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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Sesquiterpenes and oxygenated sesquiterpenes dominate the emissions of downy birches" *by* Heidi Hellén et al.

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Thank you for the valuable comments and corrections! We have considered them carefully and modified our manuscript accordingly. Please, see below the detailed answers to the comments.

General comments: The chemical identities, surface fluxes, and biological and environmental dependencies of volatile organic compound emissions into the atmosphere from downy birch trees is an important research topic for understanding the biology of these widespread tree species in higher latitudes and their interactions and feedbacks with the atmosphere. It is particularly nice to see a VOC emission study based on GCMS, as compound specific information is obtained due to the separation of isomers



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Discussion paper

(e.g. monoterpenes). I particularly found the observations of oxygenated sesquiterpenes to be extremely exciting and new, as they are rarely reported as emissions from plants. I would suggest the title of the article and the paper itself focus on this particularly novel finding. However, the authors need to discuss the limitations of the GC-MS technique as many compounds were likely missed, especially the low molecular weight OVOCs like alcohols, aldehydes, ketones, acids, esters, etc. Some of the strong conclusions mentioned in the paper would likely not stand if authors also used a method that is good for these compounds (e.g. PTR-MS).

- We added a discussion on the limitations and advantages of the GC method.

The paper is also written as if birch trees in the natural forest were studied, but reading the methods, it is clear that only a potted birch tree was used in one year and then a natural birch tree a second year.

- We now clarified this in the manuscript

In general, it is not clear to me why the authors did not select several natural birch trees growing near the instrument container to study. It's hard to extrapolate data from a single tree as being representative of downy birch emissions from the Boreal forest.

- It was not possible since we had to keep inlet lines as short as possible so that we do not lose SQTs and OSQTs in them and there was only one birch growing close enough to our measurement container.

In general, the comparison of the two datasets from different years, one using a natural tree and the other using a potted tree, and with different experimental methods rather awkward. This if further of concern since the flow rates to the instruments were different between the years. I would perhaps suggest picking only one of the data set years and focus the article on just that (perhaps moving the other to supplementary material).

- Often these kind of emission measurements are done only for a short period (e.g. two week in mid-summer) or using offline sampling with only a few samples. Here we

wanted to show how much emissions may vary in different setups/seasons. Measurements from the year 2017 were included to show the effect of stress on emissions. We now clarified this in the text. The flow rates to the instruments should not affect the results since it is taken into account and it is assumed that there are no significant losses of these compounds in the inlets when using these flows. We have studied inlet recoveries in Helin et al. (2020) and Hellén et al. (2012).

The measurements were collected during different developmental stages, but the impact of developmental stage on the emissions is poorly treated in the paper. Also with respect to discussions on stress, visible signs of damage, drought, temperature, etc., it is not clear why these occurred and when and how they impacted the emissions.

- Stress occurred only in 2017 when the measured birch was growing in the pot, due to dry zero air and too little watering. In 2019, the zero air used was humidified and the tree was growing naturally. The effect of stress in 2017 was confirmed by the strong emissions of GLVs which are known to be stress related compounds. This clarification was added to the manuscript.

Of particular concern is the fact that the study did not measure key physiological processes/variables to indicate that the vegetation was physiologically active including transpiration, stomatal conductance, and net photosynthesis rates.

- Unfortunately, these measurements were not available (see also answer to Q2 of reviewer 1). However, since most often these emissions are modelled in the atmospheric models only using temperature, they are not needed for using these results.

In particular, the use of dry zero air likely caused stomatal closure due to VPD stress, likely associated with high temperatures as well.

- We did measure RH in the chamber. In 2017 the mean RH was 31% while in 2019 it was much higher (63%) due to humidification of the zero air used for flushing the chamber. We added a comment on the possible stomatal closure in 2017 into the

manuscript in section 3.4

Regarding temperature, why was it not measured always and why was a branch outside the enclosure measured instead of the actual branch being studied inside the enclosure?

