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Sesquiterpene Emissions from Pine Trees — Identifications, Emission Rates and Flux Estimates for the Contiguous United States

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Biogenic volatile organic compound (BVOC) emissions were studied using vegetation enclosure experiments. Particular emphasis was given to sesquiterpene compounds (SQT), although monoterpenes (MT) were also characterized. SQT were detected in emissions from seven (out of eight) pine species that were examined. Thirteen SQT compounds were identified; the most abundant ones were β-caryophyllene, α-bergamotene, β-farnesene, and α-farnesene, with emission rates increasing exponentially with temperature. Regression analysis yielded exponential dependencies of both MT and SQT emissions on temperature of the form $E = E_0 \times \exp(\beta(T - T_0))$. This resulted in SQT basal emission rates (E_0 defined at $T_0 = 30$ °C) ranging between <4 and 620 ng (carbon) gdw^{-1} h^{-1} (gdw = gram dry weight). The average value of the exponential temperature response factor β for SQT emissions, taken from all experiments, was 0.17 °C^{-1}, whereas the value for monoterpenes was 0.11 °C^{-1}. The average, total SQT emissions from pines were estimated to be 9, 16, and 29% of the MT emissions at 20, 30, and 40 °C respectively. The emission factors and β-factors determined from these measurements were used to estimate pine tree MT and SQT emission distributions for the contiguous United States using MEGAN (model of emissions of gases and aerosols from nature, Guenther et al., 2006). SQT fluxes reaching 10–40 mg m^{-2} for the month of July were estimated for extensive areas of most western and southern U.S. states.

Introduction

Biogenic volatile organic compound (BVOC) emissions have long been suspected to contribute to secondary atmospheric aerosol production (1). Results from reaction chamber experiments and ambient observations have confirmed earlier speculation on the important role of BVOC in contributing to secondary organic aerosol. New data suggest that both the oxidation of the most abundant and volatile BVOC, isoprene (C_5H_8, MW = 68 g mol^{-1}, boiling point 34 °C), as well as oxidation of less volatile BVOCs including monoterpenes (MT, $C_{10}H_{16}$, MW = 136 g mol^{-1}, bp 155–175 °C) and sesquiterpenes (SQT, $C_{15}H_{24}$, MW = 204 g mol^{-1}, bp 240–275 °C)) can contribute to aerosol growth (e.g., refs 2–7). Aerosol yields are positively correlated with BVOC molecular weight. Oxidation of SQT results in the highest aerosol fraction, reaching up to 100% under certain conditions (8–15).

For more than 20 years it has been known that SQT are emitted from flowers and foliage (16); however, SQT landscape flux estimates and predictions of ambient aerosol yields are highly uncertain due to sparse and highly uncertain emission rate data. Analytical challenges and the high reactivity of SQT in ambient air have hindered successful SQT flux measurements at the ambient scale (17). As an alternative approach, enclosure measurements and scaling techniques have been used for determining SQT landscape fluxes (18–20).

In recent years we have developed and refined experimental techniques for SQT emission rate studies from deciduous and coniferous vegetation species (20–22). A high degree of variability of SQT emission rates has been observed among the 41 species studied to date. Available data show that high emitters (>100 ng gdw^{-1}h^{-1}) are found in both deciduous and coniferous families. Data generated by the present investigators as well as others (23–27) illustrate significant SQT emissions among pine trees (genus *Pinus*). More than 35 pine species are found in North America (28). The U.S. FIA (Forest Inventory and Analysis) statistics for 2002 indicate that pine trees cover ∼18% of contiguous U.S. forest areas, which is more than any other genus (29). It is also interesting to note that in recent reaction chamber experiments volatile emissions of loblolly pine were found to yield more particle formation compared to an α-pinene test mixture and to BVOC emissions from a helm oak tree. These observations were surprising as initial terpene concentrations in the loblolly pine experiment were lower than for the two comparison cases (30). This study points toward the potentially important role of BVOC emissions from loblolly pine, and possibly from other pine tree species in ambient aerosol formation. Here, we report SQT emission data from eight pine species that we have studied. These data are supplemented with observations from the aforementioned literature to develop July SQT emission distribution estimates for the contiguous U.S.

Experimental Section

Enclosure Experiments. Emission studies were performed by enclosing individual branches of pine trees with light-transparent Tedlar of Teflon bags. Detailed descriptions of the experimental protocol, materials used, flow conditions, removal of ozone in the purge and sample air, and monitoring of environmental data have been published previously (20–22, 31) and are only summarized here. After installation of the enclosure, the branch was allowed to acclimate to the enclosure conditions for 0.5–1 day, which also allowed any potential disturbance-induced BVOC bursts to subside and be purged out of the enclosure before sampling began. Typical bag purge flow rates were between 15 and 20 L min^{-1} resulting in average air turnover times of ∼3 min for a 50 L enclosure

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volume. Experiments were generally performed over 2–3 days to obtain diurnal emission profiles. A low flow (∼5 mL min⁻¹) of a multicomponent, ppmv-level reference standard (containing toluene, isopropyl-benzene, 1,2,3,4-tetrahydronaphthalene, 1,3,5-tri-isopropylbenzene and n-nonylbenzene) was doped into the purge flow. The concurrent analysis of these compounds allowed testing and correcting for possible compound losses and analytical biases. Needles were harvested after the experiment, dried for 24 h at 70 °C, and then weighed to determine the biomass dry weight (gdw).

Research Sites. Reported experiments were performed in Boulder, CO; Duke Forest, Chapel Hill, NC; the University of Michigan Biological Station (UMBS), Pellston, MI; and near Humboldt State University, Arcata, CA.

