

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**

4

5 Table S1: Parameters and Conditions of GCMS Analytical systems used.

	2008	2009	2010	Chiral analysis
GC/detector	HP 6890/MSD 5973	SHIMAZDU GC-2010, GCMS-QP2010	HP 6890/MSD 5973	TRACE GC/POLARIS Q (Thermo Finnigan)
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)	HYDEODEX- β -3P (25 m x 0.25 mm) (Machery Nagel)
Temperatures	Inject: 250 °C Detector: 250 °C	Inject: 250 °C Detector 250 °C	Inject: 240 °C Detector 240 °C	Inject: 220 °C Detector 220 °C
Injection volume	1-0.3 μ L splitless	1 μ L (split 1:2)	1 μ L splitless	1 μ L (split 30:1)
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	60 °C (5 min hold) to 140 °C at 4 °C min ⁻¹

6 ^acolumn could not separate limonene and β -phellandrene.

7 ^bcolumn could not separate γ -cadinene and δ -cadinene.

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9 **Chemical sources**

10 The following sources of chemicals were used: tridecane (Aldrich, 99+%), (1R)-(+)- α -pinene
11 (Aldrich, 98%), camphene (Supelco, 98.5%), (1S)-(-)- β -pinene (Aldrich, 99%), myrcene
12 (Fluka, \geq 95.0%), α -phellandrene (SAFC), R-(+)-limonene (Fluka, \geq 99.0%), terpinolene

1 (Fluka, ≥95.0%) β-caryophyllene (SAFC, ≥80.0%); α-humulene (Fluka, ≥98.0%);
2 germacrene-D (Treatt USA Inc., 40%); hexane (Sigma-Aldrich, n-Hexane CHROMASOLV).

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4 **BVOC Identification**

5 All MT except β-phellandrene were confirmed using retention times and mass spectra of
6 purified commercial standards. The relative response factors to tridecane used as an internal
7 standard, 100 $\mu\text{mol L}^{-1}$, were calculated and concentration was quantified by calibration
8 curves (5 points within 5-1000 $\mu\text{mol L}^{-1}$) made from the standards. The retention time and
9 mass spectrum of β-phellandrene were obtained using Angelica seed oil (Shiono Koryo
10 Kaisha, Ltd.), which contains 60% β-phellandrene. The SQT compounds β-caryophyllene, α-
11 humulene, and germacrene-D were confirmed by retention time and mass spectra of their
12 standard solutions. γ-Cadinene and δ-cadinene were identified using Hinoki essential oil
13 (Shiono Koryo Kaisha, Ltd.). Germacrene-D-4-ol was inferred from the NIST 98 MS library.
14 The response factor of standards of β-caryophyllene and α-humulene were used to quantify
15 SQT and Germacrene-D-4-ol.

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17 **Parameters for calculating OH reactivity**

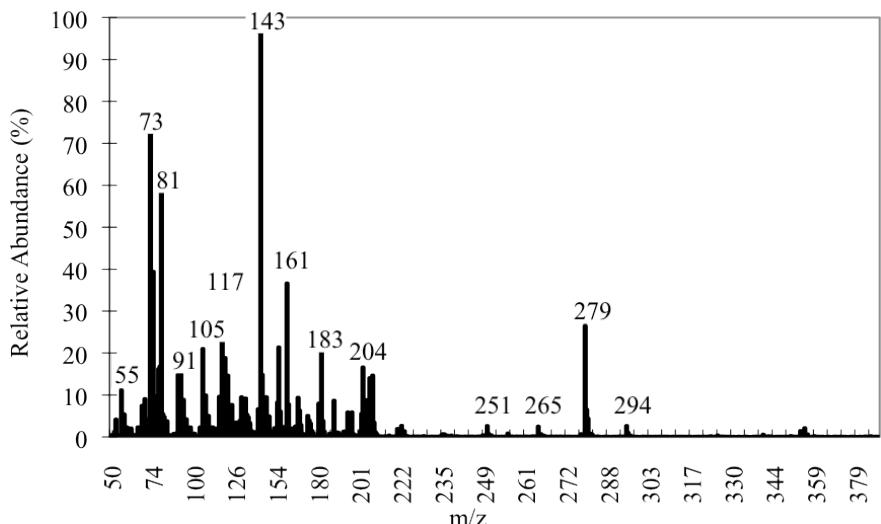
18 Rate constants at 298 K were from Atkinson and Arey (2003) and vapor pressures were from
19 Hoskovec et al. (2005). Vapor pressure not included in Hoskovec et al. (2005) were
20 calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02. Average
21 rate constant and vapor pressure for total OMT were estimated by taking the sum of
22 individual rate constant (k) or vapor pressure scaled by the individual relative composition of
23 concentration.

