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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.

This manuscript provides a large and useful dataset describing seasonal variation in BVOC emissions from Betula pubescens, the most important deciduous tree species of the Eurasian boreal forest. Of particular significance is the inclusion of a number of previously understudied compounds, sesquiterpenes and oxygenated sesquiterpenes, which are expected to play an oversized role in atmospheric chemistry due to their potentially high rates of reactivity and SOA formation. Inclusion of such reactive com-

pounds may help to reconcile discrepancies between leaf level estimates of OH reactivity and measurements of OH reactivity in the forest atmosphere. The authors have made a large number of repeated measurements on single branches across each of two growing seasons and supplemented their data set with qualitative BVOC emissions characterizations of branches of an additional 13 trees. As a consequence, they observed a great amount of variability across seasons and between tree individuals, both quantitatively and qualitatively, i.e., the chemical species composition of emissions. This high amount of variability necessarily results in a messy, somewhat confusing dataset and complicates data interpretation, but documenting the variability is itself an important result. And despite this variability, the authors were able to draw fairly robust general conclusions about seasonal trends and the relative importance of different classes of emitted BVOC over time. While I regard these emission rate data and the conclusions drawn as qualitatively valid and worthy of publication, I have a number of reservations regarding the quantitative validity of their measurements and their calculated BVOC emission factors, as outlined below. Apparently, and inevitably when a singe branch is measured repeatedly over an entire season, leaf biomass could not be measured until the end of the experiment. Therefore, biomass was necessarily estimated, in this case using a growth model developed for needles of Scots pine. Its validity for deciduous species is unaddressed. While estimates for mature leaves, when growth has slowed or stopped are likely to be quite accurate, biomass estimates during bud break and early leaf growth seem highly problematic, and errors could lead to corresponding errors in emission estimates. Given the observed high emission rates of SQT and OSQT immediately following bud break, one might wonder if underestimates of leaf biomass contribute to these high rates. Was there any effort to determine early season leaf biomass, specific leaf mass, etc. on comparable nearby branches or to validate the CASSIA model for B. pubescens?

-We did measure biomass of leaves three times over the growing season. However, as mentioned by the reviewer biomass during the bud break and early growth was modelled. Measurements of birch leaf growth were conducted at our site during years

2015 and 2016 throughout the summer beginning immediately after bud break, so the model describes the leaf growth from the beginning. Measurements included both area growth measured from photographs and specific leaf mass (g/mm2). Thus, the modelled mass growth used in this manuscript took into account both the area increment and the changing mass to area ratio. Correlation between the modeled and measured leaf growth was good during 2015 and 2016 and the modelled results seemed reasonable based on visual check when compared with the photographs taken during the study period of this manuscripts. We improved these explanations in the revised manuscript.

Branch enclosures lacking any sort of temperature control or within chamber mixing, relying solely on air flow through the chamber, inevitably experience above ambient temperatures under sunlit or partial sun conditions. The authors address this issue, characterizing the difference between ambient temperatures inside and outside the enclosure, but the over temperatures in the chamber are enormous, averaging 10 to 14 deg. under partly cloudy and sunny conditions, respectively. Given typical Q10 values for BVOC emissions, this would likely result in 2 to 4-fold increases in branch emissions within the chamber compared to those outside the chamber. Thus, reported emission rates should be viewed with some skepticism. Of course, the relevant temperature for characterizing emissions is the leaf temperature, rather than chamber air temperature. Using an infrared thermometer, the authors characterize the relationship between air temperature and leaf temperature on branches outside the chamber. As expected, these data suggest that sunlit leaves outside the measurement enclosure experience temperatures significantly above ambient, as much as 8 deg. in sunny conditions (which seems a little high). The authors use this data to suggest that, since leaves outside the chamber experience temperatures significantly above ambient air temperature, the elevated air temperature within the enclosure is not so problematic. This ignores the possibility, however, that leaf temperatures within the enclosure are also significantly elevated above chamber ambient air temperatures under partial or full sun conditions, further exacerbating the overtemperature problem. While the au-

thors maintain (p. 5, l. 22) that a flow rate of 3.0 lpm through a 6 liter enclosure was sufficient “to keep the leaf temperature close to the chamber air temperature” they offer no evidence in support of that statement. One wishes the authors had placed thermocouples on leaves inside the chamber, i.e., leaves actually measured, ideally throughout the course of the experiment, but at the very least in order to validate their assumptions regarding within chamber leaf temperatures.

