1 Supplementary Information for: **Terpene Composition Complexity Controls Secondary**
2 **Organic Aerosol Yields from Scots Pine Volatile Emissions**

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PTR-ToF-MS Data Processing

The mass scale calibration of the PTR-ToF-MS was performed using 3 compounds that were always present in mass spectra of the tree emissions: $H_3O_{18}^+$ at m/z 21.0226, NO^+ at m/z 29.998, and $C_{10}H_{17}^+$ at m/z 137.133. Furthermore, the transmission efficiency of ions with different molar masses through the PTR-ToF-MS was calibrated using a calibration gas standard containing 8 aromatic compounds with mixing ratios ~100 ppbV in nitrogen (BOC, United Kingdom). The mass scale calibration and peak fitting for PTR-ToF-MS data were done using PTR-MS Viewer software (Ionicon Analytik), and the data were further analyzed using MATLAB. For PTR-ToF-MS data-analysis of monoterpenes and sesquiterpenes, the calibration corrected molecular ions were used to calculate the emission rates of these compounds. Therefore, for monoterpenes the peak present at m/z 137.13 was used, and for sesquiterpenes the peak at m/z 205.20. The calibration of the PTR-ToF-MS with pure standards was done using a dynamic dilution system (Faiola et al., 2012; Kari et al., in review). From the calibration of pure standards the calibration factors of molecular ions of mono- and sesquiterpenes for PTR-ToF-MS in this study were calculated using the weighted averages based on GC-MS data. For monoterpenes the calibration factor used was the weighted average of the calibration factors of following compounds: α-pinene, camphene, β-myrcene, β-pinene, 3-carene, δ-limonene, and β-phellandrene for which all, except for camphene and β-phellandrene, the calibration was done using the pure compounds. For camphene and β-phellandrene the calibration factors of β-pinene and limonene was used, respectively, because of the similar structures the compounds have. The calibration factor used to correct the molecular ion of sesquiterpenes was calculated from the calibration factors of longifolene, β-caryophyllene, α-muurolene, α-amorphene, and δ-cadinene. For longifolene, and β-caryophyllene the pure standards were used for the determination of the calibration factors. For the rest of sesquiterpenes the calibration factor of α-humulene was used.

GC-MS Authentic Standards

49 An authentic terpenoid and green leaf volatile standard was run with each set of GC

50 cartridge samples. Two standard cartridges were prepared with each standard. The

51 standard contained the following compounds: α-pinene, camphene, sabinene, β-pinene,

52 β-myrcene, 3-carene, limonene, 1,8-cineole, γ-terpinene, terpinolene, linalool, E-DMNT,

53 camphor, borneol, terpinen-4-ol, α-terpineol, bornyl acetate, longifolene, trans-β-

54 farnesene, α-humulene, α-copaene, trans-caryophyllene, aromadendrene, β-elemene.

55 The green leaf volatile standard contained the following compounds: cis-3-hexen-1-ol,

56 trans-2-hexenal, 1-hexanol, 1-octen-3-ol, cis-3-hexenyl acetate, 1-chloro-octane,

57 nonanal, cis-3-hexenyl butyrate, methyl salicylate, cis-3-hexenyl isovalerate, and cis-3-

58 hexenyl tiglate. A stock solution of each mixture was prepared in 100 mL of methanol.

59 The stock solution was diluted in methanol 10:1 and 2 µL were injected onto adsorbent

60 cartridges with a micro-syringe.

