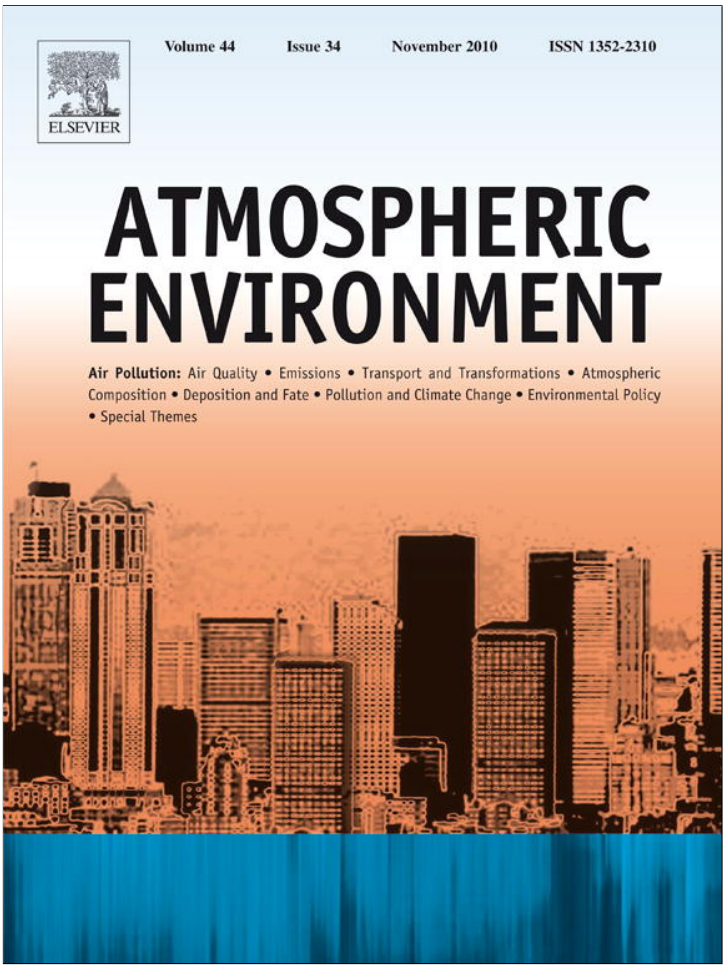

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Seasonal monoterpene and sesquiterpene emissions from *Pinus taeda* and *Pinus virginiana*

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ABSTRACT

Seasonal volatile organic compound emission data from loblolly pine (*Pinus taeda*) and Virginia pine (*Pinus virginiana*) were collected using branch enclosure techniques in Central North Carolina, USA. *P. taeda* monoterpene emission rates were at least ten times higher than oxygenated monoterpene and sesquiterpene emissions in all seasons. α-pinene and β-pinene were the most abundant emissions, while β-caryophyllene had the highest sesquiterpene emission rate from this species. β-phellandrene was the dominant compound emitted from *P. virginiana*, followed by the sesquiterpene β-caryophyllene. Sesquiterpene emissions from *P. virginiana* have not been reported in the literature previously. Summer sesquiterpene emissions from *P. virginiana* were nearly as high as monoterpene emissions, but were 4–12 times lower than monoterpene emissions in the other seasons. Oxygenated monoterpenes and 2-methyl-3-buten-2-ol were emitted at higher rates from *P. taeda* than from *P. virginiana*. Temperature response of the pinenes from *P. taeda* is similar to previously reported values used in emission models, while that for other compounds falls at the lower end of the previously reported range. Temperature response of all compounds from *P. virginiana* is in reasonable agreement with previously reported values from other pine species. There is evidence of light dependence of sesquiterpene emission after accounting for temperature response from both species. This effect is somewhat stronger in *P. taeda*. Bud break, needle expansion, and needle fall (and therefore wind events) seemed to increase monoterpene emission during non-summer seasons. In some instances springtime monoterpene emissions were higher than summertime emissions despite cooler temperatures. Emissions of individual compounds within monoterpene, oxygenated monoterpene, and sesquiterpene classes were highly correlated with each other. Compounds from different classes were much less correlated within each species. This is due to a varying temporal emission patterns for each BVOC class and suggests different production, storage, and emission controls for each. Analysis of enclosure blanks and diurnal patterns indicates that, despite precautions, disturbance due to the enclosure technique may still impact monoterpene emission rate estimates. This did not appear to affect sesquiterpene emissions.

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1. Introduction

It has long been recognized that biogenic volatile organic compound (BVOC) emissions are key inputs into atmospheric chemistry and air quality models (Guenther et al., 2000). At regional to global scales, coniferous forests are dominant contributors to terpenoid BVOC emissions. Although several studies have examined volatile organic compound emissions from the genus *Pinus*, very little data are available describing seasonal and phenological changes. Recently, several studies have described emissions of sesquiterpenes from pine species, but typically for only brief periods during the summer. Here we describe emissions of monoterpene hydrocarbons (MNT), oxygenated monoterpenes (OMT), and sesquiterpene hydrocarbons (SQT) from two widespread southern pine species, *Pinus taeda* (loblolly pine) and *Pinus virginiana* (Virginia Pine). *P. taeda* is the most abundant tree species in the southeastern United States, and its coverage is expected to increase rapidly into the middle of this century due to establishment of commercial plantations on lands previously occupied by agriculture and mixed forests. It accounts for 18.2 percent of total basal area (stem cross-sectional area at 1.37 m above ground level, an index of stocking) in southeastern US forests according to the USDA Forest Service inventory used by Geron et al. (2006). *P. virginiana* is less abundant than *P. taeda*, accounting for 2.1 percent of

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total basal area in southeastern US forests. However, it is widely distributed and a common pioneer species in the southern U.S. Its range extends more northward than *P. taeda*, and it is very common on medium to poor productivity sites from upper coastal plain to mountain habitats.

2. Materials and methods

This field study was conducted over a two-year period from June 6, 2007 to May 21, 2009 within a *P. taeda* plantation (established in 1983) in the Blackwood Division of the Duke Forest Free Atmosphere Carbon Transfer Scheme (FACTS-1) site in North Carolina (35°97′N, 79°09′W). Emission rates were determined by the using the dynamic branch enclosure technique. Only a brief summary of the most pertinent parameters will be provided here, further details are given by Helmig et al. (2006), Ortega and Helmig (2008) and Ortega et al. (2008). Branches were enclosed with FEP Teflon bags (0.127 mm film thickness) with enclosure volumes of 50–80 l. Separate bags were used to enclose each species. Branches were carefully enclosed within the bags to reduce wall contact with needles, and branches were allowed to acclimate for several hours to 1 day before sampling to minimize sampling of disturbance induced BVOC emissions. The enclosures were suspended externally to minimize contact with the needles. Since some SQT (such as the dominant SQT β-caryophyllene) rapidly react in ambient air and can be depleted during the sampling procedure in the presence of ozone (Pollmann et al., 2006) the enclosure purge (ambient) air was first passed through ozone scrubbers (activated charcoal and MnO_2 coated screens) for ozone removal. The purge flow rates into the enclosures ranged from ~18–25 l min^{-1}, resulting in typical bag residence times of ~2–4 min. Ozone in the enclosure air was periodically measured with an ozone monitor (2B Inc., Boulder, CO, USA) and found to be <2 ppb at all times. In order to a) minimize excessive heating of the air inside the enclosure and to b) reduce condensation on the bag walls from transpired water vapor, a refrigerated water trap was used on humid days in the inflowing air stream of the enclosure to lower the dewpoint and temperature of the inflowing air. Needle temperatures (and air temperature inside and outside the enclosures) were recorded with fine (Type K) shielded thermocouple wires that were attached to needles inside the bag. Photosynthetically-active radiation (PAR) was recorded with a PAR sensor (LI-190SA quantum sensor, LI-COR, Lincoln, NE, USA) outside the enclosure and corrected for small (<10%) loss through the Teflon® film. The bag enclosures were deployed from a ladder at the south edge of a clearing, allowing access to healthy foliage within three meters above ground-level (AGL). Branches from *P. taeda* and *P. virginiana* were sampled over the two year period, with alternating measurement days made on the two species. Emissions were typically measured on two days per month from each species. Five branches on 5 separate *P. taeda* tree saplings were examined, while a single branch of *P. virginiana* was studied. The age of saplings sampled ranged from 8-10 years, with the exception of the final *P. taeda* branch, which was a terminal lead on a three year old seedling with full southern exposure. The initial two *P. taeda* branches were sampled for only a brief period due to damage following a storm and excessive shading. To test for possible enclosure wall loss or VOC carryover effects "enclosure blank" measurements were made on 21 days during the study. Eight liter samples were collected from the bag enclosure before and after the emission measurements. The sampling system was operated in the same manner as in emission sampling, except the branches were excluded. Branches were harvested after the final sampling day. Needles were harvested and dried to determine final needle mass of each branch (gram dry weight). Leaf area and mass were determined on each measurement day using the methods described below. Air samples were drawn from the inside of the bag by pulling air at 200 ml min^{-1} through continuously purged 0.32 mm o.d. Teflon tubing onto solid adsorbent cartridges with a diaphragm pump operating downstream of the sample collection tubes.