-We understand the reservations of the reviewer and his arguments are valuable. However our most important aim in the measurements presented in this manuscript were to capture SQTs, OSQTs and DTs. As these compounds are normally present at low concentrations and are very easily lost on surfaces, we chose to reduce all surfaces to a bare minimum and had them inert (FEP). In addition, the dilution was chosen to be rather small, to maximize the measured signal. The used setup allowed us to measure SQTs and OSQTs, but still was not sensitive enough for DTs. The challenge of measuring these compounds can also be seen in Table 3 (as the reviewer mentions in a later comment). Unfortunately, this setup has its drawbacks, as mentioned by the reviewer, and we are aware of its limitations (i.e. chamber PAR, surface temperature, limited cooling). Especially with the cooling we could (so far) not find a good compromise that would allow to properly cool the chamber without diluting the signals too much or adding additional surfaces to the setup. We understand that these limitations are adding errors to our measurements and reported emission coefficients, however we are also quite certain that with all the suggested additions (PAR inside the chamber, surface temperature, high dilution for cooling) we could not have acquired the presented data. We see our results as a first estimate, and hope that in the future we or other researchers can/will develop better setups to measure these evasive compounds together with the suggested parameters.)

- The 3 lpm flow through the chamber was just the minimum. We changed now our manuscript to reflect the fact that the flow was 3 to 7 lpm and that in 2019 it was always >6 lpm

- We also now state the temperature effect more clearly in the first paragraph of results (section 3.1).

In a related issue, the use of PAR, measured above the enclosure, is of limited utility when trying to characterize the actual irradiation on a multitude of leaves in a branch enclosure, where leaf angle and self-shading can drastically reduce the light reaching an individual leaf. For a certainty, the average PAR received by leaves within the enclosure is significantly less than that measured above the chamber. Since at least some of the BVOC emissions result from de novo production, dependent on light, inadequate characterization of PAR represents a problem, particularly when trying to apply the Guenther et al. light algorithm to estimate emission potentials, discussed further below.

- This clearly is an issue and the uncertainty of PAR measurements is now better stated in the manuscript both in the methods and results sections. The reason for not having a PAR sensor inside the chamber is that we had to avoid all active surfaces in the chamber to be able to capture also the emissions of higher terpenes, which are very easily lost on the surfaces as shown by e.g. Helin et al. (2020). We always stress the importance of conducting additional ecosystem level measurements, which overcome the difficulties in temperature and radiation measurements. However, when concentrating in very reactive compounds like in the current study, the enclosure measurements are the only option. We have added this issue in our conclusions.

With respect to de novo emissions versus emissions from storage pools, the analysis presented here is somewhat confusing. Citing previous studies employing 13C to identify de novo production of monoterpenes in birch species or studies where emissions fell to zero upon chamber darkening, the authors quite reasonably assume that some or all of the monoterpenes measured in this study would evidence a light dependency. If one assumes that most or all of MT emissions arise de novo, why solve for solve for emission potential using only a temperature function (Table 3)?

- As presented in Table 3, using the light dependent algorithm did not improve the correlation. With only the temperature we were able to represent emissions over the growing season with relatively good confidence, so that only the temperature would be required to upscale these emissions in atmospheric models if no PAR data is available. The temperature dependent algorithm was also used to enable a comparison with earlier studies which mainly state only the temperature dependent emission potentials.

A simple darkening of their enclosures would have removed any doubt, as well as providing information regarding light dependency of other classes of BVOC, such as SQT and OSQT, some of which (including B-caryophyllene, B-farnesene and linalool, all significant emissions in this study) are at least partially the result of de novo production in other tree species (e.g., Ponderosa pine (Harley et al. 2014), although Hakola et al. (2001) report little effect of darkening on SQT emissions in B. pubescens.

- As mentioned we have done darkening experiment of B. pubescens in the earlier study (Hakola et al. 2001) and we still rely on those results. However, in future studies we will repeat this as suggested by the reviewer.

Although the authors assume that the observed SQT emissions arise from storage pools, and are therefore dependent on temperature alone, they nevertheless present data in Table 3, calculating SQT (and OSQT and ALD) emission potentials assuming both light and temperature dependencies.

- This was done to show that taking light into account did not improve the correlation.