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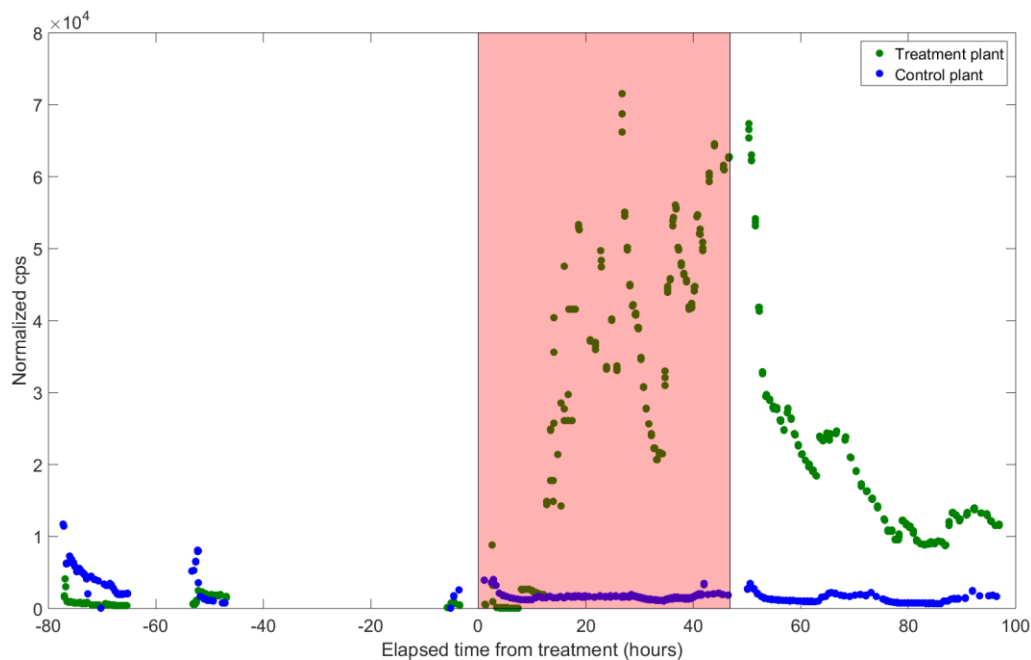
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63 Figure S1: A time-series from experiment 1 of normalized counts per second (cps) for m137, the
64 molecular ion of monoterpenes. The data was corrected with a calibration factor to account for
65 fragmentation in the PTR-ToF-MS. The shaded region denotes the herbivore exposure. The
66 m137 measured from the treatment plant emissions is shown in green and from the control
67 plant is shown in blue. Note the delay in emission increase after herbivores were applied. An

68   herbivore emission effect was not observed until after the herbivores began feeding the
69   following morning.