2.1. Biomass and leaf area determination

Following each sampling day, each needle on the enclosed branch was counted by year of growth and age cohort (flush) within year. The cohorts were numbered and a branch diagram was drawn indicating the division of cohorts. There were 1–4 smaller branchlets within each cohort. Every needle on the entire branch was counted and recorded by cohort and then added for the total branch needle count. A subsample of three needle length and basal fascicle diameter measurements per cohort were taken. The measurements are distributed among the branchlets within a cohort. For example if a cohort had only one branchlet then all three measurements were taken from that branchlet, if there were three branchlets in a cohort then one measurement per branchlet was taken.

The formulas to calculate the individual needle area vary by needle and fascicle morphology, which varies by species.

Loblolly Pine needles are in bundles (fascicles) of three with two flat interior sides to each needle. At the base of the fascicle the outside of the 3-needle fascicle forms a cylinder which tapers to a point at the last few mm.

The total fascicle needle surface area for loblolly pine is calculated as:

$$A_N = (3 + \pi) D_F L_N \quad (1)$$

where A_N is total needle area per fascicle (cm^2), L_N is needle length (cm), D_F is fascicle basal diameter (cm), and π if the ratio of a circle's circumference to its diameter.

P. virginiana needles are in fascicles of two with a flat interior side on each needle (i.e. a hemispherical cross-section). With interior flat sides adjoining, the outside of the needle fascicle forms a cylinder which tapers to a point at the last few mm.

The total fascicle needle surface area for Virginia pine is calculated as:

$$A_N = (2 + \pi) D_F L_N \quad (2)$$

The mean of the three individual needle fascicle areas per cohort was multiplied by the number of needles in the cohort yielding the needle area per cohort in cm^2. The cohort areas are summed to yield total needle surface area by growth year and branch. The slight overestimate of area due to needle taper at the point is less than 1% and is therefore negligible.

A subsample of needles are dried (48 h at 80 °C) and weighed following the final BVOC measurements on each branch. This yields a dry weight to area ratio for each cohort and allows us to calculate needle dry weight over the course of the experiment. Bud surface area is also calculated from length and diameter measurements following each BVOC measurement period.

2.2. Analysis of volatile organic compounds

Sample adsorbent tubes were thermally desorbed and focused in a custom-built thermal desorption system and analyzed via gas chromatography. Quantification was performed via flame ionization detection and identification was determined by retention time and mass spectrometry. The sampling and analysis scheme provided measurement of C_5–C_{16} chromatographible volatile organic compounds. Additional details of the analytical system are provided in Arnts (2010).

Custom packed adsorbent tubes were prepared by cutting 6 inch lengths from stock 0.25″ OD × 0.21″ ID Sulfinert tubing (Restek Corp., Bellefonte, PA) using a wet Carborundum saw. To serve as a support for the front of the adsorbent bed, a dulled tubing cutter was used to indent a small band about 1″ from the front of the tube. Tubes were de-burred and cleaned using water with Alconox detergent followed by rinses with de-ionized water, methanol and hexanes. Tubes were then baked out at 90 °C overnight. Wire mesh disk adsorbent bed retainers were custom made by obtaining type 304 stainless steel woven (twill Dutch weave) wire cloth (325 × 2300 mesh count with a nominal filter rating of 2 μm, Newark Wire Cloth Co., Clifton, NJ) and then coated by Restek to match the Sulfinert tube surface. Discs were punched out the bulk stock using a custom made 0.213″ diameter shim punch. A disk was then inserted from the rear of the tube, followed by the addition of 600 mg of Tenax-TA, a rear mesh disk and a spring clip (Perkin Elmer Inc., P/N L4071123). A subset of tubes were packed 400 mg of with Tenax TA (60/80 followed by 250 mg of Carbotrap (20/40 mesh, Supelco/Sigma–Aldrich, 595 N. Harrison Road, Bellefonte, PA 16823). The presence of the Carbotrap was used to check for breakthrough of 2-methyl-3-buten-2-ol (MBO) from the Tenax-TA. Tubes were then capped using Swagelok fittings with graphitized Vespel ferrules. Tubes were then baked out at 240 °C with clean dry nitrogen.

Tubes were returned to the laboratory where they were thermally desorbed and analyzed by gas chromatography with flame ionization detection (quantitation) and mass spectrometry (identification). Analytical details are provided in Arnts (2010) and accompanying supplementary materials. Field sample volumes were kept below breakthrough volumes to ensure quantitative results. For most of the major emissions, pure sample standards were obtained and used to establish chromatographic retention times. In cases where standards were not available, we attempted to compare published retention times along with mass spectral matching. Reported emissions are thus accompanied by a level of confidence of identification for each compound. The overall analytical process surveys chromatographable compounds from C_5 through C_{16} (thermally stable hydrocarbons, alcohols, carbonyls, aromatics, esters and ethers).

3. Discussion

3.1. Blank analysis

Analysis of the enclosure blank versus sample concentrations taken the same day allows us to assess possible contamination and enclosure "memory" effects. In general, mean enclosure blank concentrations were less than ten percent of pine enclosure values for the dominant MNT α-pinene and β-phellandrene measured on the same day. On the other hand, less abundant MNT such as γ-terpinene, limonene, and camphene featured mean enclosure blank concentration values 30–35% of the sample mean values (Fig. 1). Analysis of sample cartridge blanks (not exposed to chamber or ambient air) showed insignificant concentrations of BVOC relative to enclosure blank values. Values were typically near or below detection limits, indicating low levels of VOC carryover in the tubes or the internal surfaces of the desorption/analytical system. Quantification of these latter compounds can be complicated by potential isomerization and dehydration reactions. For instance, camphene can be created from α-pinene while γ-terpinene can be formed from dehydration of terpinic alcohols, which did show signs of minor (10–20%) bag carryover. SQT mean blank concentrations ranged from 3–19% of pine enclosure values. The highest value observed was for nopinone (40%), which is likely an oxidation product of α-pinene and/or limonene (Hallquist et al., 1999; Jaoui and Kamens, 2003). Analysis of sample cartridge blanks showed insignificant concentrations of BVOC relative to enclosure blank values. Values were typically near or below detection limits, indicating low levels of carryover in the tubes or internal surfaces of the desorption/analytical system.

An interesting pattern emerged when comparing the enclosure blanks collected before and after emission sampling. In the majority of the blanks the concentrations of dominant BVOC were lower in the first (morning) blank than the one taken later in the day. However, MNT concentrations were sometimes 2–10 times higher in the morning field blank compared to the evening field blank (especially from blanks collected prior to *P. taeda* emission sampling), although SQT concentrations were not significantly different between the two sets of blanks. This may be due to the higher composition of monoterpenes in the external surface oils of the pines (or in storage pools vulnerable to disturbance) whereas the sesquiterpenes originate from internal structures or light-driven physiological processes within chloroplasts (Duhl et al., 2008 and references therein). SQT would therefore be less affected by disturbance and deposition to the enclosure surface. If enclosure blanks taken in the morning following a sampling day when emissions were higher in the same enclosure bag, carryover due to contact during enclosure removal may therefore result in high morning blank values for MNT compared to SQT.

In general, the enclosure blank values suggest a possible bias on the order of 10 percent of total BVOC carbon. It is difficult to assign a positive or negative bias since the blank values may represent a positive systematic bias due to physical disturbance of the enclosed vegetation. Alternatively the enclosure blank values may be interpreted as a negative bias due to loss to enclosure walls which is captured during blank analysis. In either case, the compounds with the highest enclosure concentrations tended to have the lowest relative blank values.

3.2. Emission rates

The mean emissions rates (observed and standardized to 30 °C) by compound for each tree species are listed in Table 1. The relative emissions of the 14 MNT discussed in Geron et al. (2000) agrees well with the *P. taeda* emissions we observe except for β-phellandrene, which accounted for a greater proportion of MNT in the current study. This compound was also the dominant C_{10} emission from *P. virginiana*, exceeding α-pinene emissions by 66%. β-phellandrene emissions were not reported in any of the limited *P. virginiana* data of Geron et al. (2000). Emissions of Δ^3-carene from *P. virginiana* were equivalent to α-pinene in Geron et al. (2000), but were only 25% of α-pinene emissions here.

β-caryophyllene was the most abundant SQT emitted from both species, and in fact was the second most abundant compound emitted from *P. virginiana*.

α-humulene and farnesene were also emitted from these species. The monoterpene alcohol linalool was an important component of the emission from *P. taeda*.