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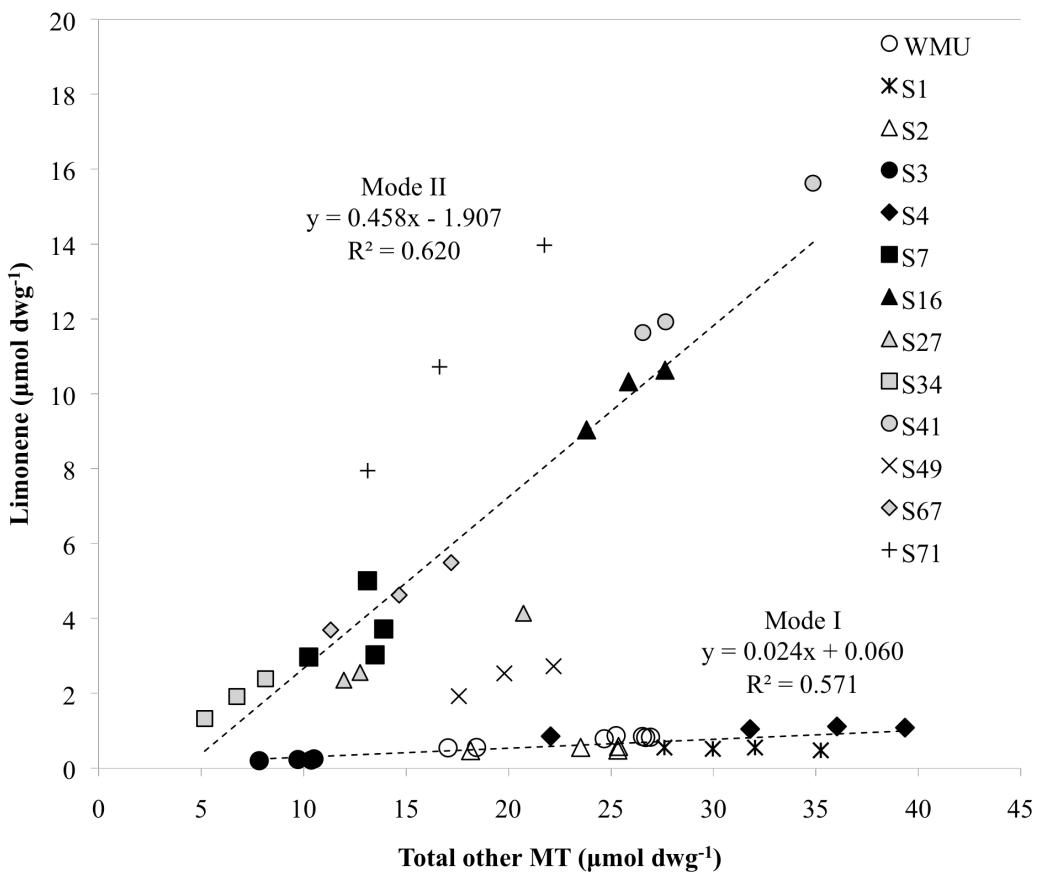
25 **References**

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27 4605-4638, 2003.
28 Hoskovec, M., Grygarova, D., Cvacka, J., Streinz, L., Zima, J., Verevkin, S. P., and Koutek, B.:
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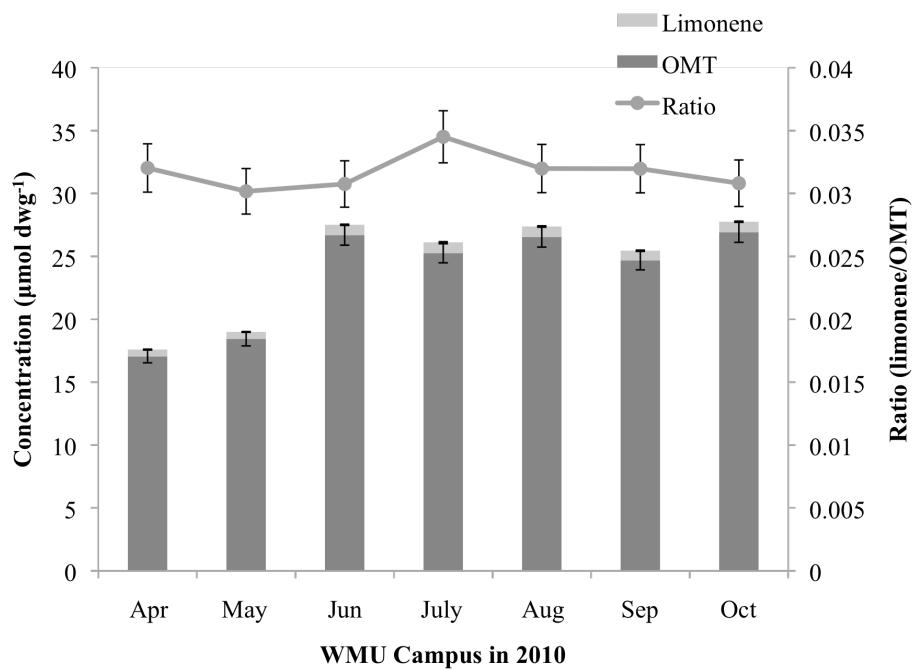
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2 Figure S1. Mass Spectrum of TMS Derivative from the SQT-ol. N-methyl-N-
3 trimethylsilyltrifluoroacetamide (MSTFA) was used to confirm the presence of the hydroxyl
4 group. 100 μ L MSTFA and 100 μ L pyridine were added to 1 mL field sample, which
5 contained 492 μ mol L⁻¹ of Germacrene D-4-ol. The solvent was heated at 75 °C for 27 h
6 while stirring. Molar mass of Germacrene D-4-ol is 222 g/mol and of Germacrene D-4-
7 ol+TMS is 294 g/mol. The peak at m/z=73 is the TMS fragment.
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2 Figure S2. Consistency throughout a growing season in the relationship between limonene
 3 and total other MT in specific trees measured in UMBS. S7, S16, S27, S34, S41, S49, S67
 4 and S71 were used as Mode II in Figure 3. WMU data, which are used in Figure S3, are
 5 included. Limonene and total other MT concentration in representative trees reflecting both
 6 modes were collected repeatedly over the growing season from June to August in 2010.

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2 Figure S3. Concentrations of limonene and total other MT (OMT) in 1-year-old needles from
3 the same tree collected on the campus of Western Michigan University (WMU) from April to
4 October in 2010 (column bars) and a time series of the ratio limonene/OMT (top line). Errors
5 bar represent analytical precision.