Chemical Analysis. Enclosure air samples typically were collected over 60 min using one of two techniques. First, an automated cartridge sampler collected samples at 200 mL min⁻¹ onto solid adsorbent cartridges (Tenax GR), which were subsequently analyzed by thermodesorption-gas chromatography (GC) with dual flame ionization (FID) and quadrupole mass spectrometer (MS) detection. In addition, a field–deployable, two-channel preconcentration and analysis instrument (also utilizing GC/MS/FID) was used (20) for on-site sampling and analysis. Both automated systems typically collected 10–12 emission samples per day over a 2–3 day period for each enclosure experiment. SQT were identified based on their mass spectra and by comparison of their chromatographic elution order (32); quantifications were achieved after determining the analyte recoveries and calibrating the GC/FID response with n-alkane (33) and SQT (21) reference standards. Further details on the chromatography systems can be found in Pollmann et al., (2005) (31) and Ortega et al. (2007) (20).

Regional Flux and Atmospheric Modeling. MT and SQT emission factors and temperature dependence relationships determined from this study were incorporated into the MEGAN biogenic emission model (model of emissions of gases and aerosols from nature, ref 34). MEGAN uses a framework that is similar to earlier biogenic emission models but has several significant improvements. These include methods for characterizing and processing land cover type and density, improved simulation of canopy environment including leaf energy balance calculations, light penetration through varying canopy types, and detailed chemical speciation. In addition, MEGAN can estimate the net emission to the atmosphere and includes a term to account for variations in canopy production and loss of particular compounds. MEGAN is a global model with a 1 km spatial resolution. The inputs for the model are based on satellite data, specific vegetation inventories, and the most recent and reliable emission factors and flux measurements. Pine MT and SQT emission variations were estimated by MEGAN as a function of temperature and pine foliar density using the parameters shown in Table 1. The standard MEGAN meteorological and land cover data for the year 2003, as described in more detail by Guenther et al. (2006)(34), were used to develop the emission estimates presented here. Please note that interannual changes in meteorological conditions and their effect on SQT emission estimates are expected to be much lower than current uncertainties in emission factors; consequently, the choice of year should not be of significance for the purpose of this estimate. Various enclosure experiments have demonstrated that agricultural crops and other trees can be significant SQT emitters. However, these were excluded from the model since the focus of this study was on pine trees.

Results and Discussion

SQT emission rates from more than 40 vegetation species, which have been studied to date, generally show high variability between species from the same genus and between different plant genera. Available data also suggest large interannual and seasonal variations in basal emission rates. However, the increasing body of data places constraints on the likely range of emissions from particular species in various geographic regions during different times of the year. New data presented here and from previously published reports also illustrate that SQT emissions from pine trees make an appreciable contribution to the overall BVOC flux and have the potential to contribute to the total biogenic secondary organic aerosol formation in landscapes with a high contribution to the overall biomass from pines.

A chromatogram from a *Pinus ponderosa* (ponderosa pine) emission sample is shown in Figure 1. Three groups of compounds can be distinguished. Five peaks resulting from the reference standard are labeled with an asterisk. Many pines trees emit a wide range of MT. MT and several identified oxygenated MT elute between 7.2–12.9 and 10.2–14.7 min, respectively. Ten SQT were identified with retention times between 18.9–22.5 min. The most abundant SQT were β-farnesene and β-caryophyllene. The total amount of carbon from SQT emissions in this particular sample is 22% of that originating from MT emissions.

A total of eight pine species were studied (Table 1), with varying numbers of samples collected during each experiment. Identified SQT with their linear temperature-programmed retention index and mass spectral identification are given in Table 2. Emission rates from the individual MT and SQT were summed and then plotted against the enclosure air temperature during the sample collection period (Figure 2). Exponential regressions ($E = E_0 \times \exp(\beta(T - T_0))$) were calculated through the summed MT and SQT data series. This fit through the data yielded basal emission rates (for $T_0 = 30$ °C) and the temperature response factor β. The derived β-factors, the calculated basal MT and SQT emission rates and the regression coefficient for each experiment are included in Table 1. MT basal emission rates are generally higher than SQT emission rates. Basal emission rates range from 0.17–4.0 for MT and from <0.004 to 0.62 μg C gdw⁻¹h⁻¹ (C = carbon) for SQT. Best estimate values for the mean MT and SQT β-factors are calculated by weighting data from each individual experiment by the number of data points and by the coefficients of the regression (R^2 values). The resulting β-factor estimates were 0.11 °C⁻¹ for MT and 0.17 °C⁻¹ for SQT (Table 1).

Other available reports of MT and SQT emissions from pine species are also included in Table 1. These data provide further evidence for SQT as important emissions from pine trees and that the emission rate and β-factor data reported here are in qualitative agreement with other observations.

The experiments at Duke expanded upon the previously reported studies in the late summer of 2004 (35). Higher daytime ambient temperatures, reaching up to 40 °C were encountered during 2005. SQT basal emission rates during August 2005 were generally lower than during September 2004; however, the calculated β-factors were well within the uncertainty of the earlier measurements. The light and temperature dependency of SQT emissions were studied by comparing daytime measurements with nighttime measurements made at elevated temperatures. The air flowing into the enclosure at nighttime was heated, thereby raising the temperature inside the enclosure to ∼10 °C above ambient nighttime levels. Results from these experiments in comparison with daytime data are shown in Figure 2. These data show that SQT nighttime emissions under elevated temperature conditions were close to daytime values at similar temperatures. The night-time SQT emissions were slightly less than daytime emissions at the same temperatures. It is possible that SQT emissions from loblolly pine have a light dependency resulting in these observations. However, the