Emissions of MNT, OMT, and SQT normalized to 30 °C were 4700, 220, and 370 ngC g^{-1} h^{-1} for all branches of *P. taeda*. Corresponding estimates for *P. virginiana* were 1570, 35, and 605 ngC g^{-1} h^{-1}. The exponential temperature adjustment of Guenther et al. (1993) was used, with $\beta = 0.09$ for MNT and OMT, and $\beta = 0.15$ for SQT (Helmig et al., 2007). These β values are reasonably consistent with calculations of β from our data, which are described below.

The total normalized SQT emission rate from *P. taeda* is consistent with the higher values observed by Helmig et al. (2007), and is only 18% lower than the *P. taeda* values reported by Helmig et al. (2006). The SQT composition emitted from this species is also consistent with that observed by these authors, although the percentage of α-cedrene is somewhat higher here than reported by Helmig et al. (2006, 2007).

MBO emissions from *P. taeda* (56 ng C g^{-1} h^{-1}) were somewhat higher than MBO emissions from *P. virginiana* (36 ng C g^{-1} h^{-1}) and were strongly light dependent in spring and summer. Nine percent of the samples collected during this study were taken with the adsorbent tubes containing the 2nd bed of Carbotrap, which has been found to cause dehydration of terpinic alcohols to their hydrocarbon analogues, which is isoprene in the case of MBO. We examined MBO emission rates from each species and could not detect this effect. The two-bed tubes did not yield higher levels of MBO on those days when both single and two bed tubes were used in emission sampling. Overall emissions of MBO from these southern pine species were over two orders of magnitude lower than MBO emissions from the western North American pine species *Pinus ponderosa*, *Pinus contorta*, and *Pinus jeffreyii* (Harley et al., 1998).

Temperature corrected (to 30 °C) branch mean *P. taeda* (Branches 1 and 3 shown in Fig. 4) emission factors ranged from 2500 to 3500 ngC g^{-1} h^{-1}, for MNT. However, Branch 2 had a mean rate of 13,000 ngC g^{-1} h^{-1}. This estimate was strongly impacted by very high rates during springtime bud-break/needle expansion and in late November of 2008, during a period of high wind, needle abscission, and likely high disturbance levels within the enclosure. It is also impacted by an extreme temperature event in July of 2008, when needle temperature inside the enclosure exceeded 54 °C as ambient temperature approached 40 °C. When these data are not considered, mean emission for this branch declined to 7000 ngC g^{-1} h^{-1}. OMT also were reduced by over 50% when these data were not considered. Branch mean temperature standardized OMT emissions ranged from 50–100 ngC g^{-1} h^{-1}, and SQT emissions ranged from 200–600 ngC g^{-1} h^{-1}.

Branch to branch variability in *P. taeda* emission composition was small compared to interspecific variation. Emission of α-pinene from the three primary branches ranged from 48–56% of MNT emission. β-pinene emissions composed from 26–29% of MNT emissions with the exception of springtime emissions from the three year old seedling, where it accounted for only 5% of monoterpene emissions. β-phellandrene emissions accounted for 7–11% of MNT emission. Linalool emission ranged from 28–33% of OMT emissions. β-caryophyllene accounted for 24–42% of total SQT emissions, while emissions of β-farnesene were somewhat more

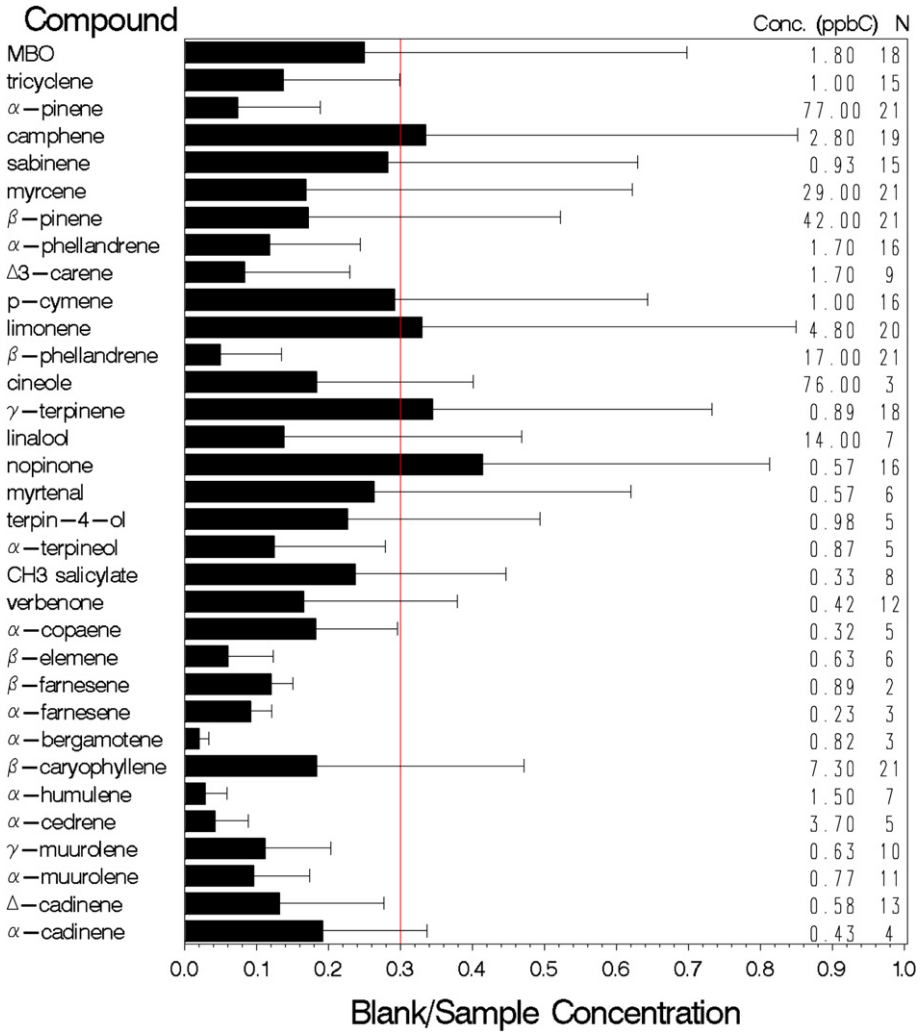

Fig. 1. Ratio of mean enclosure blank to vegetation sample concentrations for compounds with a mean vegetation sample concentration >100 pptC. The vertical line denotes a an enclosure blank to vegetation sample concentration ratio of 0.3. Compounds shown are 2-methyl-buten-2-ol (MBO), tricyclene, α-pinene, camphene, sabinene, myrcene, β-pinene, α-phellandrene, Δ^3-carene, para-cymene (p-cymene), limonene, β-phellandrene, 1,8 cineole (cineole), γ-terpinene, linalool, nopinone, myrtenal, terpin-4-ol, α-terpineol, methyl salicylate (CH_3 salicylate), verbenone, α-copaene, β-elemene, β-farnesene, α-farnesene, α-bergamotene, β-caryophyllene, α-humulene, α-cedrene, γ-muurolene, α-muurolene, Δ-cadinene, and α-cadinene. The compounds are listed by retention time on the RTX-5 column. Conc. (ppbC) denotes mean sample concentration of compound on the days when enclosure blanks were collected. *N* is number of days the compounds were detected when enclosure blanks were taken.

variable, ranging from 4–14% of total SQT emission. Primary branch #2 (2007) emitted the largest percentage of β-farnesene and featured a higher proportion of summertime measurements.

Several classes of compounds normally associated with anthropogenic activity were also detected in the enclosures, typically at concentrations less than 1 ppbC by volume. These include alkanes (octane, n-nonane), aromatics (benzene, ethyl-toluene, toluene, trimethyl-benzene, xylene), and aldehydes (benzaldehyde, hexenal, octanal, nonanal, decanal). Concentrations of these compounds in enclosure blank samples were typically greater than or well within one standard deviation of vegetation sample concentrations, so we assume that these compounds are sampling or analytical artifacts and not vegetation emissions. Aldehydes have been reported as ozone reaction products with hydrocarbons on Tenax (Strömvall and Petersson, 1992), and we cannot rule out the possibility that low levels of O_3 passing through the sampling system may have caused such an artifact. Toluene has been found to be a minor emission from some vegetation species, including *Helianthus annuus*, *Pinus sylvestris* (Heiden et al., 1999) and *P. taeda* (White et al., 2009), but we cannot detect measurable emission of this compound here, as toluene concentrations in enclosure blanks were similar to those in vegetation samples.

3.2.1. Emission correlation

Emission correlations of individual compounds for each species are shown in Fig. 2. Emissions of compounds within MNT

Table 1
List of compounds emitted from each species by study-mean descending emission rate (ER) for all seasons (and all branches for P. taeda) combined. Temperature corrected emissions (ERstd) adjusted to 30 °C using $\beta = 0.09$ and $\beta = 0.15$ for C_{10} and C_{15} compounds, respectively, are also given.

