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# Monoterpene and Sesquiterpene Emission Estimates for the United States

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Biogenic volatile organic compounds (BVOC) contribute significantly to the formation of ozone and secondary organic aerosol (SOA). The Model of Emissions of Gases and Aerosols from Nature (MEGANv2.02) is used to estimate emissions of isoprene, monoterpenes (MT), and sesquiterpenes (SQT) across the United States. Compared to the Biogenic Emission Inventory System (BEIS3.0), MEGANv2.02 estimates higher isoprene but lower MT emissions for July 2001 and January 2002. A sensitivity study of SQT and MT emission factors and algorithm parameters was conducted by assigning values to four plant functional types (PFTs) using both recent measurements and literature values. The standard deviations of the emissions factors within these PFTs were two to four times the averages because of the variation in experimental basal emissions rate data. More recently published SQT and MT basal emission rates are generally lower than those reported in the literature through 2004. With the new emissions factors, monthly average SQT emission rates for the contiguous United States are equal to 16% of the MT emissions during July and 9% of the emissions during January. The SQT emissions distribution is strongly influenced by the grass and crop PFT, for which SQT emissions data are quite limited.

## 1. Introduction

Scientists and policy makers are concerned about particulate matter with aerodynamic diameter less than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) because of its effects on human health, mortality, atmospheric visibility, and climate forcing. Emissions of biogenic volatile organic compounds (BVOC) represent a major source of

secondary organic aerosol (SOA), which in turn contributes significantly to  $\text{PM}_{2.5}$  mass. Liao et al. (1) estimated that total BVOC emissions in the United States are four times higher than VOC emissions from anthropogenic sources. Tsigaridis and Kanakidou (2) estimate that global SOA production from BVOC ranges from 2.5 to 44.5 Tg (organic mass) per year, whereas the global SOA production from anthropogenic VOC ranges from 0.05 to 2.62 Tg (organic mass) per year.

Three primary classes of BVOC form SOA: isoprene ( $\text{C}_5\text{H}_8$ ) (1, 3), which has the highest global emission but a relatively low SOA yield; monoterpenes (MT) ( $\text{C}_{10}\text{H}_{16}$ ); and sesquiterpenes (SQT) ( $\text{C}_{15}\text{H}_{24}$ ). Although SQT have lower emission rates than isoprene or MT, they may contribute significantly to SOA formation because they are very reactive and have high aerosol yields (4). Liao et al. (1) estimated that isoprene, MT, and SQT emissions contribute 58.2, 37.3, and 4.5% of biogenic SOA on an annual basis in the United States. In their study, the SQT emissions were derived from the Global Emissions Inventory Activity (GEIA), which lacks an explicit SQT emission inventory. The total BVOC emissions from the inventory were speciated based on estimates from Griffin et al. (5). In this paper we focus on SQT, because of the availability of recent emission measurements, their comparatively high aerosol yields, and because they have been less extensively studied than other BVOC.

More than 300 SQT species have been classified (6), although fewer than 30 have been identified as emitted from vegetation (7–10). Among the most common SQT,  $\beta$ -caryophyllene has been observed to be emitted from a variety of trees and agricultural plants, such as *Betula pendula*, *Pinus taeda*, *Populus tremula*, *Sambucus nigra*, *Citrus sinensis*, potato plants, sunflower, maize, leaves of tobacco, and cotton (8). Helmig et al. (7) found that SQT emissions from a variety of pine tree species are as high as 29% of MT emissions. However, SQT emissions remain highly uncertain because few quantitative emission rate measurements have been made, the available data show high variability, and because the biological pathways for SQT emissions are not well understood (11, 12). Kanakidou et al. (13) estimated that the uncertainties in global BVOC emissions could be as high as a factor of 5 for SQT and other terpenes, and a factor of 3 for isoprene.

In this study, we used the Model of Emissions of Gases and Aerosols from Nature (MEGANv2.02) to estimate isoprene, MT, SQT, and other VOC emissions for the United States. MEGANv2.02 driving variables and parametrizations for isoprene have been described previously (14). The MEGANv2.02 approach for MT and SQT is described in this manuscript, and parameters for other compounds will be described elsewhere. MEGAN is being developed with the goal of replacing regional inventories such as the Biogenic Emission Inventory System (BEIS) (version 3.0), which has been widely used to predict BVOC emissions in the United States, and global inventories such as the GEIA inventory (16). Compared to BEIS, MEGAN incorporates updated emission factors and land cover data, includes more controlling variables over the emissions, is global in scale, and is relatively easy to apply. MEGANv2.02 has been coded in FORTRAN90 for higher computational efficiency and compatibility with chemistry and transport models such as the Community Multiscale Air Quality model (CMAQ).

This paper first describes the MEGAN model and the updates made for this study (version 2.02). We summarize new emission rate data for SQT and MT that have been measured from a wide range of plants and locations across the United States. The new emission data for SQT are also

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compared to emission rates published in the literature from 1995 to 2004. MEGANv2.02 is used to combine the emission rate data with information on plant distribution, leaf area index, leaf age, and environmental conditions to produce emission flux estimates. The paper presents comparisons of isoprene and MT emission estimates from MEGANv2.02 and BEIS3.0, and compares SQT emission estimates based on the new emission rate data versus older literature data. The paper also examines contributions of individual PFTs to SQT emissions, and the chemical speciation, diurnal patterns, and light and temperature dependence of the emissions.

## 2. Materials and Methods

This study utilizes MEGANv2.02 (<http://bai.acd.ucar.edu/Megan/index.shtml>) and (14) with updates described below) to produce emission estimates that are spatially, temporally, and chemically resolved, based on measured emission rates, satellite-derived vegetative cover data, and date-, time- and site-specific environmental conditions. MEGAN is a global model with a spatial resolution of 1 km. For comparison with the MEGANv2.02 results, estimates of isoprene and MT emissions are also prepared using BEIS3.0 (available at <http://www.epa.gov/asmdnerl/biogen.html>). BEIS3.0 uses the Biogenic Emissions Landcover Database (BELD (17)) to describe vegetation cover.

