

1 **Supplementary Material**

2 **“The Atmospheric Potential of Biogenic Volatile Organic Compounds from Needles of** 3 **white Pine (*Pinus strobus*) in Northern Michigan” by Toma and Bertman**

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5 **Conditions of GCMS Analysis**

	2008	2009	2010
GC	HP 6890, MSD 5973	SHIMAZDU GC-2010, GCMS-QP2010	HP 6890, MSD 5973
Capillary column	^a HP-5MS (30 m x 0.25 mm x 0.25 μ m)	SHR5XLB (30 m x 0.25mm x 0.25 μ m)	^b Stabilwax (30 m x 0.32mm x 0.25 μ m)
Temperatures	Inject: 250 °C Detector: 250 °C	Inject: 250 °C Detector 250 °C	Inject: 240 °C Detector 240 °C
Injection volume	1-0.3 μ L splitless	1 μ L with split 1:2	1 μ L splitless
Temperature program	1) 60 °C (2 min hold) to 180 °C at 7 °C min ⁻¹ 2) 60 °C(2 min hold) to 110 °C at 7 °C min ⁻¹ , go to 180 °C at 3 °C min ⁻¹ .	60 °C (2 min hold) to 200 °C at 4 °C min ⁻¹ .	40 °C (2 min hold) to 200 °C at 4 °C min ⁻¹

6 ^adenotes that the column could not separate limonene and β -phellandrene.

7 ^bdenotes that the column could not separate γ -cadinene and δ -cadinene.

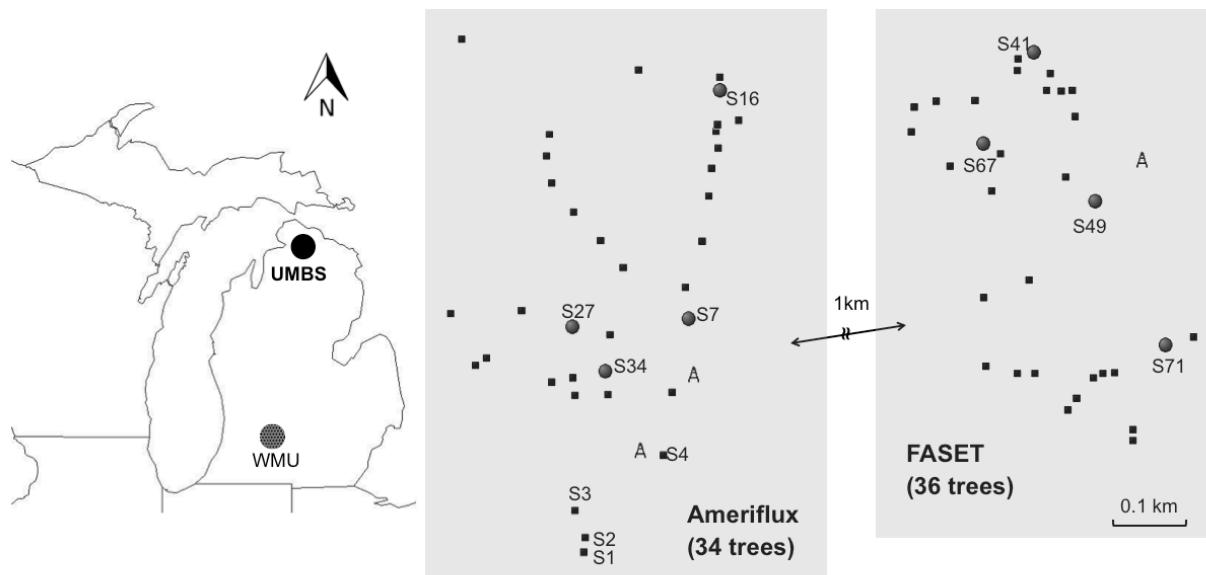
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9 **BVOC Identification Methods**

10 All MT except β -phellandrene were confirmed by retention times and mass spectra using
11 purified commercial standards. The relative response factors to internal standard, 100 μ mol L⁻¹
12 tridecane (Aldrich, 99+%), were calculated and concentration was quantified by a
13 calibration curve (5 points within 5-1000 μ mol L⁻¹) made from the standards. The following
14 sources of chemicals were used: (1R)-(+)- α -pinene (Aldrich, 98%), camphene (Supelco,
15 98.5%), (1S)-(-)- β -pinene (Aldrich, 99%), Myrcene (Fluka, \geq 95.0%), α -phellandrene (SAFC),
16 R-(+)-limonene (Fluka, \geq 99.0%), terpinolene (Fluka, \geq 95.0%). The retention time and mass

1 spectrum of β -phellandrene were obtained using Angelica seed oil (Shiono Koryo Kaisha,
2 Ltd.), which contains 60% of β -phellandrene. The SQT compounds β -Caryophyllene, α -
3 humulene, and germacrene-D were confirmed by retention time and mass spectra of their
4 standard solutions, which were supplied from SAFC, $\geq 80.0\%$; Fluka, $\geq 98.0\%$; Treatt USA
5 Inc., 40% respectively. γ -Cadinene and δ -cadinene were identified using Hinoki essential oil
6 (Shiono Koryo Kaisha, Ltd.). Germacrene-D-4-ol was inferred from the MS library, NIST 98.
7 The response factor of standards of β -caryophyllene and α -humulene were used to quantify
8 SQT and SQT-ol.

