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Flux estimates and OH reaction potential of reactive biogenic volatile organic compounds (BVOCs) from a mixed northern hardwood forest

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Abstract

Diurnal branch-level emission rates of biogenic volatile organic compounds (BVOC) including isoprene, monoterpenes (MT), and sesquiterpenes (SQT) were determined at the University of Michigan Biological Station for the tree species red maple (*Acer rubrum*), red oak (*Quercus rubra*), paper birch (*Betula papyrifera*), white pine (*Pinus strobus*), and big tooth aspen (*Populus grandidentata*). These emission rates were combined with detailed biomass distribution and meteorological data and incorporated into the canopy model, model of emissions of gasses and aerosols from nature (MEGAN), for estimating whole-canopy fluxes of isoprene. The modeled half-hour fluxes ($mg\,C\,m^{-2}\,h^{-1}$) and cumulative seasonal fluxes ($mg\,C\,m^{-2}$) compared favorably with results from direct, canopy-level eddy covariance (EC) isoprene measurements; modeled cumulative seasonal flux deviated less than 30% from the EC results. Significant MT emissions were found from four of the five tree species. MT emissions from three of these were both light- and temperature-dependent and were approximately one order of magnitude greater than light-independent MT emissions. SQT emissions were identified from three of the five tree species. The model was modified to incorporate SQT and both light-dependent and light-independent MT emissions for determining fluxes. Isoprene comprised >95% of the total terpenoid flux with MT and SQT comprising 4% and 0.3%, respectively. The average cumulative fluxes (in $mg\,C\,m^{-2}$) from June through September were 2490 for isoprene, 105 for MT, and 7 for SQT. A simple box model analysis was used to estimate the contribution of the isoprene, MT, and SQT emissions to the total OH reactivity. These results confirm that isoprene dominates OH reactions especially during daytime hours. Emissions of reactive MT and SQT increase the BVOC+OH reactivity, but are still lower than estimates of BVOC fluxes at this site necessary for affecting OH reactivity to the significant degree suggested by recent reports.

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Keywords: VOC; Oxidant; Monoterpene; Sesquiterpene; Fluxes; Biogenic emission modeling; Isoprene

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1. Introduction

The role of biogenic volatile organic compounds (BVOCs) in atmospheric chemistry has been widely discussed and summarized (e.g. Fehsenfeld et al., 1992; Fuentes et al., 2000; Monson and Holland, 2001). In addition to their role in tropospheric ozone chemistry, there is increasing evidence that significant fractions of secondary organic aerosols are composed of BVOC reaction products (Bonn et al., 2004; Claeys et al., 2004a,b; Lim et al., 2005). Studies of oxidant chemistry in forest canopies have suggested that there could be large emissions of reactive BVOC that are not detected in ambient air. These highly reactive species are suspected to play significant roles in modifying ozone and OH concentrations within forest canopies. Faloona et al. (2001) found that OH radical concentrations in a Michigan (MI) forest did not decay at night as rapidly as expected based on known reaction pathways and ambient BVOC measurements. They speculated that there must be another OH source, possibly the ozonolysis of biogenic terpenes. Di Carlo et al. (2004) found a missing OH reactivity (defined as the calculated reactivity minus the measured reactivity) from the same MI forest. They determined that this missing OH reactivity was proportional to $e^{\beta T}$ where the value of β was ∼0.1. This relationship was nearly identical to the way in which monoterpene (MT) vapor pressures and emissions increase exponentially with temperature. The investigators suggested that this phenomenon could be due to emissions of highly reactive biogenic terpenes that could not be detected using standard sampling and analysis techniques. Goldstein et al. (2004) found that a thinning experiment in a California (CA) ponderosa pine forest greatly enhanced MT emission rates as well as ozone losses. They suggested that although there were hundreds of biogenic compounds measured at the branch level, only a fraction were observed in forest air and most were likely preferentially lost due to chemical reactions rather than transported out of the canopy. In the same CA forest 3 years later, Holzinger et al. (2005) used proton transfer reaction mass spectrometry (PTR-MS) to measure relatively high concentrations of heavy ions (e.g. $m/z = 113$) that had spatial and temporal distributions consistent with expected oxidation products of biogenic terpenes. A common hypothesis in these recent studies is that there are unaccounted-for reactive biogenic emissions from forest canopies that react with OH or

ozone (and thus produce OH) that have not been adequately accounted for. With increasing interest in oxidant chemistry and aerosol formation from forested regions, accurate measurements of the biogenic precursors are necessary for inclusion into atmospheric chemistry and transport models. More conclusive BVOC measurements that substantiate the current state of knowledge regarding these processes would be valuable.

Many compounds emitted by forest vegetation, such as reactive MT and sesquiterpenes (SQT), are reactive with oxidants and contribute to aerosol nucleation and growth (Bonn and Moortgat, 2003; Lee et al., 2006). These processes can occur within the canopy rendering many commonly used above-canopy flux measurements infeasible. Therefore, in order to estimate landscape fluxes for many of these compounds, it is necessary to measure emissions at the leaf or branch level and scale these values to the canopy level by using detailed information on leaf and canopy characteristics.

In this study, emission rates of isoprene, MT, and SQT were determined from intact leaves and branches from naturally growing vegetation at a mixed northern hardwood forest in Michigan. These emissions were then used in conjunction with the canopy component of a global biogenic emission model (MEGAN = model of emissions of gasses and aerosols in nature; Guenther et al., 2006) to estimate canopy-level fluxes. Eddy covariance (EC) isoprene fluxes have been measured at this site since 1999 (Pressley et al., 2005) and were used to compare the two techniques. This, in turn, provided a means for estimating the uncertainties in extending the scaling technique to other compounds. Fluxes of these compounds were then used to estimate the BVOC + OH reaction potentials and to determine if additional insight could be gained by comparing results from these emission studies with other recent reports from direct ambient observations.

2. Experimental

2.1. Site description

The study site was the University of Michigan Biological Station (UMBS) near Pellston, MI, USA (45°30′N, 84°42′E). The tree species sampled for this scaling study composed the majority (∼95%) of the biomass around two flux towers on the property. The canopy has the biomass composition

Table 1
Canopy characteristics and model inputs for estimating landscape fluxes at UMBS. Lower and upper bound emission estimates for the highest MT emitting tree species are separated by a slash (/). Values of β for light-dependent MT are underlined

Tree species	Specific leaf mass[a]	Individual leaf area index (LAI)	% of LAI	Isoprene BER (branch)[b]	Estimated isoprene BER (leaf)[c]	Branch MT BER (temp)[d]	Leaf MT BER (light + temp)[e]	SQT BER	$\beta(MT)$[f]	$\beta(SQT)$
	($g\,m^{-2}$)	($m^2\,m^{-2}$)	(%)	($\mu gC\,g^{-1}hr^{-1}$)	($\mu gC\,g^{-1}h^{-1}$)	($\mu gC\,g^{-1}h^{-1}$)	$\mu gC\,g^{-2}h^{-1}$	$\mu gC\,g^{-1}h^{-1}$	($°C^{-1}$)	($°C^{-1}$)
Populus grandidentata	79.2 (0.14)	1.10	28.9	46.3 (21.5)	81.0	<0.1	<0.01	<0.01	n/a	n/a
Quercus rubra	71.9 (1.37)	1.01	26.6	53.5 (29.7)	93.6	<0.1	3.4/5.3	0.025	<u>0.16</u>	0.17
Acer rubrum	67.8 (1.51)	0.73	19.1	<1.0	<1.0	<0.1	0.88	0.028	<u>0.20</u>	0.16
Pinus strobus	62.6 (0.69)	0.42	11.0	<1.0	<1.0	0.36/1.4	<0.01	0.35	0.10	0.15
Betula papyrifera	71.0 (1.39)	0.33	8.7	<1.0	<1.0	0.50/0.70	4.4/7.0	<0.01	<u>0.29</u>, 0.17	n/a
Total		3.59	94.3							

[a]Standard deviations ($N = 4$) of the specific leaf masses are in parentheses.