MEGANv2.02 computes emission rates for a total of 138 chemical species based on 20 explicit and lumped chemical classifications. Isoprene, three SQT classes ( $\beta$ -caryophyllene,  $\alpha$ -farnesene, and "other" SQT), and seven MT classes (myrcene, sabinene, limonene, 3-carene, *trans*- and  $\beta$ -ocimene,  $\beta$ -pinene,  $\alpha$ -pinene, and "other" monoterpenes) are included in the 20 chemical classes. Emission rates are calculated on the basis of the following equation (14)

$$ER = \epsilon\gamma\rho \quad (1)$$

where ER is an emission rate ( $\mu\text{g}$  of compound  $\text{m}^{-2}$  of earth surface  $\text{h}^{-1}$ ),  $\epsilon$  is an emission factor that represents the net in-canopy emission rate expected at standard conditions ( $\mu\text{g} \text{m}^{-2} \text{h}^{-1}$  at 303 K),  $\gamma$  is an emission activity factor that accounts for changes due to deviations from standard conditions, and  $\rho$  is a factor that accounts for chemical production and loss within plant canopies. In this study, detailed plant canopy information is not considered so  $\rho$  is set to 1. This assumes that the first level of the chemical transport model into which the emissions will ultimately be fed will determine the chemical loss of the emission.

The emissions activity factor in MEGANv2.02 can account for effects of the canopy environment, leaf age, and soil moisture. The last effect (soil moisture) is neglected in this study, so

$$\gamma = \gamma_{\text{CE}}\gamma_{\text{age}} = \gamma_{\text{LAI}}\gamma_{\text{P}}\gamma_{\text{T}}\gamma_{\text{age}} \quad (2)$$

where  $\gamma_{\text{CE}}$  is the canopy environment factor,  $\gamma_{\text{LAI}}$  accounts for variations in leaf area index (LAI),  $\gamma_{\text{P}}$  and  $\gamma_{\text{T}}$  account for the response to changes in light and temperature, respectively, and  $\gamma_{\text{age}}$  accounts for variations due to leaf age.  $\gamma_{\text{age}}$  is calculated from a leaf age algorithm that assigns different emission activities to new, growing, mature, and old leaves.

To use results from MEGAN in atmospheric chemistry and transport models, detailed compound emissions must be combined into the lumped chemical classes that are used in gas-phase atmospheric chemical mechanisms. As part of this study, new lumping schemes for biogenic VOC compounds (18) were developed for SAPRC99 (19), RADM2 (20), RACM (21), and CBMZ (22). The lumping schemes were developed by first splitting the 20 MEGAN compound classes into 138 individual chemical compounds, and then assigning them to compound classes used in the respective chemical mechanisms. In our version of SAPRC99, for example, the

MT species are all grouped into a single compound class, TRP1. Our version of SAPRC99 includes three classes of sesquiterpenes:  $\beta$ -caryophyllene (BCARL),  $\alpha$ -humulene (AHUMUL), and other slower-reacting SQT (SSQT). Although  $\alpha$ -farnesene is treated as an explicit compound class in MEGANv2.02, it is not treated explicitly in the chemical mechanism because of the lack of data on its atmospheric chemical reactions and instead is lumped into the AHUMUL class.

To facilitate MEGAN's use, MEGANv2.0 has been coded in FORTRAN90, based on the NetCDF format and IOAPI interface ([www.cmascenter.org](http://www.cmascenter.org)). These changes significantly improved MEGAN's computational efficiency and make it compatible with the SMOKE and CMAQ models.

The primary SQT and MT PFT emission factor database developed for this study, referred to as EF-S06, was derived from basal emissions rates (BER in  $\mu\text{g} \text{gdw}^{-1} \text{h}^{-1}$ ) at 303 K and temperature dependencies derived from recent enclosure measurements (7, 9–11). These data were obtained by enclosing individual sections or whole plants in Teflon bag enclosures that were continuously purged with clean, ozone-free air. After an equilibration period, air samples from the enclosure were preconcentrated and analyzed by gas chromatography. Normalized emission rates and temperature response factors were derived by analyzing measured emission rates against the recorded temperature and light conditions in the enclosure (7). The compilation of recent measurements includes 123 observations made from 2004 to 2006. A list of the plants, sampling dates, and locations is provided in the Supporting Information (Table S1). Based on these data, emission parameters were defined for four PFTs: broadleaf trees (BT), needle leaf trees (NT), shrubs and bushes (SB), and grasses and crops (GC). After close examination of the underlying data we concluded there was no justification for finer discrimination of emissions rates by PFT, species, or sampling date, location, or season, due to the limited size and high unexplained variability of the data.

Table 1 provides a summary of the data for SQT and MT emission factors (EF), including the mean and standard deviation of the EF across plant samples in the four PFT categories, with EF determined using a BER within a canopy environment model (14) at standard conditions with a representative biomass density ( $\text{gdw} \text{m}^{-2}$ ) for the specified PFT. Since the assumed biomass density for each PFT was a fixed value (500, 750, 500, and 500  $\text{gdw} \text{m}^{-2}$  for BT, NT, SB, and GC, respectively (16)), the standard deviations of the EF in Table 1 reflect only the variability in BER across plant samples. As indicated, the variability in the EF values is high. For most compounds and PFTs, the standard deviations are a factor of 2 to four times the average emission factors. For BT and NT, the sampled plants included in the data set encompass a wide range of common species and growing regions across the United States and are expected to be reasonably representative. However, most of the measurements were made in late spring, summer, or early fall, so they are not very representative of the colder months. Seasonal dependencies of BER are expected to be significant (7, 23), but emission data and the model do not yet consider this influence. For the SB and GC categories, the database is smaller and less representative. In particular, the GC category is limited to measurements for fennel, tomato, sunflower, corn, bean, wheat, and tobacco, with no lawn or native grasses represented.

