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Atmospheric Chemistry and Physics Discussions

Interactive comment on "From emissions to ambient mixing ratios: on-line seasonal field measurements of volatile organic compounds over a Norway spruce dominated forest in central Germany" *by* E. Bourtsoukidis et al.

Anonymous Referee #3

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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

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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.

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.

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

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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.

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.

Detailed comments:

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

INTRODUCTION - 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

MATERIAL AND METHODS - 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

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- when were the extreme cases observed? were they correlated with high ambient temperatures or some other meteorological features? - 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)? 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. - 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? - 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.

RESULTS - what does DWD mean? - you name the main drivers of BVOC emissions before you have analysed 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? - 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. - Fig 2: cycles – should read circles - 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. - 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) - p 30199 line 9: 'negative isoprene fluxes can be explained only by reactions. . .' Please explain which reactions you mean? - 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

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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! - p 30204 line 12: please correct the acronym for mevalonic acid pathway. - Fig 7: explain the colour coding - 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 - Fig 8: explain the color coding. How do you take into account the growing shoot effect here?

DISCUSSION - explain CC or preferably, use the proper word (correlation coefficient) - 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 30187, 2013.