L99-140. I don't see the reason why you have to repeat in text what is known since the last 23 years. I would recommend completely removing this part. Maybe you can replace it with a smaller one, but briefly discussing the current models.

*This is a very good comment. The Emission potentials section has been rewritten, and only the key processes are named.*

L156. I strongly recommend to separate results and discussion.

*We have restructured the results and discussion to be clearer.*

L158-169. What is the reason of such presentation? I would suggest a plot or a less confusing approach that would directly allow the reader to distinguish the characteristics of each year.

*The chapter has been rewritten.*

L171. Please provide a number that indicates how much higher and how much significantly higher. Did you perform a p-test?

*We have added box and whisker plots (Fig 1 in revised MS) to provide statistics of the measurements.*

L193:198. The reasons for explaining the different seasonality are explained in a very broad way. It could also be the age of the tree, the pollution or simply the different climatic conditions.

*Unfortunately our data does not give any firm evidence what could cause the different seasonality. As you say, it can be age of the tree or climatic conditions. That is why more precise presentation is quite difficult.*

L206. SQT may serve as signaling compounds as well eg. Vickers et al., 2009.

*Vickers has been added to the text.*

L230. In Fig. 1 you present a timeline. Diurnal variability would be better illustrated in a 24h plot and accounting for all days. Please include a figure where the diel cycle is presented for all the selected periods and years separately. Maybe then the reader can understand why you chose this period separation.

*Figure 2 has been replaced by a new one as proposed by a reviewer*

L245. The figure and the following results conclude otherwise. Please reformulate the sentence. L233-L258. What is new when compared with Bäck et al. (2012)? I don't see any reason to include this tree variability in such detailed manner as it only confuses the reader and concludes on what is already known.

*Bäck et al studied the chemotypes of Scots pine. Nobody has measured chemotypes of other tree species but Scots pine and therefore our finding that also Norway spruce has different chemotypes is a new important finding.*

L277-278. Both StdErr and R2 indicate that a poor fitting for SQT during spring and early summer. I would ask to include a figure with the SQT fittings, since this is the class of VOC you are mainly investigating. At which periods was the fitting best? At which worst? What can we learn from this? Even as supplement, this is more valuable than numbers which usually are taken for granted without further investigation on the other values provided.

*See the above response to the comments on emission potentials, where also some observation & fitting plots are included. The nonlinear fitting should not be judged by R<sup>2</sup>, because this is an unjustified measure for it (e.g. Spiess and Neumeyer, 2010). The sesquiterpenes emissions in spring were low, and the number of measurements was limited. Thus the spring results are only indicative. In early and late summer, the emissions were higher, and the simple temperature algorithm is able to predict the emission potential with much closer correspondence with the observations. Some of the peak emissions were not predicted, but the tested hybrid algorithm (which has both the pool emissions and the instant light dependent emissions combined) did not bring any closer results. Thus the reason for the emission peaks may be some other stimulus which the plant responds to, but which is not included in the simple modeling approach.*

*Spiess, A. and Neumeyer, N., 2010. An evaluation of R2 as an inadequate measure for nonlinear models in pharmacological and biochemical research: a Monte Carlo approach, BMC Pharmacology 10:6. doi:10.1186/1471-2210-10-6.*

L302-316. You actually present normalized contribution to OH reactivity from the species you measured. What is the reactivity of these emission measurements? How is it comparing with past measured values? From the values reported I would expect a small total reactivity that may be insignificant when compared with direct measurements. Including only the organics you measured and in the absence of a measured reactivity value, the result is kind of misleading. It creates the impression that SQT dominate the OH reactivity which is not the case. Or is it? Please calculate the reactivity including also the inorganic species measured at the

station, report a value and compare with field measurements or from the literature. In general, I appreciate the effort to use OH reactivity, but the approach has to be slightly changed in order to address the bigger picture. I would be very impressed if SQT indeed dominate OH reactivity in a boreal environment.

*-it is not possible to include the inorganic species measured at the same site since these reactivities were calculated directly from emission measurements and not from ambient air data. Also comparing the values to the ambient air studies is not possible since the units are different. Therefore we decided to show relative values and title of the section was changed to clarify this.*

*-On the other due to high reactivity of SQTs, most of them are not detected in ambient air measurements and it is possible to estimate their share to the local chemistry only directly from the emissions measurements.*

*-At this site VOCs have higher contribution to the ambient air OH reactivity than other trace gases (NO<sub>x</sub>, CO, O<sub>3</sub>, CH<sub>4</sub>) especially in summer (Sinha et al. 2010). Monoterpenes are the main contributors to the total OH reactivity of the ambient air VOCs (Hakola et al. 2012) and based on the reactivities of the emissions, SQTs are actually more important than MTs to the local chemistry even though most of them are not detected in ambient air measurements due to the short lifetimes in air.*

*This is now clarified in the text in section 3.5*

L318-327. Your conclusions don't provide anything more than a description of the data. Please state what is the finding that makes your study suitable for publication.

*We have rewritten the conclusions.*

## **RESPONSE TO REFEREE 2**

### **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.*

Page1, 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 stress 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 necessarily from the study.

*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 PPF? 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,  $\alpha$ -pinene and b-pinene have quite similar mass spectra and the ion 93 response of b-pinene is about 10 % larger than the response of  $\alpha$ -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.

*Guenther et al. (2012) describes an update of the Model of Emissions of Gases and Aerosols from Nature (MEGAN) to version 2.1, which includes the emissions of approximately 150 specific compounds (classified into compound classes). MEGAN is a global model which is why the model parameters are set up to represent all biotopes and plant functional types in the terrestrial ecosystem. The model parameters have been developed based on the global database of Guenther et al. (1995), supplemented with results in several articles. The article cited for emissions in Europe is Karl et al. (2009), who consider a temperature dependent emission algorithm with slope value of  $0.09 K^{-1}$  based on Guenther et al. (1993) for monoterpenes, and cite the results ( $0.17K^{-1}$ ) of Helmig et al. (2007) for sesquiterpene emissions.*

*Section 2.3 Emission potentials has also been rewritten & made shorter. Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and*

*updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, doi:10.5194/gmd-5-1471-2012, 2012.*

*Guenther, A. B., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res.-Atmos., 100, 8873–8892, 1995.*

*Karl, M., Guenther, A., Köhler, R., Leip, A., and Seufert, G.: A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models, Biogeosciences, 6, 1059–1087, doi:10.5194/bg-6-1059-2009, 2009.*

*Guenther, A., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res., 98(D7), 12609–12617, 1993.*

*Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., and Sakulyanontvittaya, T.: Sesquiterpene emissions from pine trees – Identifications, emission rates and flux estimates for the contiguous United States, Environ. Sci. Technol., 41, 1545–1553, 2007.*

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 monoterpene-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 periods 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 meteorological data are not used to specify the seasonality for the measurements. The temporal 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 measurements 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 cant 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 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 trees 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  $M = M_S * \exp(\beta(T-T_S))$  for monoterpenes, and the multiplicative light factor ( $C_L$ , where  $L$  is the photosynthetically active radiation PAR) and temperature factor ( $C_T$ ) controlled model  $I = I_S * C_L * C_T$  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  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ , 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) caption 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.

Guenther, A., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, *J. Geophys. Res.* 98(D7), 12609–12617, 1993.

Guenther, A.: Seasonal and spatial variations in natural volatile organic compound emissions, *Ecological applications* 7(1), 34-45, 1997.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *J. Atmosph. Chem.* 33, 23-88, 1999.

Schuh, G., Heiden, A. C., Hoffmann, T., Kahl, J., Rockel, P., Rudolph, J., and Wildt, J.: Emissions of volatile organic compounds from sunflower

*and beech: Dependence on temperature and light intensity, Journal of Atmospheric Chemistry 27, 291-318, 1997.*

*Tingey, D. T., Turner, D. P., and Weber, J. A.: Factors controlling the emissions of monoterpenes and other volatile organic compounds. In: Trace Gas Emissions by Plants, Sharkey, T. D. et al., (eds), Academic Press, Inc. San Diego, California, 93-119, 1991.*

*Wiedinmyer, C., Guenther, A., Harley, P., Hewitt, N., Geron, C., Artaxo, P., Steinbrecher, R., and Rasmussen, R.: Global organic emissions from vegetation. In: Emissions of atmospheric trace compounds, Granier, C. et al. (eds), Kluwer Academic Publishers, Dordrecht, 115-170, 2004.*

*Wildt, J., Kley, D., Rockel, A., Rockel, P., and Segschneider, H. J.: Emission of NO from several higher plant species, J. Geophys. Res. 102(D5), 5919-5927, 1997.*

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.*

*Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, doi:10.5194/gmd-5-1471-2012, 2012.*

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 O<sub>3</sub> 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*

# 1 [Terpenoid and carbonyl emissions from Norway spruce in Finland](#) 2 [during the growing season](#)

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4  
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13  
14 **Abstract.** We present spring and summer volatile organic compound (VOC) emission rate measurements from Norway  
15 spruce (*Picea abies* L. Karst) growing in a boreal forest in southern Finland. The measurements were conducted using  
16 in situ gas-chromatograph with 1 to 2-hour time resolution [to reveal quantitative and qualitative short-term and seasonal](#)  
17 [variability of the emissions](#). The measurements cover altogether 14 weeks in years 2011, 2014 and 2015. Monoterpene  
18 (MT) and sesquiterpene (SQT) emission rates were measured all the time, but isoprene only in 2014 and 2015 and  
19 acetone and C<sub>4</sub>-C<sub>10</sub> aldehydes only in 2015. The emission rates of all the compounds were low in spring, but MT,  
20 acetone and C<sub>4</sub>-C<sub>10</sub> aldehydes emission rates increased as summer proceeded, reaching maximum emission rates in  
21 July. Late summer mean [values \(late July and August\)](#) were 29, 17 and 33 ng g(dw)<sup>-1</sup> h<sup>-1</sup> for MTs, acetone and  
22 aldehydes respectively. SQT emission rates increased during the summer and highest emissions were measured late  
23 summer (late summer mean [value](#) 84 ng g(dw)<sup>-1</sup> h<sup>-1</sup>) concomitant with highest linalool emissions [most likely due to](#)  
24 [stress effects](#). The between-tree variability of emission pattern was studied by measuring seven different trees during  
25 the same afternoon using adsorbent tubes. Especially the contributions of limonene, terpinolene and camphene were  
26 found to vary between trees, whereas proportions of  $\alpha$ - and  $\beta$ -pinene were more stable. [Our results show that it is](#)  
27 [important to measure emissions on canopy level due to irregular emission pattern, but reliable SQT emission data can](#)  
28 [be measured only from enclosures](#). SQT emissions contributed more than 90 % of the ozone reactivity most of the  
29 time, and about 70 % of [the](#) OH reactivity during late summer. The contribution of aldehydes [to OH reactivity](#) was  
30 comparable to the [one](#) of MT during late summer, 10 %-30 % most of the time.