Pinus taeda	ng C g^{-1} h^{-1}				*Pinus virginiana*	ng C g^{1} h^{-1}			
	ID	*N*	ER	ERstd		ID	*N*	ER	ERstd
α-pinene	A	163	1289	2442	β-phellandrene	A	90	387	894
β-pinene	A	163	678	1297	β-caryophyllene	A	90	267	341
myrcene	A	163	338	593	α-pinene	A	90	233	548
β-phellandrene	A	163	201	372	β-pinene	A	90	131	329
β-caryophyllene	A	163	100	163	Myrcene	A	90	89	230
Linalool	A	124	82	72	β-farnesene	A	76	63	51
Limonene	A	163	71	153	Δ3-carene	A	90	58	133
β-farnesene	A	96	59	60	α-humulene	A	90	54	64
MBO	A	152	53	56	Limonene	A	90	44	97
Camphene	A	163	39	89	Δ-cadinene	A	90	28	72
α-cedrene	C	72	36	45	MBO	A	62	25	36
Linalool oxide	B	45	24	24	α-phellandrene	A	90	24	52
α-humulene	A	149	24	31	terpinolene	A	75	21	39
α-phellandrene	A	120	21	45	Camphene	A	89	17	45
α-bergamotene	B	151	19	23	pentadecane	A	86	15	92
α-terpinene	A	96	19	45	α-terpinene	A	75	12	28
nopinone	B	152	15	29	γ-terpinene	A	89	9.9	23
γ-terpinene	A	138	14	26	α-muurolene	C	62	9.8	36
p-cymene	A	163	13	32	p-cymene	A	89	9.8	25
Nerolidol	B	111	13	8.2	Sabinene	A	89	9.5	25
Δ-cadinene	A	130	12	35	α-copaene	B	62	9.3	21
β-terpineol	A	93	11	49	Nopinone	B	62	7.6	20
γ-muurolene	C	100	11	17	γ-muurolene	C	72	7.3	30
α-muurolene	C	135	11	19	β-elemene	C	62	5.9	10
Tricyclene	A	149	10	22	Tricyclene	A	75	5.1	11
Sabinene	A	112	9.2	22	α-cadinene	C	62	5.0	29
β-gurjunene	C	93	8.8	10	Camphor	A	76	4.9	12
α-farnesene	A	50	17	44	CH_3 salicylate	B	62	4.4	12
Terpinolene	A	25	8.5	27	α-terpineol	A	62	4.1	6.6
Camphor	A	163	8.3	18	Verbenone	B	62	4.0	8.6
α-cadinene	C	40	6.9	6.5	Terpin-4-ol	A	62	2.8	4.2
Ledene	C	93	6.1	6.0	α-thujene	B	75	2.7	6.8
α-copaene	A	163	5.6	10	2-methylfuran	B	62	2.5	4.2
Verbenone	B	163	5.5	12	Linalool	A	62	0.4	0.6
CH_3 salicylate	B	152	5.0	11					
α-terpineol	A	149	4.6	6.0					
β-elemene	C	135	4.5	6.0					
Terpin-4-ol	A	163	4.1	8.1					
Myrtenal	C	112	3.6	10					
Bornyl acetate	A	60	3.6	5.0					
Sabina ketone	B	56	3.2	4.0					
1,8 cineole	A	152	2.7	5.8					
Borneol	C	151	2.6	2.6					
Cis-3-hexenol	A	93	2.4	7.2					
α-cubebene	A	112	2.0	4.2					
β-bourbonene	C	73	1.9	2.5					
2-heptanone	A	93	1.7	3.8					

ID column denotes level of confidence in identification: A = confirmed by retention time and mass spec using standard, B = excellent library match and within range of reported retention indices as compiled by NIST (http://webbook.nist.gov/chemistry/cas-ser.html), C = mass spectral match and poor agreement with reported retention indices.

Other compounds detected from *Pinus taeda* (<50 observations and emission rate < 6 ng C g^{-1} h^{1}) include β-sesquiphellandrene, α-thujene, β-himachalene, germacrene D, β-caryophyllene oxide, β-cedrene, and a sesquiterpene (CAS 16728-9) lacking published retention time data.

Other compounds detected from *Pinus virginiana* (<20 observations and emission rate < 6 ng C g^{-1} h^{1}) include bornyl acetate, β-farnesene-(Z), β-terpineol, γ-gurjunene, 3-hexen-1-ol acetate, and a sesquiterpene (CAS 16728-9).

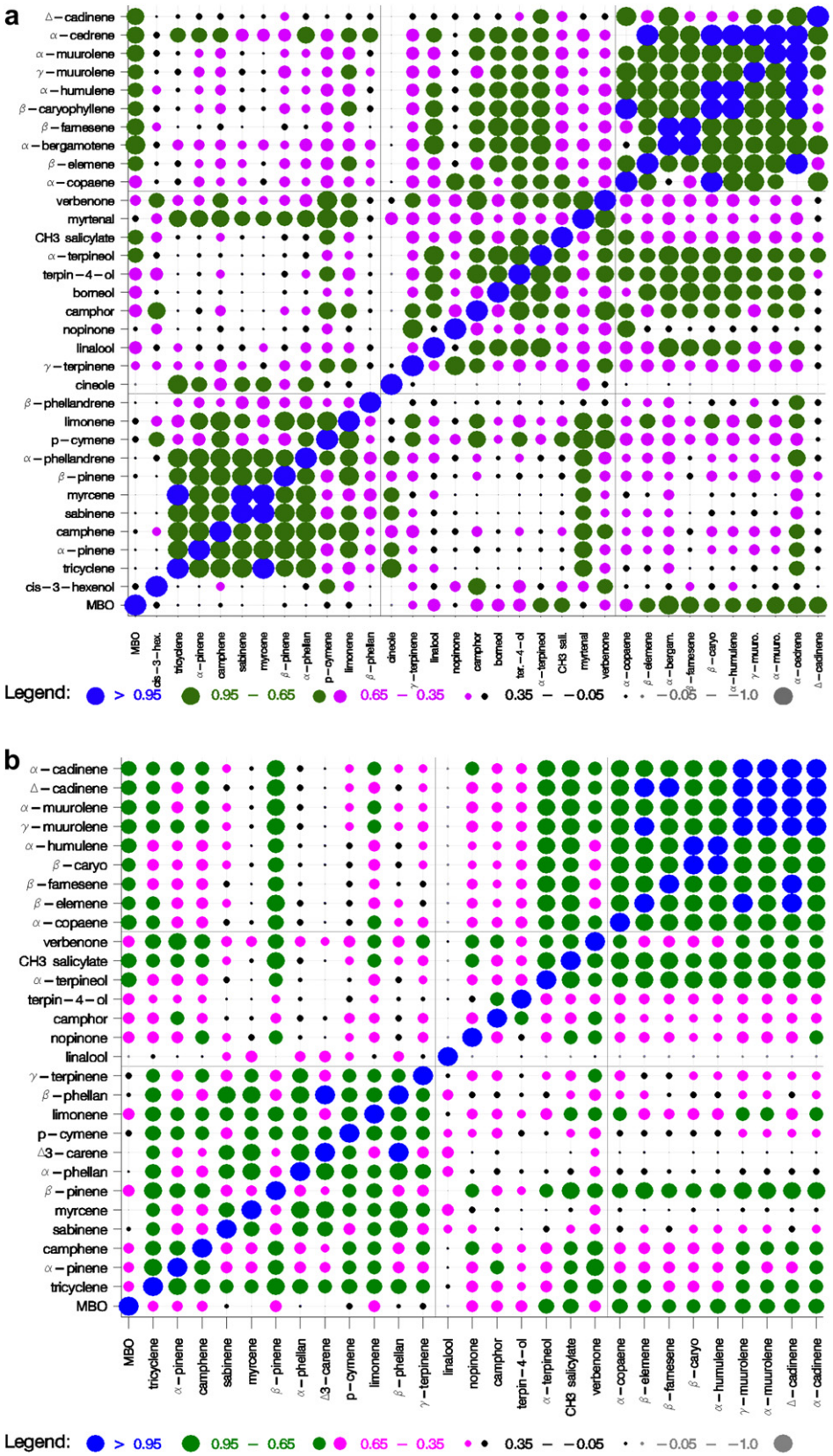

Fig. 2. a. Emission rate correlations between 33 compounds emitted from *Pinus taeda*. Correlations > 0.20 are significant at the $\alpha = 0.05$ level. b. Emission rate correlations between 29 compounds emitted from *Pinus virginiana*. Correlations > 0.20 are significant at the $\alpha = 0.05$ level. The solid gray horizontal and vertical lines separate monoterpene, oxygenated monoterpene, and sesquiterpene compound classes. Compounds are shown by increasing column retention time.

