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Atmospheric Chemistry and Physics
Discussions

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

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We wish to thank Referee 2 for valuable comments that improved our manuscript in many ways.

- 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. . - 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 RËĘ2<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? Rˆ2 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 Rˆ2 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. α-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. α-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. α-pinene and limonene emissions measured and predicted using the temperature dependent emission algorithm in the late summer period.

Figure 6. β-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 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. 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 measuremtns 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 O3 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 O3 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 re-formulate 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 Rˆ2, 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 (NOx, CO, O3, CH4) 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.

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