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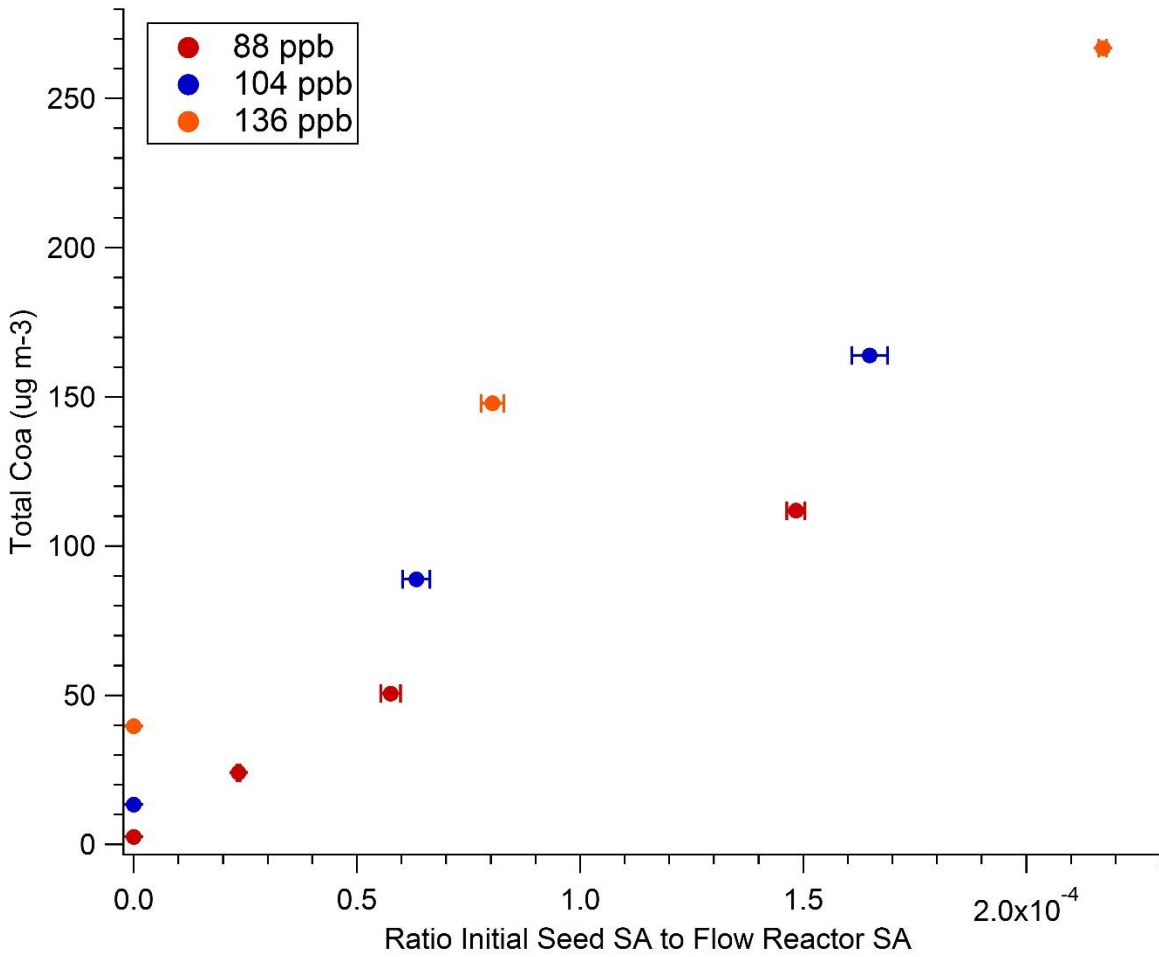
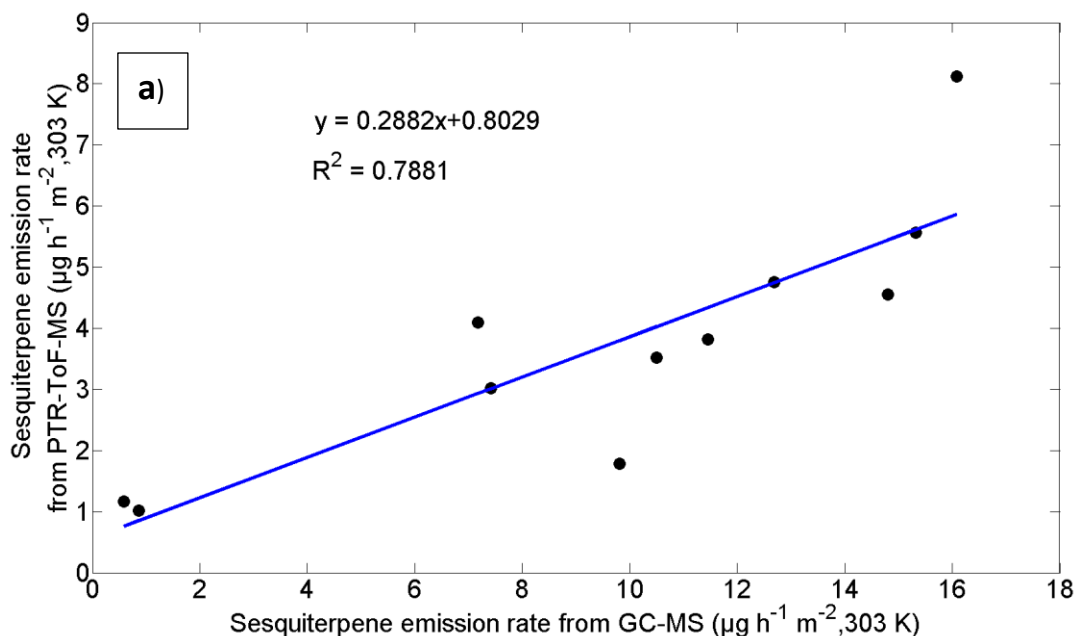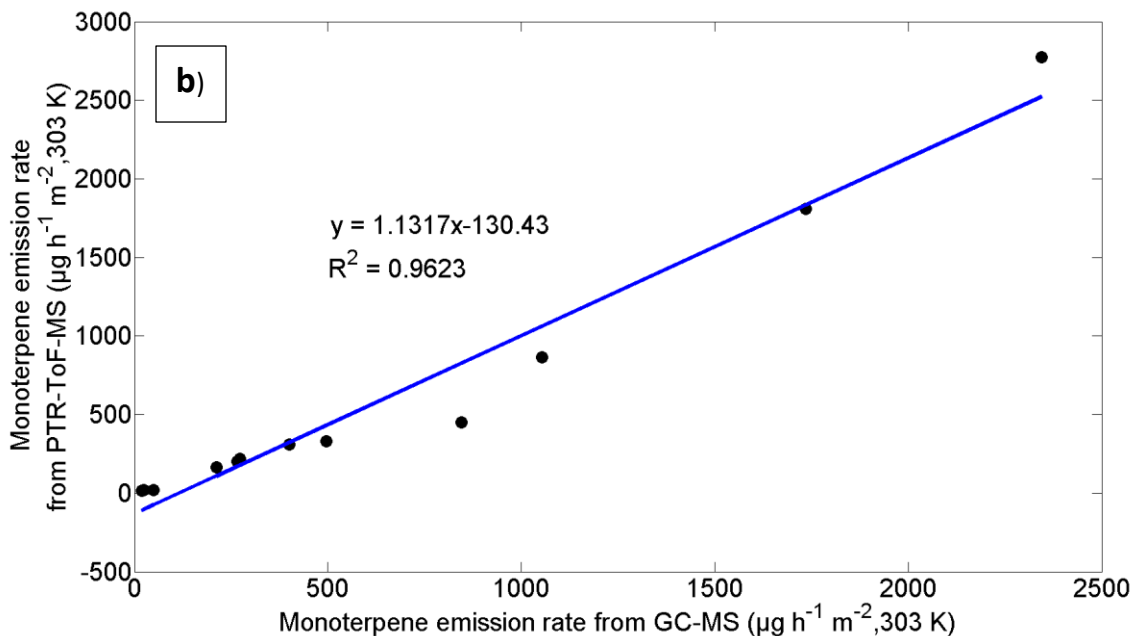Figure S2: SOA mass yield versus the ratio of the initial seed particle surface area ($S_{s,i}$) to the flow reactor surface area (S_f) for three different α-pinene mixing ratios. Yields were strongly dependent on seed surface area. For example, SOA mass yield from 88 ppb reacted α-pinene increased from 1% without any seed to nearly 11% with high seed.