[b]Mean basal emission rate (BER) of branch enclosure experiments performed during 2003 and 2005. Standard deviations of isoprene emission rates are listed in parentheses.

[c]The leaf-level BER shown here were obtained by multiplying branch-level BER by 1.75 according to recommendations from Guenther et al. (1994).

[d]Basal emission rate for individual monoterpenes that were found to be dependent on temperature only.

[e]Basal emission rate for individual monoterpenes that were found to be dependent on light and temperature. The leaf-level emissions rates shown here were obtained by multiplying the branch-level BER by 1.75 following the same procedure as for isoprene (see footnote c).

[f]Underlined numbers indicate values obtained by regression of emission rate vs. temperature at light levels (PPFD) greater than $500\,\mu mol\,m^{-2}\,s^{-1}$. *Betula papyrifera* exhibited both light-dependent and temperature only emissions of MT which are considered separately (separated by a comma).

listed in Table 1. The overstory leaf area index (LAI) for this site is $3.8 \, m^2 \, m^{-2}$ with a mean canopy height of 22 m. Long-term EC isoprene fluxes were measured from the UMBS-flux tower from 1999 until 2002 and on the PROPHET tower since 2003. More detailed information that describes this site and the two flux towers can be found in Carroll et al. (2001) and Schmid et al. (2003).

2.2. Materials and methods

Branch-level BVOC emission rates (generally measured between 15 June and 15 August during the 2003 and 2005 growing seasons) were determined from red maple (*Acer rubrum*), red oak (*Quercus rubra*), paper birch (*Betula papyrifera*), white pine (*Pinus strobus*), and big tooth aspen (*Populus grandidentata*). Specific leaf mass and LAI values listed in Table 1 represent averages from 26 litter traps ($0.18 \, m^2$ per trap) in the 1.3 ha plot (60 m radius) within the fetch of the UMBS-flux tower. These five species account for approximately 95% of the overstory leaf area, with the two dominant isoprene emitters (*Q. rubra* and *P. grandidentata*) contributing ~56% of the total (see Table 1). The primary emphasis of the 2003 experiments was to obtain branch-level isoprene emission rates. Dynamic enclosures (described below) were used to contain the biomass, as 200 ml samples from the enclosures were collected onto multi-stage adsorbent cartridges (Air Toxics, Perkin Elmer) using a gas-tight glass syringe. These were analyzed on-site within 24 h using thermo-desorption gas chromatography with flame ionization detection (GC-FID). Calibration of this GC-FID was performed using a 213 ppbv 2,2-dimethyl-hexane standard (Scott Specialty Gasses, Longmont, CO) at least twice per week. Additional samples were collected in 2003 for verifying MT identifications. This was done by collecting two emission samples from each tree species at UMBS and storing the adsorbent catridges on ice. They were later analyzed in our laboratory using the GC-FID-mass spectrometry (MS) system described by Pollmann et al. (2005). Positive identifications of the different MT and SQT were achieved using a combination of matching mass spectra to a NIST library and comparing GC retention times to those published by Adams (1989).

In 2005, the primary objective was to measure diurnal profiles of MT and SQT. Sampling and analysis were performed at the site using a field-deployable system with simultaneous GC-FID and GC-MS. The two-stage sampling/analysis system consisted of two pairs of cartridges containing a combination of solid adsorbents in series to trap BVOC in the volatility range from C_5 (isoprene) to C_{15} (SQT). The first stage was used to collect hourly samples at a sample flow rate of $150 \, ml \, min^{-1}$. This resulted in sample volumes of $\sim 7-12 \, l$ (for MT and SQT). The first stage traps were heated and analytes were transferred (under H_2 flow) to second-stage microtraps (cooled to $-15 \,^\circ C$) with subsequent rapid thermal desorption and injection onto two pairs of chromatography columns. The entire process of sample collection/focusing, thermal desorption, chromatography, and data collection was performed in the field, thus eliminating the need for transferring and storing samples. Ozone was removed from the sampling stream using a combination of MnO_2-coated copper screens and sodium thiosulfate-impregnated glass-fiber filters. The detection limit for MT and SQT using these techniques was $\sim 1 \, ng \, C$. This equates to a mixing ratio of $\sim 2.5 \, pptv$ for MT and SQT in a 10 l gas sample collected from vegetation emitting at a rate of $0.01 \, \mu g \, C \, g^{-1} h^{-1}$ (using a typical 50 l branch enclosure under a sweep flow rate of $15 \, l \, min^{-1}$). The estimated uncertainties of these emission measurements are $\pm 20\%$ of MT and $\pm 35\%$ for SQT.

Dynamic enclosures were placed on live, sunlit branches during the middle of the growing seasons as indicated above. The bag enclosed a volume of $\sim 50 \, l$ and was made of 0.05 mm Teflon film (FEP), which is 95% transparent to photosynthetic photon flux density (PPFD). Leaf temperature, enclosure air temperature, relative humidity, PPFD, and ambient ozone concentrations were measured every 10 s, and average values were recorded every minute. A high-capacity, $55 \, l \, min^{-1}$ oil-free pump (Medo Corporation, Hannover Park, IL) was used to provide sweep air through the enclosure at $15 \, l \, min^{-1}$. Background hydrocarbons were removed by placing a 0.75 l steel container filled with charcoal (Fisher brand 05-685A, 6–14 mesh) in-line. A specially designed set of MnO_2-coated copper screens (OBE Corporation, Fredericksberg, TX) were used to eliminate ozone from the sweep air. Sodium thiosulfate-impregnated glass-fiber filters were used immediately upstream of the adsorbent cartridges as an additional precaution against potential BVOC sampling losses from reactions with ozone (Helmig, 1997). A quantitative, ppm-level internal standard composed of five aromatic compounds was added to the enclosure sweep air at

5 ml min⁻¹ to monitor the recoveries of compounds of varying volatilities. Disturbances to the leaf and needle surfaces were minimized as much as possible. Enclosures were allowed to equilibrate approximately 24 h prior to sampling. Experiments were typically performed for 2–3 days so that diurnal emission profiles could be established. Leaf areas of fresh leaves and needles were measured using a leaf area meter (Licor 3100C, Lincoln, NE) equipped with a standard lens as well as a fine resolution lens (which was necessary for pine needles). Dry weights were determined after placing leaves (or needles) in a drying oven at 70 °C for 24 h. Sunlit leaves from the top of the canopy were used to determine specific leaf density for use in the model. During the 2005 sampling period, emissions were also measured with a leaf cuvette using the procedures described in Harley et al. (1996). Although the quantitative data for this study were taken from the branch enclosure experiments, the leaf cuvette was invaluable in demonstrating the light dependencies of BVOC emissions as light and temperature could be independently controlled.