TABLE 1. Pine Tree Experiments, Dates, Temperature Range of Observations, Total Number of Samples Analyzed (and Number of Samples in Which MT and SQT Were Identified), Mean Basal MT Emission Rate, Mean Basal SQT Emission Rate, MT β-factor (with Coefficient of Exponential Regression), and SQT β-factor (with Coefficient of Exponential Regression)

common name	scientific name	sampling date[a]	min T (°C)	max T (°C)	no. samples total (MT/SQT)	MT BER (μg gdw^{-1}h^1)	SQT BER (μg gdw^{-1}h^1)	MT β (°C^{-1})(R^2)	SQT β (°C^{-1})(R^2)	reference
gray pine	*Pinus sabiniana*	**Mar 22–24, 2005**	**23**	**33**	**7 (7/7)**	**4.0**	**0.06**	**0.21 (0.59)**	**0.29 (0.94)**	**this study**
scots pine	*Pinus sylvestris*	**May 26–31, 2005**	**19**	**31**	**10 (10/0)**	**1.7**	**<0.004**	**0.28 (0.91)**	**n/a**	**this study**
ponderosa pine	*Pinus ponderosa*	Jul 19–20, 2005	26	43	8 (8/8)	0.27	0.02	0.10 (0.81)	0.16 (0.96)	
ponderosa pine	*Pinus ponderosa*	Aug 23–24, 2005	11	33	8 (8/8)	0.73	0.11	0.12 (0.84)	0.15 (0.88)	
ponderosa pine	*Pinus ponderosa*	**MEAN ± STDEV**				**0.50 ± 0.32**	**0.07 ± 0.06**	**0.11 ± 0.01**	**0.15 ± 0.01**	**this study**
shortleaf pine	*Pinus echinata*	**Sep 13–14, 2005**	**11**	**24**	**10 (10/10)**	**0.15**	**0.09**	**0.13 (0.55)**	**0.07 (0.09)**	**this study**
beach pine	*Pinus contorta*	**Sep 14, 2005**	**14**	**14**	**1 (1/1)**	**0.17[b]**	**0.10[b]**	**n/a**	**n/a**	**this study**
white pine	*Pinus strobus*	Jun 17–19, 2005	19	28	10 (10/6)	0.18	0.03	n/a	n/a	
white pine	*Pinus strobus*	Jun 27–28, 2005	21	43	15 (15/15)	1.4	0.35	0.09 (0.89)	0.05 (0.44)	
white pine	*Pinus strobus*	Jun 27–28, 2005	21	43	8 (8/8)	1.0	0.02	0.07 (0.58)	0.09 (0.37)	
white pine	*Pinus strobus*	Jul 27–28, 2005	13	29	14 (14/0)	0.36	<0.01	0.17 (0.89)	n/a	
white pine	*Pinus strobus*	**MEAN ± STDEV**				**0.74 ± 0.57**	**0.10 ± 0.17**	**0.11 ± 0.05**	**0.07 ± 0.03**	**this study**
red pine	*Pinus resinosa*	Jul 5–Jul 6, 2005	15	34	18 (18/9)	0.80	0.08	0.10 (0.49)	0.26 (0.68)	
red pine	*Pinus resinosa*	Jul 5–6, 2005	23	26	3 (3/3)	0.99	0.14	n/a	n/a	
red pine	*Pinus resinosa*	Jul 23–24, 2005	15	40	16 (16/8)	0.05	0.03	0.08 (0.36)	0.21 (0.79)	
red pine	*Pinus resinosa*	**MEAN ± STDEV**				**0.61 ± 0.50**	**0.08 ± 0.06**	**0.09 ± 0.01**	**0.24 ± 0.03**	**this study**
loblolly pine	*Pinus teada*	Aug 8–9, 2005	22	34	12 (12/12)	0.06	0.07	0.10 (0.60)	0.21 (0.70)	
loblolly pine	*Pinus teada*	Aug 9–12, 2005	20	40	29 (28/29)	0.21	0.12	0.07 (0.46)	0.16 (0.90)	
loblolly pine	*Pinus teada*	Aug 9–12, 2005	20	40	17 (17/17)	0.23	0.26	0.08 (0.57)	0.14 (0.80)	
loblolly pine	*Pinus teada*	**MEAN ± STDEV**				**0.17 ± 0.09**	**0.15 ± 0.10**	**0.08 ± 0.02**	**0.17 ± 0.04**	**this study**
loblolly pine	*Pinus teada*	Sep 22–25, 2004	15	37	23 (21/23)	0.37	0.62	0.08 (0.40)	0.17 (0.80)	
loblolly pine	*Pinus teada*	Sep 22–26, 2004	13	31	19 (19/18)	0.60	0.39	0.12 (0.34)	0.17 (0.63)	
loblolly pine	*Pinus teada*	Sep 20–23, 2004	7	34	34 (34/31)	0.29	0.17	0.08 (0.43)	0.16 (0.57)	
loblolly pine	*Pinus teada*	Sep 24–25, 2004	11	32	10 (10/10)	0.32	0.21	0.10 (0.73)	0.16 (0.88)	
loblolly pine	*Pinus teada*	**MEAN ± STDEV**				**0.47 ± 0.16**	**0.35 ± 0.20**	**0.09 ± 0.02**	**0.16 ± 0.01**	**this study**
		MEAN of all species ± STDEV				0.95 ± 1.24	0.11 ± 0.10	0.14 ± 0.07	0.16 ± 0.08	
		MED of all species ± STDEV				0.50 ± 1.24	0.08 ± 0.10	0.11 ± 0.07	0.16 ± 0.08	
		weighted MEAN ± STDEV[c]						0.11 ± 0.01	0.17 ± 0.05	
loblolly pine	*Pinus teada*						**<0.1**			**Helmig et al., 1999b (23)**
white pine	*Pinus strobus*						**<0.1**			**Helmig et al., 1999b (23)**
lodgepole pine	*Pinus contorta*						**0.3**			**Helmig et al., 1999b (23)**
scotts pine	*Pinus sylvestris*					**1.0–5.1**	**<0.01–0.16**	**0.08–0.19**	**0.16–0.19**	**Tarvainen et al., 2005 (24)**
scotts pine	*Pinus sylvestris*						**<0.001–0.087**			**Hakola et al., 2006 (25)**
scotts pine	*Pinus sylvestris*					**0.33–1.5**	**0.005–0.16**	**0.09**	**0.19**	**Hakola et al., 2006[d] (26)**
scotts pine	*Pinus sylvestris*					**up to 1.33**	**see footnote e**			**Holzke et al., 2006 (27)**