The set of recent emission rate measurements was used to estimate the chemical speciation of MT and SQT emissions as well as the total emission rates. The most abundant SQT observed were  $\beta$ -caryophyllene,  $\alpha$ -farnesene, *cis*- and  $\beta$ -farnesene,  $\alpha$ -humulene, [Z]-,  $\alpha$ -, and *trans*-bergamotene, and  $\beta$ -bourbonene. MEGANv2.02 treats  $\beta$ -caryophyllene and  $\alpha$ -farnesene explicitly, because they contributed the largest

**TABLE 1. Mean and Standard Deviation of Emissions Factors (EF) by PFT, for SQT and MT compounds in EF-S06 and EF-D06<sup>a</sup>**

emission cases	BT EF ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	NT EF ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	SB EF ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	GC EF ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )
	Sesquiterpenes			
EF-S06	(37)	(40)	(18)	(18)
$\alpha$ -farnesene	22.2 $\pm$ 46.3	14.2 $\pm$ 18.6	1.8 $\pm$ 4.2	21.2 $\pm$ 40.4
$\beta$ -caryophyllene	18.6 $\pm$ 38.8	12.1 $\pm$ 15.8	4.2 $\pm$ 9.7	25.4 $\pm$ 48.3
other sesquiterpenes	46.7 $\pm$ 97.5	55.0 $\pm$ 71.7	21.5 $\pm$ 49.8	55.1 $\pm$ 104.8
total sesquiterpenes	87.5	81.3	27.6	101.8
EF-D06	(12)	(1)	(1)	(9)
$\alpha$ -farnesene	76.1	78.7	20.0	20.9
$\beta$ -caryophyllene	63.7	67.0	45.7	25.0
other sesquiterpenes	160.2	304.2	234.3	54.1
total sesquiterpenes	300.0	450.0	300.0	100.0
	Monoterpenes			
EF-S06 and EF-D06	(43)	(35)	(12)	(18)
myrcene	22.1 $\pm$ 46.6	85.8 $\pm$ 112.0	20.9 $\pm$ 35.5	5.6 $\pm$ 18.2
sabinene	14.3 $\pm$ 30.2	41.9 $\pm$ 54.6	17.3 $\pm$ 29.4	8.0 $\pm$ 26.1
limonene	40.7 $\pm$ 85.7	98.9 $\pm$ 129.0	173.9 $\pm$ 295.6	41.5 $\pm$ 135.4
3-carene	5.0 $\pm$ 10.6	43.5 $\pm$ 56.8	6.1 $\pm$ 10.4	17.2 $\pm$ 56.1
<i>trans</i> - and $\beta$ -ocimene	134.4 $\pm$ 283.3	3.9 $\pm$ 5.1	103.0 $\pm$ 175.1	14.3 $\pm$ 46.6
$\beta$ -pinene	40.6 $\pm$ 85.6	91.7 $\pm$ 119.6	45.0 $\pm$ 76.6	21.9 $\pm$ 71.6
$\alpha$ -pinene	36.1 $\pm$ 76.0	225.9 $\pm$ 294.8	51.2 $\pm$ 87.0	57.2 $\pm$ 186.9
other monoterpenes	155.9 $\pm$ 328.7	281.2 $\pm$ 366.9	318.3 $\pm$ 541.2	158.1 $\pm$ 516.1
total monoterpenes	449.2	872.6	735.8	323.7
biomass density (gdw $\text{m}^{-2}$ )	500	750	500	500

<sup>a</sup> Values in parentheses are the number of samples. BT, NT, SB, and GC represent broadleaf tree, needle leaf tree, shrub-bush, and grass-crop categories, respectively.

fraction of the total SQT emission rate across all of the samples. The other SQT are grouped together. The most abundant MT observed in the recent data were *trans*-ocimene,  $\alpha$ -pinene,  $\beta$ -pinene, limonene,  $\beta$ -myrcene, and 3-carene, which contributed an average of 70% of the total MT emission rate across all of the samples.

For purposes of comparison with SQT emissions estimates based on the recent data (EF-S06), a second emission factor data set, referred to as EF-D06, was prepared, exclusively using total SQT emission rates from plant enclosure measurements reported in the literature from 1995 to 2004. Emissions of MT, isoprene, and other biogenic compounds were unchanged from EF-S06. For the second SQT emission factor data set (EF-D06), quantitative emissions rate data from eleven studies (24–35) were compiled and grouped into the four PFT categories. Comparison of reported emission rates indicated that emission data for several BT and SB reported by Helmig et al. (30, 31) were especially high. SQT emissions can be artificially enhanced in response to disturbance of the vegetation during installation of the enclosure system (8) and references therein). Later studies have used improved enclosure techniques and allowed longer equilibration before data are collected. Consequently, these earlier data were not included when average BERs were calculated. With the Helmig et al. (30, 31) data excluded, only one measurement each remained for plants in the NT and SB PFT categories. Consequently, the available data for all the woody plants — BT, NT, and SB — were combined, and the same SQT BER value of 0.6  $\mu\text{g gdw}^{-1} \text{h}^{-1}$  was used for all three PFTs. A BER value of 0.2  $\mu\text{g gdw}^{-1} \text{h}^{-1}$  was estimated for the GC PFT. The total EF-D06 SQT EF thus differs between the NT, BT, and SB PFTs due to only the differences in their assumed biomass densities and the chemical speciation of SQT from each PFT, which was kept the same as in the EF-S06 model.