A fast isoprene sensor (FIS) (Guenther and Hills, 1998) was used to measure isoprene concentrations for the EC isoprene flux calculations. The Teflon inlet line (1.27 cm ID) and sonic anemometer (Applied Technologies, Inc., Longmont, CO) were co-located towards the NW at 31 m above the ground (1.4 times canopy height) on the UMBS-flux tower. Sample air was pumped to the FIS located in a shelter at the bottom of the tower. Further details on the isoprene flux measurements are provided in Pressley et al. (2005). These fluxes were used to verify the accuracy of the scaling technique.

2.3. Model description

The canopy component of a global biogenic emission model (MEGAN; Guenther et al., 2006) was used for estimating landscape fluxes of isoprene, MT, and SQT. MT and SQT emissions are primarily driven by temperature, which can be parameterized by a β-factor (i.e. ER $\propto e^{\beta T}$). Branch-level emission rate measurements were plotted as a function of temperature and an exponential curve fit was used to determine the β-factors for each terpenoid class and each tree species (see Table 1). Basal emission rates are defined as those occurring at a temperature of 30 °C and a PPFD of 1000 μmol m⁻² s⁻¹. These rates as well as β-values from the species studied at UMBS are listed in

Table 1. *Q. rubra* and *A. rubrum* exhibited light-dependent MT emissions while *P. strobus* exhibited MT emissions that were only a function of temperature. *B. papyrifera* was found to exhibit both light-dependent and light-independent MT emissions. Since light and temperature were co-dependent variables in these experiments, the basal emission rates and β-factors for light-dependent MT emissions were obtained by first normalizing the emissions to standard light conditions and then plotting the remaining values against temperature and finding the best fit exponential regression curve through the data. The normalization was accomplished by dividing the original emission rates by the light correction factor for isoprene given in Guenther et al. (1993). SQT were emitted from three of the five tree species surrounding the tower as shown in Table 1. However, other native tree species in the area (but not present in the footprint of the PROPHET tower) were also found to be SQT emitters. These include balsam fir (*Abies balsamea*), white spruce (*Picea glauca*), jack pine (*Pinus banksiana*), and red pine (*Pinus resinosa*). American beech (*Fagus grandifolia*) contributes ∼5% of the leaf area in the flux footprint and was determined to be a negligible BVOC emitter in earlier screening experiments. Therefore, the leaf area contribution from American beech was included in the scaling study, but assigned an emission rate of zero. The total BVOC flux was estimated as

$$\text{Flux}_{\text{BVOC,total}} = \sum_i \sum_j \left[\sum_{k=1}^{5} F_{i,j,k} \right], \qquad (1)$$

where i represents the various emitting species in the canopy (e.g. pine, oak, aspen, etc.), j represents the individual BVOC (isoprene, MT, SQT, etc.), and k represents each of five vertical layers within the canopy (see below). Therefore, the model was run for each i, j combination independently, and the results were added. Other model inputs include absolute humidity (g H_2O per kg air), wind speed (m s⁻¹), canopy type (conifer forest, mixed forest, broadleaf forest, etc.), air temperature (°C), PPFD (μmol m⁻² s⁻¹), latitude, time of day, drought index, and day of year (DOY). With these inputs, emissions were calculated for shade and sun leaves at each of five levels within the canopy based on vertical temperature changes and light attenuation. Half-hourly meteorological data from 2001 were used for this analysis and the results were compared to EC fluxes for the same time period. The 2001

data were representative of all the available years in terms of date of last frost, leaf-out date, and average daily and cumulative seasonal isoprene fluxes.

Branch-level basal emission rates from the two dominant isoprene emitters varied between 10 and $90\,\mu g\,C\,g^{-1}\,h^{-1}$. The average emission rates were $53.5\,\mu g\,C\,g^{-1}\,h^{-1}$ for *Q. rubra* ($N = 14$, $\sigma = 29.7$, median $= 56.1$), and $46.3\,\mu g\,C\,g^{-1}\,h^{-1}$ for *P. grandidentata* ($N = 10$, $\sigma = 21.5$, median $= 44.9$). Because of self-shading and varying leaf orientations that occur within a branch enclosure, isoprene emission rates are lower than what would be obtained if all leaves were exposed to a PPFD of $1000\,\mu mol\,m^{-2}\,s^{-1}$. Therefore, the average branch-level isoprene emission rates were multiplied by a scaling factor (1.75) as described in Guenther et al. (1994) to correct for this effect. The resulting values constitute the leaf-level emission rates used in the model (sixth column of Table 1). Since leaf-level emission rates are required as model inputs, this scaling factor was applied to both branch-level isoprene and light-dependent MT emissions. This was not necessary for light-independent emissions, where leaf orientation does not affect emission rates.

The branch-level MT and SQT emission rates determined from the 2005 measurements were used to model whole-canopy fluxes. Emissions of MT were always exponentially dependent on temperature. Significant light-dependent MT emissions were also observed from the broadleaf species. In the following discussions, it is noteworthy that when individual MT are referred to as being "light-dependent" or "light-independent", the temperature dependence always exists. To account for light-dependent MT emissions, the model was modified to include a light response similar to the isoprene light response algorithms developed by Guenther et al. (1991). Since MT emissions from *B. papyrifera* were found to be both light-dependent and light-independent, they were treated separately. The dominant light-dependent MT emitted from all deciduous species was *trans*-ocimene, primarily from *Q. rubra* and *B. papyrifera*. The average of the β-factors was $0.10\,°C^{-1}$ for the light-independent MT and $0.16\,°C^{-1}$ for the SQT emissions (Table 1). *P. strobus* (white pine) exhibited the highest SQT and light-independent MT emissions. The most abundant MT from *P. strobus* (accounting for ~74% of the total MT emissions) were α-pinene, β-pinene, camphene, d-limonene, and *para*-cymene. The average SQT speciation from

P. strobus included β-cubebene, α-gurjunene, δ-cadinene, α-cedrene, α-humulene, β-selinene, and α-muurolene, with the last three accounting for 77% of the total SQT emissions from this tree species. Other reactive SQT (α-farnesene and caryophyllene) were identified in emission samples from *Q. rubra*.

After estimating whole-canopy BVOC fluxes from this forest site, the OH reactivities from the various terpenoid compounds were estimated. Rate constants for reaction with OH (k_{OH}) were derived from published values or by estimates based on molecular structure. For modeling purposes, a value of $8.7 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ was calculated using a weighted average of the rate constants from the major MT identified for light-independent MT+ OH reactions. Similarly, a value of $k_{OH} = 25 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ was used for the light-dependent MT + OH and SQT + OH reaction rate coefficients. A value of $k_{OH} = 9.97 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ was chosen for isoprene. Further discussion regarding the selection of these values is included in Appendix A.