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## 31 32 **1 Introduction**

33 The boreal forest is the largest terrestrial biome, forming an almost continuous belt around the northern hemisphere.  
34 The boreal forest zone is characterized by a short growing season and a limited number of tree species. The most  
35 common tree species are Scots pine, Norway spruce and silver and downy birch and they produce and emit vast  
36 amounts of biogenic volatile organic compounds (VOCs) (Bourtsoukidis et al., 2014a, b; Bäck et al., 2012; Cojocariu

38 et al., 2004; Grabmer et al., 2006; Hakola et al., 2001, 2006; Tarvainen et al., 2005; Yassaa et al., 2012). The  
39 compounds are mainly isoprene, monoterpenes (MT), sesquiterpenes (SQT) and oxygenated volatile organic  
40 compounds (OVOCs) (Tarvainen et al., 2007). There **js** a variety of factors controlling these emission, both biotic  
41 (Pinto-Zevallos et al., 2013; Joutsensaari et al., 2015) and abiotic stress (Vickers et al., 2009; Bourtsoukidis et al.,  
42 2012; Bourtsoukidis et al., 2014c) factors can initiate or alter VOC emissions. Abiotic stress factors have been  
43 reviewed by Loreto and Schnizler (2010). Terpenes for example relieve oxidative and thermal stresses of trees. Many  
44 stress factors can also interact and cause additive effects (Niinemets, 2010; Holopainen and Gershenson, 2010).  
45 Biotic stresses such as acarid species infestation have been shown to initiate farnesene and linalool emissions in  
46 spruce seedlings (Kännaste et al., 2008). **Emission potentials and composition varies a lot between different tree**  
47 **species (Guenther et al. 2012).** However, there is also a lot of variation in the emissions of different individuals of the  
48 same tree species. Bäck et al. (2012) showed that Scots pine trees of the same age, growing in the same environment,  
49 emit very different monoterpene selections. These so called different chemotypes cause uncertainties in emission  
50 modelling.

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51 **In the atmosphere VOCs are oxidized, which affects the tropospheric ozone formation (Chameides et al., 1992) and**  
52 **contribute to the lifetime of methane by consuming hydroxyl radicals. In addition reaction products of VOCs also**  
53 **participate in the formation and growth of new particles (Tunved et al., 2006).** In smog chamber studies secondary  
54 organic aerosol (SOA) yields for different hydrocarbons and even for different MTs have been found to vary  
55 considerably (Griffin et al., 1999). Jaoui et al. (2013) studied SOA formation from SQT and found that the high  
56 reactivity of SQT produced generally high conversion into SOA products. Furthermore, they found that the yields were  
57 dependent on the oxidant used and were highest for nitrate radical (NO<sub>3</sub>) reactions. Of the SQT acidic products, only  
58 β-caryophyllinic acid has been observed in ambient samples (Jaoui et al., 2013; Vestenius et al., 2014). Due to their  
59 high reactivity, SQT are not usually found in ambient air. Hakola et al. (2012) detected longifolene and isolongifolene  
60 in boreal forest air during late summer. Hence, the best way to evaluate the atmospheric impact of SQTs is to measure  
61 them from emissions.

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Vegetation produces and emits vast amounts of biogenic volatile organic compounds (VOCs), especially in the densely forested boreal regions (Hakola et al., 2001, 2006; Tarvainen et al., 2005), which are mainly monoterpenes (MT), sesquiterpenes (SQT) and oxygenated volatile organic compounds (OVOCs). In the atmosphere these compounds are oxidized, which affects the tropospheric ozone formation (Chameides et al., 1992) and contribute to the lifetime of methane. In addition reaction products of VOCs also participate in the formation and growth of new particles (Tunved et al., 2006).

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62 In addition to isoprene and MTs and SQTs, plants emit also large amounts of oxygenated compounds i.e. alcohols,  
63 carbonyl compounds and organic acids (Koppmann and Wildt, 2007). OVOCs containing six carbon atoms (C<sub>6</sub>) are  
64 emitted directly by plants often as a result of physical damage (Fall et al., 1999; Hakola et al., 2001). Saturated  
65 aldehydes (**hexanal, heptanal, octanal, nonanal, and decanal**) have also been found in direct emissions of plants (Wildt  
66 et al., 2003) as well as methanol, acetone and acetaldehyde (Bourtsoukidis et al. 2014b). ▽

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67 In the present study we conducted on-line gas-chromatographic measurements of emissions of MTs and SQTs as well  
68 as C<sub>4</sub>-C<sub>10</sub> saturated aliphatic carbonyls from Norway spruce (*Picea abies* L. Karst) branches. Although Norway spruce  
69 is one of the main forest tree species in Central and Northern Europe, there are relatively **limited amount of data** on its  
70 emissions (Hakola et al., 2003; Grabmer et al., 2006; Bourtsoukidis et al., 2014a and b, Yassaa et al. 2012). **Rinne et**  
71 **al. (2009) identified knowledge gaps concerning VOC emissions from boreal environment and concluded that there is**  
72 **a lack of knowledge in non-terpenoid emissions from most of the boreal tree species. They also pointed out that**  
73 **chemotypic variations are not well enough understood to be taken into account in emission modelling. To fill this**

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90 [knowledge gap we conducted BVOC emission measurements from Norway spruce. On-line gas-chromatograph mass](#)  
91 [spectrometer \(GC-MS\) was chosen because](#) in addition to detection of individual MTs it allows sensitive detection of  
92 SQTs, which is often difficult to perform under field conditions. The on-line measurements were considered essential  
93 for evaluating the factors affecting emission rates, for example their temperature and light dependence. Our campaigns  
94 cover periods of years 2011, 2014 and 2015 during spring and summer, altogether about 14 weeks. In 2015 also  
95 carbonyl compounds were added to the measurement scheme, since there is no earlier data of their emissions.

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## 96 2 Methods

### 97 2.1 VOC measurements

98 The measurements were conducted at the SMEAR II station (Station for Measuring Forest Ecosystem-Atmosphere  
99 Relations, 61°51'N, 24°18'E, 181 a.s.l) in Hyytiälä, southern Finland (Hari and Kulmala 2005) in 2011, 2014, and  
100 2015. The measurements took place in spring/early summer 2011 (two weeks in April, five days in May and three days  
101 in June), spring/summer 2014 (one week in May, two weeks in June and one week in July), and summer 2015 (one  
102 week in June and two weeks in August) [and they were conducted using an in situ gas-chromatograph.](#)

103 [Two different trees were measured; tree 1 in 2011 and tree2 in 2014 and 2015.](#) The selected trees were growing in a  
104 managed mixed conifer forest (average tree age ca 50 years), and located about 5 meters from the measurement  
105 container. The height of the tree 1 in 2011 was about 10 meters [\(age about 40 years\).](#) [The measured branch was a](#)  
106 [fully sunlit, healthy lower canopy branch pointing towards a small opening at about 2 meters height. In 2014 and](#)  
107 [2015 a younger tree \(tree 2, ca. 1 m tall, age ca 15 years\) about 5 meters away from the tree used in 2011 was](#)  
108 [selected for the study. The branches were placed in a Teflon enclosure and the emission rates were measured using a](#)  
109 [dynamic flow through technique. The setup is shown in supporting material.](#) The volume of the cylinder shape  
110 transparent Teflon enclosure was approximately 8 litres and it was equipped with inlet and outlet ports and a  
111 [thermistor \(Philips KTY 80/110, Royal Philips Electronics, Amsterdam, Netherlands\) covered with Teflon tubing](#)  
112 [inside the enclosure.](#) [The photosynthetically active photon flux density \(PPFD\) was measured just above the](#)  
113 [enclosure by quantum sensor \(LI-190SZ, LI-COR Biosciences, Lincoln, USA\).](#)

Deleted: The samples were collected at a height of about 2 meters from a fully sunlit, healthy lower canopy branch pointing towards a small opening. In 2014 and 2015 a younger tree (ca. 1 m tall, age ca 15 years) about 5 meters away from the tree used in 2011 was selected for the study. The branches were placed in a Teflon enclosure and the emission rates were measured using a dynamic flow through technique.

Deleted: (Philips KTY 80/110, Royal Philips Electronics, Amsterdam, Netherlands)

114 The flow through the enclosure was kept at about 3-5 litres  $\text{min}^{-1}$ . Ozone was removed from the [incoming](#) air using  
115 [manganese oxide \(MnO<sub>2</sub>\) coated copper nets.](#) The emission rates were measured using [the on-line GC-MS. From the](#)  
116 [enclosure outlet port air was directed through the 6 m long fluorinated ethylene propylene \(FEP\) inlet line \(i.d. 1/8](#)  
117 [inch\) to the GC-MS with the flow of ~0.8 L/min. Subsamples were taken from this main flow with the flow of 40-60](#)  
118 [ml/min directly into](#) the cold trap of a thermal desorption unit (Perkin Elmer ATD-400) packed with Tenax TA in 2011  
119 and Tenax TA/Carbopack-B in 2014 and 2015. The trap material was changed since isoprene was found not to be  
120 retained fully in the cold trap in 2011. The trap was kept at 20°C during sampling to prevent water vapour present in  
121 the air from accumulating into the trap. The thermal desorption instrument was connected to a gas chromatograph (HP  
122 5890) with DB-1 column (60 m, i.d. 0.25 mm, f.t. 0.25  $\mu\text{m}$ ) and a mass selective detector (HP 5972). One 20-minutes

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141 sample was collected every other hour. The system was calibrated using liquid standards in methanol injected on Tenax  
142 TA-Carbopack B adsorbent tubes. The detection limit was below 1 pptv for every MT- and SQT.