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a)

$y = 0.2882x+0.8029$

$R^2 = 0.7881$

Sesquiterpene emission rate from PTR-ToF-MS (μg h^{-1} m^{-2},303 K)

Sesquiterpene emission rate from GC-MS (μg h^{-1} m^{-2},303 K)

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b)

$y = 1.1317x-130.43$

$R^2 = 0.9623$

Monoterpene emission rate from PTR-ToF-MS (μg h^{-1} m^{-2},303 K)

Monoterpene emission rate from GC-MS (μg h^{-1} m^{-2},303 K)

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80 Figure S3: Inter-comparison between PTR-ToF-MS and TD-GC-MS measurements for
81 sesquiterpene emissions (a), and monoterpene emissions (b). TD-GC-MS cartridge samples
82 were collected immediately downstream of the plant enclosure to minimize sampling line
83 losses. The PTR was connected to an automated valve system with long sampling lines. There
84 were minimal sampling line losses of monoterpenes, and high losses of sesquiterpenes. PTR
85 sesquiterpene concentrations were corrected for loss by multiplying PTR values by 3.27 based
86 on the slope in (a). Sesquiterpenes were also corrected for fragmentation patterns from
87 standard runs (Kari et al., in preparation).
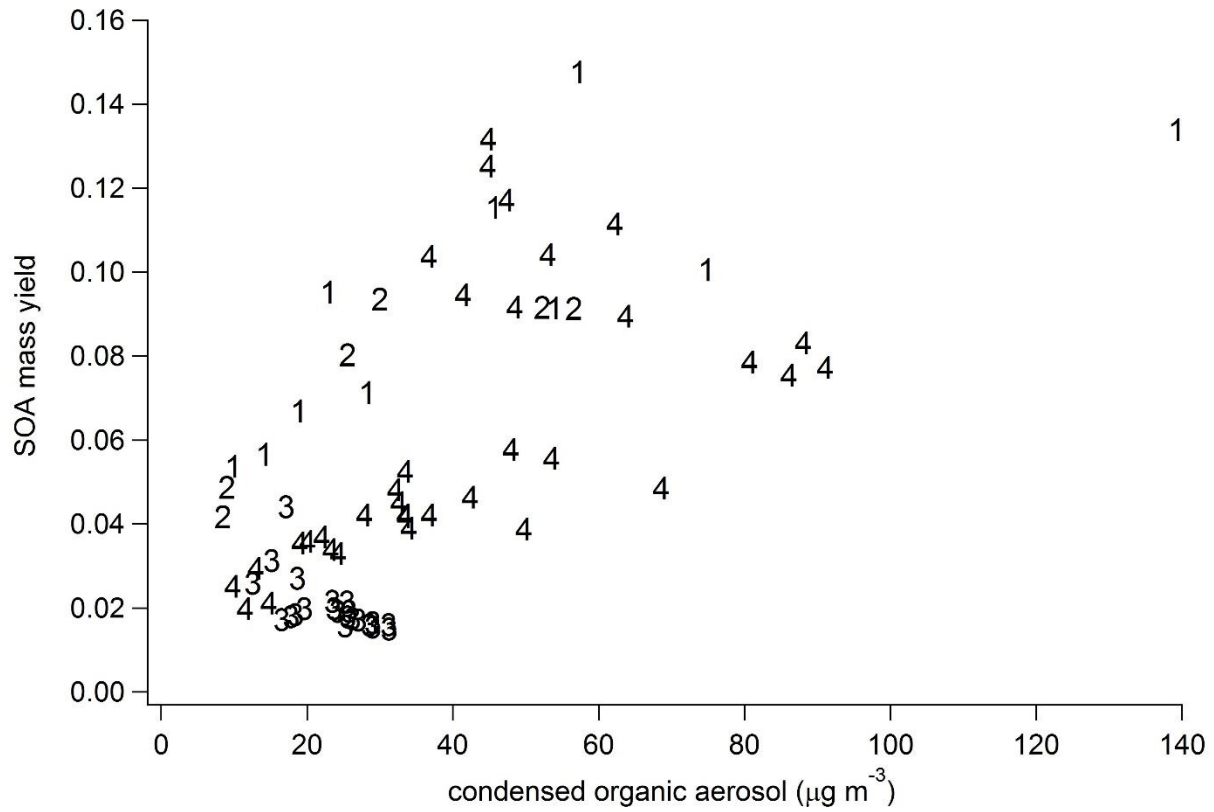
90 Figure S4: SOA mass yields during active feeding periods. Marker numbers denote the
91 experiment number. Generally, SOA mass yields were higher during active feeding periods in
92 experiments 1 and 2 than they were in experiments 3 and 4.

Table S1: Average basal emission rates ($\mu g\ m^{-2}\ h^{-1}$, 303 K) of plant volatiles during each experimental phase (pre-treatment, active feeding, and post-treatment) for each experiment. Errors are provided in parentheses and were propagated from the standard deviations of duplicate cartridge samples analyzed via TD-GC-MS. bdl=below detection limit.