and SQT classes were highly correlated with each other. OMT exhibited varying degrees of correlation with each other, and later eluting OMT (α-terpineol, methyl salicylate, and verbenone from *P. virginiana*) compounds were highly correlated with SQT emissions, suggesting similar storage and volatility driven emission controls. Correlations between MNT and SQT were much lower within each species, likely due to a varying temporal emission patterns influenced by different production, storage, and emission controls. MBO is much more highly correlated with SQT than MNT emissions, which may suggest a seasonal and/or light effect on SQT emissions. Linalool, α-terpineol, and terpin-4-ol emissions from *P. taeda* are also more highly correlated with MBO and SQT than MNT. Myrtenal and cineole, on the other hand, were more highly correlated with MNT. Hakola et al. (2006) found that both linalool and 1,8-cineole were well correlated with SQT but not MNT in *P. sylvestris*. Toluene and

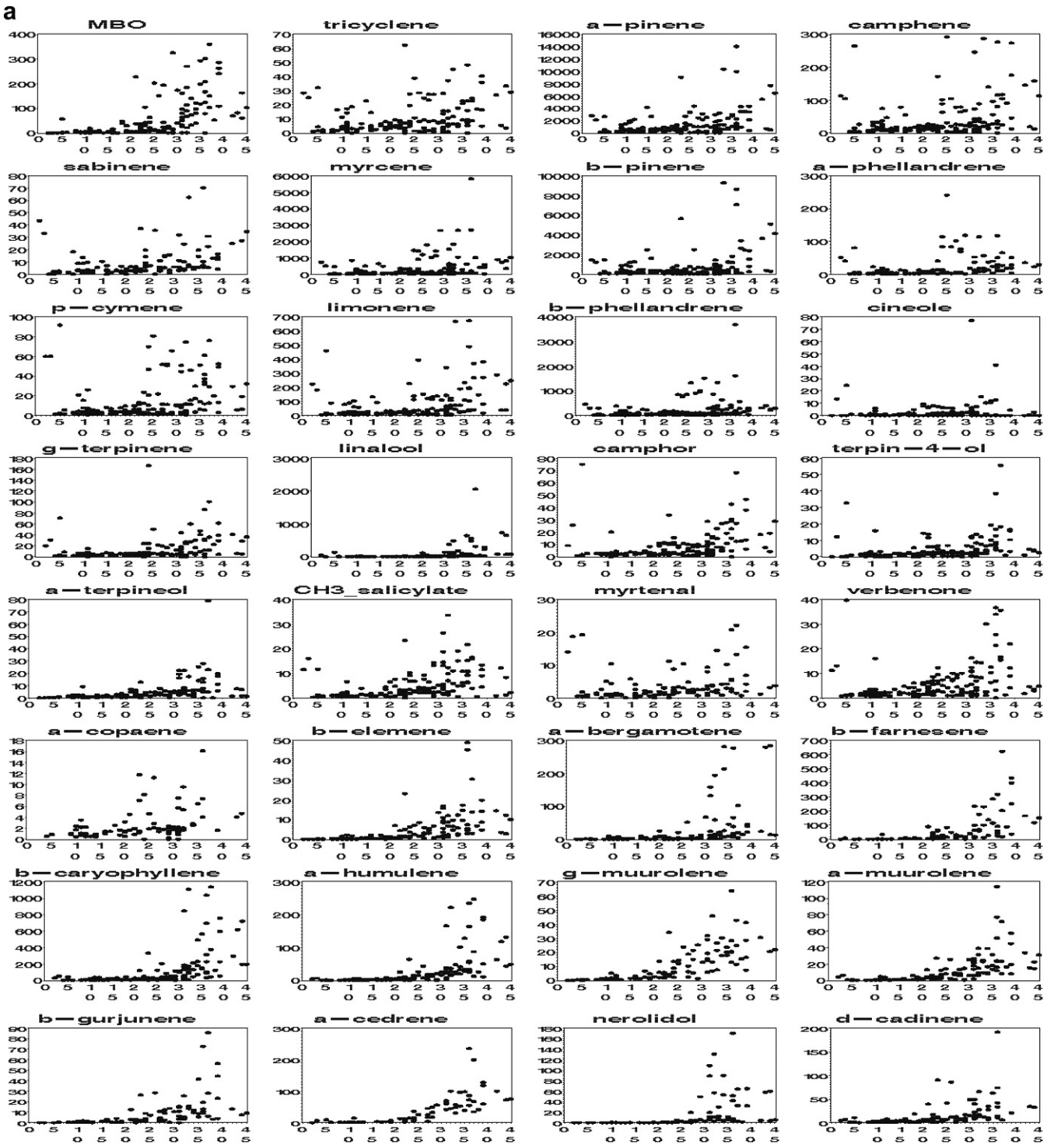

Fig. 3. a. Emission rate (ngC $g^{-1}h^{-1}$) versus leaf temperature (°C) for the top 32 compounds emitted from *Pinus taeda*. b. Emission rate (ngC $g^{-1}h^{-1}$) versus leaf temperature (°C) for the top 32 compounds emitted from *Pinus virginiana*.

trimethylbenzene were uncorrelated with BVOC emissions from either species.

3.2.2. Temperature effects

The exponential parameter β is determined by the vapor pressure dependent rate of BVOC emission increase with leaf temperature. It is typically determined empirically from short-term experiments where leaf temperature is changed on temporal scales of minutes to hours, yet the resulting parameter estimates have been used to derive BVOC inventories at monthly, annual, and even multi-decadal scales associated with globally changing environmental variables (Monson et al., 2007). Factors affecting β at fine time scales could be quite different from those driving seasonal or interannual temperature dependence.

Fig. 3 shows individual compound emissions versus leaf temperature. Exponential functions were fit to emissions of individual compounds from the main *P. taeda* branch and *P. virginiana* of the form:

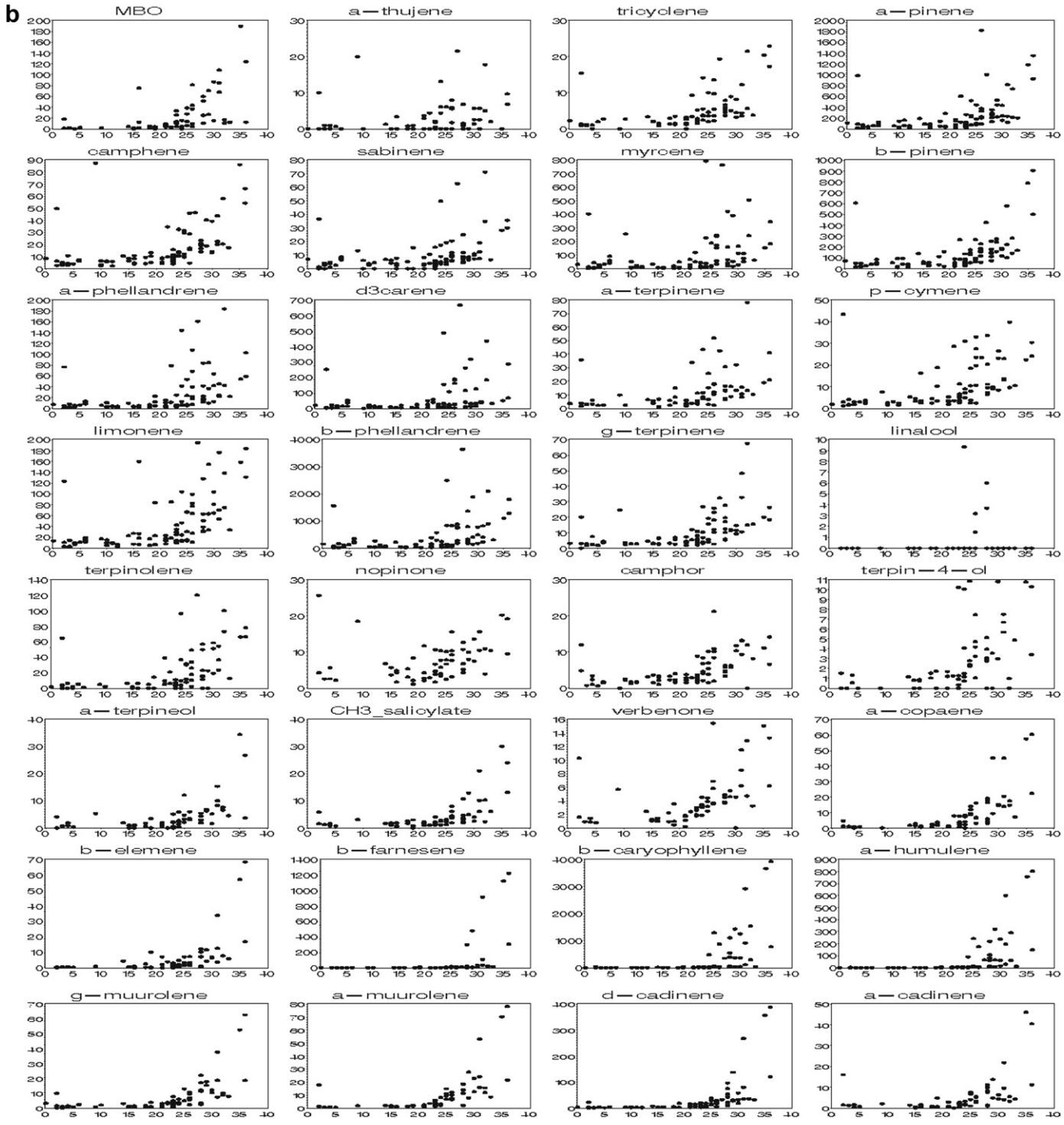

Fig. 3. (*continued*).