[a] Sampling Locations: Grey Pine, Scotts Pine, NCAR greenhouse experiments (Boulder, CO); Ponderosa Pine, Boulder, CO; Shortleaf Pine, Beach Pine, Arcata, CA; White Pine, Red Pine, UMBS, MI; Loblolly Pine, Duke, NC. [b] Emission rate determined from one individual sample, not normalized. [c] Weighted mean and standard deviation were calcualted by multiplying β-factors from individual experiments with number of samples and regression coefficient for each experiment and normalizing. [d] Data from a debudded branch (after removal of buds) were also reported, but are not included in the data listed here. [e] No normalized SQT emission rates were determined, maximum mean daytime individual compound emission rates of 9 identified SQT was 0.047 μg gdw^{-1}h^{-1}.
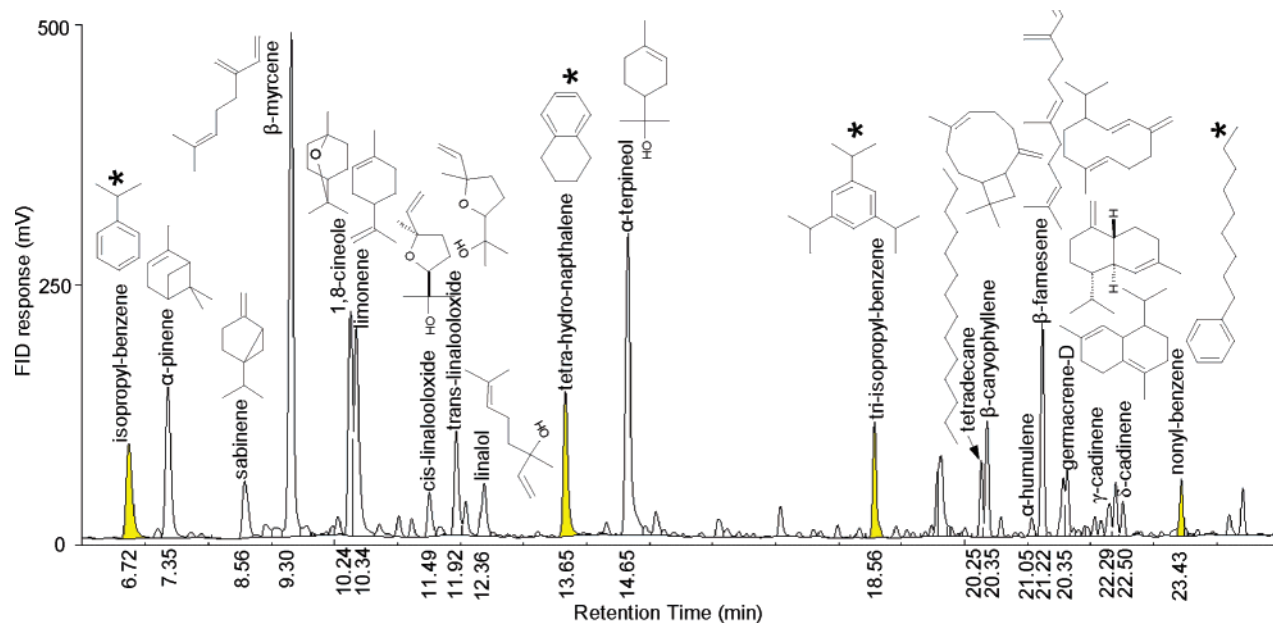
FIGURE 1. Chromatogram (plotted as the flame ionization detector (FID) response) from a ponderosa pine emission sample. Ponderosa pine was found to be both a significant monoterpene (retention times 7.2–14.7 min) and sesquiterpene (18.9–22.5 min) emitter. Eight sesquiterpenes were identified (identifications are indicated in the chromatogram). Shaded peaks (also labeled with an asterisk) are the aromatic compounds from the reference standard that was added to the enclosure air at a known concentration and controlled flow rate.

TABLE 2. SQT and Related Compounds Identified in Emission Samples from Pine Trees with Their CAS Registry Number, Gas Chromatography Retention Index (RI) on DB-1, and Mass Spectral Fragmentation Data[a]