143 The following compounds were included in the calibration solutions: 2-methyl-3-buten-2-ol (MBO) (Fluka), camphene  
144 (Aldrich), 3-carene (Aldrich), p-cymene (Sigma-Aldrich), 1,8-cineol (Aldrich), limonene (Fluka), linalool (Aldrich),  
145 myrcene (Aldrich),  $\alpha$ -pinene (Sigma-Aldrich),  $\beta$ -pinene (Fluka), terpinolene (Fluka), bornylacetate (Aldrich),  
146 longicyclene (Aldrich), isolongifolene (Aldrich),  $\beta$ -caryophyllene (Sigma), aromadendrene (Sigma-Aldrich),  $\alpha$ -  
147 humulene (Aldrich),  $\beta$ -farnesene (Chroma Dex). Isoprene was calibrated using gaseous standard from National  
148 Physical Laboratory (NPL). We had no standard for sabinene and therefore it was quantified using the calibration curve  
149 of  $\beta$ -pinene, because both species elute close each other and their mass spectra are similar. Therefore the results for  
150 sabinene are only semi-quantitative, but it enables the observations of diurnal and seasonal changes. Compared to off-  
151 line adsorbent methods this in situ GC-MS had clearly lower background for carbonyl compounds and in 2015 we  
152 were able to measure also acetone/propanal and C<sub>3</sub>-C<sub>10</sub> aldehyde emission rates. The aldehydes included in the  
153 calibration solutions were: butanal (Fluka), pentanal (Fluka), hexanal (Aldrich), heptanal (Aldrich), octanal (Aldrich),  
154 nonanal (Aldrich) and decanal (Fluka). Unfortunately, acetone co-eluted with propanal and the calibration was not  
155 linear due to high acetone background in adsorbent tubes used for calibrations.

**Moved down [1]:** We had no standard for sabinene and therefore it was quantified using the calibration curve of  $\beta$ -pinene. This "calibration" is not quantitative, but it enables to observe diurnal and seasonal changes.  $\beta$ -Pinene was chosen, because their mass spectra are quite similar and they elute close to each other.

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## 156 2.2 Calculation of emission rates

157 The emission rate is determined as the mass of compound per needle dry weight and per time according to

$$159 E = \frac{(C_2 - C_1)F}{m} \quad (1)$$

**Deleted:** 2-methyl-3-buten-2-ol (MBO), camphene, 3-carene, p-cymene, 1,8-cineol, limonene, linalool, myrcene,  $\alpha$ -pinene,  $\beta$ -pinene, terpinolene, bornylacetate, longicyclene, isolongifolene,  $\beta$ -caryophyllene, aromadendrene,  $\alpha$ -humulene,  $\beta$ -farnesene. Isoprene was calibrated using gaseous standard from NPL (National Physical Laboratory). Compared to off-line adsorbent methods this in situ GC-MS had clearly lower background for carbonyl compounds and in 2015 we were able to measure also acetone and C<sub>4</sub>-C<sub>10</sub> aldehyde emission rates. The aldehydes included in the calibration solutions were: butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal. Unfortunately, acetone co-eluted with propanal and the calibration was not linear due to high acetone background in adsorbent tubes used for calibrations. ¶

161 Here C<sub>2</sub> is the concentration in the outgoing air, C<sub>1</sub> is the concentration in the incoming air, and F is the flow rate  
162 into the enclosure. The dry weight of the biomass (m) was determined by drying the needles and shoot from the  
163 enclosure at 75 °C for 24 hours after the last sampling date. We also measured needle leaf areas and the specific leaf  
164 area SLA is 136 m<sup>2</sup> g<sup>-1</sup>.

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## 165 2.3 Emission potentials

166 A strong dependence of biogenic VOC emissions on temperature has been seen in all emission studies of isoprene,  
167 MTs, and SQTs (e.g. Kesselmeier and Staudt 1999; Ciccioli et al. 1999; Hansen and Seufert 2003; Tarvainen et al.  
168 2005; Hakola et al. 2006). The temperature dependent pool emission rate is usually parameterized using a log-linear  
169 formulation

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170

198  
199  $E(T) = E_s \exp(\beta(T - T_s))$  (2)  
200

201 where  $E(T)$  is the emission rate ( $\mu\text{g g}^{-1} \text{h}^{-1}$ ) at leaf temperature  $T$  and  $\beta$  is the slope  $\frac{d \ln E}{dT}$  (Guenther et al. 1993).  $E_s$  is  
202 the emission rate at standard temperature  $T_s$  (usually set at 30 °C). The emission rate at standard temperature is also  
203 called the emission potential of the plant species, and while it is sometimes held to be a constant it may show variability  
204 related to e.g. season or the plant developmental stage (e.g. Hakola et al. 1998, 2001, 2003, 2006; Tarvainen et al.  
205 2005, Aalto et al 2014).

206 Besides the temperature-dependent nature of the biogenic emissions, light dependence has been discovered already in  
207 early studies of plant emissions (e.g. the review of biogenic isoprene emission by Sanadze 2004 and e.g. Ghirardo et  
208 al 2010). The effect of light on the emission potentials is based on the assumption that the emissions follow similar  
209 pattern of saturating light response which is observed for photosynthesis, and the formulation of the temperature effect  
210 is adopted from simulations of the temperature response of enzymatic activity. The algorithm formulation is given e.g.  
211 in Guenther et al. 1993 and Guenther 1997.

212 In this work we have carried out nonlinear regression analysis with two fitted parameters, arriving at individual  
213 standard emission rates and slope values for the modelled MTs and SQTs compounds during each model period. The  
214 compounds analysed with the temperature dependent pool emission rate were the most copiously emitted MTs and  
215 SQTs, other MTs, other SQTs, acetone and sum of aldehydes. The light and temperature controlled instant emission  
216 rates were obtained for isoprene. An alternative modelling approach was tested using a hybrid emission algorithm,  
217 which has both the temperature-dependent pool emission and the light and temperature controlled instant emission  
218 terms.

219  
220  
221  
222 **2.4 Chemotype measurements**

223 In order to estimate the between-tree variability of the emissions, we conducted a study in 2014, where we made  
224 qualitative monoterpane analysis from six different spruces (trees 3-8) growing in a same area not farther than about  
225 10 metres from each other. All the trees were about 1 m high and naturally regenerated from local seeds. A branch was  
226 enclosed in a Teflon bag and after waiting for 5 minutes we collected a 5 minute sample on a Tenax TA/Carbopack-B  
227 tube and analysed later in a laboratory using Perkin-Elmer thermodesorption instrument (TurboMatrix 650) connected  
228 to Perkin-Elmer gas-chromatograph (Clarus 600) mass spectrometer (Clarus 600T) with DB-5 column. The samples  
229 were taken during one afternoon on 24 June 2014.

**Deleted:** The slope value  $\beta$  is typically obtained from experimental data. Based on literature reviews, the value 0.09 is normally recommended to be used in MT emission modelling (Fehsenfeld et al. 1992; Guenther et al. 1993).

**Deleted:** mono- and sesquiterpene

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**Deleted:** The compounds analysed with the temperature dependent emission rate were the sum of MTs, the sum of SQTs, the sum of aldehydes and acetone.

**Deleted:** Besides the temperature-dependent nature of the biogenic emissions, light dependence has been discovered already in early studies of plant emissions (e.g. the review of biogenic isoprene emission by Sanadze 2004 and e.g. Ghirardo et al 2010). The effect of light on the emission potentials is based on the assumption that the emissions follow similar pattern of saturating light response which is observed for photosynthesis (Guenther et al. 1993). The formulation of the temperature effect is adopted from simulations of the temperature response of enzymatic activity (Guenther et al. 1993). The parameterization for isoprene emissions taking into account both the light and temperature dependence then is

**Deleted:**  $E(L, T) = E_s C_L C_T$  (3)

Here  $E(L, T)$  is the emission rate as a function of photosynthetically active photon flux density  $L$  ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) and leaf temperature  $T$  (K).  $E_s$  is the emission rate at standard conditions of radiation and temperature (usually set at 1000  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$  and 30 °C) (Guenther et al. 1993; Kesselmeier and Staudt 1999; Wiedinmyer et al. 2004).  $C_L$  and  $C_T$  are dimensionless environmental correction factors, accounting for the light and temperature effects on the emissions, with the formulations

$C_L = \frac{\alpha c_{L1} L}{\sqrt{1 + \alpha^2 L^2}}$  (4)

$C_T = \frac{\exp\left(\frac{c_{T1}(T - T_s)}{RT_s^2}\right)}{c_{T3} + \exp\left(\frac{c_{T2}(T - T_M)}{RT_s^2}\right)}$  (5)

Here  $R$  is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>). The factors  $\alpha$  (0.0027),  $c_{L1}$  (1.066),  $c_{T1}$  (95 000 J mol<sup>-1</sup>),  $c_{T2}$  (230 000 J mol<sup>-1</sup>),  $c_{T3}$  (0.961), and  $T_M$  (314 K) are empirical constants obtained from experimental data (Guenther et al. 1993; Guenther 1997). In this study a nonlinear regression analysis with the light and temperature dependent emission rate was carried out for the isoprene emissions.

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**Deleted:** When also the tree that was continuously measured in that day was added to the analysis, we had altogether 7 trees for this qualitative analysis.

**Deleted:** sample on a Tenax

281 **2.4 Calculating the reactivity of the emissions**

282 We calculated the total reactivity of the emissions ( $TCRE_x$ ) by combining the emission rates ( $E_i$ ) with reaction rate  
283 coefficients ( $k_{i,x}$ ).

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284  $TCRE_x = \sum E_i k_{i,x}$

(3)

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285 This determines approximately the relative role of the compounds or compound classes in local OH, and O<sub>3</sub>  
286 chemistry. The reaction rate coefficients are listed in Table 1. When available, temperature-dependent rate  
287 coefficients have been used. When experimental data was not available, the reaction coefficients have been estimated  
288 with the AopWin™ module of the EPI™ software suite ([https://www.epa.gov/tsca-screening-tools/epi-suitetm-](https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface)  
289 [estimation-program-interface](https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface), EPA, U.S.A).