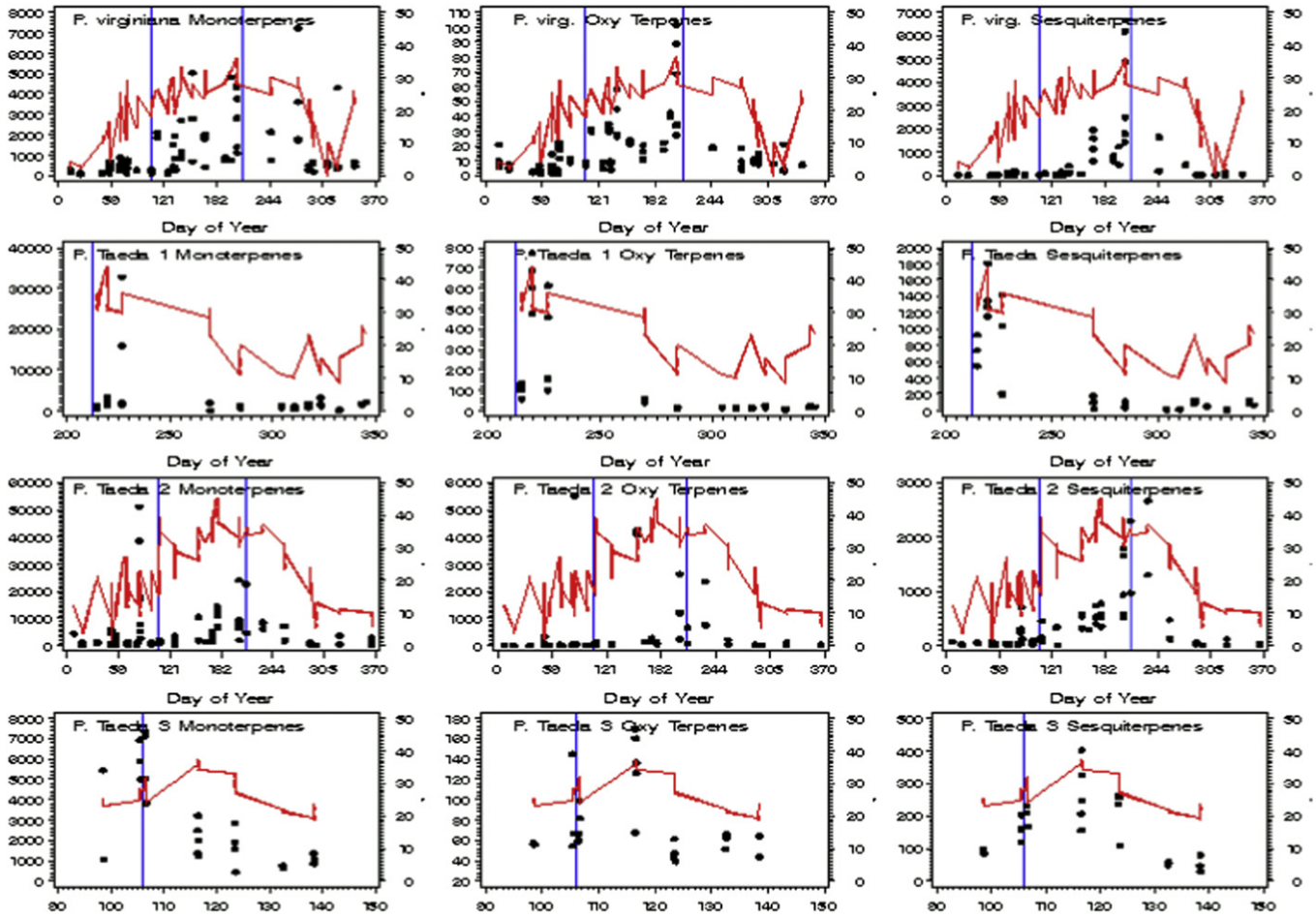

Fig. 4. Seasonal emission patterns of monoterpenes, oxygenated monoterpenes, and sesquiterpenes from 3 *Pinus taeda* branches and the *Pinus virginiana* branch. Red solid line denotes leaf temperature (°C) shown on the right vertical axis. Blue vertical lines denote day 106 (mid-April) and day 212 (end of July). Left axes units are emissions in ngC g(dry weight)$^{-1}$ h^{-1}. Note changes in axes scales.

Table 2
Temperature normalized ($\beta = 0.09$ for monoterpenes and oxygenated terpenes, $\beta = 0.15$ for sesquiterpenes) emissions (ng C g^{-1} h^{1}) by compound class and season for *Pinus taeda* (Branch 2 as shown in Figure 4) and *P. virginiana*. Values in bold type indicate a seasonally significant difference at $P = 0.01$.

Pinus taeda				
Compound	Winter ($n = 33$)	Spring ($n = 22$)	Summer ($n = 22$)	Fall ($n = 10$)
	Mean (Std dev.)	Mean (Std dev.)	Mean (Std dev.)	Mean (Std dev.)
Monoterpene	10,500 (17,500)	27,000 (76,000)	4360 (4000)	3800 (6000)
Oxygenated Terpene	210 (600)	1500 (7300)	200 (260)	120 (170)
Sesquiterpene	560 (1000)	820 (470)	360 (240)	380 (590)
Pinus virginiana				
Compound	Winter ($n = 31$)	Spring ($n = 24$)	Summer ($n = 16$)	Fall ($n = 18$)
	Mean (Std dev.)	Mean (Std dev.)	Mean (Std dev.)	Mean (Std dev.)
Monoterpene	1480 (1300)	1590 (1900)	1980 (1050)	2950 (2340)
Oxygenated Terpene	33 (48)	31 (18)	32 (15)	34 (31)
Sesquiterpene	250 (220)	127 (80)	**1840** (1150)	395 (285)

$$ER = \alpha e^{\beta(T_l - T_s)} \quad (3)$$

where ER is emission rate in ng g(needle dry weight)$^{-1}$ h^{-1}, α and β are parameters determined by empirical fit to the data, T_l and T_s are observed leaf and standard (30 °C) temperatures, respectively, and e is the base of natural logarithms.

P. taeda β estimates ranged from 0.07 to 0.10 for α- and β-pinene and showed little difference between annual and summer-only estimates. Other MNT yielded β estimates ranging from 0.03 to 0.07 and were generally lower when calculated from only the summer data. OMT showed a similar annual range in β estimates, but showed no significant temperature dependence in the summer only data. This suggests that lower production or pool depletion of these compounds may be occurring in the summer months in *P. taeda*. SQT yielded β estimates from 0.05 to 0.08 from seasonal data, but saw similar relative reductions in β estimates as *P. virginiana* when calculated from only the summer data.

P. virginiana MNT β values ranged from 0.07 to 0.16 with a mean of 0.09, while OMT had slightly higher values on average, near 0.10. SQT β values ranged from 0.15 to 0.33 (mean = 0.23, β-caryophyllene = 0.23) when calculated from data for all seasons, but ranged from 0.13 to 0.24 (mean = 0.17, β-caryophyllene = 0.13) when calculated from only summer observations. The difference between summer and annual β values may be due to lower SQT synthase activity in mid fall through mid-spring seasons, and therefore lower SQT emission potential at lower temperatures

observed from fall through early spring. This is supported by light dependence in SQT (farnesene etc) emissions observed from (Harrewijn et al., 2002 and references therein). Conversely, MNT β estimates increased when only summer values were considered (mean $\beta = 0.13$). This may be due to increased production during warm summer conditions, but also could be driven by elevated emissions during cooler weather events such as bud expansion or needle fall. OMT emissions from *P. virginiana* showed little change in β estimates when fit to summer data versus data for all seasons.

