

Interactive comment on “The atmospheric potential of biogenic volatile organic compounds from needles of White Pine (*Pinus strobus*) in Northern Michigan” by S. Toma and S. Bertman

Anonymous Referee #2

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This study examines the influences of location within the canopy, year, and phenotypic differences on needle concentrations of terpenoid volatile organic compounds. It attempts to apply these results to changes in atmospheric chemistry, and it also presents some interesting results of a little studied, highly reactive sesquiterpene species found within the needles. This latter result is of special interest, given recent papers on the unknown OH reactivity in forests (e.g. Sinha et al., 2010). However, I think that for this paper to be published, the introduction and some of the results sections may need to be rewritten. Many references are needed to motivate the methods adopted within this paper. Finally, the many ideas contained within this paper seem very scattered, and the order of presentation of the data is not clear. For the rest of this review, I refer to

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pages by the last two letters, e.g. 26852, Line 10 will be replaced by P52L10, and I use MT to abbreviate ‘monoterpenes’, as in the paper.

Abstract: When reporting percentages, it would help to state the number of samples.

Introduction: If the potential for VOC to serve as a source of aerosols is relevant for this study, I recommend devoting a paragraph to this subject, and citing additional sources, such as Hao et al. (2011 -see references). It would be extremely helpful to clearly delineate when the subject is ‘BVOC content’ of a forest, meaning the concentrations of BVOC found within leaves, BVOC emissions, meaning the amount of BVOC emitted from leaves into the ambient atmosphere, and BVOC ambient concentrations, which is the concentration of BVOC found in the atmosphere. In the introduction, these ideas appear together, without clearly explaining the link between them. Additionally, it is unclear if the focus is on ‘forest health’ or ‘air quality and production of aerosols’ (P51L29).

Materials and Methods: I recommend stating in this section that the forests are generally identical, as noted later in the paper on P53L10. If you need to refer to something in the supplement multiple times, it may be best to include it in the paper, so it may be best to include figure S1 in the actual paper, rather than the supplement.

Section 3.1: It is not evident to this reviewer how the different biosynthetic pathways relate to the ambient summer temperatures. This last paragraph needs to be clarified, and should probably have additional sources cited.

Section 3.2: Note that although the light environments are different, there can also be a temperature difference of several degrees between the top and bottom of a forested environment (e.g. Gu et al., 1999).

If the number density of insect larvae varies with altitude, you should provide some evidence. Additionally, it would be interesting to see a direct comparison of overstory and understory trees, I note that only in 2008 are the ‘bottom’ overstory concentrations

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of MT+SQT close to the concentrations in the understory. Are the concentrations from the 'lower' overstory trees statistically significantly different from the concentrations in the understory trees? If not, this would lend confidence to the conclusion about the changes in terpene concentrations as the understory becomes the overstory.

Section 3.3: It makes sense to note that the difference between BVOC concentrations reported in the gas-phase and BVOC concentrations measured in needles might be due to the volatility of different terpenes, since to first order, the high concentrations where the BVOCs are produced result in diffusion to the lower concentration areas (the ambient atmosphere) where the BVOCs are deposited or reacted away. A big-leaf model (e.g. Pleim and Ran, 2009) might help make this matter more clear.

Section 3.4: I strongly recommend that this section be extended, in light of the many papers about missing OH reactivity above forests. The authors state 'little is known about its gas-phase properties'. I recommend the authors leave no stone unturned in searching the literature for references to the atmospheric effects. Some additional background, or some calculations, would strengthen your conclusions.

Section 3.5: This the conclusions of this section – that there can be phenotypic differences in productions of BVOCs within a tree population is interesting, but this section needs significant improvement. It would help, first of all, to present some of the literature that have also found genotypic variation in BVOC production within a population of trees. I question the statement that trees of both modes were within 2m of each other at UMBS, since not all of the trees used in Figure 2 are seem to be labeled on the map in Figure S1. To fix this, you may want to label all the trees in the map, produce a table with each tree number, which analysis it was used in, and what its 'mode' was in Figure 2. Additionally, it would help to explain why 2008 was not included in the analysis. It seems like different years and trees are used for different analyses, and little scientific motivation is provided. As an example, tree S16 is present in the seasonal trend study, but S41 is not – especially since it was one of the more clearly 'defining' trees for the second mode.

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For all of the line fits in Figure 2 and referenced Figure S3, you should indicate the goodness of fit. You only label two trees that have a 'very different' ratio of Limonene/ α -pinene so this makes it somewhat difficult to accept the conclusions. I strongly suggest that the authors adopt the term 'OH reactivity' (e.g. Sinha et. al, 2010) instead 'loss of hydroxyl radical. First, the terms presented are 'loss rates', and not absolute losses. Second, since OH is produced quickly during the day, and is also quickly reacted away, it may be more accurate to use the term 'OH reactivity' and not 'OH loss'.

What is the basis for scaling BVOC emissions with needle concentration and temperature based on Raoult's law? It would help to provide some background as to the validity, and the potential drawbacks, of application of this method.

Summary Describe what the different behavior between MT and SQT was, and what you mean by 'annual change'.

Finally, I recommend that a thorough grammar review be undertaken. A partial, but not complete, list follows:

P51L6: Should be 'temperature and light corrections'

P51L5: You do not define "MT"

P51L16: "Time requirements" – needs to be more specific.

P51L21: Are you talking about estimating BVOC content of the forest needles, BVOC emissions rates, or BVOC atmospheric concentrations. It is unclear.

P53L26: 'Given that 2009 was a cooler summer.' is a sentence fragment.

P54L11: terpenes emission should be 'terpene emissions'.

P54L25: This sentence needs to be rewritten.

P57L1: " the ratio did not change as the seasons changed" might be clearer to say: "did not change throughout the summer".

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P58L3: 'was calculated' should be 'were calculated'

References: Gu, L. et al.: Micrometeorology, biophysical exchanges and NEE decomposition in a two-story boreal forest – development and test of an integrated model, *Agricultural and Forest meteorology*, 94, 125-148, 1999

Sinha et al.: OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions, *Environ. Sci. Technol.*, 44, 6614–6620, 2010

Hao, L. Q., et al.: Mass yields of secondary organic aerosols from the oxidation of α -pinene and real plant emissions, *Atmos. Chem. Phys.*, 11, 1367-1378, doi:10.5194/acp-11-1367-2011, 2011

Pleim, J. and Ran, L. Surface Flux Modeling for Air Quality Applications, *Atmosphere*, 2, 271-302; doi:10.3390/atmos2030271, 2011.

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