Emissions of MT and SQT depend strongly on temperature (7, 29, 36). Although light-dependence is less certain, Hansen and Seufert (36) suggest that including both light and temperature dependence to describe  $\beta$ -caryophyllene emissions results in a more accurate prediction of short-term variations than using temperature-dependence alone. The

temperature dependence of MT and SQT emissions is described in MEGANv2.02 using the relationship

$$\gamma_T = \exp[\beta(T - T_s)] \quad (3)$$

where  $\beta$  is a temperature dependence parameter [ $\text{K}^{-1}$ ] and  $T_s$  is a standard reference temperature, taken here as 303 K. All of the recent data for which temperature-dependence information was available were combined to estimate values of  $\beta$  without differentiating by PFT. The resulting values (mean  $\pm$  1 $\sigma$ ) are  $\beta = 0.13 \pm 0.07 \text{ K}^{-1}$  for MT ( $n = 59$  plant samples) and  $\beta = 0.16 \pm 0.09 \text{ K}^{-1}$  for SQT ( $n = 46$  plant samples).

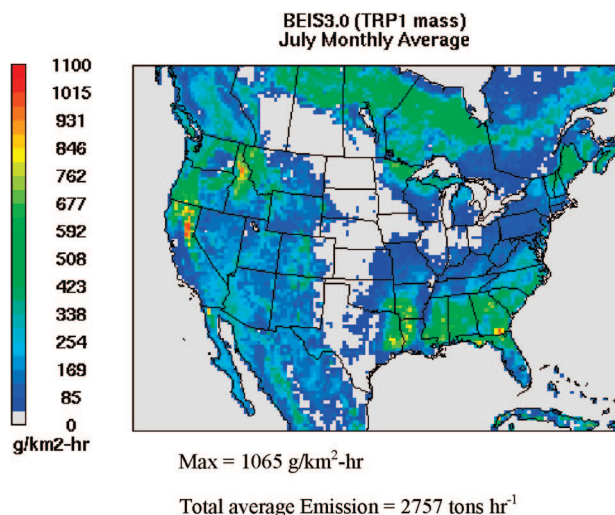
Guenther et al. (16) characterize the light dependence of MT emissions based on two alternative emissions processes: first, light- and temperature-dependent direct emissions from chloroplasts without storage, and second, purely temperature-dependent emissions from storage pools. In MEGANv2.02, a fraction of emissions from the various compounds and categories have a light-dependence. This light-dependence fraction (LDF) modulates emissions according to the fractions assigned to each process

$$ER = \epsilon \gamma_{\text{age}} \gamma_{\text{LAI}} \gamma_T [\gamma_P \text{LDF} + (1 - \text{LDF})] \quad (4)$$

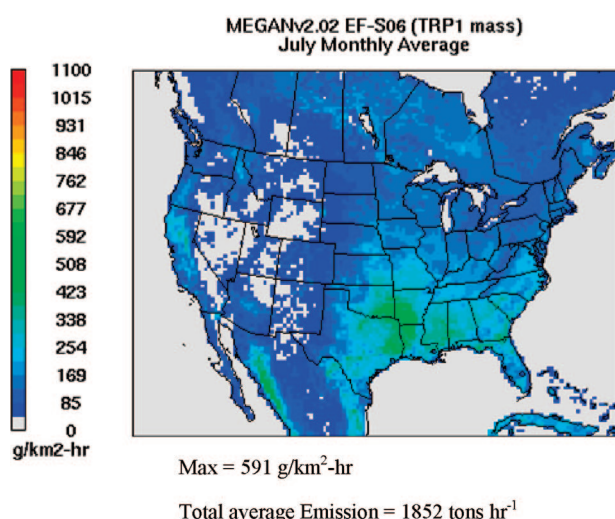
Because of the lack of available data, we assume that 50% of SQT emissions occur through the light- and temperature-dependent route. The fraction of emissions that is light- and temperature-dependent ranges from 5 to 10% for most MT compounds, except for *trans*- and  $\beta$ -ocimene, for which LDF is 0.8.

MEGANv2.02 requires time- and location-specific solar radiation and ambient temperature information to compute the light and temperature dependency of emissions. For this study, meteorological fields for the contiguous United States domain for July 1–31, 2001, and January 1–30, 2002, were derived from fifth generation Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (MM5) output, processed by the Meteorology Chemistry Interface Processor version 2.0 (MCIP2) (Russell and Park, 2003, Georgia Institute of Technology, personal communication). The domain resolution is 36 km, with 147  $\times$  111 cells starting from 40N and 97W, with a vertical resolution of 9 layers.

## Monoterpene Emission



## Monoterpene Emission



**FIGURE 1.** Monthly average of MT emissions fluxes for July estimated from BEIS 3.0 (upper panel) and MEGANv2.02 with EF-S06 (lower panel) for July.

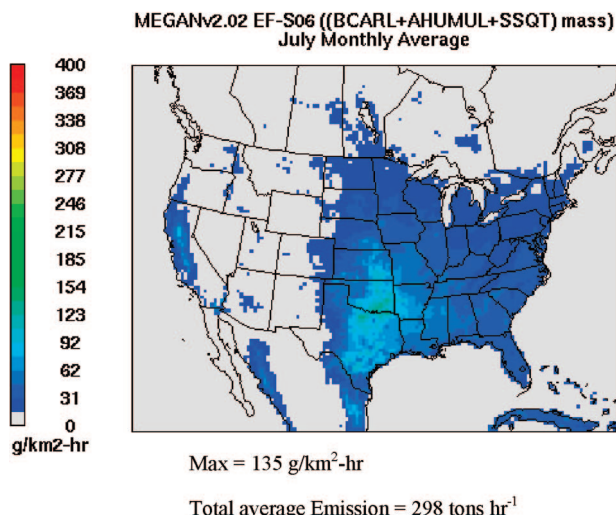
MEGANv2.02 also requires PFT and LAI distributions. PFT distribution data used in this study are based on 2001 MODIS satellite data and are described in Table 4 of Guenther et al. (14) as the MEGAN-P database. The resulting distributions by PFT are shown in the Supporting Information (Figure S1). Data from 2001 were used because they were all that were available at the time. The PFT distributions are assumed to be constant because the changes in land cover are assumed to be negligible over a 1-year period. In contrast, LAI varies both temporally and spatially. In this study, July and January monthly average 2003 LAI data for the domain are estimated from MODIS satellite data (MEGAN-L database in Table 4 of Guenther et al. (14)).