- Unfortunately we did not have any system to measure leaf temperatures inside the chamber since our surface thermometer was not able to measure through the FEP-film of the chamber. We did measure chamber temperature continuously. In addition, we have to be very careful with the materials since SQTs and OSQTs are very easily lost on the surfaces and therefore we tried to avoid installing any additional equipment inside the chamber. We assumed that zero air flow into the chamber was enough to keep leaf temperature close to the chamber temperature. Also with some thermocouple for leaf temperature measurements, one would measure only one or a few leafs while other leaves in the chamber in different light conditions may have very different temperatures. Getting the correct leaf temperature measurements in these kind of measurements is challenging, but in future we hope to get a better system for this.

The paper does report diurnal patterns of emissions which in my opinion is more important the growing season.

- We report both patterns, as their significance depends on interest of the reader. In case the interest lies in physiological processes, the diurnal pattern will be more informative, however, if the interest is in global modeling, the seasonal pattern will be of more use. Our intentions were aiming more to global modeling (as can be seen by the absence of key parameters for physiological processes), still we hope the results can be helpful in both areas.

Specific comments

Title: The title is perhaps misleading as the study did not measure all possible VOCs from the trees, and it does not indicate which tissue the emissions are deriving from

and the environmental/biological conditions.

- It is never possible to measure all VOCs simultaneously, as estimations go to over 1000000 VOCs with less than 11 carbon atoms (Goldstein et al. 2007). Terpenes and terpenoids clearly dominate VOC emissions (Sindelarova et al. 2014). We covered major SOA precursors while missing lighter more volatile compounds. To clarify we changed the title to 'Sesquiterpenes and oxygenated sesquiterpenes dominate the VOC (C5-C20) emissions of downy birches'.

Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the Earth's atmosphere, Environ. Sci. Technol., 41, 1514–1521, https://doi.org/10.1021/es072476p, 2007)

Sindelarova et al., Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years, ACP, doi:10.5194/acp-14-9317-2014

Could the dominant VOCs change under drought or high temperature stress?

- Yes, huge amounts of GLVs are emitted due to stress also in this study. In addition, for example, farnesene is known to be related to stress emissions. This is discussed in the manuscript in section 3.4.

What about from stems or roots as apposed to leaves?

- Stem and root emissions are expected to be low compared to needle/leaf emissions (Vanhatalo et al. 2020 and Mäki et al 2019).

Vanhatalo A, Aalto J, Chan T, Hölttä T, Kolari P, Rissanen K, Kabiri K, Hellén H and Bäck J (2020) Scots Pine Stems as Dynamic Sources of Monoterpene and Methanol Emissions. Front. For. Glob. Change 2:95. doi: 10.3389/ffgc.2019.00095.

Mari Mäki, Hermanni Aaltonen, Jussi Heinonsalo, Heidi Hellén, Jukka Pumpanen & Jaana Bäck: Boreal forest soil is a significant and diverse source of volatile organic compounds. Plant Soil, https://doi.org/10.1007/s11104-019-04092-z, 2019.

https://link.springer.com/article/10.1007%2Fs11104-019-04092-z.

What about the phenological dependence of VOC emissions from leaves as has previously been described for broadleaf species? https://acp.copernicus.org/articles/16/6441/2016/

- Our manuscript describes the seasonality of different terpene/terpenoid groups. We have divided the emissions to seasons: budbreak, early and late growing season. One of our conclusions is: “Due to high variability of the emissions over the growing season, it is clear that estimating birch emissions should take into account the seasonality of emission potentials”

Abstract: The abstract is very long and lacks critical structure (suggest the authors review a widely accepted format for abstracts and adhere to it) http://www.cbs.umn.edu/sites/default/files/public/downloads/Annotated_Nature_abstract.pdf I am not really following the motivation of the study. It seems that little data is not really something that is scientifically motivating. Why not start with a broader perspective discussing key uncertainties of VOC emissions from the Boreal forest and the missing OH reactivity problem?

- We reformulated the abstract.

What does, “almost throughout the summer” mean?

- We removed this and state now that SQTs and OSQTs were the main emitted ‘terpenes’ (and not ‘compounds’)

Are mean emissions the most useful here? I would suggest reporting emissions separately for bud break, early, late, and main growing season.