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290 **3. Results and discussion**

291 **3.1 Weather patterns during the measurements**

292 According to the statistics of the Finnish Meteorological Institute, the weather conditions in Finland were close to  
293 normal during the growing season in the years the measurements were carried out. The main features of the weather  
294 patterns are characterised here briefly to provide an average estimate of the conditions in the measurement years  
295 compared with the long-term average conditions in Finland.

296 In 2011, the spring was early and warm. Thermal spring (mean daily temperature above 0°C) started in the whole  
297 country during the first few days of April. The average temperatures were higher than the normal long-term average  
298 temperatures. In addition to the warm temperatures, April had very little precipitation. The same pattern continued in  
299 May, with slightly higher temperatures than the normal long-term average. Towards the end of the month the weather  
300 turned more unstable, with more rains and cooler night temperatures. The average temperature in June was a little over  
301 two degrees higher than the normal long-term average, and there were some intense thunderstorms.

302 In 2014, the weather conditions in May were quite typical, with the average temperatures close to the long-term average  
303 values in all parts of the country. The month started with temperatures cooler than the long-term average, and the cool  
304 period continued for about three weeks. After the cool period the weather became warmer with a south-eastern air  
305 flow, and hot (over 25°C) air temperatures were observed in southern and central parts of the country. Towards the  
306 end of May, cooler air spread over the country from the northeast, and the temperature drops could be high in eastern  
307 Finland. May was also characterised with precipitation, especially in eastern Finland. June started with a warm spell,  
308 but towards the end the weather was much cooler, with the average temperatures 1 to 2 degrees lower than the long-  
309 term average. The precipitation was regionally quite variable in June, the amount could be doubly the long-term  
310 average in some areas, while the amounts were only half of it in many places in central Finland. July was much warmer  
311 than the long-term average temperatures, especially in western Finland and in Lapland. July also had very little rain.

317 In 2015, the June average temperatures were 1 to 2 degrees below the long-term averages, especially in the western  
318 parts of central Finland, and southern Lapland. There were also more rain showers than normally. In July the cold spell  
319 and rainy days continued, with the average temperatures below the long-term averages, especially in the eastern parts  
320 of the country. Highest precipitation rates were measured in the southern and western coastal regions, and in the eastern  
321 parts of the country. In August the warmth returned after two cooler months, with average temperatures 1 to 2 degrees  
322 above the long-term average values. August also had very little rain, except for some parts in eastern Finland and in  
323 Lapland.

324 The observed mean temperature and precipitation amounts at the Juupajoki weather station in Hyttiälä during each  
325 measurement month in 2011, 2014, and 2015 are shown in Table 2.

### 326 3.2 Variability of the VOC emissions

327 Seasonal mean emission rates of isoprene, 2-methyl-3-buten-2-ol (MBO), MTs and SQTs are presented in Table 3  
328 and Fig 1. Typical diurnal variations of the most abundant compounds for each season are shown in Fig. 2. Since  
329 most of the emission rates of the measured compounds were higher in late summer than in early summer, we  
330 calculated the spring (April and May), early summer (June to mid-July) and late summer (late July and August) mean  
331 emissions separately. This describes the emission rate changes better than monthly means.

332 Isoprene emission rates were low in spring and early summer, but increased in August. In spring emission rates were  
333 below detection limit most of the time and early and late summer means were  $1.3 \pm 3.7$  and  $6.0 \pm 12$  ng g(dry weight)<sup>-1</sup>  
334 h<sup>-1</sup>, respectively. The highest daily maxima isoprene emissions were about 70-80 ng g(dw)<sup>-1</sup> h<sup>-1</sup>, but usually they  
335 remained below 20 ng g(dw)<sup>-1</sup> h<sup>-1</sup>. Our measured values (Table 3) match very well with the measurements by  
336 Bourtsoukidis et al (2014b) who report season medians varying from 1.6 ng g(dry weight)<sup>-1</sup> h<sup>-1</sup> in autumn to 3.7 ng  
337 g(dry weight)<sup>-1</sup> h<sup>-1</sup> in spring. However, while the highest emission rates were measured in late summer in the present  
338 study, Bourtsoukidis et al. (2014b) found highest emission rates in spring.

339 MT emission rates were below 50 ng g(dw)<sup>-1</sup> h<sup>-1</sup> most of the time in April, May and still in the beginning of June for  
340 every measurement year, below 50 ng g(dw)<sup>-1</sup> h<sup>-1</sup> most of the time. At the end of June the MT emission rates started to  
341 increase (about 30 %) to the level where they remained until the end of August, the daily maxima or their sum  
342 remaining below 300 ng g(dw)<sup>-1</sup> h<sup>-1</sup>. In comparison with the study by Bourtsoukidis et al. (2014b), MT emission rates  
343 in Finland are four to ten times lower than those measured in Germany and their seasonal cycles are different. As with  
344 isoprene, they measured the highest MT emission rates during spring, whereas our highest emissions take place late  
345 summer. Median seasonal values reported by them are 203.1, 136.5 and 80.8 ng g(dw)<sup>-1</sup> h<sup>-1</sup> for spring, summer and  
346 autumn, respectively. Our averages are 8, 21 and 28 ng g(dw)<sup>-1</sup> h<sup>-1</sup> for spring, early summer and late summer,  
347 respectively (Table 3).

348 A substantial change in the emission patterns took place at the end of July, when SQT emission rates increased up to  
349 3-4 times higher than the MT emission rates at the same time (Table 3). Such a change in emissions was not observed

**Deleted:** In 2011, the spring was early and warm. According to the statistics of the Finnish Meteorological Institute the thermal spring started during the first three days of April, with the average temperatures exceptionally high and very little precipitation. The same pattern continued in May, but the weather turned more unstable towards the end of the month, with more rains and cooler night temperatures. The average temperature in June was a little over two degrees higher than normal, and there were some intense thunderstorms. Table 2 shows the mean temperatures and rain amounts during each measurement month.¶

In 2014, the weather conditions in May were quite typical, with the average temperatures close to the long-term average values. June started with a warm spell, but towards its end the weather was exceptionally cold, and the average temperatures in June were 1 to 2 degrees lower than usual. July was exceptionally warm in the whole country.¶

In 2015, the June average temperatures were again 1 to 2 degrees below the long-term averages, and there were more rain showers than normally. In July the cold spell and rainy days continued, but in August the warmth returned, with the average temperature 1 to 2 degrees above the long-term average values. August also had exceptionally little rain. ¶

**Deleted:** Since most of the emission rates of the measured compounds were higher in late summer than in early seasonsummer, we calculated the spring (April and May), early summer (June to mid-July) and late summer (late July and August) mean emissions separately. This described the emission rate changes better than monthly means. Seasonal mean emission rates of isoprene, 2-methyl-3-buten-2-ol (MBO), MT and SQT are presented in Table 3 and typical diurnal variations of the most abundant compounds for each season are shown in Fig. 1.

**Deleted:** Norway spruce is known to be a low isoprene emitter and a moderate MT emitter (Kesselmeir and Staudt, 1999; Grabner et al., 2006; Bourtsoukidis et al., 2014a, b). Our study confirmed these earlier results, although the seasonal pattern of emissions was clearly different. Isoprene emission rates were low early summer, but increased towards August and late summer mean emission rate was 6 ng g(dry weight)<sup>-1</sup> h<sup>-1</sup>. The highest daily maxima isoprene emissions were about 70-80 ng g(dw)<sup>-1</sup> h<sup>-1</sup>, but usually they remained below 20 ng g(dw)<sup>-1</sup> h<sup>-1</sup>. MBO emission rates were even lower than isoprene, the late summer mean was 2.4 ng g(dw)<sup>-1</sup> h<sup>-1</sup>.

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393 in ~~the~~ study by Boutsoukidis et al. (2014b). ~~Instead of late summer increase, they observed again highest emissions~~  
394 ~~already during the spring (118.6 and 64.9 ng g(dw)<sup>-1</sup> h<sup>-1</sup> in spring and summer, respectively) after which emissions~~  
395 ~~significantly declined. Moreover,~~ they report that MTs dominated the Norway spruce emissions through the entire  
396 measuring period (April-November), SQT emission rates being equal to MT emission rates during spring, but only  
397 about half of MT emission rates during summer and about 20 % during autumn. One potential explanation for such a  
398 different seasonality ~~and emission strengths~~ may lie in the differences between site specific factors such as soil moisture  
399 conditions, local climate ~~(winter in Germany is much milder and the trees do not face as dramatic change as in Finland~~  
400 ~~when winter turns to spring)~~, stand age or stress factors. ~~The tree measured in Germany was much older (about 80~~  
401 ~~years)~~. In a boreal forest, late summer normally is the warmest and most humid season favouring high emissions, as  
402 was also the case in our study periods. On the contrary, in central Germany July was relatively cold and wet, and  
403 according to the authors, reduced emissions were therefore not surprising (Boutsoukidis et al 2014b).

404 Another interesting feature ~~can be seen~~ in the specified emission rates of different compounds. In the ~~present~~ study the  
405 main SQT in spruce emissions was  $\beta$ -farnesene. About 50% of the SQT emission consisted of  $\beta$ -farnesene and its  
406 maximum emission rate (155 ng g(dw)<sup>-1</sup> h<sup>-1</sup>) was measured on the afternoon of 31 July 2015. ~~Two other identified~~  
407 ~~SQTs were  $\beta$ -caryophyllene and  $\alpha$ -humulene. There were two more SQTs, which~~ also contributed significantly to the  
408 total SQT emission rates, but since ~~no calibration~~ standards ~~were available~~ for these ~~,~~ their quantification is only  
409 tentative. Linalool emissions increased simultaneously with SQT emissions ~~(Fig. 1) reaching maximum concentrations~~  
410 ~~during late summer in August~~, in the same way as was previously observed in the measurements of Scots pine  
411 emissions in the same forest in southern Finland (Hakola et al., 2006), where emissions were found to increase late  
412 summer concomitant with the maximum concentration of the airborne pathogen spores, and Hakola et al. (2006)  
413 suggested a potential defensive role of the conifer ~~linalool and~~ SQT emissions. Several other reports point to similar  
414 correlations between SQT (in particular  $\beta$ -farnesene) and oxygenated MTs such as linalool emissions and biotic  
415 stresses in controlled experiments. For example, increases in farnesene, methyl salicylate (MeSA) and linalool  
416 emissions were reported to be an induced response by Norway spruce seedlings to feeding damage by mite species  
417 (Kännaste et al. 2009), indicating that their biosynthesis might prevent the trees from being damaged. Interestingly,  
418 the release of  $\beta$ -farnesene seemed to be mite specific and attractive to pine weevils, whereas linalool and MeSA were  
419 deterrents. Blande et al. (2009) discovered pine weevil feeding to clearly induce the emission of MTs and SQTs,  
420 particularly linalool and (E)- $\beta$ -farnesene, from branch tips of Norway spruce seedlings. Also, in a licentiate thesis of  
421 Petterson (2007) linalool and  $\beta$ -farnesene were shown to be emitted due to stress. The emissions from Norway spruce  
422 increased significantly after trees were treated with methyljasmonate (MeJA). Martin et al (2003) discovered that MeJA  
423 triggered increases in the rate of linalool emission more than 100-fold and that of SQTs more than 30-fold. Emissions  
424 followed a pronounced diurnal rhythm with the maximum amount released during the light period, suggesting that they  
425 are induced de novo after treatment. Our study shows that such major changes in emission patterns can also occur in  
426 trees in field conditions, and without any clear visible infestations or feeding, indicating that they probably are systemic  
427 defence mechanisms rather than direct ones (Eyles et al 2010).