The isoprene EF map of Guenther et al. (14) is used to estimate isoprene emissions. MT and SQT emission factors are based on the EF-S06 and EF-D06 data sets. Emission factors for other VOC are similar to those described by Guenther et al. (15).

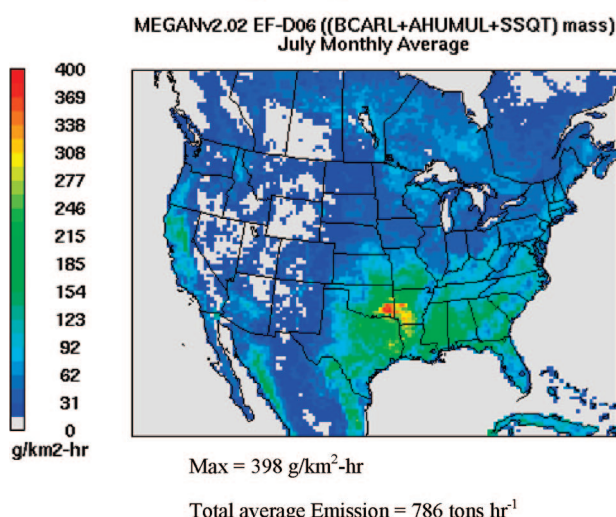
### 3. Results and Discussion

The distributions of the isoprene emissions estimated by MEGANv2.02 and BEIS3.0 are generally similar, though the

## Sesquiterpene Emission



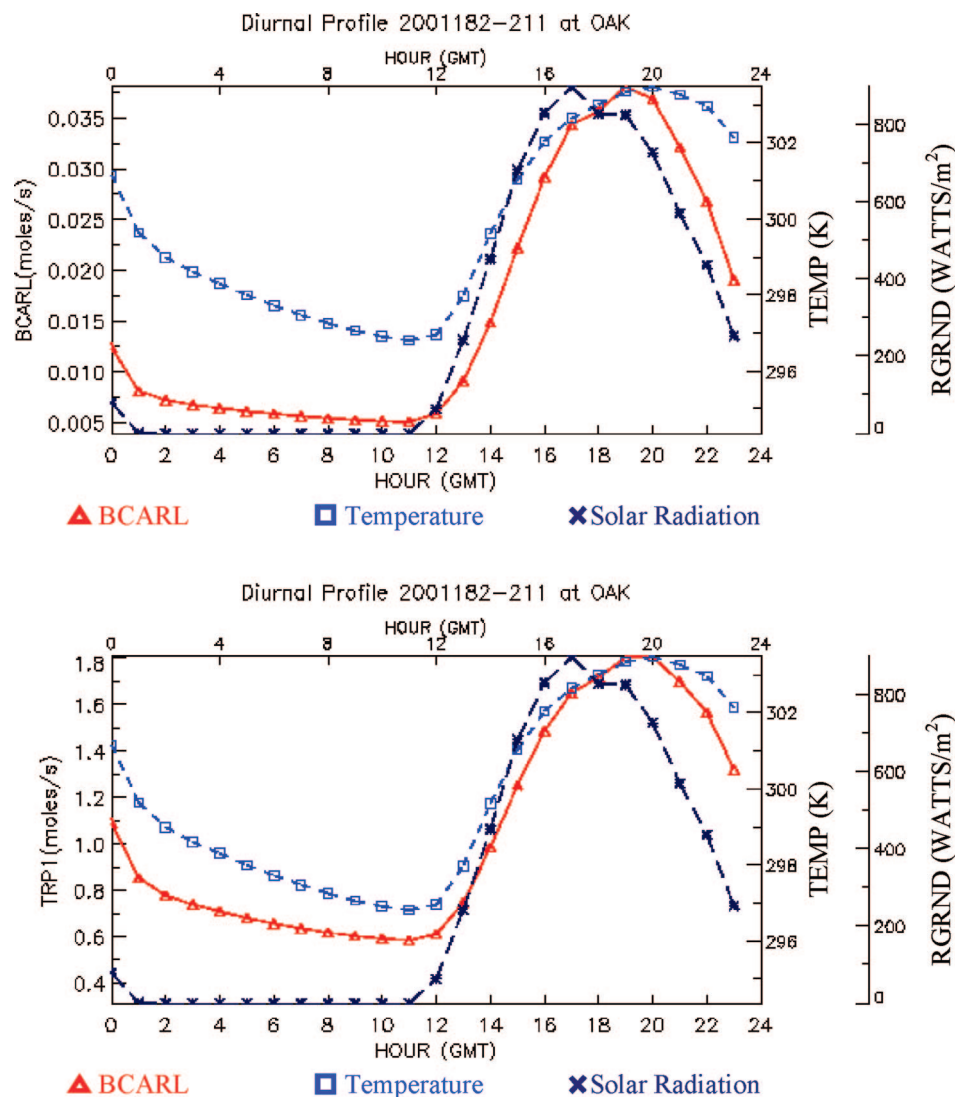
## Sesquiterpene Emission



**FIGURE 2.** Monthly average of SQT emissions fluxes estimated for July from EF-S06 (upper panel) and EF-D06 (lower panel) for July.

maximum monthly average emissions fluxes (concentrated in eastern Oklahoma and western Arkansas) are higher with MEGANv2.02 than BEIS3.0 (Figure S2 in the Supporting Information). Summing emissions over the full modeling domain, the monthly average hourly isoprene emissions rate for July is 7400 tons h<sup>-1</sup> with BEIS3.0 versus 12100 tons h<sup>-1</sup> with MEGANv2.02. In January (results not shown), the average hourly emissions rate is 170 tons h<sup>-1</sup> with BEIS3.0 versus 360 tons h<sup>-1</sup> with MEGANv2.02, with wintertime isoprene emissions in both cases occurring primarily along the California coast, in the southeastern United States, and in Mexico. The differences between MEGANv2.02 and BEIS3.0 isoprene emission estimates are primarily due to the EF used by these models.