3.2.3. Light effects

We examined possible light dependence for individual compounds by fitting the temperature function of Guenther et al. (1993) to the emission rate of each compound from each species as discussed above. The residuals from this equation are then plotted against PAR and regression analysis performed. No temperature dependence was indicated for any of the C_{10} compounds emitted from *P. virginiana*. However, several SQT compounds were correlated with PAR, suggesting possible light dependence. Residual SQT emissions from *P. taeda* were also significantly related to PAR ($\text{Prob} > F < 0.05$ for all data, $\text{Prob} > F < 0.10$ for summer only observations. As in other field studies, the high degree of correlation between PAR and leaf temperature complicates the identification of the PAR relationship (Duhl et al., 2008 and references therein), although the distinct contrast in the pattern of regression residuals of MNT versus SQT suggest there is a light-driven difference in the production and/or emission of SQT from these pines. This was also confirmed using multiple linear regression techniques, where *P. taeda* SQT emissions showed a statistically significant relationship with PAR even after adjustment for leaf temperature effects. MNT showed no such PAR response. This PAR effect was less pronounced in *P. virginiana*, possibly due to lower range of PAR observed and/or smaller number of emission measurements. However, the lack of SQT light dependence and strong seasonal variation of caryophyllene is very similar observations of this compound from *P. sylvestris* by Tarvainen et al. (2005). Bouvier-Brown et al. (2009) found α-farnesene emissions from *Pinus ponderosa* to be dependent mainly on temperature whereas α-bergamotene and β-farnesene emissions are temperature and light-dependent. In our data, β-farnesene does appear to exhibit light dependence. Duhl et al. (2008) summarized SQT light dependence across several plant types and compounds and noted contrasting light relationships for a given compound between plant species, which complicates representation of PAR effects in BVOC emission models.

3.2.4. Seasonal patterns

Seasonal emission patterns of total MNT, OMT, and SQT emissions from each branch are shown in Fig. 4. Summer and fall MNT emissions seem to follow the pattern described by Keenan et al. (2009), where emissions peak with temperature in mid to late summer. However, their model of seasonality does not capture the spring peaks we observe from *P. taeda* in late March to April. This time period corresponds to that of budbreak and needle growth. MNT emissions during this time period were often higher than summertime emissions even though leaf temperatures were

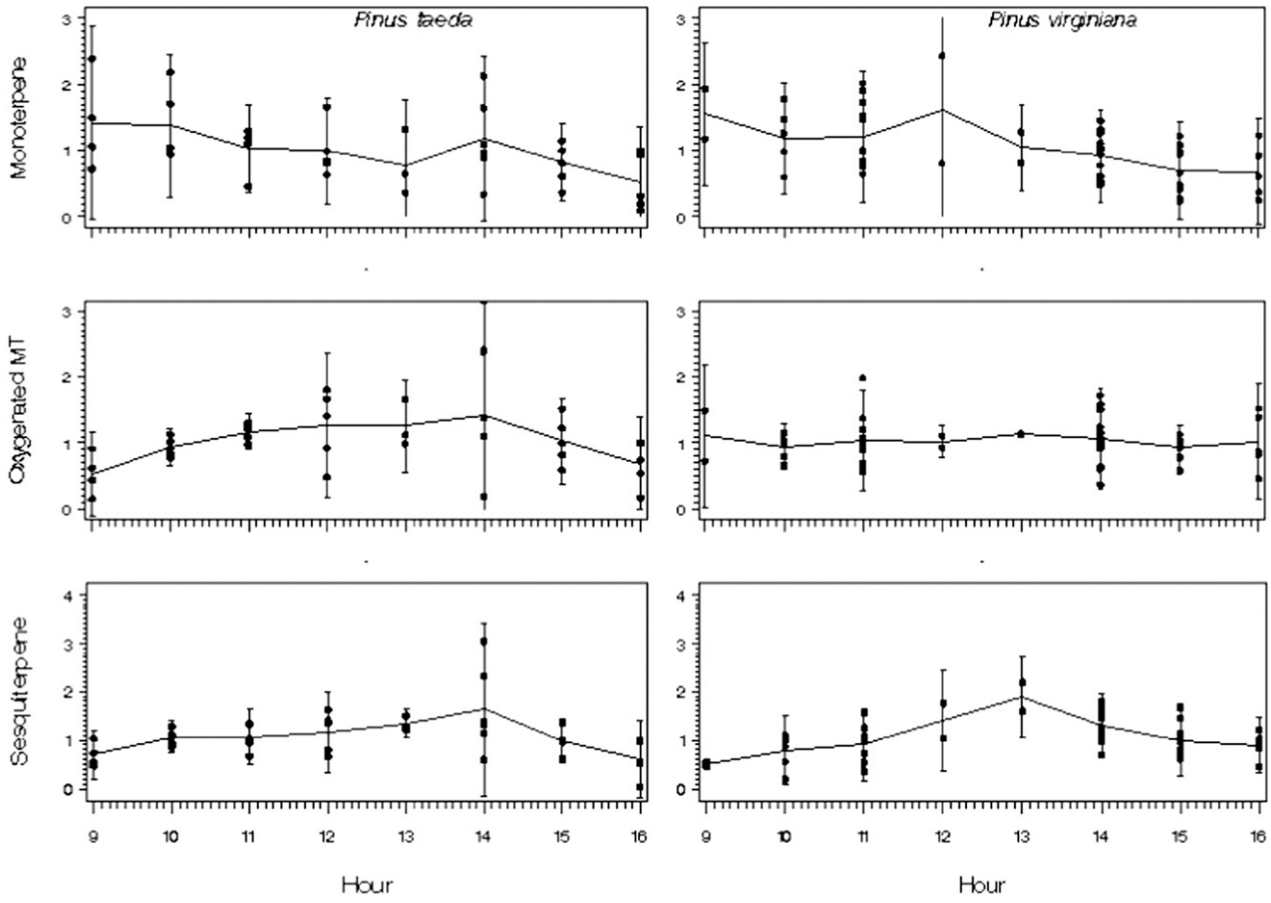

Fig. 5. Diurnal emission patterns of normalized (divided by respective daily mean) of monoterpenes, oxygenated monoterpenes, and sesquiterpenes from *Pinus taeda* and *Pinus virginiana*. Data are from late spring through early fall. Vertical bars denoted +/− one standard deviation.

typically lower. This effect was present but less pronounced in *P. virginiana*, and in OMT from both species. There also appears to be elevated MNT emissions associated with the time of maximum autumnal litterfall from both species. Elevated springtime MNT emissions were also noted by Kim (2001), who found that slash pine (*Pinus elliottii*) and loblolly pine (*P. taeda*) had highest emission rates associated with bud expansion in the spring. β-pinene was the most abundant compound emitted from *P. elliottii* terminal buds in contrast to the needles where α-pinene dominated. SQT emissions from our study, on the other hand, showed seasonal peaks in mid- to late summer from both species.

Seasonal variation in temperature-standardized rates is shown in Table 2. Examination of standardized rates allows us to identify seasonal departures from the exponential temperature relationship. The normalized C_{10} compounds showed no appreciable seasonal cycle in *P. virginiana*. C_{10} compounds emissions from *P. taeda* also showed no pronounced seasonal cycle, although spring and winter did show somewhat higher standardized emissions, mostly due to the higher late winter and early spring emissions discussed above. Kim (2001) also found no seasonal pattern in standardized *P. taeda* MNT emissions, but observed strong seasonal MNT emission variation from *P. elliotti* in Florida, where standardized emissions peaked in the summer months.

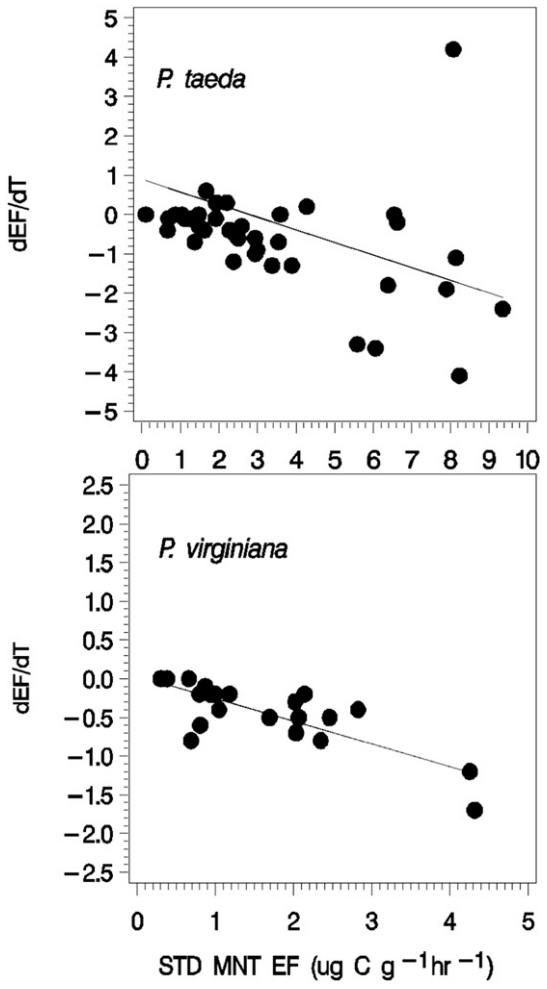

Fig. 6. Daily first derivative (dEF/dT) of normalized MNT EF plotted versus daily mean EF for *Pinus taeda* and *Pinus virginiana*. Data shown are for days with mean leaf temperature exceeding 10 °C. Solid lines represent significant ($P < 0.0001$) least squares regressions fit to the data, slope for each species is ~ 0.3 μgC g^{-1}.