428 In 2015 we measured also acetone/~~propanal~~ and C<sub>4</sub>-C<sub>10</sub> aldehyde emission rates. The total amount of the~~se~~ measured  
429 carbonyl compounds was comparable to the amount of MTs (Table 3) although with our method it was not possible to

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**Deleted:** done in a spruce forest in Germany

**Deleted:** Instead of late summer increase especially in SQT emissions (in our data from 0 to 84 ng g(dw)<sup>-1</sup> h<sup>-1</sup>), they observed highest MT and SQT emissions already during the spring (203 and 119 ng g(dw)<sup>-1</sup> h<sup>-1</sup>, respectively) after which emissions significantly declined, median MT emissions being 136 and 80 ng g(dw)<sup>-1</sup> h<sup>-1</sup> and SQT emissions 65 and 21 ng g(dw)<sup>-1</sup> h<sup>-1</sup> during summer and autumn, respectively. Further

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446 measure emissions of the most volatile aldehydes, formaldehyde and acetaldehyde, which are also emitted from trees  
447 in significant quantities (Cojocariu et al., 2004, Koppmann and Wildt, 2007; Boursoukidis et al., 2014b). [In summer](#)  
448 [2015](#), the carbonyl compounds consisted mainly of acetone (30 %), and the shares [for the other compounds were as](#)  
449 [follows:](#) nonanal (21%), decanal (17%), heptanal (14%), hexanal (10%) and pentanal (5%). The shares of butanal and  
450 octanal were less than 2% each. [The seasonal mean values are shown in Table 3. Aldehydes with shorter carbon](#)  
451 [backbones \(butanal, pentanal, hexanal\) have higher emissions in early summer like most MTs, while aldehydes with](#)  
452 [longer carbon backbones \(heptanal, octanal, nonanal, decanal\) have higher emissions in late summer similarly to SQTs.](#)  
453 Diurnal variability of the emission rates of MT and SQT, acetone/[propanal](#) and larger aldehydes are shown in Fig. 2.  
454 They all show similar temperature dependent variability with maxima during the afternoon and minima in the night.  
455 The SQT daily peak emissions were measured two hours later than MT and aldehyde peaks.

456

### 457 3.3 Tree to tree variability in emission pattern

458 When following the emission seasonality, we discovered that the MT emission patterns were somewhat different  
459 between the two trees measured. The tree measured in 2011 (tree 1) emitted mainly  $\alpha$ -pinene in May, whereas the tree  
460 measured in 2014 and 2015 (tree 2) emitted mainly limonene in May ([Table 4](#)). As summer proceeded the contribution  
461 of limonene emission decreased in both trees and the share of  $\alpha$ -pinene increased in tree 2. The species specific Norway  
462 spruce emissions have been measured earlier at least by Hakola et al. (2003) and Boursoukidis et al. (2014a). The  
463 measurements by Hakola et al. covered all seasons, but only a few [daytime samples](#) for each season, whereas the  
464 measurements by Boursoukidis et al. covered three weeks in September–October in an Estonian forest. The main MTs  
465 detected in the Estonian forest were  $\alpha$ -pinene (59 %) and 3-carene (26 %), but also camphene, limonene,  $\beta$ -pinene and  
466  $\beta$ -phellandrene were [detected](#). In the study by Hakola et al. (2003) the MT emission composed mainly of  $\alpha$ -pinene,  $\beta$ -  
467 pinene, camphene and limonene, but only very small amounts of 3-carene were observed, similarly to the present study.  
468 This raises a question whether spruces would have different chemotypes in a similar way as Scots pine has (Bäck et  
469 al., 2012).

470 In order to find out how much variability there was between the trees [in monoterpene emission pattern](#), we conducted  
471 a study [in June](#) in 2014, where we made qualitative analysis from six different spruces growing in a same area (labelled  
472 as tree 3 - tree 8). The results for MT emissions are shown in [Figure 3](#). SQT emissions were not significant at that time  
473 ([about 1 ng g\(dw\)<sup>-1</sup> h<sup>-1</sup>](#)). As expected, the MT emission pattern of the trees was quite different; terpinolene was one  
474 of the main MT in the emission of four trees whereas tree 3 [emitted only 3%](#) terpinolene. Also limonene and camphene  
475 contributions were varying from few percent to about third of the total MT emission. All the measured trees emitted  
476 rather similar proportions of  $\alpha$ - and  $\beta$ -pinene. The shares of myrcene,  $\beta$ -pinene and 3-carene were low in every tree.  
477 Since different MTs react at different rates in the atmosphere ([Table 1](#)), the species specific measurements are  
478 necessary when evaluating MTs influence on atmospheric chemistry. [Currently, air chemistry models very often use](#)  
479 [only single branch measurements and this can lead to biased results when predicting product and new particle](#)

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499 [formation](#). This study and the study of Scots pine emissions by Bäck et al. (2012) show that species specific  
500 measurements are necessary, but also that flux measurements [are](#) more representative than branch scale emission  
501 measurements and averaging over larger spatial scale may be better suited for air chemistry models.

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### 502 3.4 Standard emission potentials

503 The standard emission potentials were obtained by fitting the measured emission rates to the temperature dependent  
504 pool emission algorithm (equation 2) and the light and temperature dependent algorithm (equations 3-5) described in  
505 section 2.2). For the temperature dependent algorithm, the nonlinear regression was carried out with two fitted  
506 parameters, yielding both the emission potentials and individual  $\beta$  coefficients for each compound group. With the  
507 light and temperature dependent algorithm, only emission potentials were obtained. The compounds' [emissions](#) fitted  
508 using the temperature dependent pool emission algorithm were [the ones of the most](#) abundant MT, SQT [and the sum](#)  
509 [of carbonyls](#) for each season, while the analysis with the light and temperature dependent emission algorithm was  
510 carried out for isoprene emissions. In the analysis, obvious outliers and other suspicious data were not included. The  
511 excluded values typically were the first values obtained right after starting a measurement period, which might still  
512 show the effects of handling the sample branch. The isoprene emissions obtained in 2011 were not taken into account  
513 in the analysis as they were not properly collected on the cold trap. This was fixed in 2014 and 2015 by changing the  
514 adsorbent material. An approach with a hybrid algorithm, where the emission rate is described as a function of two  
515 source terms, de novo synthesis emissions and pool emissions, was also tested. However, the results were not  
516 conclusive.

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517 The standard emission potentials of isoprene, the selected MT and SQT, acetone and C<sub>4</sub>-C<sub>6</sub> aldehyde sums are presented  
518 in Table 5. Emission potentials are given as spring, early summer, and late summer values. The coefficient of  
519 determination (R<sup>2</sup>) is also given, even though it is an inadequate measure for the goodness of fit in nonlinear models  
520 (e.g. Spiess and Neumeyer, 2010). A more reliable parameter for estimating the goodness of fit is the standard error of  
521 the estimate, which [is](#) also given.

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522 The summertime emission potentials of MT and SQT reflect the typical behaviour of the temperature variability in  
523 summer, with low emissions in spring and high emissions in the higher temperatures of late summer. The variability  
524 of the emission potential during the growing season and between the individual compounds is large. In late summer  
525 limonene and  $\alpha$ -pinene had [the highest MT](#) emission potentials. SQT exhibit a similar [behavior as monoterpene](#)  
526 [emission potentials](#) with very low springtime and early summer emission potentials while the late summer emission  
527 potential is high. [In a review by Kesselmeier and Staudt \(1999\) the reported standard emission potentials \(30°C, 1000](#)  
528  [\$\mu\text{mol m}^{-2} \text{s}^{-1}\$ \) of Norway spruces for monoterpenes vary from 0.2 to 7.8  \$\mu\text{g}\(\text{dry weight}\)^{-1} \text{h}^{-1}\$  and in a study by](#)  
529 [Bourtsoukidis et al. \(2014b\) mean emission potential of Norway spruce was 0.89  \$\mu\text{g}\(\text{dry weight}\)^{-1} \text{h}^{-1}\$  for all data](#)  
530 [\(spring, summer, fall\). Our standardized MT emission potentials are lower than earlier reported values being 0.1  \$\mu\text{g}\$](#)   
531  [\$\text{g}\(\text{dry weight}\)^{-1} \text{h}^{-1}\$  during late summer, when they were at their highest.](#)

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539 This is the first time we have applied fitting the traditional temperature-based emission potential algorithms to  
540 measured carbonyl emissions, and based on the spruce emission results, the approach appears to be applicable also on  
541 these compounds. The best fit was obtained with the temperature dependent algorithm. The temporal variability of the  
542 emission potential was similar to MT- and SQTs. Unfortunately, acetone/[propanal](#) and [C4-C10](#) aldehyde measurements  
543 were only carried out during the last measurement campaign, but the emission pattern possibly indicates a midsummer  
544 maximum, because emissions were clearly identified in June, and already decreasing in late July-August. The isoprene  
545 emissions, fitted with the light and temperature emission algorithm, also reflect the light/temperature pattern of  
546 summer, with low emissions in spring and high emissions in late summer.