Figure 1 shows the monthly average emissions of MT estimated with BEIS3.0 and MEGANv2.02. In this case, the maximum monthly average fluxes, located in the northwestern and southeastern regions of the United States and in Canada, are higher with BEIS3.0 than with MEGANv2.02. Summing emissions over the full modeling domain, the average hourly emissions rate for July is 2800 tons h<sup>-1</sup> with



**FIGURE 3.** Monthly average diurnal profiles for July at Oakmont, MS, for (a)  $\beta$ -caryophyllene emissions, surface temperature, and solar radiation reaching the ground (upper panel) and (b) monoterpene emissions, surface temperature, and solar radiation reaching the ground (lower panel).

BEIS3.0 versus 1850 tons  $\text{h}^{-1}$  with MEGANv2.02. In January (results not shown), the average hourly emissions rate over the full domain is 370 tons  $\text{h}^{-1}$  with BEIS3.0 versus 120 tons  $\text{h}^{-1}$  with MEGANv2.02, with wintertime MT emissions focused along the western and southern borders of the continent. The differences between MEGANv2.02 and BEIS3.0 MT emission estimates are again due primarily to differences in EF.

As shown in Table 1, the NT PFT has the highest MT EF for a given land area, followed by the SB, BT, and GC PFTs, in that order. However, biogenic emissions not only depend on EF but also on plant distribution, light intensity, and temperature. To identify the relative contributions of emissions from different PFTs, we ran MEGANv2.02 with EF-S06 with EF for each of the individual PFT, setting EF of the other PFT to zero. Results from these runs are shown in the Supporting Information, as maps of monthly average emissions for each PFT for July (see the Supporting Information, Figure S3). Over the domain, the average hourly MT contributions from each category are 240 tons  $\text{h}^{-1}$  from BT, 650 tons  $\text{h}^{-1}$  from NT, 420 tons  $\text{h}^{-1}$  from SB, and 540 tons  $\text{h}^{-1}$  from GC. The NT PFT accounts for the majority of MT emissions in southern Canada, and the northwestern and southeastern United States, with the GC PFT accounting for most emissions in the middle of the continent. Even though

the EF for the GC PFT is the lowest of the four, there is significant GC coverage in the middle of the country, causing the GC PFT to be the second largest MT emitter overall.

Figure 2 shows the monthly average emissions of SQT estimated with EF-S06 and EF-D06. Comparisons with BEIS3.0 were not included because it does not have a distinct SQT class (though some modelers have estimated SQT emissions in BEIS as a fixed fraction of MT and other biogenic emissions (37)). As shown in Figure 2, for much of the domain, monthly average SQT emission rates estimated using older BER data from the literature (EF-D06) are much higher than those estimated on the basis of the newer BER measurements (EF-S06). For the modeling domain as a whole, the average hourly SQT emissions rate for July is 300 tons  $\text{h}^{-1}$  with the EF based on only the new measurements, versus 790 tons  $\text{h}^{-1}$  based on the older values. Monthly average emissions rates estimated for January (not shown) are low in both cases; about 30 tons  $\text{h}^{-1}$  for the whole domain with the older data or 12 tons  $\text{h}^{-1}$  with the new data. The new SQT emissions are equal to 16 and 9.4% of the MT emissions for July and January.

The differences in domain-wide total emission rates reflect the sharply higher EF used in EF-D06 for the BT, NT and SB categories. The reasons why the older data are so much higher are not well understood. One possibility may be that

researchers making earlier measurements of SQT emissions might have focused their efforts on plants that were expected to have high emissions, thereby biasing the summarized results. Another possibility is that current researchers have gone to greater lengths to minimize plant disturbances, which are known to induce SQT emissions (7, 8, 10). In contrast to the other PFTs, EF-S06 and EF-D06 use similar EF assignments for the GC category. However, the similarity may be coincidental, as there are few measurements in this PFT category to support the values used in either model. This highlights the need for more measurements from plants in the GC category. Further expansion of the database of SQT emissions measurements is clearly needed, including measurements focused on understanding seasonal variations and responses to environmental conditions and plant disturbance. Natural disturbances could enhance emissions rates above the values being measured in the well equilibrated and undisturbed enclosure experiments in the recent studies (8). In the meantime, we recommend EF-S06 as providing the most up-to-date and representative SQT emissions estimates for the United States.

As with MT, the relative contributions of different PFTs to SQT emissions were determined through a series of four EF-S06 runs that each included emissions from a single PFT. Results for July are shown in the Supporting Information (Figure S4). As indicated in Table 1, based on recent measurements, the PFT with the highest SQT EF is the GC category, followed in descending order by BT, NT and SB. When the EF are combined in MEGANv2.02 with information on plant distributions and environmental conditions, SQT emissions are dominated by the GC category, which produces an average of 174 tons  $\text{h}^{-1}$  over the domain for July. The BT category produces SQT emissions at an average rate of 50 tons  $\text{h}^{-1}$ , mostly in the eastern United States, while the NT category produces SQT emissions at an average rate of 54 tons  $\text{h}^{-1}$ , primarily in the southeastern United States, eastern Canada and the Northwest coast. The peak SQT emissions shown in Figure 2 for July in Oklahoma and Arkansas are from a combination of dense GC cover, high temperatures and high light intensity. The SQT emissions for GC could be biased high due to the EF used for that category, which was estimated from a small number of samples and low variety of plants. Moreover, the density of GC is high in the United States based on the satellite-derived LAI, and this enlarges the contribution from the GC EF.