SQT common name	CAS registry number	RI	mass spectrum M/Z fragment (% relative abundance)
cubebene <alpha->	17699–14–8	1337	119(100), 105(92), 161(72), 41(44), 91(34), 93(29)
copaene <alpha->	3856–25–5	1362	119(100), 105(81), 161(63), 93(56), 91(42), 92(33)
bourbonene <beta->	5208–59–3	1369	81(100), 80(82), 123(69), 79(34), 41(18), 77(14)
cubebene <beta>	13744–15–5	1379	161(100), 204(67), 107(57), 66(46), 133(34), 189(32)
elemene <beta->	33880–83–0	1379	93(100), 81(83), 67(79), 68(63), 41(56), 53(52)
cedrene <alpha->	11028–42–5	1398	119(100), 161(47), 93(45), 105(34), 77(28), 91(24)
caryophyllene	87–44–5	1403	93(100), 69(84), 41(77), 91(74), 79(69), 133(59)
SQT1411		1411	161(100), 105(49), 91(44), 93(30), 79(29), 119(29)
neryl acetone	3879–26–3	1420	43(100), 205(50), 187(28), 91(28), 41(23), 77(17)
bergamotene <[Z]-alpha-trans->	13474–59–4	1427	93(100), 119(83), 69(43), 41(40), 91(35), 77(26)
humulene <alpha->	6753–98–6	1437	93(100), 80(35), 121(23), 92(19), 91(17), 41(17)
farnesene <cis-beta->	18794–84–8	1444	69(100), 93(62), 41(55), 67(21), 133(21), 79(21)
muurolene <gamma->	30021–74–0	1456	161(100), 119(57), 106(56), 93(52), 91(50), 79(48)
germacrene D	23986–74–5	1461	161(100), 91(63), 105(58), 81(43), 79(41), 119(38)
selinene <beta->	17066–67–0	1471	41(100), 93(90), 79(84), 105(80), 107(77), 81(72)
germacrene B	15423–57–1	1480	121(100), 93(81), 107(54), 91(45), 41(41), 79(41)
muurolene <alpha->	10208–80–7	1485	105(100), 93(48), 41(44), 94(44), 91(42), 161(35)
farnesene <alpha->	502–61–4	1491	93(100), 69(62), 41(61), 79(49), 107(48), 55(48)
cadinene <gamma->	483–76–1	1492	161(100), 93(76), 91(69), 79(59), 105(56), 119(53)
cadinene <delta->	39029–41–9	1502	161(100), 119(76), 134(74), 105(64), 91(57), 204(45)
nerolidol <cis->	142–50–7	1515	69(100), 41(54), 93(49), 71(45), 43(35), 73(34)
nerolidol <trans->	40716–66–3	1545	69(100), 93(65), 41(62), 71(46), 43(45), 55(33)
SQT1555		1555	93(100), 94(50), 119(40), 120(40), 77(30), 117(30)
cedrol	77–53–2	1579	95(100), 150(86), 151(65), 43(52), 71(46), 81(37)

[a] SQT species that could not be positively identified were labeled according to their retention index (e.g., SQT1411, SQT1555).

differences were not statistically significant, and this remains an open question. These data also further confirm that SQT emissions from Loblolly pine are strongly modulated by temperatures during both day and night.

As mentioned above, SQT emission rates have a stronger temperature dependency (β-factor) than MT, although the absolute SQT emissions are typically lower. SQT emission factors were scaled against MT observed in the same samples. On average, SQT were 12% (median = 16%) of the MT basal emission rate at 30 °C. Since MT and SQT exhibited different temperature response curves, this ratio is dependent on temperature, increasing, for example, from 9% at 20 °C to 29% at 40 °C (using the median emission rate values).

A summary of identified SQT with their percentage contribution to the overall SQT flux is listed in Table 3. These fractional numbers were then multiplied by the total SQT emission rate from each experiment and normalized to yield the data shown in the last two columns of this table. The most important compounds emitted were β-caryophyllene, α-bergamotene, β-farnesene, and α-farnesene, which together make up approximately 70% of identified SQT. Interestingly, the SQT speciation from loblolly pine was different in the 2004 and 2005 samples, although experiments were performed at the same site and on the same stand of trees. These findings imply either seasonal or year-to-year changes in SQT emission patterns or differences between
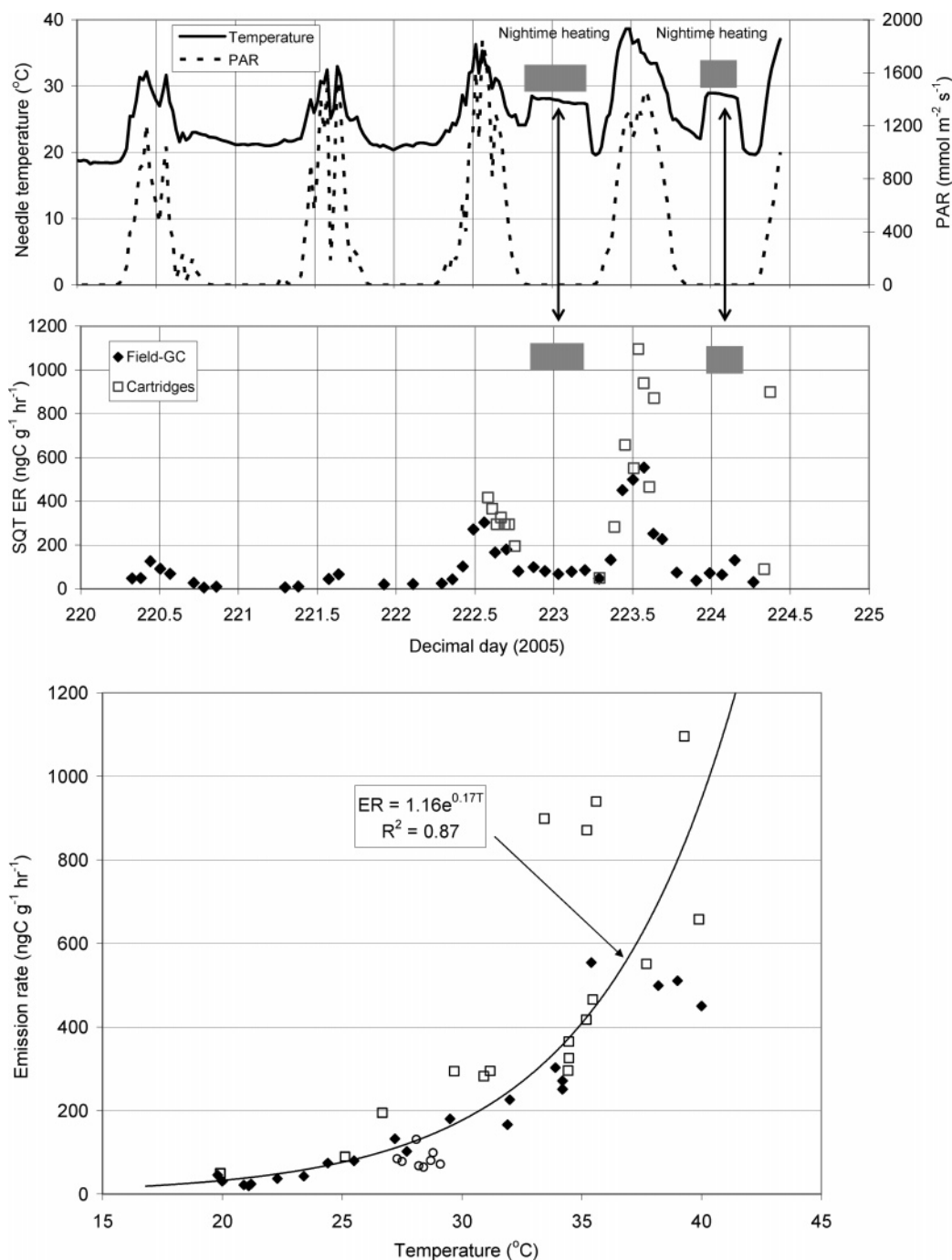
FIGURE 2. Sesquiterpene (SQT) emission rate (ER) data from an enclosure experiment on a loblolly pine tree at Duke Forest. The upper window shows the temperature and light record (photosynthetically active radiation (PAR)) and observed total SQT emission rates, measured with both adsorbent cartridges and the on-line field gas chromatography (GC) instrument. The time period when the air flowing into the enclosure was heated is indicated by the shaded area. The lower panel shows total SQT emission rates plotted against the mean needle temperature inside the enclosure. Data taken using adsorbent cartridges are indicated with open squares (□), field GC data points are filled diamonds (◆), and data from the nighttime heating experiment (using the field GC) are designated by the open circles (○) in the lower graph. The exponential fit curve excludes the nighttime heating experiments but incorporates both the field GC as well as cartridge data.