3. Results and discussion

3.1. Isoprene

Measured and modeled emission rates of all compounds (isoprene, MT, and SQT) are expressed in $\mu g\,C\,g^{-1}$ (biomass) h^{-1} and whole-canopy fluxes are given in either $\mu g\,C\,m^{-2}\,h^{-1}$ for half-hour averages or in $mg\,C\,m^{-2}$ (ground area) for cumulative multi-day fluxes. The available meteorological and isoprene flux data for 2001 start at DOY 158 (7 June) and end at DOY 267 (24 September). Fig. 1 A shows the modeled isoprene fluxes from DOY 180 (29 June) through DOY 200 (19 July) together with the EC measurements. This time period was chosen as representative of midsummer values with a range of different meteorological conditions, including warm cloud-free conditions as well as days in which there was significant rain. In addition, this period had relatively few periods of missing data. The modeled uncertainty range was obtained by using the mean $\pm 1\sigma$ values for basal emission rates for the isoprene emitters as indicated in Table 1. The average of the modeled results is within the measured flux uncertainty bounds (estimated to be less than $\pm 40\%$; Pressley et al., 2005). A close comparison of the two data sets shows that the onset of isoprene fluxes from the forest canopy occurs later in the day than is predicted by the
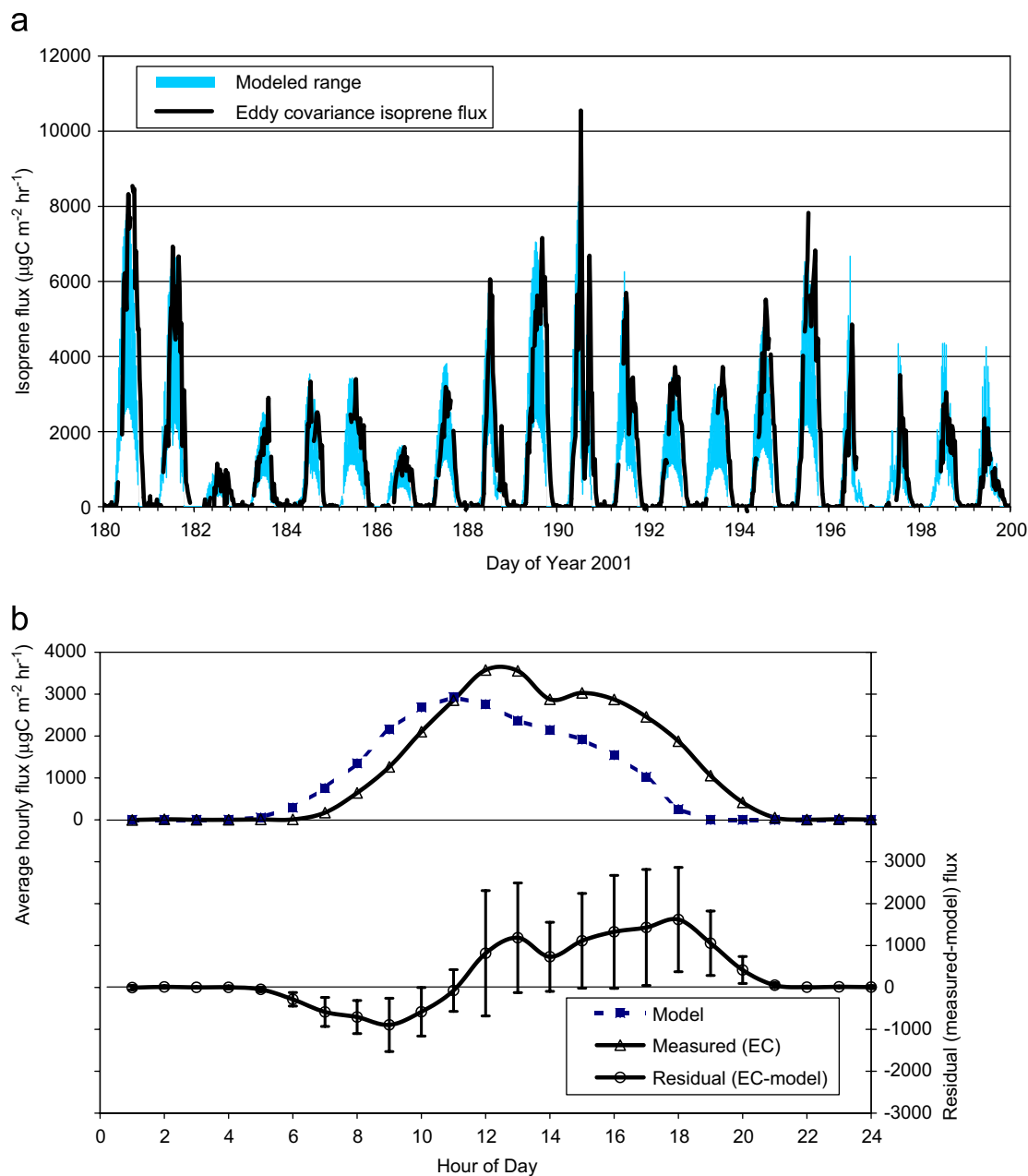
a

b

Fig. 1. (a) (Top): mean modeled half-hour isoprene fluxes with comparison to eddy covariance fluxes for DOY 180–200, 2001 (9 July–19 July). The shaded area indicates the range of modeled results using the mean $\pm 1\sigma$ leaf-level basal emission rates for *Quercus rubra* and *Populus grandidentata*. (b) (Bottom): average hour residual (measured–modeled) fluxes for each hour during the same period shown in (a). Error bars represent ± 1 standard deviation.

model. Fig. 1b shows the hourly means of these measured and modeled fluxes as well as the difference (between measured and modeled fluxes) during these 20 days. The model generally overpredicts the flux during the mornings and underpredicts the fluxes in the afternoons, which is a similar finding as that reported by Sillman et al. (2002).

Isoprene emissions are controlled by both environmental (light and temperature) as well as physiological processes. Isoprene is very volatile and is not stored to any considerable degree in the leaf tissues. Therefore, isoprene is emitted shortly after it is produced. Isoprene synthase is an enzyme found in the soluble form in leaf stroma as well as

bound to thylakoid membranes (Wildermuth and Fall, 1998). This enzyme combined with Mg^{2+} ions converts dimethylallyl diphosphate (DMAPP) into isoprene (Fall and Wildermuth, 1998). An induction period of up to 30 min is required for both photosynthesis and isoprene production (and therefore emission) when a leaf is exposed to light after a period of darkness (Sharkey et al., 1991). Similarly, emissions can continue for over an hour after light is abruptly removed (Fall and Monson, 1992). These effects demonstrate that there is a delay between the environmental stimuli that initiate and sustain isoprene production, and the time when emissions actually occur. The differences in the modeled vs. measured landscape fluxes shown in Fig. 1 are likely due to these effects. In addition, fluxes are also influenced by boundary layer development and temperature variations within the canopy. On a typical sunny day, the analyses of surface energy budgets show that latent and sensible heat fluxes from the canopy lag behind increases in PPFD measured above the canopy (Pressley et al., 2005). Similarly, canopy components will hold heat (even as irradiance and above-canopy air temperatures have decreased) and positive heat fluxes will continue into the evening. The two aforementioned

processes were not considered in this particular modeling study. These comparisons suggest that incorporation of both the delayed emissions from leaf physiological processes and a more accurate description convective transport offer opportunities for future model improvements.