The article this far has focused on monthly average emissions rates. However, BVOC emissions are expected to vary substantially from hour to hour due to the influence of meteorological factors. Figure 3 shows monthly average diurnal profiles of monoterpene (TRP1) and  $\beta$ -caryophyllene (BCARL) emissions from MEGANv2.02 with EF-S06 at Oak Grove, MS, one of the locations in the SEARCH monitoring network (<http://www.atmospheric-research.com/studies/SEARCH/index.html>). In each figure, emissions are plotted together with surface temperature (1.5 m above ground level) and incoming solar radiation. As expected on the basis of the assumptions used in MEGANv2.02, SQT emissions drop off more sharply at night than MT emissions because a greater fraction of SQT emissions are treated as both light- and temperature-dependent, and because of the stronger temperature-dependence of the SQT emissions.

A wide range of values of the temperature dependence parameter,  $\beta$ , have been reported for both MT and SQT. Values of  $\beta$  from the recent measurements considered in this study ranged from 0.03 to 0.29  $\text{K}^{-1}$  for SQT and  $-0.05$  to 0.35  $\text{K}^{-1}$  for MT. All PFTs in MEGANv2.02 apply the same temperature and light dependencies for SQT. To examine the influence of this parameter on SQT emission estimates, EF-S06 was rerun with  $\beta = 0.07 \text{ K}^{-1}$  and 0.25  $\text{K}^{-1}$ , corresponding to a range of  $\pm$  one standard deviation from the

mean value of 0.16  $\text{K}^{-1}$ . The results of these sensitivity analysis cases for July are shown in the Supporting Information (Figure S5). Increasing the value of  $\beta$  to 0.25  $\text{K}^{-1}$  intensifies the emissions in the portion of the domain with average temperatures above the base temperature of 303 K, and lowers the emissions in areas with lower temperatures. Overall, emissions in this case are about the same as in the base case, averaging 307 tons  $\text{h}^{-1}$ . In the opposite case, reducing  $\beta$  to 0.07  $\text{K}^{-1}$  increases the emissions in lower temperature areas and decreases them in areas with higher temperatures. Although the case with  $\beta = 0.07 \text{ K}^{-1}$  has lower peak emissions than the other two cases, the total emissions for the domain are highest in this case, averaging 386 tons  $\text{h}^{-1}$ . This is due to the increase in emissions over the large portion of the domain with relatively low temperatures. The change of  $\beta$  by 56% ( $\pm\sigma$ ) changes the total emission by 3% to 30% for July and 48% to 240% for January. Improved understanding of temperature dependencies, including refined estimates of variations across plant species, would clearly improve the SQT emissions estimates.

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## Supporting Information Available

Table S1 and Figures S1–S5 (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) Liao, H.; Henze, D. K.; Seinfeld, J. H.; Wu, S.; Mickley, L. J. Biogenic secondary organic aerosol over the United States: Comparison of climatological simulations with observations. *J. Geophys. Res.* **2007**, *112*, D06201.
- (2) Tsigaridis, K.; Kanakidou, M. Global modeling of secondary organic aerosol in the troposphere: a sensitivity analysis. *Atmos. Chem. Phys.* **2003**, *3*, 1849–1869.
- (3) Henze, D.; Seinfeld, J. H. Global secondary organic aerosol from isoprene oxidation. *Geophys. Res. Lett.* **2006**, *33*, L09812.
- (4) Griffin, R. J.; Cocker, D. R.; Flagan, R. C.; Seinfeld, J. H. Organic aerosol formation from the oxidation of biogenic hydrocarbons. *J. Geophys. Res.* **1999**, *104*, 3555–3567.
- (5) Griffin, R. J.; Cocker, D. R.; Seinfeld, J. H.; Dabdub, D. Estimate of global organic aerosol from oxidation of biogenic hydrocarbons. *Geophys. Res. Lett.* **1999**, *26*, 2721–2724.
- (6) Joulain, D.; Konig, W. A. *Atlas of Spectral Data of Sesquiterpene Hydrocarbons*; EB-Verlag: Hamburg, Germany, 2001.
- (7) Helmig, D.; Ortega, J.; Duhl, T.; Tanner, D.; Guenther, A.; Harley, P.; Wiedinmyer, C.; Milford, J.; Sakulyanontvittaya, T. Sesquiterpene emissions from pine trees - identifications, emission rates and flux estimates for the contiguous United States. *Environ. Sci. Technol.* **2007**, *41*, 1545–1553.
- (8) Duhl, T. R.; Helmig, D.; Guenther, A. Sesquiterpene emissions from vegetation: a review. *Biogeosci. Discuss.* **2007**, *4*, 3987–4023.
- (9) Matsunaga, S. N.; Guenther, A. B.; Greenberg, J. P.; Potosnak, M.; Papiez, M.; Hiura, T.; Kato, S.; Nishida, S.; Harley, P.; Kajii, Y. Sesquiterpene and oxygenated sesquiterpene emission measurements from desert and forest vegetation using a liquid extraction technique. Manuscript submitted to *Atmos. Environ.*
- (10) Papiez, M. R. The impacts of reactive terpene emissions from plants on air quality in Las Vegas, NV. M.S. Thesis, University of Reno, Reno, NV, 2007.