individuals of the same species. This assumption is well supported by results from two other studies, which similarly reported seasonally changing SQT emission patterns as well as differences in the SQT emission patterns from different Scots pine trees (*26*, *27*). Holzke et al. (2006) (*27*) present a more in-depth analysis of physiological parameters that potentially determine changes in the emissions of these compounds, based on seasonal measurements of MT and SQT. SQT have also been shown to be emitted at increased

rates from a variety of other vegetation as a response to various biological and environmental stress factors (e.g., *26*, *36*–*43*). Short-term changes in SQT speciation and total emission rates during the 2004 and 2005 experiments were not detected. However, it is possible that some of the differences between the 2 years may have been influenced by long-term responses to previous stimuli, which are only observable on longer time scales. Most notably, the 2005 measurements were conducted approximately six weeks

TABLE 3. Percentage Contribution of Individual SQT ($\pm$ Standard Deviation) to the Total SQT Flux Observed[a]

SQT	pine species (number of individual trees studied)								AVG	rank	weighted AVG	weighted Rank
	gray (1)	ponderosa (2)	shortleaf (1)	beach (1)	white (3)	red (3)	loblolly 2005 (3)	loblolly 2004 (4)				
cubebene <alpha->		4 ($\pm$1)							0.5	15	0.3	14
copaene <alpha->		1 ($\pm$0)							0.2	18	0.1	20
bourbonene <beta->		1 ($\pm$1)							0.1	21	0.1	24
cubebene <beta>					4 ($\pm$7)	4 ($\pm$6)			2.4	8	0.8	11
elemene <beta->							1 ($\pm$2)		0.2	19	0.2	16
cedrene <alpha->						1 ($\pm$2)	1 ($\pm$2)		0.6	13	0.3	15
caryophyllene		22 ($\pm$9)		6	7 ($\pm$13)		26 ($\pm$8)	67 ($\pm$3)	15.1	3	30.1	1
SQT1411		2 ($\pm$0)							0.3	17	0.2	19
neryl acetone							1 ($\pm$1)		0.1	22	0.1	21
bergamotene <[Z]-alpha-trans->			100	77			9 ($\pm$6)	13 ($\pm$8)	24.9	1	22.5	2
humulene <alpha->		10 ($\pm$7)			5 ($\pm$9)		8 ($\pm$2)	13 ($\pm$4)	5.7	6	6.7	5
farnesene <cis-beta->	77	27 ($\pm$23)		3	3 ($\pm$5)	41 ($\pm$30)	17 ($\pm$12)	8 ($\pm$1)	20.2	2	15.6	3
muurolene <gamma->		10 ($\pm$1)					1 ($\pm$1)		1.3	11	0.7	12
germacrene D		10 ($\pm$0)		5					1.9	10	1.2	7
selinene <beta->					8 ($\pm$14)	3 ($\pm$5)			3.6	7	1.1	9
germacrene B							1 ($\pm$1)		0.1	23	0.1	22
muurolene <alpha->				1	13 ($\pm$22)		26 ($\pm$32)		8.1	5	5.2	6
farnesene <alpha->	20			4	57 ($\pm$51)	55 ($\pm$34)	1 ($\pm$2)		10.5	4	11.8	4
cadinene <gamma->		7 ($\pm$2)				1 ($\pm$1)	2 ($\pm$3)		1.2	12	0.8	10
cadinene <delta->		6 ($\pm$2)		5	2 ($\pm$4)				2.1	9	1.1	8
nerolidol <cis->							1 ($\pm$2)		0.1	20	0.2	18
nerolidol <trans->							5 ($\pm$8)		0.6	14	0.7	13
SQT1555	3								0.3	16	0.2	17
cedrol							1 ($\pm$1)		0.1	24	0.1	23
average Σ SQT bas. emis. rate (μg gdw^{-1}h^{-1})	0.06	0.07	0.09	(0.10)	0.10	0.08	0.15	0.35				

