RC: The manuscript is dealing with detailed measurements of emissions of biogenic volatiles from a Norway spruce tree in central Germany over one year, and exploring the environmental factors affecting emission rates. The paper also presents a method for calculating the ambient mixing ratio from enclosure measurements. The methods (shoot enclosures, PTR-MS analysis) are suitable for this aim and the analyses are in principal well performed, although there are some issues that need to be clarified and should be considered in revision. Especially impressive are the emission rate measurements of the very reactive sesquiterpenes, which normally can not be measured in field conditions in such a high time resolution. The study also shows significant emissions of oxygenated compounds, which are less studied topic in the abundant literature of BVOC emissions from trees.

The results clearly indicate that emission rates from spruce shoots are varying greatly between seasons, that the diurnal patterns also differ between seasons, and several potential environmental drivers for these variations are discussed. The seasonal patterns of sesquiterpenes emissions seem to differ a lot from monoterpenes and oxygenated VOCs, which is an important, novel finding and may provide important insights to atmospheric reactivity analyses.

AC: We would like to thank anonymous reviewer #3 for acknowledging the importance of our study and for providing us with fruitful feedback that will improve the final form of our manuscript.

RC: I have three main concerns. First, although the study is very thoroughly investigating the potential relationships between environmental drivers and emissions, and thus doing a good job in fulfilling the aim: 'The main goal of this study is to address the dominant factors determining the driving forces of VOC emissions from Norway spruce', the factors they are analysing are merely physical drivers, and not much attention is paid on physiological drivers, which are nevertheless discussed (synthesis pathways for example). The production and emission pathways are closely linked to many plant physiological processes, such as carbon uptake, transpiration and growth. Since no physiological measurements were performed (photosynthesis, transpiration), it is very difficult to judge which processes were involved in regulating emissions of different compound groups. Nevertheless the authors discuss and speculate these processes but are forced to be rather speculative and vague in argumentation.

AC: We recognize the weaknesses that occur from missing physiological measurements. Certainly, carbon uptake, photosynthesis and transpiration would have strengthened our argumentation. The cited publication by Laothawornkitkul et al. (2009) is best in summarizing the current knowledge and complexity between plant metabolism and VOC emissions. Their review is underlining the needs to determine VOC emission on the VOC species level to be able to relate to the specific metabolic pathways. In the revised version we will make careful note of the lack of measured physiological parameters when discussing these points. We will also raise this point in the discussion as an aim for future work.

RC: My second main concern relates to this issue as well. The correlation coefficients were calculated separately for a number of combinations of classified environmental factors, but the classification does not follow any logic based on tree physiological state, instead it is based on only the arbitrarily classified physical factors such as temperature or O3 concentration. This is leading to very biased analysis. For example, a 9.5 C temperature in summer is probably rather low (or night-time!), but in spring or fall (April or September) it may well be close to the daily maximum temperature. Thus, using a Gaussian distribution over a long time period when the state of the plant is dramatically changing, is not justified. Further, in these analysis no effect of light was taken into account, although light is important for monoterpene emissions as well (see e.g. Ghirardo et al 2010 and your own table 2 as well). For these reasons, I can not see how the analysis is giving any useful insight to the emission dynamics and therefore recommend leaving it out from the manuscript.

AC: Given the fact that the measurements site is located in a highly variable environment, we came up with the idea of using the Gaussian distributions in order to investigate the emissions under a variety of changing atmospheric and meteorological parameters. Nevertheless, the reviewer is correct. Similar temperatures will affect seasonal emissions in a different way as it can be seen from the temperature dependencies at table 2. These β-factors do not change dramatically, but indeed they suggest different emission responses. Therefore, the revised manuscript will not include the analysis performed under the filtered 12 atmospheric conditions group.

RC: The third concern is about calculating emission rates when the shoot is growing inside the enclosure (as I believe it was in this case). You do not present any estimates on the actual shoot biomass change over the season, but nevertheless calculate emissions

per dry weight. This means that you will strongly underestimate springtime emissions if you use the shoot dry weight in the end of the season, even if the emission rates from young (growing) and old foliage would be the same. However, there are also indications that new shoots would be much stronger emitters of e.g. monoterpenes and methanol than the mature ones (Aalto et al 2013 BGD). Please clarify, and correct if possible.

AC: As we have reported in Bourtsoukidis et al. (2012), the dry mass weight during the growing season has been extrapolated by length measurements. These measurements have been performed in almost daily basis during the growing period (Dittmann A., Bachelor thesis, Frankfurt University, 2012; http://www2.uni-frankfurt.de/45685032/Bachelorarbeit_AnnaDittmann.pdf). Additionally fresh grown needles from another branch were dried and weighted, since mature and fresh needles weight have a different mass for the same length. Of course this may add some uncertainty on the calculated weight during the growing period, but it does not underestimate the emissions in a substantial way, as if we were using the final needle weight. For avoiding similar misconceptions we will clarify this process as following (ACPD version P30195L23):

"Hereafter, biogenic emissions were quantified in ng $g(dw)^{-1}$ h^{-1}. The dry weight was determined by cutting the branch after the measurements and drying the needles for a week at $70^{o}C$ in a temperature controlled oven, until constant weight was achieved. During the growing period, frequent length measurements were performed and the dry weight was calculated from the observed relationship between mass and length. "

Additionally, the very interesting study of Aalto et al. will be cited in the revised manuscript.