- (11) Ortega, J.; Helmig, D.; Daly, R. W.; Tanner, D. M.; Guenther, A. B.; Herrick, J. D. Approaches for quantifying reactive and low volatility biogenic organic compound emissions by vegetation enclosure techniques — Part B: Applications for quantifying monoterpene and sesquiterpene emission rates. Manuscript submitted to *Chemosphere*.
- (12) Wiedinmyer, C.; Guenther, A.; Harley, P.; Hewitt, C. N.; Geron, C.; Artaxo, P.; Steinbrecher, R.; Rasmussen, R. Global Organic Emissions from Vegetation. In *Emissions of Atmospheric Trace Compounds*; Granier, C., Artaxo, P., Reeves, C. E., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 2004.
- (13) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. Organic aerosol and global climate modeling: a review. *Atmos. Chem. Phys.* **2005**, *5*, 1053–1123.
- (14) Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron, C. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* **2006**, *6*, 3181–3210.
- (15) Guenther, A.; Geron, C.; Pierce, T.; Lamb, B.; Harley, P.; Fall, R. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. *Atmos. Environ.* **2000**, *34* (12–14), 2205–2230.
- (16) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* **1995**, *100*, 8873–8892.
- (17) Kinnee, E.; Geron, C.; Pierce, T. United States land use inventory for estimating biogenic ozone precursor emissions. *Ecol. Appl.* **1997**, *7*, 46–58.
- (18) Sakulyanontvittaya, T. Secondary Organic Aerosol from Sesquiterpenes and Other Biogenic Emissions in United States. Ph.D. Thesis, University of Colorado, Boulder, CO, 2007.
- (19) Carter, W. P. L. *Implementation of the SAPRC-99 Chemical Mechanism into the Models-3 Framework. Report to the U.S. Environmental Protection Agency*; U.S. EPA: Washington, D.C., 2000.
- (20) Stockwell, W. R.; Middleton, P.; Chang, J. S. The second generation regional acid deposition model chemical mechanism for regional air quality modeling. *J. Geophys. Res.* **1990**, *95*, 16,343–16,367.
- (21) Stockwell, W. R.; Kirchner, F.; Kuhn, M. A new mechanism for regional atmospheric chemistry modeling. *J. Geophys. Res.* **1997**, *102*, 25,847–25,879.
- (22) Zaveri, R. A.; Peters, L. K. A new lumped structure photochemical mechanism for large-scale applications. *J. Geophys. Res.* **1999**, *104*, 30,387–30,415.
- (23) Ortega, J.; Helmig, D.; Guenther, A.; Harley, P.; Pressley, S.; Vogel, C. Flux Estimates and OH Reaction Potential of Reactive Biogenic, Volatile Organic, Compounds (BVOCs) from A Mixed Northern Hardwood Forest. *Atmos. Environ.* **2007**, *41*, 5479–5495.
- (24) Agelopoulos, N. G.; Chamberlain, K.; Pickett, J. A. Factors affecting volatile emissions of intact potato plants, *Solanum tuberosum*: variability of quantities and stability of ratios. *J. Chem. Ecol.* **2000**, *26*, 497–511.
- (25) Arey, J.; Crowley, D. E.; Crowley, M.; Resketo, M.; Lester, J. Hydrocarbon emissions from natural vegetation in CA South-Coast-Air-Basin. *Atmos. Environ.* **1995**, *29*, 2977–2988.
- (26) Arimura, G.; Huber, D. P. W.; Bohlmann, J. Forest tent caterpillars (*Malacosoma Disstria*) induce local and systemic diurnal emissions of terpenoid volatiles in hybrid poplar (*Populus Trichocarpa* × *Deltoides*): cDNA cloning, functional characterization, and patterns of gene expression of (–)-Germacrene D Synthase, PtdTPS1. *Plant J.* **2004**, *37*, 603–616.
- (27) Ciccio, P.; Brancaloni, E.; Frattoni, M.; Di Palo, V.; Valentini, R.; Tirone, G.; Seufert, G.; Bertin, N.; Hansen, U.; Csiky, O.; Lenz, R.; Sharma, M. Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes. *J. Geophys. Res.* **1999**, *104*, 8077–8094.
- (28) Hakola, H.; Laurila, T.; Lindfors, V.; Hellen, H.; Gaman, A.; Rinne, J. Variation of the VOC emission rates of birch species during the growing season. *Boreal Env. Res.* **2001**, *6*, 237–249.
- (29) Hansen, U.; Seufert, G. Terpenoid emission from *Citrus sinensis* (L.) OSBECK under drought stress. *Phys. Chem. Earth B* **1999**, *42*, 681–687.
- (30) Helmig, D.; Klinger, L. F.; Guenther, A.; Vierling, L.; Zimmerman, P.; Geron, C. Biogenic volatile compound emissions. I. Identifications from three sites in the U.S. *Chemosphere* **1999**, *38*, 2163–2187.
- (31) Helmig, D.; Klinger, L. F.; Guenther, A.; Vierling, L.; Zimmerman, P.; Geron, C. Biogenic volatile compound emissions. II. flux potentials from three sites in the U.S. *Chemosphere* **1999**, *38*, 2189–2204.
- (32) Konig, G.; Brunda, M.; Puxbaum, H.; Hewitt, C. N.; Duckham, S. C.; Rudolph, J. Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species. *Atmos. Environ.* **1995**, *29*, 861–874.
- (33) Martin, D. M.; Gershenson, J.; Bohlmann, J. Induction of volatile terpene biosynthesis and diurnal emission by methyl jasmonate in foliage of Norway spruce. *Plant Physiol.* **2003**, *132*, 1586–1599.
- (34) Schuh, G.; Heiden, A. C.; Hoffmann, Th.; Kahl, J.; Rockel, P.; Rudolph, J.; Wildt, J. Emissions of volatile organic compounds from sunflower and beech: dependence on temperature and light intensity. *J. Atmos. Chem.* **1997**, *27*, 291–318.
- (35) Zhang, Q.; Birgersson, G.; Junwei, Z.; Lofstedt, C.; Lofqvist, J.; Schlyter, F. Leaf volatiles from nonhost deciduous trees: variation by tree species, season, and temperature, and electrophysiological activity in *Ips Typographus*. *J. Chem. Ecol.* **1999**, *25*, 1923–1943.
- (36) Hansen, U.; Seufert, G. Temperature and light dependence of  $\beta$ -caryophyllene emission rates. *J. Geophys. Res.* **2003**, *108*, 4801.
- (37) Morris, R. E.; Koo, B.; Guenther, A.; Yarwood, G.; McNally, D.; Tesche, T. W.; Tonnesen, G.; Boylan, J.; Brewer, P. Model sensitivity evaluation for organic carbon using two multipollutant air quality models that simulate regional haze in the southeastern United States. *Atmos. Environ.* **2006**, *40*, 4960–4972.

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