If one examines Fig. 3, the lack of a light dependency for SQT and OSQT emissions is indeed called into question. If one compares the early season data for MT, SQT and OSQT emissions, the shape of the responses is almost identical. That is, all show very low (but not zero) nighttime emissions, followed by a more than 10-fold increase during the day. This large an increase is very unlikely to be explained simply by a 17 deg temperature change, requiring a Q10 of over 5. With respect to MT, this large increase is easily explained by including a light response. But what about SQT and OSQT?

Again, a simple darkening of the enclosure would have helped resolve the issue.

- For less volatile STQs and OSQTs the temperature dependence is expected to be higher than for MTs due to their lower vapour pressures. As mentioned earlier, we also relied on our earlier darkening results where sesquiterpenes emissions did not decrease significantly during darkening.

Throughout the MS, seasonal means of emissions are reported. If I understand correctly, these are simply the means of all measurements made during a given season. This has some information value. But since the majority of measurements were apparently made during periods of darkness or low light and low nighttime temperatures(using data points in Fig. 3 as a guide), seasonal means significantly underestimatemean midday maximal emissions. For example, the early seasonal mean of all SQTemissions is 692, while the midday maximum in Fig. 3 is well over 2000. Using sea-sonal means of all data seriously underestimates the significance of midday emissions,of greatest importance for most atmospheric chemistry issues. Nowhere in the MS are mean daily maxima of emissions reported. Similarly, reporting only seasonal means ofPAR (including nighttime PAR) and temperature is of modest values; reporting daytimemeans or maxima would be of more use.

- We now added afternoon means to sections 3.1.2 and 3.1.3 and to the appendix table A1. In addition, a comment on this was added into the reformulated abstract. In Fig. 2, standard deviations of the measured emission rates are also shown.

Given the issues related to leaf temperature and PAR incident on leaves, I have very little confidence in any of the emission potential estimates provided in the manuscript. In addition to the temperature and light issues, I have some issues with the general procedures used to determine emission potentials. If I understand correctly (the au-thors don't present much detai) all of the data in a given season are lumped together and the data are fit to either the Guenther temperature algorithm or the light and temperature algorithms. I am unsure how ppropriate, or useful, this is, particularly if the majority of

the data is obtained under conditions of darkness and relatively low temper-ature. If I've misunderstood how these emission potentials are arrived at, I apologize,but more detail about the procedure might be warranted. Finally, given the consider-able variability in emissions even within a given season (Fig. 6), I question the utility of publishing seasonal mean values. The utility of calculating these emission potentials by the methods employed is further called into question by Table 3, in which almost half of the determinations are not considered sufficiently robust to report, while others generate unrealistic estimates of Beta.

- Emission potentials are mainly calculated for atmospheric modelling. For these models there is little benefit for daily emission factors since it is not possible to include very detailed data. In addition, for calculating daily emissions potentials, there is only a few measurement points, which may lead to deviations in the potentials. Therefore seasonal mean emission potentials are more representative for the use in modelling even though, at the moment, even seasonality is not often taken into account in these models. Often emission studies are only from short campaign or only from a few manual samples taken over the growing season and seasonality is not detected that easily.

- Unrealistic values in Table 3 are due to the low amount of values above the detection limits of our instruments. Thus, the values detected being very low and close to the detection limits have high uncertainties. We added a note about this to the caption of the table. Some of the compounds were measured for the first time exactly because the values are low as these compounds are usually lost easily to surfaces.

Thus, I recommend that the authors focus more on the measured emission rates and less on the attempts to determine emission capacities. They should present their emission data, being straightforward about the enclosure temperature issues and the resulting impact on their measurements. Having done so, they can still draw reasonable conclusions regarding the suite of BVOCs emitted by B. pubescens, the seasonal and tree to tree variability, and about the importance of previously unreported OVOC or OSQT emissions.

- We still hope to present the emission potentials (even with these uncertainties) since without parameterizing emissions somehow it is not possible to estimate their possible impacts in the atmosphere using atmospheric models. As shown by the emission algorithms, there is a clear correlation with temperature, and even with uncertainties measuring the temperature, these can give a first estimate on the possible emissions. Hopefully, in the future, we have better methods (maybe ecosystem scale flux measurements) to estimate emissions of these highly reactive compounds with strong potential for aerosol production in the atmosphere as well.

A few other issues require some attention, as follows.

Abstract, line 24. See comments above regarding the reporting of seasonal means).

The abstract was reformulated with a comment on afternoon maxima.