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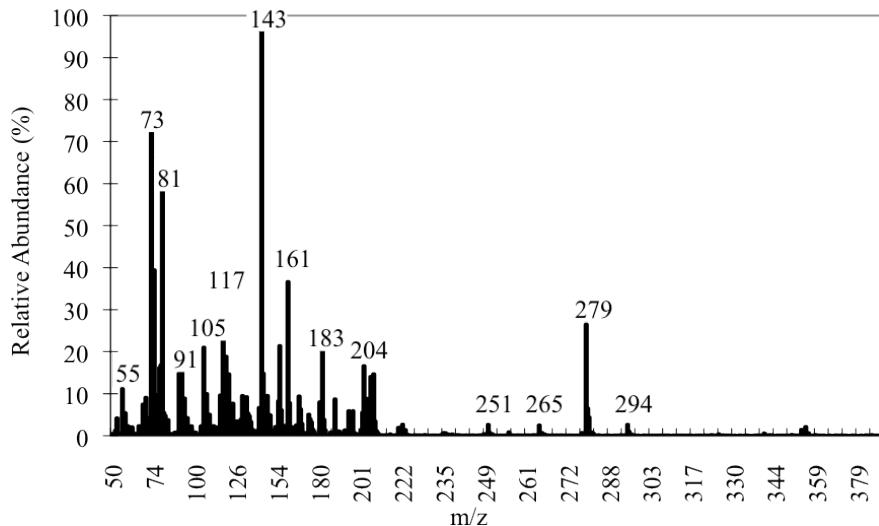


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12 Figure S1. Distribution of individual trees within the sampling site at UMBS. FASET is an
13 experimentally disturbed forest where early successional tree species were girdled in spring
14 2008 to make way for late successional species. (square: represents each understory tree,
15 circle: trees that have relatively high concentration of limonene.).

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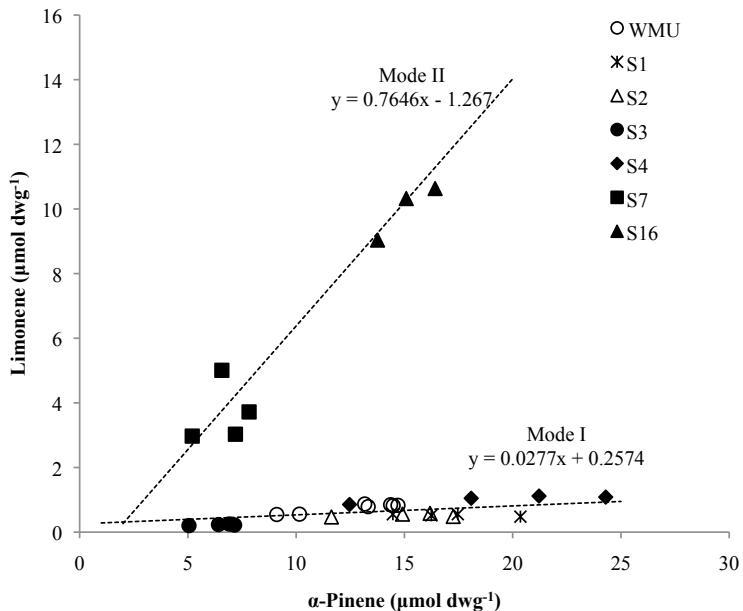
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4 Figure S2. Mass Spectrum of TMS Derivative from the SQT-ol. N-methyl-N-
5 trimethylsilyltrifluoroacetamide (MSTFA) was used to confirm the presence of the hydroxyl
6 group. 100 μ L MSTFA and 100 μ L pyridine were added 1mL field sample, which contains
7 492 μ mol L⁻¹ of SQT-ol. The solvent was heated at 75 °C for 27 h while stirring. Molecular
8 weight of Germacrene D-4-ol is 222 and Germacrene D-4-ol+TMS is 294. 73 is TMS
9 fragment.

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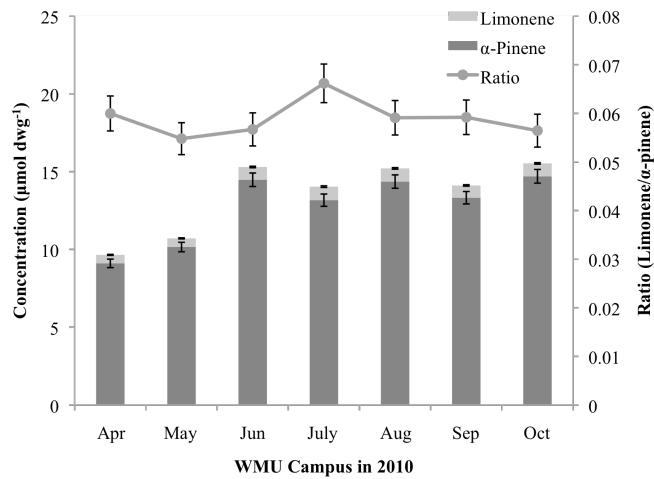


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4 Figure S3. Seasonal trend in the relationship between limonene and α -pinene in specific trees
5 measured in UMBS. Limonene and α -pinene concentration in representative trees reflecting
6 both modes were collected repeatedly over the growing season from June to August in 2010.

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10 Figure S4. Seasonal trend in the ratio of limonene and α -pinene in needles collected on the
11 campus of Western Michigan University (WMU) from April to October in 2010. Errors bar
12 represent analytical precision.

1 **The parameters for calculating the relative contribution to OH loss**
2 The parameters at 298 K, k (α -pinene; 7.43×10^{-11} , limonene; $1.64 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
3 (Atkinson and Arey, 2003), P° (α -pinene; 560.9, limonene; 201.8 Pa) (Hoskovec et al., 2005).
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5 **References**

- 6 Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103,
7 4605-4638, 2003.
- 8 Hoskovec, M., Grygarova, D., Cvacka, J., Streinz, L., Zima, J., Verevkin, S. P., and Koutek, B.:
9 Determining the vapour pressures of plant volatiles from gas chromatographic retention data, *J.*
10 *Chromatogr. A*, 1083, 161-172, 2005.

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