Fig. 2 shows the ranges of cumulative isoprene fluxes using mean $\pm 1\sigma$ values for basal emission rates from Table 1. The mean cumulative (end-of-season) modeled flux is $2490 \, mg \, C \, m^{-2}$. Similar to Fig. 1, when the upper estimates of basal emission rates are used, the scaling approach yields values closest to the data obtained from EC. For comparison, the maximum estimated uncertainty of the measured fluxes (40%) is plotted as well. Sampling periods for which there were complete meteorological data but missing measured fluxes were excluded from the modeled cumulative fluxes so that the comparisons were not biased. This is the reason for the brief periods where the data series become horizontal (most notably DOY 171 and DOY 215). Because the cumulative fluxes are additive, time periods with missing data cannot contribute to the cumulative flux. Therefore, the modeled and measured cumulative fluxes are most likely underestimated. Using the 40% uncertainty
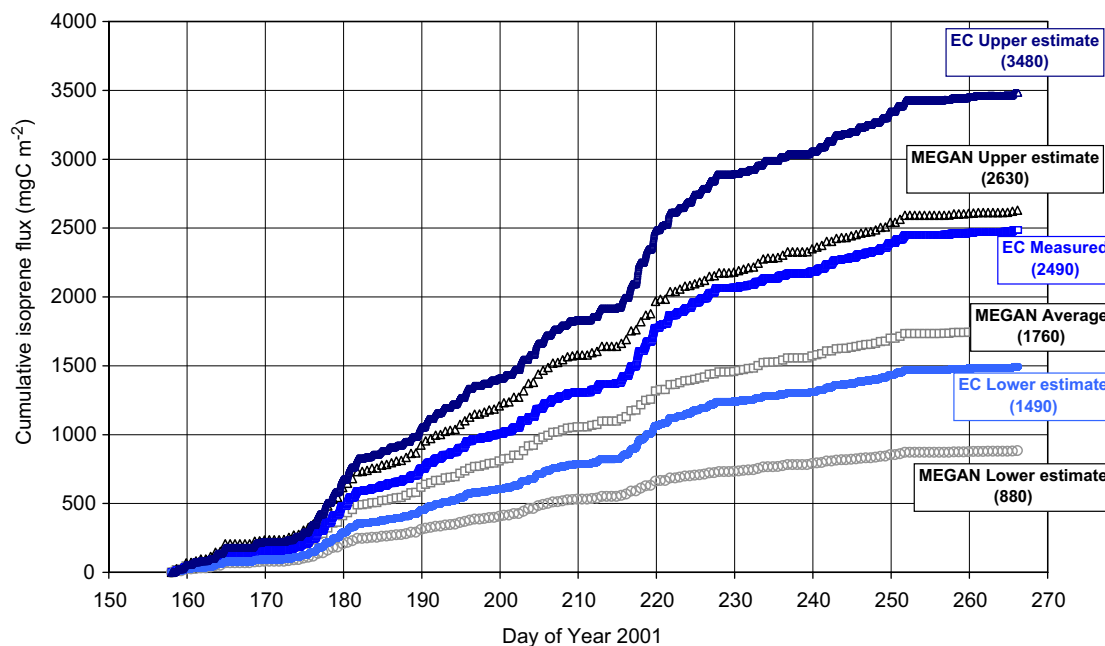

Fig. 2. The 2001 cumulative isoprene fluxes from 7 June (DOY 158) to 24 September (DOY 267). The average estimate (labeled MEGAN average) assumes the mean basal emission rates for both isoprene emitting tree species. The low and high estimates for the modeled fluxes (black open symbols) are the same ones used for Fig. 1. The EC results include the $\pm 40\%$ uncertainty range.

bounds mentioned above, the 2001 measured cumulative EC fluxes ranged between 1490 and 3480 mg C m^{-2}. It is encouraging that both the daily patterns of isoprene fluxes are captured well by the model (Fig. 1) and that the cumulative flux estimates (Fig. 2) are well within the uncertainties of the measured results.

3.2. Monoterpenes and sesquiterpenes

Three of the five tree species included in this study exhibited light-dependent MT emissions, which were dominated by *trans*-ocimene. Fig. 3 shows an example of measured MT emissions from an *A. rubrum* tree. Emissions were scaled to a standard temperature condition (30 °C) by dividing the original emissions by a temperature correction factor defined by Guenther et al. (1991). If the MT emissions were only temperature-dependent, these normalized values should have no further dependencies. However, the data clearly follow the changes in light levels, which implies an additional light-dependency of these emissions. This is also demonstrated in Fig. 4, which shows *trans*-ocimene emission rates from another *A. rubrum* as a function of light. This particular experiment was performed in a leaf cuvette where leaf temperature was held at a constant 30 °C.

Fig. 5 shows a 10-day period (29 June–9 July 2001) of modeled SQT and MT (light-dependent and light-independent) fluxes along with the concurrent light and temperature conditions. These results were calculated using the mean values of the measured branch-level emission rates given in Table 1 and the same meteorological data used for the isoprene analysis above. Typical daytime maximum MT fluxes are 150−180 µg C m^{-2} h^{-1} compared to 4000−8000 µg C m^{-2} h^{-1} from isoprene. Typical daytime fluxes of SQT are ~30% and ~5% of the light-independent MT and total MT fluxes, respectively. After isoprene, the light-dependent MT fluxes are the next largest contributors during full solar irradiance. These fluxes are approximately one order of magnitude greater than the light-independent MT fluxes. The cumulative MT and SQT fluxes with lower and upper bound error estimates (derived from the uncertainties in Table 1) are shown in Fig. 6. The cumulative MT and SQT fluxes are significantly less than isoprene fluxes (105 and 7 mg C m^{-2} compared to 2490 mg C m^{-2}) and represent 4.2% and 0.3% of the total terpenoid flux from this forest with the majority of the MT contribution being light-dependent. It should be noted that these modeling results are based on emission measurements made during the middle of the summer. However, the total emissions as well as
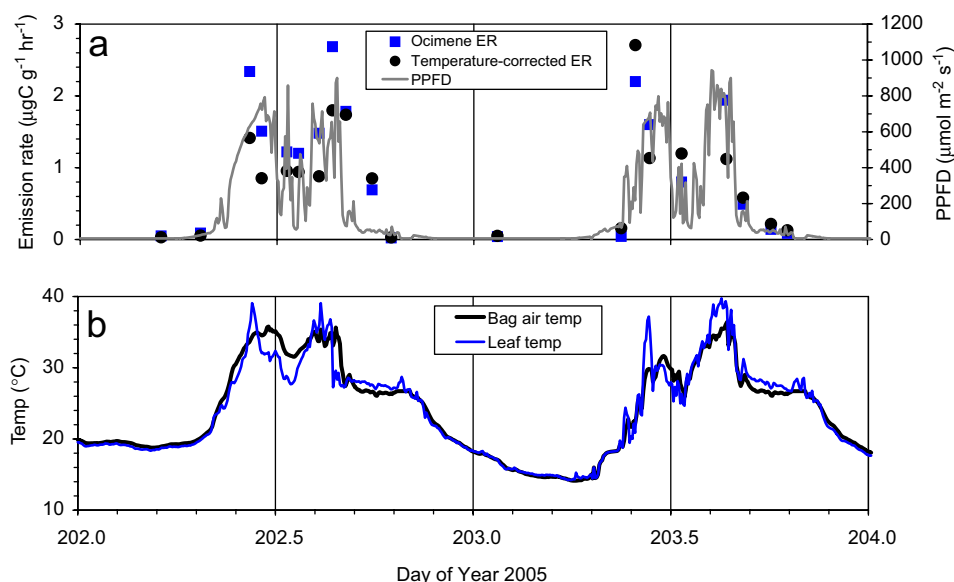