547 In late summer when isoprene emissions were a bit higher the emission model fits the data better and the emission  
548 potential for isoprene was  $56.5 \text{ ng g(dry weight)}^{-1} \text{ h}^{-1}$ . [In a review by Kesselmeier and Staudt \(1999\) the reported](#)  
549 [standard emission potentials \( \$30^\circ\text{C}\$ ,  \$1000 \mu\text{mol m}^{-2} \text{ s}^{-1}\$ \) of isoprene vary from  \$0.34\$  to  \$1.8 \mu\text{g g\(dry weight\)}^{-1} \text{ h}^{-1}\$ . Our](#)  
550 [standardized late summer mean \( \$56.5 \text{ ng g\(dry weight\)}^{-1} \text{ h}^{-1}\$ \) is much lower than these earlier reported values.](#)

### 551 3.5 [Relative reactivity of emissions](#)

552 [In summer in ambient air at this site most of the known OH reactivity \(which is ~50 % of the total measured OH](#)  
553 [reactivity\) is coming from the VOCs \(Sinha et al. 2010; Nölcher et al. 2012\). Other trace gases \( \$\text{NO}\_3\$ ,  \$\text{CO}\$ ,  \$\text{O}\_3\$ ,  \$\text{CH}\_2\$ \)](#)  
554 [have a lower contribution. Of these VOCs, aromatic hydrocarbons have only minor contribution compared to the](#)  
555 [terpenoids \(Hakola et al. 2012\). In these ambient air studies contribution of SQTs has been much lower than MTs, but](#)  
556 [those results are misleading, since lifetimes of most SQTs are so short that they can not be detected in ambient air and](#)  
557 [estimation of their contribution to the local reactivity is possible only directly from the emissions. Here we studied the](#)  
558 [relative role of different BVOCs to the reactivity of Norway spruce emissions.](#)

559 The relative contribution from each class of compounds to the total calculated [OH and  \$\text{O}\_3\$](#)  reactivity of the emissions  
560 [TCRE<sub>OH</sub> and TCRE<sub>O<sub>3</sub></sub>, respectively](#), is depicted in Fig. 3. Nitrate radicals are likely to contribute also significantly to  
561 the reactivity, but since the reaction rate coefficients were not available for the essential compounds like  $\beta$ -farnesene,  
562 the nitrate radical reactivity [is not shown](#). SQT are very reactive towards ozone and they clearly dominate the ozone  
563 reactivity. Isoprene contribution is insignificant all the time towards ozone reactivity, but it contributes 20-30 % of OH  
564 reactivity, although the emission rates are quite low. SQT dominate also OH reactivity during late summer due to their  
565 high emission rates, but early summer MT [contribution is](#) equally important. Contribution of acetone to the TCRE<sub>OH</sub>  
566 was very small (~0.05% of total reactivity), but reactivity of C<sub>4</sub>-C<sub>10</sub> aldehydes was significant, averagely 15% and  
567 sometimes over 50% of the TCRE<sub>OH</sub>. Of the aldehydes decanal, nonanal and heptanal had the highest contributions. It  
568 is also possible to measure total OH reactivity directly and in the total OH reactivity measurements by Nölscher et al.  
569 (2013) the contribution of SQTs in Norway spruce emissions also in Hyttiälä was very small (~1%). This is in  
570 contradiction to our measurements, where we found very high share of SQTs (75% in late summer). Nölscher et al.  
571 (2013) found also very high fraction of missing reactivity (>80%) especially in late summer. [Their measurements](#)  
572 [covered spring, summer and autumn](#). Emissions of C<sub>4</sub>-C<sub>10</sub> aldehydes, which were not studied by Nölscher et al. (2013)  
573 could explain part of the missing reactivity.

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#### 583 4 Conclusions

584 Norway spruce VOC emissions were measured in campaigns in 2011, 2014 and 2015. Measurements covered  
585 altogether 14 spring and summer weeks. The measured compounds included isoprene, MT and SQT and in 2015 also  
586 acetone and C<sub>4</sub>-C<sub>10</sub> aldehydes. MT and SQT emission rates were low during spring and early summer. MT emission  
587 rates increased to their maximum at the end of June and declined a little in August. A significant change in SQT  
588 emissions took place at the end of July, when SQT emissions increased substantially. The seasonality is different from  
589 that observed earlier in Germany (Bourtsoukidis et al. 2014b). There Norway spruce emissions (isoprene, MT, SQT)  
590 were highest in spring and declined thereafter. The difference in seasonality can be due to different ages of the  
591 measured trees (10-15 years in the current study, 80 years in Bourtsoukidis et al. 2014b), different climate or different  
592 stress factors. These same factors can also cause lower emission rates measured now in comparison with other studies.  
593 The effect of age to the emission potentials should be studied.

594 In August SQT were the most abundant group in the emission,  $\beta$ -farnesene being the most dominant compound. SQT  
595 emissions increased simultaneously with linalool emissions and these emissions were suggested to be initiated due to  
596 stress effects. To our knowledge this is the first time when  $\beta$ -farnesene and linalool emissions have been shown to  
597 increase simultaneously in natural conditions, although they have been shown to increase in the emissions together due  
598 to stress effects. Of the measured compounds, SQTs had highest impact on local O<sub>3</sub> and OH chemistry. This clearly  
599 shows the importance of considering also SQTs in atmospheric studies in boreal environment.

600 Acetone and C<sub>4</sub>-C<sub>10</sub> aldehyde emissions were highest in July, when they were approximately at the same level as MT  
601 emissions. C<sub>4</sub>-C<sub>10</sub> aldehydes contributed as much as MT to the OH reactivity during late summer, but early summer  
602 only about half of the MT share in early summer. This demonstrates that also emissions of other BVOCs than the  
603 traditionally measured terpenoids are important and should be included in atmospheric studies.

604 The MT emission pattern varies a lot from tree to tree. During one afternoon in June we measured emission pattern of  
605 six different trees growing near each other and especially the amounts of terpinolene, camphene and limonene were  
606 varying. Due to inconsistent emission pattern the species specific emission fluxes on canopy level should be conducted  
607 in addition to the leaf level measurements for more representative measurements. However, only leaf level  
608 measurements produce reliable SQT data.

#### 609 Acknowledgements

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628 [determining the specific leaf area of the needles.](#)

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802 **Table 1: OH and O3 reaction rate coefficients used in reactivity calculations.**

Species	$k_{OH}$ (cm <sup>3</sup> s <sup>-1</sup> )	Reference	$k_{O3}$ (cm <sup>3</sup> s <sup>-1</sup> )	Reference
Isoprene	$2.7 \cdot 10^{-11} \cdot e^{390/T}$	Atkinson et al. (2006) <sup>a</sup>	$1.03 \cdot 10^{-14} e^{-1995/T}$	Atkinson et al. (2006) <sup>a</sup>
2-Methyl-3-buten-2-ol	$6.3 \cdot 10^{-11}$	Atkinson et al. (2006) <sup>a</sup>	$1.0 \cdot 10^{-17}$	Atkinson et al. (2006) <sup>a</sup>
$\alpha$ -Pinene	$1.2 \cdot 10^{-11} \cdot e^{440/T}$	Atkinson et al. (2006) <sup>a</sup>	$8.05 \cdot 10^{-16} \cdot e^{-640/T}$	IUPAC <sup>b</sup>
Camphene	$5.33 \cdot 10^{-11}$	Atkinson et al. (1990a)	$6.8 \cdot 10^{-19}$	IUPAC <sup>b</sup>
Sabinene	$1.17 \cdot 10^{-10}$	Atkinson et al. (1990a)	$8.2 \cdot 10^{-17}$	IUPAC <sup>b</sup>
$\beta$ -Pinene	$1.55 \cdot 10^{-11} \cdot e^{467/T}$	Atkinson and Arey (2003)	$1.35 \cdot 10^{-15} \cdot e^{-1270/T}$	IUPAC <sup>b</sup>
Myrcene	$9.19 \cdot 10^{-12} \cdot e^{1071/T}$	Hites and Turner (2009)	$2.65 \cdot 10^{-15} \cdot e^{-520/T}$	IUPAC <sup>b</sup>
3-Carene	$8.8 \cdot 10^{-11}$	Atkinson and Arey (2003)	$4.8 \cdot 10^{-17}$	IUPAC <sup>b</sup>
<i>p</i> -Cymene	$1.51 \cdot 10^{-11}$	Corchnoy and Atkinson (1990)	$< 5.0 \cdot 10^{-20}$	Atkinson et al. (1990b)
Limonene	$4.2 \cdot 10^{-11} \cdot e^{401/T}$	Gill and Hites (2002)	$2.8 \cdot 10^{-15} \cdot e^{-770/T}$	IUPAC <sup>b</sup>
1,8-Cineol	$1.11 \cdot 10^{-11}$	Corchnoy and Atkinson (1990)	$< 1.5 \cdot 10^{-19}$	Atkinson et al. (1990)
Linalool	$1.59 \cdot 10^{-10}$	Atkinson et al. (1995)	$\geq 3.15 \cdot 10^{-16}$	Grosjean and Grosjean (1998)
Terpinolene	$2.25 \cdot 10^{-10}$	Corchnoy and Atkinson (1990) <sup>a</sup>	$1.6 \cdot 10^{-15}$	IUPAC <sup>b</sup>
Bornylacetate	$1.39 \cdot 10^{-11}$	Coeur et al. (1999)	-	
Longicyclene	$9.35 \cdot 10^{-12}$	AopWin <sup>TM</sup> v1.92	-	
Isolongifolene	$9.62 \cdot 10^{-11}$	AopWin <sup>TM</sup> v1.92	$1.0 \cdot 10^{-17}$	IUPAC <sup>b</sup>
$\beta$ -Caryophyllene	$2.0 \cdot 10^{-10}$	Shu and Atkinson (1995) <sup>a</sup>	$1.2 \cdot 10^{-14}$	IUPAC <sup>b</sup>
$\beta$ -Farnesene	$1.71 \cdot 10^{-10}$	Kourtchev et al. (2012)	$1.5 \cdot 10^{-12} \cdot e^{-2350/T}$	IUPAC <sup>b</sup>
$\alpha$ -Humulene	$2.9 \cdot 10^{-10}$	Shu and Atkinson (1995) <sup>a</sup>	$1.2 \cdot 10^{-14}$	IUPAC <sup>b</sup>
Alloaromadendrene	$6.25 \cdot 10^{-11}$	AopWin <sup>TM</sup> v1.92	$1.20 \cdot 10^{-17}$	AopWin <sup>TM</sup> v1.91
Zingiberene	$2.87 \cdot 10^{-10}$	AopWin <sup>TM</sup> v1.92	$1.43 \cdot 10^{-15}$	AopWin <sup>TM</sup> v1.91
Acetone	$8.8 \cdot 10^{-12} \cdot e^{-1320/T} + 1.7 \cdot 10^{-14} \cdot e^{423/T}$	Atkinson et al. (2006) <sup>a</sup>	-	
Butanal	$6.0 \cdot 10^{-12} \cdot e^{410/T}$	Atkinson et al. (2006) <sup>a</sup>	-	
Pentanal	$9.9 \cdot 10^{-12} \cdot e^{306/T}$	Thévenet et al. (2000)	-	
Hexanal	$4.2 \cdot 10^{-12} \cdot e^{565/T}$	Jiménez et al. (2007)	-	