RC: Abstract: p. 30189, line 3: 'Highest emission deviations' - please mention also in the abstract what is compared with your temperature algorithm (deviations to what?)

AC: The last sentences of the abstract have been modified as following:

"Finally, we evaluate the temperature dependent algorithm that describes the temperature dependent emissions by grouping the data in ten different temperature regimes. Highest deviations between the algorithm and the measurements were observed for monoterpenes. The observed discrepancy was attributed to the additional light dependency of monoterpene emissions that was observed"

INTRODUCTION

RC: - p. 30189, line 17: Paarsonen should be Paasonen - p. 30190, line 1: Lucia should be Llusiá - please use the most current IPCC estimates for warming - p. 30190, line 22: what does faster production mean? do you refer to the biosynthesis or the atmospheric reactions? please specify or delete. - p. 30190, line 29: Kivimanpaa should read Kivimäenpää

AC: P30189, L17: will be corrected

P30190, L1: it will be corrected and the current IPCC estimates for warming will be presented

P30190, L22: the “faster production” will be deleted

P30190, L29: will be corrected

MATERIAL AND METHODS

RC: please give some more information on the ecosystem and site: o age, height, diameter and canopy structure (height of lowest living branches) of trees o stand density and amount of other species o slope of the stand

AC: we will add this information to this section as suggested and we will further include to publications that include photos of the site of interest:

“The managed forest ecosystem is somewhat more than 60 years old. The dominant spruce trees reach a maximum height of about 17m, while lowest living branches can be found also in 2m height at the edge of the forest, where measurements took place. Further information on the forest characteristics can be found in Crowley et al. (2010) and Bonn et al. (2013). ”

RC: when were the extreme cases observed? were they correlated with high ambient temperatures or some other meteorological features?

AC: The extreme cases were observed under mechanical stress, usually occurred under strong winds. Following the above comment we will add:

“… and the dry weight was calculated from the observed relationship between mass and length. All the data up to 2 hours after the length measurements were excluded from the data analysis in order to exclude artificial, mechanically induced emissions. Additional mechanical stress has been observed under strong winds and these results are embodied in Table 1. “

RC: did you check the chamber wall and tubing losses also in field conditions? were they depending on RH, as observed by Kolari et al (Atmospheric Environment 62: 344-351)?

AC: The losses have been calculated only in the laboratory, where dependencies on the RH have been observed similar to Kolari et al. (2012). This detail will be also inserted in our material and methods.

RC: were there compound-specific differences in losses? - The chamber in Ruuskanen et al is not leak tight, as shown also in Kolari et al (2012) - Did you allow the shoot to grow inside the enclosure? If so, how did you determine the dry biomass (you use the total dry needle biomass of the enclosed branch) at a given time, when it is changing during the growth period? Please give more explanation.

AC: -Yes, the losses were compound-specific and we will add this in detail.

- The "leak tight" was an expression mistake as can be understood by our ambient mixing ratio calculation approach. We will correct that in the revised version.

-As explained in the "major concerns" section the biomass was extrapolated by length measurements (Dittmann A. Bachelor thesis, Frankfurt University, 2012)

RC: the Eq 1 is missing the explanation for kchem. I presume kVOC . [O3] is referring to that? What other chemical losses can be occurring and how important they are in the final outcome?

AC: - yes, the detailed k_{chem} will be explained in the revised version

-Chemical losses are the losses that primarily occurred due to the reactions with ozone. Further chemical gas-phase reactions will contribute only to a minor extend during the time of residence within the plant cuvette. The loss due to reactions with ambient ozone is not important for the oxygenated species but it does affect the highly reactive SQT emission rates as discussed in Bourtsoukidis et al. (2012).

RC: Why do you need to calculate absolute humidity? There is no justification why this should be more important than relative humidity. please explain in the beginning of Chapter 2.6.

As discussed within the final sentences of this chapter, in the absence of physiological parameters, absolute humidity values were calculated as "support to indicate the leaf to air vapor pressure deficit (VPD) which is the driving force for transpiration and stomatal behavior." At different temperatures you will find different absolute water deficits (VPD) though the relative humidities are similar. The absolute water content denotes the missing amount of water as the driving force. (see: VON WILLERT, D.J., MATYSSEK, R., HERPPICH, W.: Experimentelle Pflanzenökologie. Georg-Thieme-Verlag Stuttgart. 1995 page 113. In this context ‘relative humidity’ is just a reference value that needs to be linked to temperature.