Fig. 3. *Trans*-ocimene emission rates from an *Acer rubrum*; 21–22 July 2005 at UMBS. Upper figure (a) shows light levels (photosynthetic photon flux density, PPFD), original emission rates (■), and temperature-corrected emission rates (●). Lower figure (b) shows air and leaf temperatures for this experiment. Temperature-corrected emission rates were calculated by dividing the original emissions by a temperature correction (C_T) using the MT algorithm from Guenther et al. (1991) and the air temperature shown in (b).
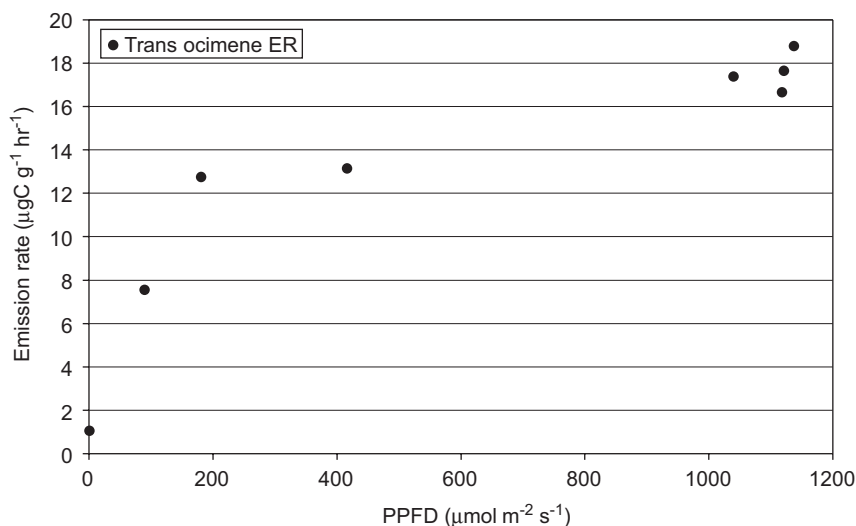
Fig. 4. *Trans*-ocimene emission rate vs. light (PPFD) for an *Acer rubrum* leaf cuvette experiment (31 July 2005) at UMBS. Leaf temperature was held at a constant 30 °C.
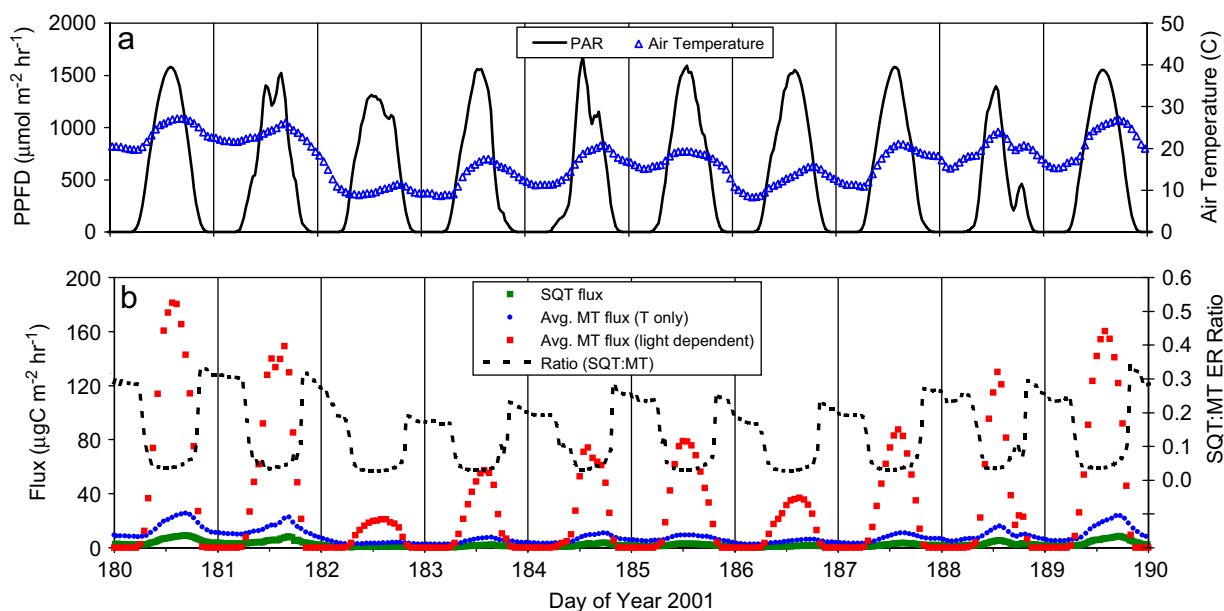

Fig. 5. Modeled half-hour fluxes of MT and SQT at UMBS from 29 June to 9 July 2001. Air temperature and PPFD are in the upper panel (a). MT and SQT fluxes are in the lower panel ((b); left-hand *y*-axis). SQT:MT ratios are plotted on the second (right) *y*-axis in the lower panel (b).

the MT and SQT speciation can change. For example, Pressley et al. (2004) found emission rates from Douglas fir (*Pseudotsuga menziesii*) to decrease from May to September, whereas Western hemlock (*Tsuga heterophylla*) emissions remained relatively constant. Hakola et al. (2006) demonstrated that average MT basal emission rates from two Scots

pine (*Pinus sylvestris*) enclosures varied by ~40% over the course of a growing season (March to October) with emissions being highest in late spring (May and June). Holzinger et al. (2006) showed variable MT β-factors (as described in Section 2.3) from a ponderosa pine plantation that led to underestimating winter and spring fluxes by up to
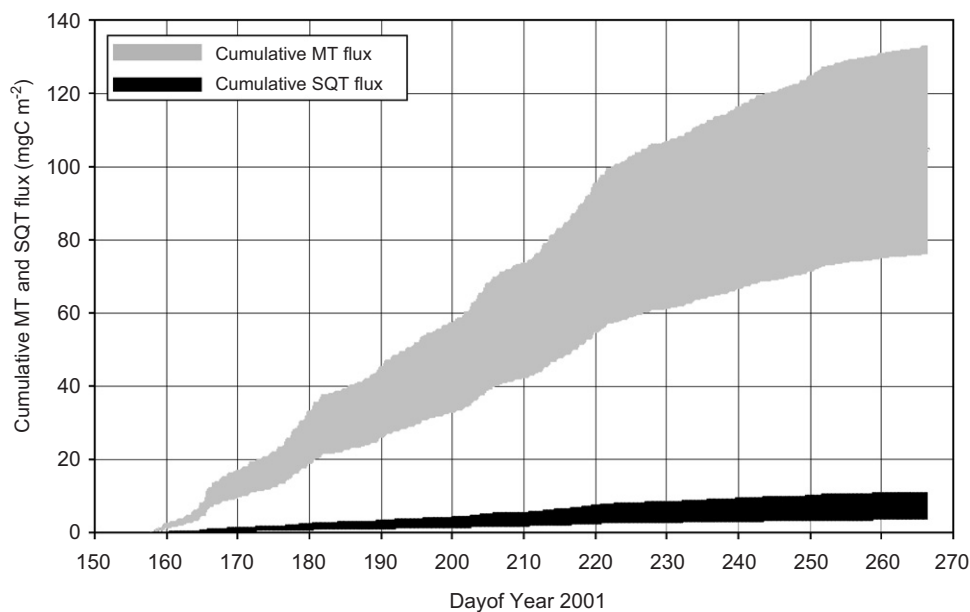
Fig. 6. Modeled 2001 cumulative MT and SQT fluxes from 7 June (DOY 158) to 24 September (DOY 268). The shaded gray area represents the MT flux ranges calculated from the upper and lower estimates of branch-level emission rates in Table 1 ($\pm 27\%$). The uncertainty of the SQT fluxes is estimated to be $\pm 50\%$ which is indicated by the range of the black area.

130% when using estimates based on a temperature-only relationship and a constant value of β. However, since summer fluxes contributed the majority of the cumulative amount, the annual underestimate was closer to 30%. The midsummer emission rates and β-factors estimated here are appropriate for comparing OH reactivities (Section 3.4) with previous reports from this site. However, seasonal variability of MT emissions for this site has not been determined. It is likely that similar changes in emissions as just described would cause annual cumulative MT fluxes from UMBS to be higher than the estimates presented in Fig. 6.