[a] These ratios were then multiplied with the overall SQT emission rate to obtain a weighted average contribution of individual SQT and a ranking of the importance of individual compounds. SQT species that could not be positively identified have been labeled with their retention index (e.g., SQT1411, 1555).

earlier than in 2004, when day and nighttime temperatures were overall higher.

Only a few individual SQT compounds have been studied to determine their atmospheric reaction rate constants. Most SQT undergo rapid reactions in the atmosphere with both OH and ozone, resulting in atmospheric lifetimes on the order of seconds to a few hours (44). Available data suggest that SQT reactivity increases with the number of available double bonds (db) in the molecule, e.g., β-caryophyllene (2 db) and α-humulene (3 db) are among the most reactive SQT (31). It is noteworthy that all of the most abundant SQT (Table 3) have either 2 or 4 db. Therefore, as a class, the total SQT emissions from these pines are estimated to have reactivity comparable to β-caryophyllene, which has been found as one of the most reactive compounds among SQT investigated so far (31, 44, 45).

Figure 3 shows the MEGAN distribution of pine SQT emission factors for the contiguous U.S. MEGAN uses an area average emission factor based on plant species composition and species-specific emission factors, which represents the net emission expected at standard conditions (air temperature of 30 °C and leaf area index of 5). The month of July was chosen for a pilot study, as the relatively high average July temperatures were expected to yield the highest sensitivity toward SQT emissions. Also, the typically observed high ozone and particulate loadings during the month of July motivate the investigation of SQT emission rates during that time of year. Please note that only two of the emission measurements were obtained during the month of July (ponderosa pine and white pine). Potential seasonal differences in SQT emission rates are neglected in the emission modeling, so our results should only be considered a first order-of-magnitude estimate. Monthly pine emission rates shown in Figure 3 illustrate the stronger temperature dependence 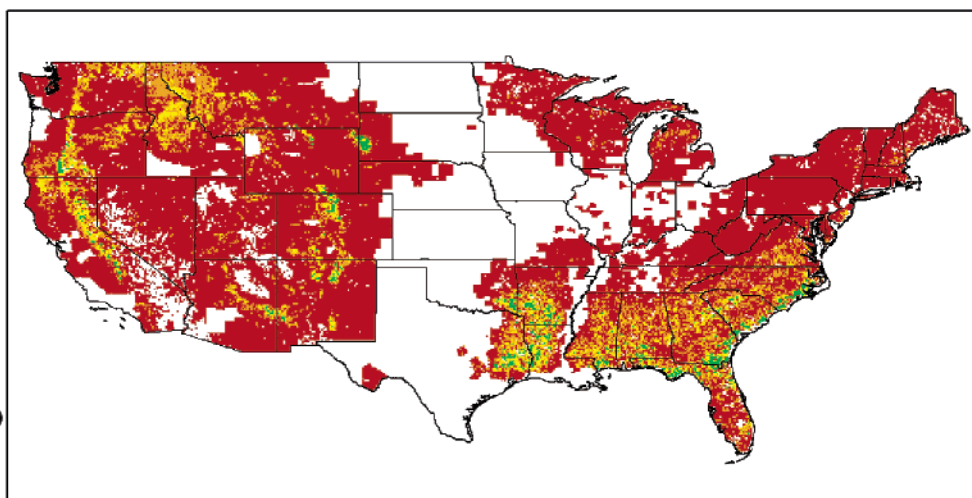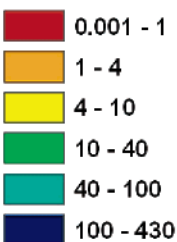of SQT emissions which are <5% of MT emissions in cooler regions and >15% in warmer regions. While monthly MT fluxes from pine trees can reach >100 mg m^{-2}, maximum monthly SQT fluxes of 10−40 mg m^{-2} were calculated. The highest SQT landscape fluxes are predicted for the southeastern U.S. and mountainous regions of the western U.S. (e.g., Rocky Mountains, Sierra Nevada Mountains, and Black Hills). High SQT fluxes in these regions are driven by both the high biomass density of pine trees as well as warm July conditions.

