

## ***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 #1**

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#### General comments:

The paper, “The atmospheric potential of biogenic volatile organic compounds from needles of white pine (*Pinus strobus*) in northern Michigan”, by Toma and Bertman addresses an important issue in the study of BVOC emissions, namely the interspecific variability of terpenoid compounds and how that variation can impact atmospheric chemistry. While the paper is generally well written, it lacks some rigor in developing the principle conclusions presented. First, the paper needs to build a stronger case to link leaf BVOC content to atmospheric emissions. Second, the increase in OH reactivity due to limonene should be considered for the sum of BVOCs rather than a binary

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system with  $\alpha$ -pinene for the ‘true’ atmospheric potential to be realized. The specific areas where the manuscript could be improved are listed below.

Specific comments:

\* Lines 17-19, page 26851. The crux of the paper is that leaf concentrations are directly related to atmospheric emissions. The authors propose that the “atmospheric potential” or OH reactivity can be inferred from the leaf BVOC composition without measuring any leaf emissions. This point deserves a more complete treatment especially since one of the two provided references (Lerdau et al., 1994) did not find this relationship for all terpene species (i.e.,  $\Delta$ -carene).

\* The wording of the final sentence in Introduction is much too strong for what is ‘reported’ in the manuscript. It leaves the reader expecting a link between BVOC levels and genetic diversity as well as an analysis of the genetic diversity of pine populations. Support is not provided for either of those. Consider rewording to match the results in the paper.

\* Section 3.2. The explanation of why BVOC leaf concentrations were higher in the top of the canopy compared to bottom of the canopy should focus more on BVOC biosynthesis rather than what is known on emissions (temperature and light dependencies). Leaf-level emissions are not relevant to explain the leaf concentrations.

\* Section 3.5. The discussion of environmental factors to explain the chemotype variation observed is unclear. Noting that  $\alpha$ -pinene/limonene ratios were invariant for individual trees over a growing season does not fully eliminate differences in their environmental growing conditions. Alternative environmental factors should be fully elucidated and supported with additional data. Was the age of tree or leaf type (across modes) considered (Loreto et al., 2000)? Did the light environment differ between the two modes (sun vs. shade)? Could one mode have been resource limited (nitrogen or water) or stressed (e.g., competition from a nearby canopy dominant)? Leaf-level biological exchange data (e.g., assimilation rates, stomatal conductance) would greatly

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help clarify leaf-level environmental differences between the two modes. Finally, it is not clear from the supplemental figure, S1, that “tress of both modes were within 2 m of each other” if using figure S3 to identify trees of differing modes.

\* Section 3.5. The authors hypothesize that the chemotype variation is due to genetic variation (page 26857) after ruling out environmental variation but provide no support or citations for this assertion (e.g., could it be due to the high level of genetic variation among populations (Buchert, 1994)). Is there prior work on genetic variation and BVOC synthesis? Have gene studies on UMBS white pines been conducted? What could explain the small pockets of genetically different trees within the forest?

\* Section 3.5. Regarding the calculation of the impact of Mode II trees (elevated limonene) on OH reactivity. The 11% increase in OH reactivity is based on a binary system of only limonene and  $\alpha$ -pinene (equations 1-3) yet those two compounds only account for  $\sim$ 30-50% of the terpenes measured. Since the title of the paper concerns the atmospheric potential of these BVOCs, it seems more appropriate to consider the relative increase in OH reactivity due to limonene based on the full terpene profile measured. While it is biologically interesting that two modes were observed, the atmospheric implication of such should not be overstated.

Technical corrections:

- \* Provide full name prior to the first use of an abbreviation (see OH, NO<sub>x</sub>, and MT).
- \* Check the consistency of spelling and punctuation of chemical compounds throughout the paper including tables and figures. For example, germacrene-D is also presented as germacrene D.
- \* Check the use of “terpene(s)” throughout paper. Some instances should be singular and are plural and vice-versa.
- \* Line 20, page 26857. Should read “the relative contribution to OH loss”.
- \* Line 2-3, page 26858. Subject-verb agreement. “contributions were calculated” or

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“contribution was calculated”.

\* Line 20, page 26858. “MT and SQT needle concentrations showed. . .”

\* Edit Figure S3 caption as the figure does not illustrate a “seasonal trend”.

#### References:

Buchert G. P. 1994 Genetics of white pine and implications for management and conservation. *Forestry Chronicle* 70: 427-434

Lerdau, M., Dilts, S. B., Westberg, H., Lamb, B. K., and Allwine, E. J. 1994 Monoterpene emission from ponderosa pine, *J. Geophys. Res.*, 99, 16609–16615.

Loreto, F., Nascetti, P., Graverini, A. and Mannozi, M. 2000 Emission and content of monoterpenes in intact and wounded needles of the Mediterranean Pine, *Pinus pinea*. *Functional Ecology*, 14: 589–595. doi: 10.1046/j.1365-2435.2000.t01-1-00457.x

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