3.3. Comparison of modeled MT fluxes to previous measurements

The emission estimates presented here are from a mixed forest where detailed biomass data are available. However, this region is composed of heterogeneous vegetation types depending on soil properties, elevation changes, and anthropogenic disturbances. Other conifer species growing in the area include red pine (*Pinus resinosa*), Eastern hemlock (*Tsuga canadensis*), jack pine (*Pinus banksiana*), balsam fir (*Abies balsamea*), white spruce (*Picea glauca*), black spruce (*Picea mariana*), and Eastern white cedar (*Thuja occidentalis*). These were

all found to be MT emitters with SQT identified in at least four of these species. Therefore, the modeled results presented here are likely to be representative of secondary growth mixed forests common to the region, but other areas in this region are expected to exhibit different emission ratios of various BVOC as well as different total BVOC fluxes. Guenther et al. (1995) predicted July mean MT fluxes of $\sim 0.15-0.25\,\mathrm{g\,C\,m^{-2}\,month^{-1}}$ for Northern United States forests which translate to average hourly fluxes of $\sim 200-350\,\mu\mathrm{g\,C\,m^{-2}\,h^{-1}}$. Maximum daily fluxes are expected to be approximately twice the average values assuming typical diurnal (sinusoidal) temperature cycles. Lee et al. (2005) measured MT fluxes in August above a *Pinus ponderosa* plantation in California using two different techniques and observed MT fluxes generally between ~ 2 and $4\,\mu\mathrm{mol\,m^{-2}\,h^{-1}}$ $(240-480\,\mu\mathrm{g\,C\,m^{-2}\,h^{-1}})$. Finally, Spirig et al. (2005) measured MT fluxes in July above a beech and birch dominated forest in NW Germany using PTR-MS and observed maximum MT daytime fluxes between ~ 0.4 and $0.6\,\mu\mathrm{mol\,m^{-2}\,s^{-1}}$ $(1400-2100\,\mu\mathrm{g\,C\,m^{-2}\,h^{-1}})$, which were approximately 25% of the isoprene fluxes at that site. Typical maximum daytime MT fluxes from the modeling study presented here $(\sim 100-200\,\mu\mathrm{g\,C\,m^{-2}\,h^{-1}})$ are less than those observed in the publications listed above. The various

MT fluxes from these studies are not directly comparable to our results since they are from different sites with different vegetation and different light and temperature regimes (and of course different time periods). However, our modeled results are of a similar magnitude as fluxes reported in these other studies, which provides greater confidence in the current scaling technique. Although the SQT emissions are a small percentage of the total, these results are the first estimates from the UMBS site.

3.4. Effect of terpenoid emissions on OH reactivity

The total OH reactivity (inverse of OH lifetime) is calculated by (Kovacs et al., 2003)

$$k_{OH}^* = \sum k_{OH+VOC_i}[VOC_i] + k_{CO}[CO] \\ + k_{SO_2}[SO_2] + k_{NO_2}[NO_2] + \cdots, \qquad (2)$$

where k_{OH}^* represents the reactivity (in units of s^{-1}) and the quantities in brackets indicate concentrations. The asterisk (*) is used to differentiate this value from the reaction rate coefficients with OH (k_{OH+VOC} in units of $cm^3 s^{-1} molecule^{-1}$). The studies of Faloona et al. (2001) and of Di Carlo et al. (2004) discussed OH reactivity from this same forest site by considering the measured ambient concentrations of various biogenic and anthropogenic hydrocarbons ([VOC$_i$]) in addition to CO, NO, NO$_2$, and methane. Based on direct OH concentration measurements and detailed reaction mechanisms, Faloona et al. (2001) suggested that the anomalously high nighttime OH concentrations observed could be due to ozonolysis of highly reactive BVOC. Di Carlo et al. (2004) observed disagreements between measured and predicted OH reactivity that had an exponential dependence on temperature. This relationship closely matched temperature-dependent MT emissions and thus they argued that unmeasured highly reactive BVOC containing at least one carbon double bond (C=C) were likely responsible for this observation. We investigated the contribution of our modeled flux results to OH reactivity to determine if some of the compounds measured from enclosures, but not included in the aforementioned studies, could be responsible for the missing OH reactivity. Several highly reactive MT and SQT were observed in the enclosure samples (e.g. trans-ocimene, α-terpinene, β-caryophyllene) but were not included in the calculations of Di Carlo et al.

(2004) since they were not detected in ambient air. These compounds react rapidly with O$_3$ and OH. With such short atmospheric lifetimes, it is not surprising that some of these compounds that were observed from enclosures (where oxidant scrubbing was employed) were not detected in ambient air. Without ambient VOC concentrations, direct comparisons of OH reactivity (for these additional identified compounds) were not possible using Eq. (2). Therefore, we defined a BVOC reactivity rate (R_{BVOC} in units of s^{-2}) as

$$R_{BVOC} = P_{BVOC}k_{OH+BVOC}, \qquad (3)$$

where P_{BVOC} is the BVOC production rate (molecules $cm^{-3} s^{-1}$) from the canopy and $k_{OH+BVOC}$ is the rate coefficient defined in Eq. (2). A box model analysis was applied to the canopy to estimate BVOC production rates from the modeled and measured fluxes. Production rates (molecules $cm^{-3} s^{-1}$) were calculated by dividing that BVOC fluxes (mg C m^{-2}s^{-1}) by the vertical column of 8.8 m, which is portion between 50% and 95% of the 22 m canopy height. This region represents the majority of the leaf biomass at this site (Schmid et al., 2003). When considering total OH reactivity (Eq. (2)), there are many complications because of time-varying OH concentrations, temperature effects, and, in particular, BVOC reaction products. Carter and Atkinson (1996) characterized a significant number of the isoprene oxidation reactions and their by-products, but the atmospheric oxidation reactions of MT and SQT are much less characterized. The parent BVOC molecules as well as reaction products can be reactive with other oxidants (O$_3$, NO, NO$_2$) and these reactions can also be a source of OH radicals (Paulson and Orlando, 1996; Aschmann et al., 2002). We considered the first order reactions of the parent molecules (isoprene, MT, and SQT) with OH. However, OH can react with the oxidation products of the initial reactions, which suggests that MT and SQT could be a greater sink for OH radicals based on the number of carbon atoms per molecule. For example, two primary products of the isoprene + OH reaction are methacrolein and methyl vinyl ketone. These molecules as well as further reaction products have reaction rate coefficients of $k_{OH} \sim 10^{-11} cm^3 molecule^{-1} s^{-1}$ (Carter and Atkinson, 1996), which are of the same order of magnitude of the initial isoprene + OH reaction (see Table S1 in Appendix A). The following estimates of OH reactivity rates are conservative since MT

and SQT have 2 or 3 times the number of carbon atoms as isoprene and can therefore potentially be a correspondingly greater OH sink with respect to gas-phase reactions.