- This was corrected

Is bud break supposed to be different from early growing season?

- Yes, there was a clear difference. During the budbreak period, when there was a

bud, emissions were very small, and when the leaf started to grow fast (early growing season) emissions increased a lot. A better description of the various periods has been added to the section 2.1.

If no significant isoprene emissions, I would probably not mention that in the abstract.

- We removed isoprene from the abstract.

“Variable levels of emissions of MTs, C5-C10 aldehydes and GLVs were detected”. Variable with what?

- This sentence was removed.

Why are emission values of isoprene listed (below detection limits), but emisisons of these other compounds are not explicitly listed?

- Isoprene data was removed.

“On average SQT and OSQT emissions were 5 and 6 times higher than MT emissions, but variation over the growing season was high and during the late growing season MTs were the main compound group emitted.” Do the authors mean total monoterpene emissions and total SQT+OSQT emissions? It is not clear here.

- This was clarified.

“Of the SQTs, _-caryophyllene and _-farnesene were the main compounds emitted in 2019, while in 2017 also high, possibly stress-induced emissions, of _-farnesene were detected.” It is clear that there are interannual variability in the emissions, but this sentence does not summarize the key differences.

- Abstract was reformulated.

Regarding stress induced emissions, what is the stress? How do we know that this represents natural emissions and not from an artificial stress by the measurement methods? “due to drought and high chamber temperature”. Was temperature in the

chamber not controlled? High enclosure temperatures are often artifacts of many enclosure studies due to improper temperature control. Do the authors consider these emissions natural or artificial high temperature stress emissions?

- The stress was 'artificial' since in 2017 the birch was growing in a pot and, in addition, dry zero air was used for flushing the chamber. In 2019 a natural tree and humidified zero air were used and we did not detect stress related compounds. This has now been clarified in the manuscript.

If the OSQTs are being tentatively identified, how certain are the authors about the reported identity of any of the compounds?

- As explained in section 2.3, they were tentatively identified based on the comparison of the mass spectra and retention indexes (RIs) with NIST mass spectral library (NIST/EPA/NIH Mass Spectral Library, version 2.0). This is a standard method for identifying compounds in GC-MS analysis. This identification should then be confirmed by authentic standards. However, in this case these standards were not commercially available. Based on our own experience, this tentatively identification is usually correct, but sometimes it could be some very similar compound, for example a cis- or trans- isomer. We would say that the identification is much more certain than in for example in PTR-MS analysis. Here we really separate different compounds (also isomeres) in the chromatograph and all individual compounds have specific EI mass spectra and retention index.

What happened during the last two days of the experiment that is different from the other days?

- This is discussed in section 3.1.1. It could be related to the senescence of the leaves.

How does the composition of monoterpenes change throughout a day and season as a function of temperature? How does this correspond to previous studies on broad leaf monoterpene emissions as a function of leaf temperature?

https://onlinelibrary.wiley.com/doi/full/10.1111/pce.12879

-Our monoterpene emissions were very low and often below detection limits. Therefore, we studying their changes in more detail is not justified in our opinion.

Introduction “Monoterpenes (MTs) and sesquiterpenes (SQTs) are the major biogenic volatile organic compounds (BVOCs) emitted from the boreal forest.” Why have the authors ignored oxygenated VOCs which have very high emission rates from not only the Boreal forest, but many other ecosystems as well. I understand that the current study if focused on MTs, SQTs, and GLVs, but the lack of inclusion of oxygenated VOCs like low molecular weight acids, esters, alcohols, aldhehydes, ketones, etc. is not justified.

- We corrected this by adding at the beginning ‘in addition to oxygenated VOCs and isoprene’. In the third paragraph of the introduction there is also more information on OVOC emissions. In addition, we state now better in the experimental section that our measurements were missing these VOCs.