	Exp #	Pre-Treatment		Active		Post-Treatment	
		Control	Treatment	Control	Treatment	Control	Treatment
α-pinene	1	30.8 (4.9)	4.2 (0.3)	20.2 (1.0)	247.9 (20.8)	1.2 (0.1)	13.1 (0.4)
	2	15.0 (0.4)	8.5 (0.1)	6.0 (0.3)	462.9 (34.2)	6.7 (0.4)	431.4 (6.8)
	3	2.9 (0.3)	2.3 (0.1)	2.3 (0.09)	164.1 (24.0)	1.8 (0.04)	57.8 (6.5)
	4	8.1 (0.3)	9.6 (0.7)	8.0 (0.2)	239.1 (7.9)	3.8 (0.2)	32.1 (2.2)
camphene	1	12.3 (1.9)	1.7 (0.1)	6.5 (1.1)	292.2 (56.1)	0.3 (0.05)	6.9 (0.3)
	2	3.2 (0.3)	6.1 (0.03)	1.3 (0.3)	239.9 (19.4)	0.7 (0.06)	75.7 (2.4)
	3	1.9 (0.2)	0.9 (0.03)	1.7 (0.1)	84.0 (8.3)	1.3 (0.03)	18.1 (1.9)
	4	2.7 (0.1)	3.2 (0.3)	0.9 (0.05)	9.6 (3.5)	0.9 (0.1)	6.9 (0.7)
β-pinene	1	1.6 (0.1)	1.4 (0.1)	0.9 (0.05)	134.1 (16.6)	0.07 (0.004)	0.8 (0.02)
	2	0.7 (0.03)	2.0 (0.02)	0.8 (0.2)	128.2 (14.4)	0.4 (0.04)	108.4 (2.5)
	3	0.5 (0.03)	0.4 (0.01)	0.4 (0.02)	12.5 (2.7)	0.4 (0.05)	3.1 (0.3)
	4	0.6 (0.02)	0.9 (0.08)	0.4 (0.03)	10.3 (1.3)	0.2 (0.01)	1.2 (0.06)
β-myrcene	1	1.9 (0.3)	1.3 (0.02)	1.3 (0.1)	564.0 (63.6)	0.08 (0.01)	2.9 (0.06)
	2	1.3 (0.08)	1.0 (0.01)	2.6 (0.8)	123.2 (2.2)	1.7 (0.06)	71.1 (0.7)
	3	0.6 (0.03)	0.5 (0.02)	0.5 (0.02)	36.1 (2.2)	0.4 (0.02)	6.2 (0.5)
	4	1.5 (0.08)	17.6 (1.4)	0.5 (0.02)	63.5 (3.4)	0.2 (0.01)	3.6 (0.2)
Δ-3-carene	1	26.7 (2.0)	bdl	16.8 (0.8)	2.0 (0.4)	1.1 (0.07)	0.03 (0.003)
	2	6.8 (0.2)	bdl	6.4 (1.5)	1.2 (0.05)	3.3 (0.07)	0.3 (0.2)
	3	7.4 (0.5)	5.7 (0.1)	4.6 (0.1)	448.1 (27.8)	3.4 (0.02)	129.4 (8.0)
	4	9.8 (0.4)	22.8 (1.9)	4.6 (0.1)	302.6 (12.9)	1.6 (0.05)	33.9 (1.0)
p-cymene*	1	13.6 (5.2)	1.1 (0.5)	25.1 (4.4)	1584.2 (280.8)	10.0 (6.7)	47.3 (28.8)
	2	16.7 (10.1)	15.5 (12.1)	7.5 (3.6)	766.7 (109.9)	0.9 (0.06)	305.3 (50.0)
	3	16.1 (10.9)	12.4 (6.5)	7.6 (5.3)	185.8 (62.2)	1.5 (0.3)	62.7 (11.4)
	4	5.2 (2.5)	4.2 (0.9)	0.3 (0.1)	10.9 (4.0)	1.1 (0.4)	11.7 (3.2)
limonene	1	1.9 (0.3)	1.3 (0.1)	1.0 (0.2)	356.3 (48.9)	0.06 (0.01)	4.6 (0.2)
	2	0.6 (0.09)	3.0 (0.09)	0.4 (0.09)	538.4 (28.6)	0.3 (0.03)	186.7 (3.6)
	3	0.2 (0.02)	2.3 (0.08)	0.2 (0.03)	115.6 (9.2)	0.1 (0.05)	17.7 (1.9)
	4	7.1 (0.3)	1.4 (0.2)	2.2 (0.1)	22.5 (7.9)	0.8 (0.04)	2.2 (0.3)