Fig. 1. Early dates in 2017 should be 24-28/5 (although I find 24-28 May preferable)

- The dates on the photos are correct. They simply do not always match with the measurement days. Unfortunately, we do not have photos from all days, since they were taken during site visits, which happened a few times each month. Nevertheless, these photos show the development of the leaves.

Reconcile p. 5, line 12 in which losses are “negligible” with p. 15, line 19 in which significant (?) losses are implied for high MW OSQTs.

- We clarified this in the manuscript by changing the sentences on p. 5 to ‘For most target compounds losses in these sampling lines and chamber are expected to be negligible as demonstrated by the acceptable recoveries observed in the laboratory tests (Helin et al., 2020; Hellén et al., 2012), and since high flow rates were used. Even though the only OSQT (caryophyllene oxide) studied had also acceptable recovery (>80%), some losses of higher molecular weight compounds (i.e. diterpenes) in the chamber were detected and therefore it is possible that there are some losses of higher OSQTs also in the current study and our OSQT emission rates are underestimated.’

and on p. 15 to ‘In our earlier tests we have detected some losses of higher molecular weight compounds into our chamber and particularly in the instrument (Helin et al. 2020).’

p. 2, line 35. “These OSQTs are expected to be highly reactive and to have higher-comparative secondary organic aerosols yields. . .” Likely true, but please provide areference.

- To our knowledge, there are no studies on the SOA yields of OSQTs, but we added into the manuscript that this assumption was based on the larger size and lower vapour pressure of these molecules.

p. 4, line 15. How long was the branch enclosed in the chamber during measurements?How soon after enclosing the branch was sample collection begun?

- In 2017 the measured branch was enclosed for 1 to 2 weeks. In 2019 same branch was enclosed before the bud brake and during the early growing season measurements between 6/5-7/6, and after that for 1-2 weeks at the time. After closing the chamber sample collection started immediately, but results from first samples were removed. This clarification was added to the manuscript.

p. 5, line 9. What was the sampling duration? I.e., how large a sample collected?

- We have described this already on page 6 line 16-17 and therefore we do not repeat it here.

p. 5, line 22. I’m not convinced that a flow rate of 3 lpm through a 6 liter enclosure issufficient to ensure that leaf temperatures remain close to enclosure temperature. Dothe authors have evidence? Measuring temperature of leaves outside the enclosuredoes not adequately characterize leaf temperatures within the chamber. Why wereleaf temperatures not measured on leaves inside the enclosure, ideally on a continuousbasis, but certainly for brief periods to test these assumptions under varying levels ofirradiance?

- 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. In future studies we will set up a system to measure leaf temperature. Of course this will also give an estimate of one or a few leaves while the leaves in the chambers are in very variable light conditions and we need to be very careful with the materials since SQTs and OSQTs are very easily lost on the surface materials. So far, we have not found a good compromise for that problem. However we still hope that the presented results have their value, even with the additional errors.

p. 6, line 11. Empty chamber blanks were subtracted. Please give some idea of themagnitude of these corrections. Can they be considered negligible?

- For terpenes, blank was negligible, but for aldehydes in 2017 it was between 3 to 7 ng g-1 h-1. This was added to the manuscript.

p. 7, line 16. Since you are "solving" for E30, shouldn't the form of the equation be:

E30 = E/(exp(Beta*(T-Ts)))

Of more significance, what value of Beta was used, or were Beta and E30 solvedfor simultaneously? It appears from Table 3 that they were solved for simultaneously,with values of Beta ranging from 0.03 to 0.15. Guenther 93 reported a range of Betavalues for different species varying from 0.057 to 0.144 and uses a mean value ofBeta=0.09. I see no reason why the temperature dependency of emissions for a sin-gle species should vary so widely, and in the absence of experimental determinationof Beta (emission measurements while varying leaf temperature under otherwise con-stant conditions), I think choosing a constant value for Beta would be the wiser course.

- The equation was reformulated as suggested by the reviewer. Beta was solved simultaneously. In earlier studies it has been shown that temperature sensitivity of emissions maybe be higher in northern areas and there can be differences even with the same tree during the season and due to stress. In addition, Beta=0.09 would be valid only for

MTs and their emissions were minor. For SQTs and OSQTs with lower vapour pressures, Beta-values are expected to be higher, however, there are no standardized beta values for them (most probable due to low amount of available data). For clarification we added to the manuscript that Beta was solved simultaneously.

p. 8, line 20. "This was the case particularly in SQT and OSQT emissions." It's not clear to me what this sentence refers to. Are you implying that SQT and OSQT are primarily released from storage pools? Based on what evidence? The daily pattern of emissions of MT, SQT and OSQT in Fig. 3 are almost indistinguishable (discussed further above).