Heptanal	2.96·10 <sup>-11</sup>	Albaladejo et al. (2002)	-
Octanal	3.2·10 <sup>-11</sup>	AopWin™ v1.92	-
Nonanal	3.6·10 <sup>-11</sup>	Bowman et al. (2003)	-
Decanal	3.5·10 <sup>-11</sup>	AopWin™ v1.92	-

803 <sup>a</sup>IUPAC recommendation

804 <sup>b</sup>IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (<http://iupac.pole-ether.fr>).

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814 **Table 2: Mean temperatures (°C) and rain amounts (mm) during each measurement month in Hyytiälä.**

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	2011		2014		2015	
	temp	rain	temp	rain	temp	rain
April	4.5	17.4				
May	9.3	44.3	9.4	57.4		
June	15.8	65.3	11.8	94.8	11.9	81.5
July			18.6	44.1	14.6	86.7
August					15.2	12.6

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818 **Table 3: Seasonal mean emission rates of isoprene, 2-methylbutenol (MBO), MT, SQT, acetone and C<sub>4</sub>-C<sub>10</sub>**  
 819 **carbonyls in ng g(dw)<sup>-1</sup> h<sup>-1</sup>. “na” means that the compounds were not included in the analysis. Spring is April-**  
 820 **May, early summer 1.6-15.7 and late summer 16.7-31.8. bdl = below detection limit. Values are averages and**  
 821 **standard deviations for the three measurement years (2011, 2014, 2015). Other SQT = sum of all other SQTs**  
 822 **in emissions. The number of the measurements each season is in parentheses.**

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	<u>average</u>	<u>stdev</u>	<u>average</u>	<u>stdev</u>	<u>average</u>	<u>stdev</u>
	<u>spring</u>	<u>spring</u>	<u>early</u>	<u>early</u>	<u>late</u>	<u>late</u>
			<u>summer</u>	<u>summer</u>	<u>summer</u>	<u>summer</u>
<u>isoprene</u>			<u>1.3</u>	<u>3.7</u>	<u>6.0</u>	<u>12</u>
<u>MBO</u>			<u>2.1</u>	<u>4.2</u>	<u>2.4</u>	<u>3.8</u>
<u>Camphene</u>	<u>1.1</u>	<u>1.8</u>	<u>2.9</u>	<u>4.4</u>	<u>3.8</u>	<u>4.1</u>
<u>3-Carene</u>	<u>0.3</u>	<u>0.7</u>	<u>1.1</u>	<u>1.7</u>	<u>0.9</u>	<u>0.6</u>
<u>p-cymene</u>	<u>0.3</u>	<u>0.6</u>	<u>0.9</u>	<u>1.8</u>	<u>0.5</u>	<u>0.5</u>
<u>Limonene</u>	<u>2.7</u>	<u>3.4</u>	<u>6.1</u>	<u>12.2</u>	<u>7.7</u>	<u>9.5</u>
<u>Myrcene</u>	<u>0.2</u>	<u>0.4</u>	<u>1.7</u>	<u>3.7</u>	<u>3.9</u>	<u>5.1</u>
<u>α-Pinene</u>	<u>2.1</u>	<u>3.4</u>	<u>5.8</u>	<u>11.1</u>	<u>9.6</u>	<u>11</u>
<u>β-Pinene</u>	<u>1.0</u>	<u>2.2</u>	<u>1.8</u>	<u>6.2</u>	<u>0.9</u>	<u>1.1</u>
<u>Sabinene</u>	<u>0</u>	<u>0.1</u>	<u>0.5</u>	<u>1.5</u>	<u>0.9</u>	<u>1.6</u>
<u>terpinolene</u>	<u>0</u>	<u>0.2</u>	<u>0.1</u>	<u>0.4</u>	<u>0.3</u>	<u>0.9</u>
<u>bornylacetate</u>	<u>0</u>	<u>0.2</u>	<u>0.5</u>	<u>2.0</u>	<u>1.1</u>	<u>2.1</u>
<u>1,8-Cineol</u>	<u>0.7</u>	<u>0.7</u>	<u>2.1</u>	<u>3.9</u>	<u>1.8</u>	<u>2.2</u>
<u>linalool</u>	<u>na</u>		<u>1.4</u>	<u>2.2</u>	<u>7.9</u>	<u>12</u>
<u>β-carvophyllene</u>	<u>0</u>	<u>0</u>	<u>0.4</u>	<u>2.1</u>	<u>7.2</u>	<u>5.9</u>
<u>β-farnesene</u>	<u>0</u>	<u>0</u>	<u>1.1</u>	<u>4.3</u>	<u>42</u>	<u>29</u>
<u>other SQT</u>	<u>0.1</u>	<u>0.4</u>	<u>1.4</u>	<u>4.7</u>	<u>35</u>	<u>30</u>
<u>Acetone</u>	<u>na</u>		<u>17</u>	<u>11</u>	<u>17</u>	<u>9.0</u>
<u>Butanal</u>	<u>na</u>		<u>2.0</u>	<u>0.7</u>	<u>0.3</u>	<u>0.3</u>
<u>Pentanal</u>	<u>na</u>		<u>4.1</u>	<u>1.1</u>	<u>2.4</u>	<u>0.9</u>
<u>Hexanal</u>	<u>na</u>		<u>5.0</u>	<u>3.0</u>	<u>4.9</u>	<u>2.1</u>
<u>Heptanal</u>	<u>na</u>		<u>5.2</u>	<u>1.2</u>	<u>7.5</u>	<u>2.4</u>
<u>Octanal</u>	<u>na</u>		<u>0.3</u>	<u>0.1</u>	<u>0.4</u>	<u>1.1</u>
<u>Nonanal</u>	<u>na</u>		<u>6.3</u>	<u>2.3</u>	<u>9.9</u>	<u>4.5</u>
<u>Decanal</u>	<u>na</u>		<u>5.6</u>	<u>2.3</u>	<u>7.4</u>	<u>3.8</u>

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834 **Table 4: Average monthly abundances (%) of emitted MTs. T1 (tree1) includes 2011 and T2 2014 and 2015**  
835 **measurements. The number of the measurements each month is in parentheses.**

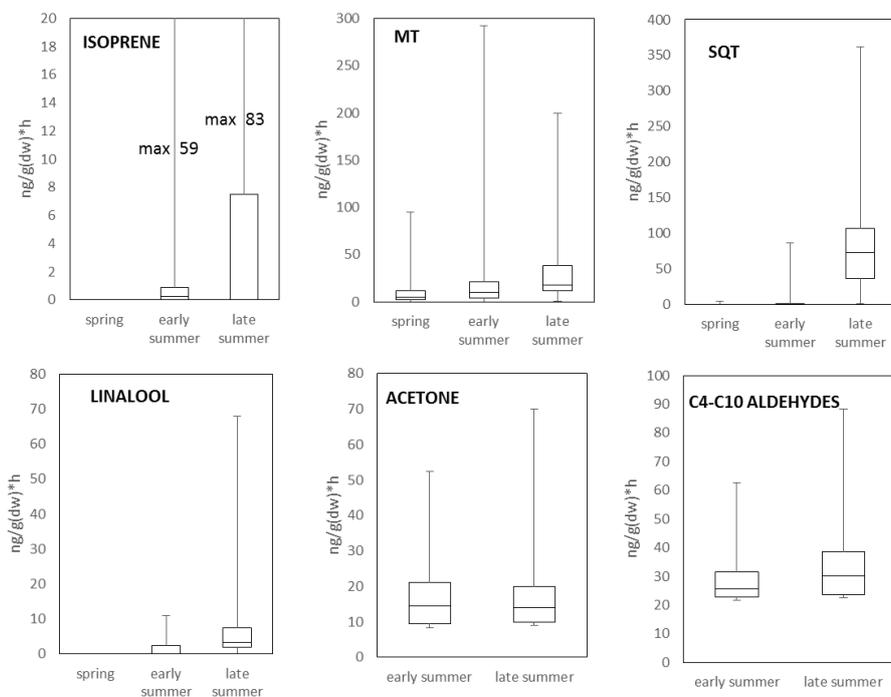
	$\alpha$ -Pinene	Camphene	Sabinene	$\beta$ -Pinene	Myrcene	$\Delta^3$ -Carene	p-Cymene	Limonene	Terpinolene
April, T1 (160)	34	19	0	18	1	5	6	18	0
May, T1 (48)	59	9	1	7	1	1	9	10	3
June, T1 (34)	7	25	16	0	34	3	9	4	0
May, T2 (129)	16	11	0	10	5	5	2	51	0
June, T2 (396)	27	15	0	15	5	5	4	29	0
July, T2 (128)	32	15	2	5	7	5	2	27	1
Aug T2 (134)	34	11	3	3	15	3	1	29	1