RESULTS

RC: what does DWD mean?

AC: Please see P30192,L15 (it means Deutsche Wetterdienst which is the German meteorological organization)

RC: you name the main drivers of BVOC emissions before you have analyzed the relationships of these drivers to emissions (p 30196, line 22 to 30197, line 2). I think you should first present the data, explore the relationships and only after then name these factors as the main drivers?

AC: The intention was to provide a brief overview of the site’s climatology, focusing on the parameters that have shown stronger correlations. It generally known since many years that temperature and light and the main drivers of BVOC emission and therefore we took this information for granted. Nevertheless, we will revise this sentence according to your suggestion:

“Figure 2 presents a climatological overview of temperature, global radiation, ozone and absolute humidity since 1997, along with the seasonal observations of these parameters during the measuring period.”

RC:Table 1: how did you define the mechanical stress, or is this only your speculation? You do not mention a hard storm in the chapter 3.1., where you speculate on weather effects.

AC: We define mechanical stress induced emissions as the extremely high emissions, observed after a known, possibly damaging process. Since the cuvette was moving under strong winds, these periods were subject to tree mechanical stress, occurred at the branch area in contact with the cuvette. This resulted in extremely high emissions, observed after a known situation. This is a) the installation process, b) the length measurements and c) strong winds.

RC: Fig 2: cycles – should read circles

AC: thank you, it's now corrected

RC: How did the drought affect the emissions? You do not show soil moisture values, and only indicate that the year was exceptionally dry (without any values for precipitation). Drought has been in many cases affecting emissions very strongly.

AC: unfortunately our soil moisture data are incomplete, missing large periods. The definition of "exceptionally dry" was derived from the reported observations of the German meteorological service (DWD) for the site of interest.(http://www.dwd.de/bvbw/appmanager/bvbw/dwdwwwDesktop?_nfpb=true&_pageLabel=P28800190621308654463391&T176000365321293013118840gsbDocumentPath=BEA__Navigation%2FKlima__Umwelt%2FKlimaatlas.html%3F__nnn%3Dtrue&lastPageLabel=P27200165321293012986287)

RC:Methanol emissions during growth period: it has been found that they indeed can be very high during the period when the shoot is growing. But did you have a growing shoot enclosed, and how were the emission rates calculated? (See my comment above)

AC: Yes, the enclosed branch contained shoots growing during the enclosure period. As explained above, the dry weight was extrapolated from periodic length measurements its relation to dry weight biomass weight and interpolation for times in between.

RC: p 30199 line 9: 'negative isoprene fluxes can be explained only by reactions: : :' Please explain which reactions you mean?

AC: The dominant reaction is the one with OH and it will be inserted in the text.

RC: what do you mean by 'Constitutive emissions' ? I presume from the discussion that you mean it as opposite for stress-induced emissions? But you use it very confusing manner: For example for isoprene: Constitutive emissions during night were within the uncertainty range of zero but their strength during the day is closely correlated with global radiation.' (p30201 line 1.3) There should not be any isoprene emissions at night, since the isoprene emission always is very strongly light dependent. Please clarify!

AC: Constitutive emissions are those associated with life processes (growth, development, reproduction, communication), thus are caused by the plant itself instead of external processes and factors and indeed in this context it can be confusing for the reader. In the revised version we will delete the "constitutive" in order to avoid misconceptions.

RC: p 30204 line 12: please correct the acronym for mevalonic acid pathway.
AC: thank you for noticing

RC:Fig 7: explain the colour coding
AC: The color coding is just emphasizing the strength of the correlations. Nevertheless, considering your 2nd major concern this figure won't be a part of the revised manuscript

RC:chapter 3.5: I recommend changing the title to 'Calculated ambient mixing ratios'; since here you use the box model with measurements inside the open enclosure. Now the title is misleading
AC: We would prefer to keep the title as is since the manuscript is mainly dealing with the emission rates. Additionally, every measurement technique usually refers to a certain reference such as gas measurements and because of the budget approach our approach works in a rather similar way.

RC: Fig 8: explain the color coding. How do you take into account the growing shoot effect here?
AC: The colors represent the months for each season and we will add the legend. The growing shoot was taken into account as explained above.

DISCUSSION

RC: explain CC or preferably, use the proper word (correlation coefficient)
AC: the abbreviation has been explained in P30201L14. Nevertheless we will use once more the proper word

RC: I have strong doubts against arguing that co-occurring emissions are linked to identical destruction pathways (p. 30207 line 22-23). This is oversimplifying. The co-occurrence simply means that the emissions are correlated to same environmental drivers (T, light, O3: : :), however the causal link between individual compounds is by

no means clarified by these correlations. - the language should be checked, in many cases there are spelling mistakes and wrong structures.

AC: After considering both reviews and the absence of physiological parameters measured, we will not include the discussion subchapter that deals with diel cycles.