β-phellandrene*	1	0.6 (0.09)	0.1 (0.1)	0.5 (0.03)	26.5 (3.6)	bdl	0.3 (0.01)
	2	0.8 (0.08)	1.1 (0.01)	2.3 (0.7)	212.4 (1.4)	1.2 (0.01)	134.5 (2.2)
	3	0.4 (0.02)	2.2 (0.09)	0.2 (0.01)	102.6 (8.6)	0.2 (0.02)	11.3 (0.8)
	4	13.5 (0.7)	22.6 (2.0)	5.1 (0.2)	138.4 (4.3)	1.2 (0.06)	8.1 (0.3)
Other MT**	1	9.0 (0.5)	1.3 (0.1)	4.9 (0.4)	705.7 (58.4)	0.3 (0.02)	9.0 (0.4)
	2	3.5 (0.4)	3.1 (0.08)	2.1 (0.3)	296.4 (18.3)	1.7 (0.1)	105.7 (2.7)
	3	7.4 (0.4)	4.6 (0.2)	7.1 (0.3)	259.0 (8.6)	2.2 (0.01)	36.1 (0.8)
	4	4.3 (0.6)	7.5 (0.2)	1.5 (0.03)	92.3 (5.3)	1.0 (0.05)	10.4 (0.4)
longifolene	1	0.4 (0.002)	bdl	0.5 (0.03)	0.1 (0.1)	bdl	bdl
	2	0.7 (0.02)	0.2 (0.1)	0.6 (0.02)	0.3 (0.01)	0.4 (0.005)	0.3 (0.01)
	3	0.1 (0.007)	0.2 (0.01)	0.1 (0.007)	0.9 (0.03)	0.07 (0.07)	0.6 (0.01)
	4	0.3 (0.01)	0.1 (0.006)	0.2 (0.004)	0.2 (0.009)	0.1 (0.006)	0.09 (0.004)
β-caryophyllene	1	2.7 (0.3)	bdl	1.4 (0.1)	0.6 (0.04)	0.06 (0.006)	0.05 (0.003)
	2	1.5 (0.07)	0.5 (0.01)	0.3 (0.02)	2.7 (0.2)	0.1 (0.01)	1.1 (0.02)
	3	0.1 (0.06)	bdl	0.1 (0.003)	0.1 (0.007)	0.2 (0.01)	0.1 (0.02)
	4	0.5 (0.03)	1.8 (0.09)	0.3 (0.008)	1.5 (0.09)	0.02 (0.009)	0.1 (0.005)
β-farnesene	1	bdl	0.7 (0.05)	bdl	2.3 (0.2)	bdl	0.1 (0.01)
	2	1.7 (0.8)	2.1 (0.02)	bdl	bdl	bdl	bdl
	3	0.1 (0.02)	0.2 (0.01)	0.9 (0.2)	1.1 (0.1)	bdl	0.1 (0.01)
	4	2.4 (0.1)	1.6 (0.2)	0.3 (0.013)	0.2 (0.01)	bdl	0.05 (0.005)
Other SQT**	1	38.2 (0.6)	3.6 (0.1)	24.3 (1.0)	20.8 (0.6)	1.2 (0.04)	2.9 (0.06)
	2	31.2 (0.7)	18.5 (0.1)	8.7 (0.2)	70.6 (2.5)	6.7 (0.3)	56.4 (1.0)
	3	5.7 (0.3)	0.8 (0.1)	4.3 (0.2)	9.2 (0.2)	3.2 (0.01)	9.3 (0.1)
	4	3.9 (0.1)	8.7 (0.2)	2.6 (0.05)	15.2 (0.6)	0.7 (0.03)	7.5 (0.2)

*These compounds were not included in the GC standard and thus these BER values are semi-quantitative. MS quantitation was performed using the terpinolene standard as a proxy. Terpinolene was selected as a proxy because of similarity in structure to β-phellandrene.

**Many of the compounds in the "other" categories were not included in the GC standard. A proxy was chosen from the standard compounds based on structural and mass spectral similarity. These BER values are also semi-quantitative. Compounds in the other monoterpenoids category include the following: tricyclene, β-fenchene, α-fenchene, sabinene, α-phellandrene, α-terpinene, 1,8-cineole, β-ocimene, γ-terpinene, terpinolene, camphor, borneol, bornyl acetate, and 10 unidentified monoterpenes. The unidentified monoterpenes had clear monoterpene mass spectra, but NIST identification matched them with monoterpenes that had known different retention times. Compounds in the other sesquiterpenes category include the following: α-copaene, β-elemene, junipene, isolongifolene, α-humulene, β-cubebene, valencene, murolene,

α-amorphene, δ-cadinene, cadina-1,4-diene, and two unidentified compounds that clearly had a sesquiterpene NIST spectra match, but the match was not consistent with other known sesquiterpene retention times.