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840 Table 5: Standard (30 °C) MT, SQT, acetone and C<sub>4</sub>-C<sub>10</sub> aldehyde emission potentials obtained in 2011, 2014 and  
841 2015. For isoprene the standard (1000 μmol photons m<sup>-2</sup> s<sup>-1</sup>, 30 °C) emission potentials are from the 2015 campaign.  
842 The standard emission potential E<sub>s</sub> and the β coefficient are given with the standard error of the estimate (StdErr, in  
843 parenthesis). R squared and the number of measurements (N, in parenthesis). The fits were made for the spring  
844 (April - May), early summer (June – mid July) and late summer (late July – August) periods.  
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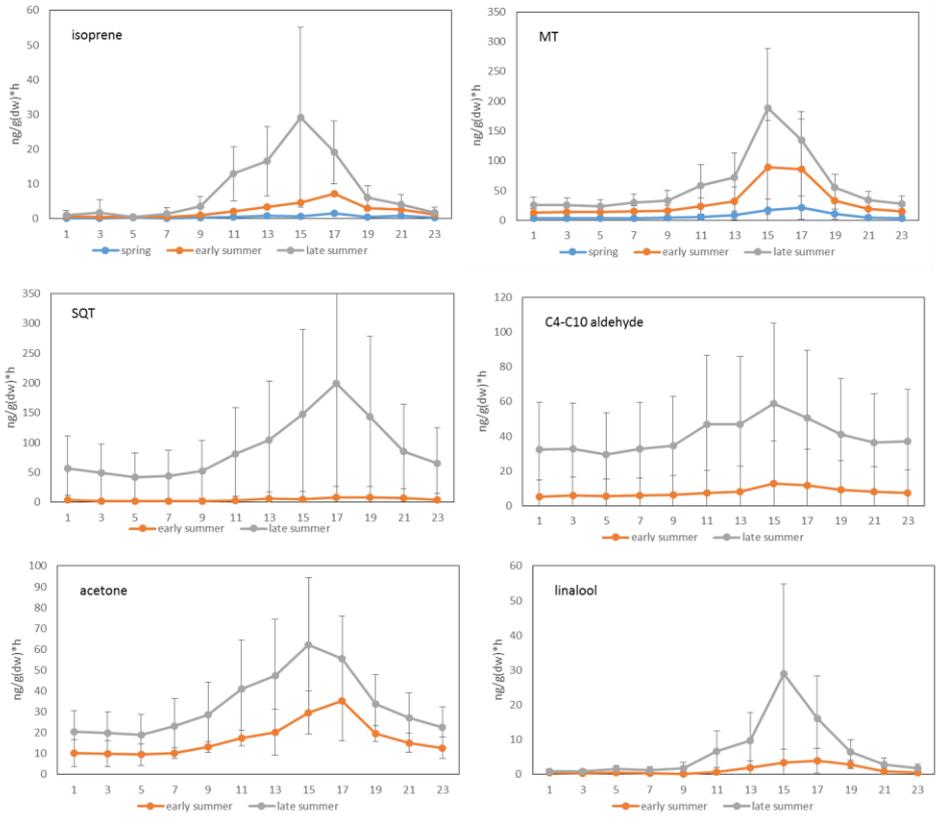
	Es (StdErr) ng/g(dw)*h	β K-1 (StdErr)	R2 (N)
<b>Spring</b>			
α-pinene	11.6 (0.7)	0.097 (0.006)	0.423 (331)
camphene	2.5 (0.4)	0.045 (0.009)	0.071 (323)
β-pinene	1.9 (0.2)	0.044 (0.007)	0.119 (324)
myrcene	0.6 (0.1)	0.010 (0.011)	0.007 (157)
limonene	5.0 (0.8)	0.032 (0.008)	0.049 (321)
other MT	2.9 (0.2)	0.085 (0.005)	0.433 (329)
β-caryophyllene	0.2 (0.1)	0.018 (0.059)	0.026 (6)
β-farnesene	-	-	- (0)
other SQT	0.7 (0.3)	0.046 (0.029)	0.029 (72)
<b>Early summer</b>			
α-pinene	14.1 (1.0)	0.058 (0.006)	0.145 (489)
camphene	7.0 (0.3)	0.060 (0.004)	0.230 (492)
β-pinene	5.2 (0.6)	0.062 (0.010)	0.076 (426)
myrcene	5.8 (0.3)	0.078 (0.005)	0.326 (356)
limonene	16.7 (0.9)	0.069 (0.005)	0.239 (497)
other MT	7.0 (0.3)	0.074 (0.004)	0.385 (499)
β-caryophyllene	4.8 (1.3)	0.018 (0.019)	0.023 (54)
β-farnesene	6.9 (1.8)	0.012 (0.018)	0.007 (90)
other SQT	6.2 (0.7)	0.055 (0.010)	0.087 (238)
acetone	50.8 (7.2)	0.066 (0.010)	0.362 (71)
aldehydes	59.1 (4.4)	0.043 (0.005)	0.503 (71)
<b>Late summer</b>			
isoprene	56.5 (4.2)		0.473 (70)
α-pinene	39.3 (4.1)	0.153 (0.017)	0.359 (163)
camphene	7.7 (1.2)	0.064 (0.016)	0.094 (161)
β-pinene	2.5 (0.3)	0.075 (0.015)	0.160 (120)
myrcene	21.1 (2.0)	0.191 (0.019)	0.476 (154)
limonene	32.3 (3.6)	0.155 (0.018)	0.336 (163)
other MT	9.9 (1.1)	0.133 (0.016)	0.298 (153)
β-caryophyllene	11.0 (1.2)	0.020 (0.010)	0.032 (129)
β-farnesene	76.9 (7.5)	0.060 (0.010)	0.183 (162)
other SQT	67.3 (8.2)	0.059 (0.013)	0.132 (157)
acetone	31.8 (2.2)	0.061 (0.007)	0.313 (163)
aldehydes	36.8 (3.0)	0.008 (0.007)	0.009 (163)

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850 **Figure 1: Season mean box and whisker plots of isoprene, MT, SQT, acetone, C4-C10 aldehydes (butanal,**  
 851 **pentanal, hexanal, heptanal, octanal, nonanal and decanal) and linalool. Boxes represent second and third**  
 852 **quartiles and vertical lines in the boxes median values. Whiskers show the highest and the lowest observations.**  
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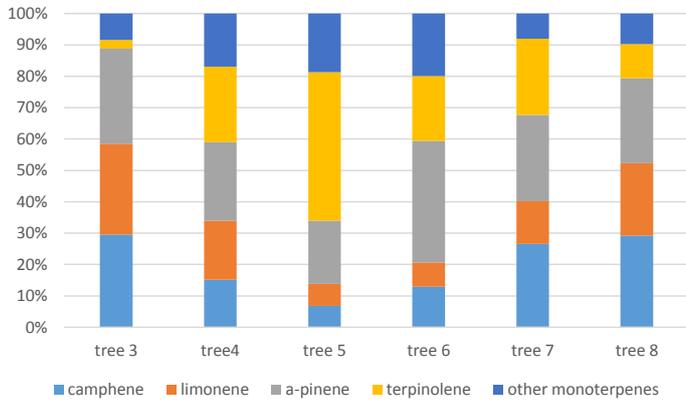
857 **Figure 2:** Mean diurnal variations of different compound groups in each season. Spring refers to April and  
 858 May, early summer June-mid July, late summer mid July-August. Aldehydes are sum of all C<sub>4</sub>-C<sub>10</sub> aldehydes  
 859 (butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal).

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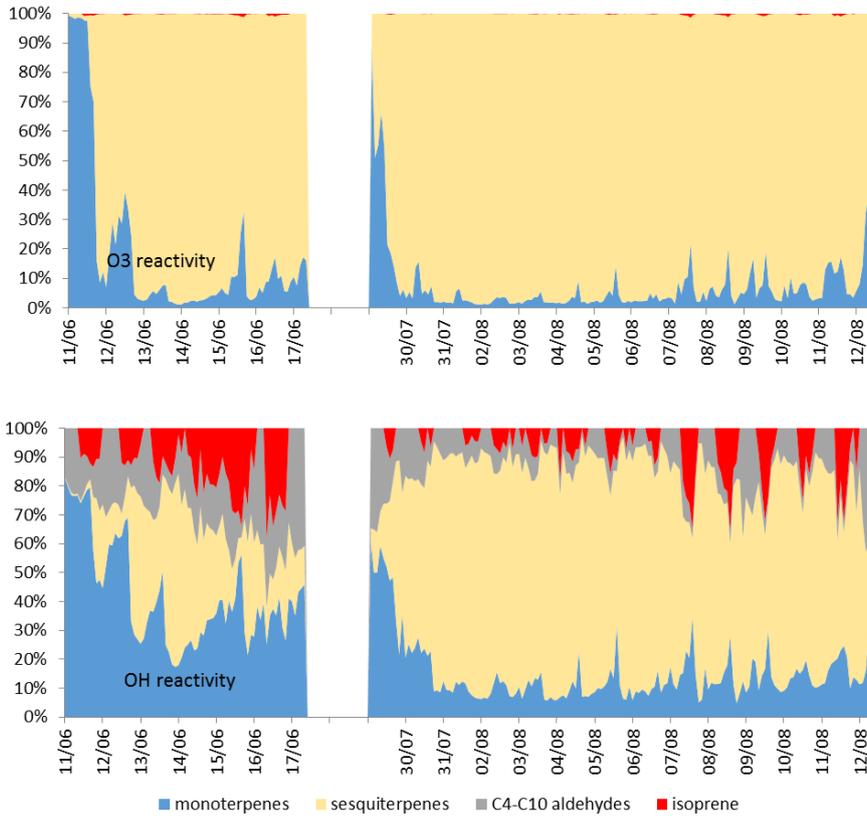
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Deleted: Variability of the most abundant emitted compounds during spring, early and late summer together with enclosure temperature. The most abundant MT were  $\alpha$ -pinene and limonene and most abundant SQT  $\beta$ -caryophyllene and  $\beta$ -farnesene. Aldehydes are sum of all C<sub>4</sub>-C<sub>10</sub> carbonyls (butanal, pentanal, hexanal, heptanal, octanal, nonanal and decanal).¶



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**Figure 3: Relative abundances of emitted monoterpenes in six different spruce individuals on 24 June 2014.**



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 882 **Figure 4. Relative  $O_3$  and OH reactivity of emissions for two periods in early and late summer 2015. The**  
 883 **compounds and reaction coefficients used for reactivity calculations are presented in Table 1.**

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