MEGAN estimates regional net emissions from a terrestrial ecosystem into the atmosphere. A comparison of isoprene flux estimates from MEGAN with locally performed measurements was recently presented by Ortega et al., (2007) (20). Similar to the experiments reported here, this work was based on branch enclosure measurements and up-scaling, and included an evaluation of these findings by comparison with measured, above-canopy fluxes. Flux estimates for isoprene agreed to within ∼30%, with the branch-enclosure-scaled calculations from MEGAN typically yielding somewhat lower values than measured isoprene fluxes (20). For the reasons mentioned above, comparisons of whole canopy SQT fluxes with estimates of SQT fluxes from MEGAN are not possible. However, the good agreement obtained for isoprene suggests that the branch enclosure measurements with modeled fluxes by MEGAN yields realistic flux estimates. Isoprene, due to its higher volatility and slower reaction than most of the important SQT, is expected to escape the canopy to a larger, and likely quantitative (100%) fraction. The emissions shown in Figure 3 assume that all of the MT and SQT emitted from pine trees escape into the above-canopy atmosphere. Please note that these results most likely overestimate SQT fluxes because rapid reactions can occur before SQT escape the canopy environment (17). Therefore, the resulting rates are expected to be representative of the sum of the primary emissions and secondary compounds
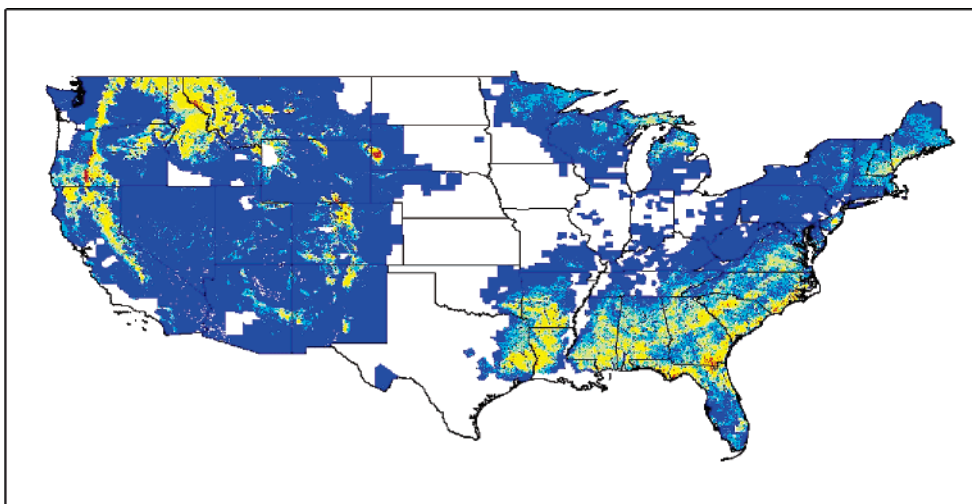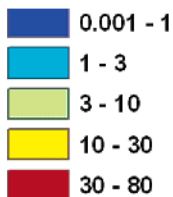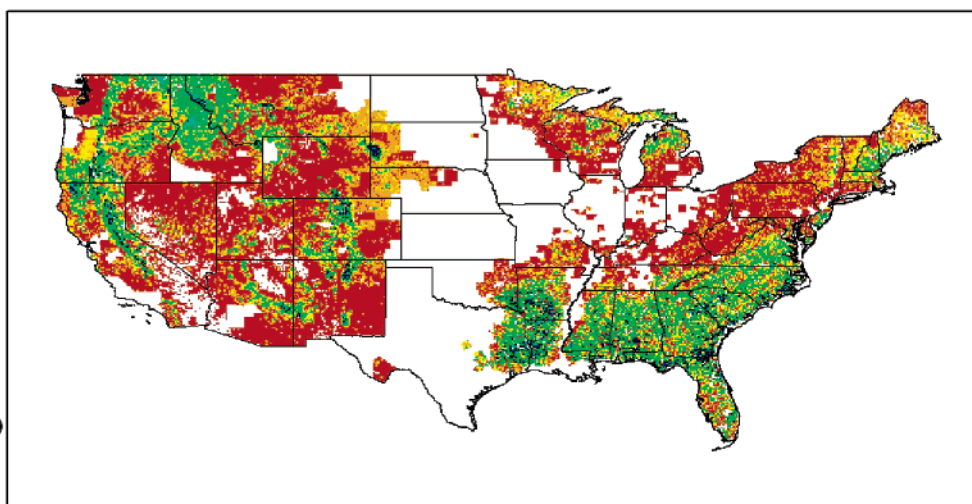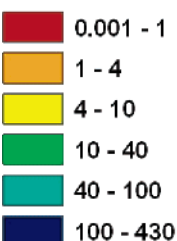
FIGURE 3. Contiguous U.S. distribution of pine sesquiterpene emission factors (μg m^{-2} h^{-1}, top panel), July 2003 pine SQT emissions (mg m^{-2}, middle panel), and July 2003 pine monoterpene emissions (mg m^{-2}, bottom panel) estimated by MEGAN using a spatial resolution of ~1 km^2. The emission factor and emissions shown here assume that all of the sesquiterpenes and monoterpenes emitted by pine trees are emitted into the atmosphere. Since these compounds can be oxidized before escaping the canopy, the values shown are more representative of the emission of primary compounds plus secondary products.

(oxidation products and secondary organic aerosol). SQT emissions from other coniferous and broadleaf tree species as well as from agricultural vegetation were omitted due to the sparseness of available quantitative emission rate data at this time. However, our experiments performed on several of these species to date have found significant SQT emissions (although somewhat lower than pine emissions). Conse-

quently it is anticipated that inclusion of emission rates from other vegetation will result in a substantial increase of total SQT landscape flux estimates.

Field experiments reported here were mostly performed during the spring through fall seasons. The seasonal variations in SQT and MT emissions are increasingly recognized. Several studies have reported strong seasonal changes of MT

emission rates, with generally higher values during the late spring to early summer and lower emissions during the fall (e.g., refs 46−50). The available studies on SQT (24−27, 51) suggest that, similar to MT, seasonal changes in SQT basal emission rates appear to be significant, with highest rates occurring during the early to mid-growing season and SQT basal emission rates possibly peaking ~1 month after MT (26). These observations indicate that a description of SQT emissions solely based on temperature and light may be inadequate. Other parameters, such as seasonal variations in physiological growth, and past weather influences (rain, cloud cover, heating degree days, etc.) should also be considered to accurately describe SQT fluxes. This task will require concurrent long-term emission rate and physiological measurements in order to better parametrize the seasonal changes in SQT emissions.

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