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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.

Anonymous Referee #1

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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 compounds 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 ob-

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served 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?

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 overtemperatures in the chamber are enormous, averaging 10 to 14 deg. under partly cloudy and sunny conditions, respectively. Given typical Q10 values

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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 authors 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.

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.

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)? 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. 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. 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.

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 underestimate mean midday maximal emissions. For example, the early seasonal mean of all SQT emissions is 692, while the midday maximum in Fig. 3 is well over 2000. Using seasonal 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 of PAR (including nighttime PAR) and temperature is of modest values; reporting daytime means or maxima would be of more use.

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 authors 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 appropriate, or useful, this is, particularly if the majority of the data is obtained under conditions of darkness and relatively low temperature. 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 considerable 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.

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 re-

sulting 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.

A few other issues require some attention, as follows.

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

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

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.

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 a reference.

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?

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

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

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

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 solved for 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 Beta values for different species varying from 0.057 to 0.144 and uses a mean value of Beta=0.09. I see no reason why the temperature dependency of emissions for a single species should vary so widely, and in the absence of experimental determination of Beta (emission measurements while varying leaf temperature under otherwise constant conditions), I think choosing a constant value for Beta would be the wiser course.

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).

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?

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. . ."

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.

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

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).

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?

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

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).

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