- We removed this unclear sentence from the manuscript

Fig. 3. Please indicate whether these are plots of individual days within each season or plots of seasonal means? If individual days, which of the days shown in Fig. 6 (in which emission potentials varied widely within a season) was chosen? Is it representative, i.e. typical daily behavior?

-Seasonal means were used and this was now clarified in the figure caption.

p. 10, lines 3 and 22. As I've indicated, I question the value of reporting mean emission rates by season. However, if you choose to do so, saying that "seasonal mean emission rates were 5 – 690" conveys very little information and is actually confusing. Something like "Mean emission rates in 2017 were significantly higher in May (692) than in June-July (226) or August (5). Similarly, in 2019. . ."

- We changed these sentences as suggested by the reviewer to 'Mean emission rates in 2017, when measured tree was growing in the pot, were significantly higher in early (692 ng gdw-1 h-1) than in main (226 ng gdw-1 h-1) or late (5 ng gdw-1 h-1) growing season. Similarly, in 2019, when a naturally growing tree was measured, mean SQT emission rates in early season were 505 ng gdw-1 h-1, while in in main or late season they were only 41 and 14 ng gdw-1 h-1, respectively.'

p. 11, line 8. As discussed, GLV emissions are clearly associated with leaf damage/ stress. Given that, seasonal mean values are more or less meaningless. I suggest eliminating Table A2 and stressing the highest values of GLV emissions as representing stress or damage responses.

- Good remark. We removed these for GLVs.

p. 13, line 19 and elsewhere. Was OSQT9 identified as 14-hydroxy-_-caryophyllene acetate or not? If so, refer to it by name; if not, say "tentatively identified as . . ."

- We did not have an authentic standard for it and therefore it was only tentatively identified and the manuscript was corrected accordingly.

p. 15, line 5 "Emission potentials showed a very high variation between the seasons." This is true, but emission potentials also showed large variation within seasons (Fig.6).

- We changed the sentence accordingly

Fig. 6. Are these emission potentials (ET30 or E30,day) calculated assuming no de novo, i.e., light-dependent emissions? Even though, MT emissions at least are assumed to be largely light-dependent? This graph appears to show extremely high SQT and OSQT emission potentials for a single day, May 18, after which emission potential drops throughout most of the early growing season. Given this extreme within season variability, is it reasonable to lump all seasonal data together to arrive at a seasonal mean emission potential?

- These are only temperature dependent emissions. We tested also light and temperature algorithm but it did not give any better R2 values. Also with light and temperature algorithm, the emission potentials were high on 18 May. These emission potentials could be due to budbreak. It has been shown earlier that budbreak causes high emissions possibly due to stored compounds in the buds. We think that even though there are strong daily variations, it was still clear that emissions were clearly higher during the early growing season, which is also shown by these seasonal means. When mod-

elers are using emission potentials in atmospheric models, they most often use only one emission potential for the whole year and here our aim was to show that there are strong variations between the season and emissions may vary, especially in early growing season. To make this very clear, we are hoping to show also these seasonal averages. Very often emission measurements are based only on a few samples or on short (e.g. 2 -4 week period) during the main growing season, but here we had in situ GC-MS measurements over the whole growth period.

Why are bud break data shown as below detection limit when values are reported in Figs. 2 and 3?

- There were not enough data points for the calculation of temperature dependence. This is now clarified in the caption of Figure 6.

I can't help but be struck by the following. Up to 15 May, all emissions are apparently below detection limit, while three days later emissions of all terpenoids have been initiated, with SQT and OSQT emissions at their seasonal high. It is a shame that measurements weren't conducted over the intervening 3 days to better understand the onset of emissions and the possible roll of storage pools (although as indicated above, I wonder if some of the reported rates may be artificially high if estimates of leaf biomass is underestimated in these small and rapidly expanding leaves).

- We are also sad to have missed this crucial moment. We intended to measure continuously over the summer, however, these measurements are very challenging and there are often problems and malfunction with the instruments. Unfortunately one malfunction happened exactly during that time.

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