Standardized SQT emissions from *P. virginiana* were 4–12 times higher during summer than in other seasons. Hakola et al. (2006) observed a similar pronounced summer peak in SQT emissions. This suggests that summertime synthesis and/or pool accumulation of SQT in this species, likely in mature 2nd year needles, which has been observed in *P. sylvestris* by Hakola et al. (2006). *P. taeda* showed no statistically significant seasonal pattern in standardized SQT emission. However strong summer peaks in SQT (not standardized) are apparent in Fig. 4.

Springtime peaks in MNT and OMT were investigated to determine if moisture or wind disturbance may have affected emission rates. Kim (2001) found needle wetness seemed to inhibit MNT emissions from *P. elliottii*, while the opposite effect was observed for *P. taeda*. Initial emissions rates (at least 10 times higher for slash pine) may have influenced these contrasting effects (Kim, 2001). Here, however, no association with needle wetness or wind disturbance was noted.

Although we did not design this study to discuss tree age effects, age showed no obvious impact on *P. taeda* BVOC emissions, as the 3 three old seedling did not emit at significantly different rates than the 8–10 year old saplings. Kim (2001) found that four year old *P. elliottii* trees emitted pinenes, limonene, and β-phellandrene at rates at least 6 times higher than seven year old trees during early and mid-spring.

3.2.5. Diurnal patterns

Since our data were collected between 8 AM and 5 PM local time, complete diurnal cycles could not be evaluated. However, we observe that monoterpene emissions from both species exhibited little change from 0900 to 1600, although a slight declining trend is apparent (Fig. 5). MNT pool depletion may be occurring during the day. This is supported by a more marked decline in the summertime MNT diurnal pattern, when expected residence time of MNT in storage pools is expected to be shortest (Schurgers et al., 2009) making pool depletion more likely. On the other hand, the daily change (dEF/dT) of normalized MNT EF plotted versus daily mean EF for both *Pinus* species (for all days with mean leaf temperature exceeding 10 °C) suggests that the days with the highest rate of diurnal decrease in MNT EF were associated with the highest average EF (Fig. 6). This could be interpreted as evidence against pool depletion and instead, may indicate a physical or thermal disturbance resulting from enclosure of the branches. Micrometeorological flux measurements at the canopy level would very helpful in understanding these effects.

Diurnal OMT emissions (Fig. 5) showed little variability, although midday peaks are evident on average. Linalool dominates OMT from *P. taeda*, while OMT from *P. virginiana* were much lower than that from *P. taeda* and were not dominated by any single compound. SQT emissions showed a more pronounced pattern, with emissions peaking in early afternoon from both species. A declining pattern is not apparent in SQT from either species, and light dependence of SQT may help account for the midday peaks in these emissions.

Duhl et al. (2008) report that all studies measuring SQT during multiple times of day found significant diurnal variability. Pool depletion and/or humidity effects may contribute to this variability. No link between diurnal variability and stomatal closure or CO_2 uptake were found in the studies reviewed by these authors.

4. Conclusions

Emissions of MNT from *P. virginiana* are reasonably consistent with limited data reported previously, although the abundance of β-phellandrene in the MNT profile is unique. MBO and OMT from from *P. virginiana* are lower than those from *P. taeda*. Summertime emissions of SQT were dominated by β-caryophyllene and were

higher than reported from other *Pinus* species. Since this study focused on only one branch from this species, additional observations are warranted.

Although most of the *P. taeda* MNT emission rate data from this study fall within the range of rates used in current BVOC emission models, roughly 5% of observations significantly exceed these rates. These data and those from other recent efforts have shown that factors other than leaf temperature can have large influences on MNT, OMT, and SQT emissions. Bud elongation and needle expansion seem to be common triggers for increased springtime MNT emissions across several studies. However, quantitative representation of these effects for use in modeling remains difficult. Other recent studies (Schurgers et al., 2009) showing seasonal controls on MNT pool regeneration and depletion may also help explain seasonal variation associated with resource and BVOC substrate availability. However, this is also a new concept, and empirical factors needed to incorporate these effects into regional emission models are lacking.

A future application of these data is to test the ability to scale to canopy levels by comparing enclosure BVOC emission estimates to BVOC emission fluxes determined from relaxed eddy accumulation (REA) techniques. Seasonal comparisons of emission from these independent approaches should provide insight into the general applicability of the enclosure data, including emission rate changes associated with leaf expansion and litterfall. In particular, litterfall effects my be less significant at the stand level since the enclosure emission increases are likely to be offset to some degree by decreased branch foliar mass. Nonetheless, seasonal, phenological, and needle age cohort effects in the genus *Pinus* have not been thoroughly examined and represent large uncertainties in BVOC emission models.

Genetic characteristics of important industrial conifers such as *P. taeda* are continually evolving on the landscape through the effects of genetic manipulation and tree improvement programs. Since approximately one billion seedlings of this species are planted in the southern U.S. annually, this should be considered in emission studies and BVOC emission models.

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References

Arnts, R.R., 2010. Evaluation of adsorbent sampling tube materials and Tenax-TA for analysis of volatile biogenic organic compounds. Atmospheric Environment 44, 1579–1584.

Bouvier-Brown, N.C., Goldstein, A.H., Gilman, J.B., Kuster, W.C., de Gouw, J.A., 2009. In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry. Atmospheric Chemistry and Physics 9, 5505–5518.

Duhl, T.R., Helmig, D., Guenther, A., 2008. Sesquiterpene emissions from vegetation: a review. Biogeosciences 5, 761–777.

Geron, C., Guenther, A., Greenberg, J., Karl, T., Rasmussen, R., 2006. Biogenic volatile organic compound emissions from desert vegetation of the southwestern US. Atmospheric Environment 40, 1645–1660.

Geron, C., Rasmussen, R., Arnts, R.R., Guenther, A., 2000. A review and synthesis of monoterpene speciation from forests in the United States. Atmospheric Environment 34, 1761–1781.

Guenther, A., Zimmerman, P.R., Harley, P., 1993. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. Journal of Geophysical Research 98, 12,609–612,617.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., Fall, R., 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. Atmospheric Environment 34, 2205–2230.

Hakola, H., Tarvainen, V., Back, J., Ranta, H., Bonn, B., Rinne, J., Kulmala, M., 2006. Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. Biogeosciences 3, 93–101.

Hallquist, M., Wangberg, I., Ljungstrom, E., Barnes, I., Becker, K.H., 1999. Aerosol and product yields from NO_3 radical-initiated oxidation of selected monoterpenes. Environmental Science and Technology 33, 553–559.

Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A., Vasconcellos, P., 1998. Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere. Journal of Geophysical Research 103, 25,479–425,486.

Harrewijn, P., van Oosten, A.M., Piron, P.G.M., 2002. Natural terpenoids as messengers. A multidisciplinary study of their production, biological functions and practical applications.

Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., Sakulyanontvittaya, T., 2007. Sesquiterpene emissions from pine trees – identifications, emission rates and flux estimates for the contiguous United States. Environmental Science and Technology 41, 1545–1553.

Helmig, D., Ortega, J., Guenther, A., Herrick, J.D., Geron, C., 2006. Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US. Atmospheric Environment 40, 4150–4157.

Jaoui, M., Kamens, R.M., 2003. Mass balance of gaseous and particulate products from b-Pinene/O_3/Air in the absence of light and b-Pinene/NOx/air in the presence of natural sunlight. Journal of Atmospheric Chemistry 45, 101–141.

Keenan, T., Niinemets, Ã., Sabate, S., Gracia, C., Penuelas, J., 2009. Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties. Atmospheric Chemistry and Physics 9, 4053–4076.

Kim, J.-C., 2001. Factors controlling natural VOC emissions in a southeastern US pine forest. Atmospheric Environment 35, 3279–3292.

Ortega, J., Helmig, D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – Part A. Chemosphere 72, 343–364.

Ortega, J., Helmig, D., Daly, R.W., Tanner, D.M., Guenther, A.B., Herrick, J.D., 2008. Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – Part B: Applications. Chemosphere 72, 365–380.

Pollmann, J., Helmig, D., Hueber, J., Tanner, D., Tans, P.P., 2006. Evaluation of solid adsorbent materials for cryogen-free trapping-gas chromatographic analysis of atmospheric C2-C6 non-methane hydrocarbons. Journal of Chromatography A 1134, 1–15.

Schurgers, G., Arneth, A., Holzinger, R., Goldstein, A.H., 2009. Process-based modelling of biogenic monoterpene emissions combining production and release from storage. Atmospheric Chemistry and Physics 9, 3409–3423.

Strömvall, A.-M., Petersson, G., 1992. Protection of terpenes against oxidative and acid decomposition on adsorbent cartridges. Journal of Chromatography 589, 385–389.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., Kulmala, M., 2005. Temperature and light dependence of the VOC emissions of Scots pine. Atmospheric Chemistry and Physics 5, 989–999.