Very long and confusing sentence, please revise: “A recent study (Praplan et al. 2019) showed that currently known oxidation products are able to explain only a minor fraction (< 4.5%) of the missing reactivity in the air of boreal forest and large fractions of missing reactivity, which was not explained by isoprene, MTs or SQTs, have been found directly in the emissions of main boreal tree species (Nölcher et al. 2013, Praplan et al., 2020).”

- This was reformulated.

The intro seems to conclude that the “missing OH reactivity” are not due to sesquiterpenes or monoterpenes, yet the authors do not convincingly demonstrate this with references. These measurements are highly technical and often a particular GC-MS configuration is not suitable for all of them. Thus, I feel that this strong statement is not justified.

- This conclusion was made by Praplan et al. (2019). The GC-MS set up used by

Praplan et al. (2019) was able to detect all monoterpenes and sesquiterpenes. The GC-MSes and the OH reactivity measurements used the same inlet line and it was confirmed that these terpenes are not able to explain the missing reactivity. Our GC-MS cannot measure oxygenated compounds having more than one or two oxygen atoms and for example nitrogen containing compounds, but is able to detect all hydrocarbons in the range having 5 to 15 (or 20) carbon atoms with detection limits ∼1-10 ng/m3.

I also am not confortable with the description in the intro that low molecular weight OVOCs have been well characterized from the Boreal forest. A handful of published measurements is far from being well characterized.

- This was changed to 'have been characterized'.

I would include more background information on the biology and distrubtion/abundance of downy birch (Betula pubescens) across the world. It would be great if the authors could take more of a global perspective of their results, putting it into perspective with other ecosystems, rather than the focus on only Finland.

- More information with wider perspective on downy birch was added.

It's better to remove any phrases about, "this is the first time. . .."

- This was removed.

From the paper. If written well, these statements will not be necessary, and can instead be reserved for the letter to the editor.

Methods Please describe the Carbon number range that the experimental setup is able to quantify by GC-MS. It is likely that all VOCs lower than 5 carbon atoms were missed or poorly quantiative due to breakthrough by this technique, especially with the warm temperature of the cold trap (25 C).

- Yes this is true and we discarded all their results since they were not quantitative. However, with our method it is possible to detect all compounds having a vapour pres-

sure corresponding to alkanes with 5 to 20 carbon atoms. From an atmospheric point of view, these compounds are highly interesting compared to lighter compounds due to their high reactivity and strong potentials to form SOA compared to, for example methanol, formaldehyde or acetone, which are also known to be emitted by many plants. With a PTR-MS you would be able to detect light OVOCs, but you would miss molecular level information on terpenes, which is highly important for estimating their atmospheric impact. Traditional PTR-MS are not very sensitive and quantitative for SQTs (or OSQTs) and it is highly probably that we would have missed them totally. Their measurements would be possible with a Vocus-PTR-TOF, for example, but molecular level information would still be missing. Then, in oder to detect for example ethene, which is known to be emitted, one would need another type of GC. Hakola et al. (1998) have also measured ethene emissions of birches, but they were found to be low compared to terpenes. We added to the manscript the carbon number range measured and comment on missing low molecular weight compounds to the section 2.2

Please show an example chromatogram (GC-MS) of both the standard, blank, as well as an enclosure air sample.

- Examples of chromatograms were added to the appendix.

How was the data on leaf growth rates used in the analysis?

- The model for leaf growth was only giving the estimate of the daily leaf weight and the leaf growth rate was calculated from it. It was used in Fig. 6 to relate the high emission rates with the fast leaf growth.

It is not clear why a separate branch enclosure was used with the results deemed semiquantitative (from a separate tree). It's not clear why this is presented in the paper.

- It was done to show that it is not just our birch which is emitting these newly identified compounds (OSQTs). For example, Scots pines are known to have different chemo-

types, which emit different set of monoterpenes. We wanted to confirm if this is the case for the Downy birch. We added some explanation with a reference to paper about the chemotypes of Scots pine (Bäck et al., 2012) to the manuscript.

Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q., and Boy, M.: Chemodiversity of a Scots pine stand and implications for terpene air concentrations, Biogeosciences, 9, 689-702, doi:10.5194/bg-9-689-2012, 2012.

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