The values calculated for reactivity rate are independent of the OH concentration, which was not measured directly during the 2003 or 2005 growing seasons at UMBS. The reaction rate constants ($k_{BVOC+OH}$) are listed in Appendix A. Reactivity rates for MT and SQT (defined in Eq. (3)) were calculated from the modeled fluxes for each half-hour period shown in Fig. 5. Measured half-hour fluxes were used to calculate the isoprene reactivity rates. Periods where measured (EC-FIS) isoprene fluxes were missing were gap-filled by interpolating between adjacent time periods. Fig. 7 shows a 5-day period (DOY 190–195) of reactivity rates plotted as a time series. It is evident that isoprene comprises nearly all of the total reactivity during the day. However, the addition of ocimene greatly increases the reactivity of non-isoprene BVOC, and nighttime MT and SQT are estimated to account for ~50% of the total rate. Fig. 8 shows the percentage contributions to the total BVOC reactivity rate from each of the terpenoid

classes. During daylight hours, isoprene contributes over 90% of the total reactivity from this forest. At night, MT and SQT constitute more of the total. This graph is somewhat deceptive because although contributions of MT and SQT to the total are greater, the nighttime reactivity rate from all compounds is reduced due to lower temperatures and absence of light. Isoprene and ocimene production essentially cease at night, and light-independent MT and SQT production rates are reduced by approximately an order of magnitude.

These reactivity rates (in units of s^{-2} from Eq. (3)) and OH reactivities (Eq. (2); in units of s^{-1}; Kovacs et al., 2003; Di Carlo et al., 2004) are not directly comparable. Although both quantities depend on the OH reaction rate coefficients, the former quantity depends on the BVOC production rates, and the latter depends on the ambient BVOC concentrations. Ambient isoprene concentrations during this study period ranged between 10 and 500 pptv at night ($\sim 10^8 - 10^{10}$ molecules cm^{-3}) and were ~5 ppbv (10^{11} molecules cm^{-3}) during the middle and afternoon hours of typical July days. Using these measured ambient mixing ratios (from
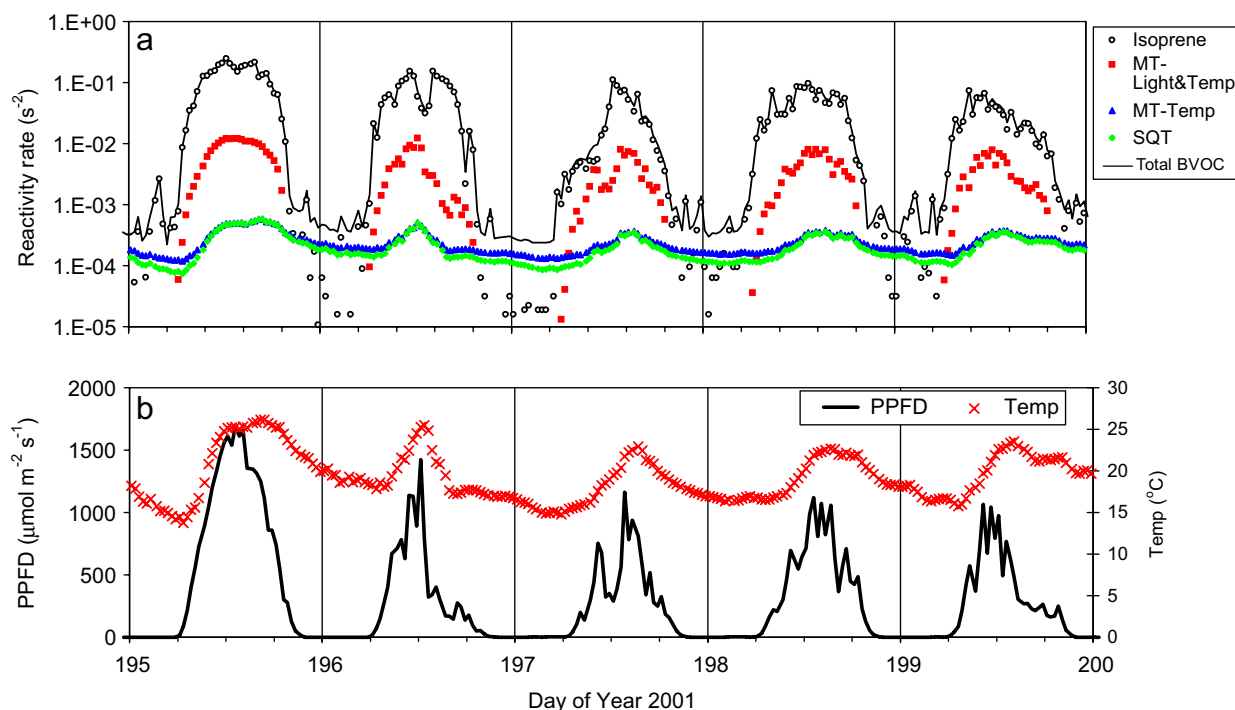

Fig. 7. (a) Top: reactivity rates of isoprene (○), light-dependent MT (□), light-independent MT (−), SQT (+), and total BVOC (solid line) calculated using Eq. (3) for 14 July–19 July 2001. Note that the y-scale is logarithmic. (b) Bottom: ambient light and temperature conditions for each day.
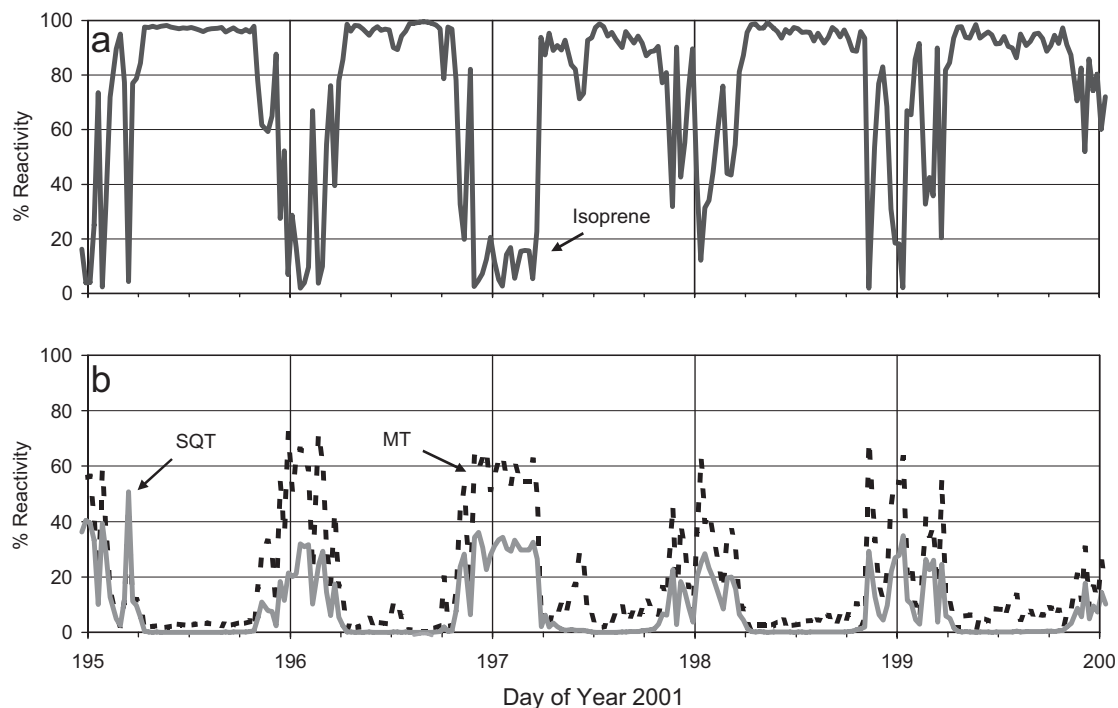
Fig. 8. Modeled BVOC reactivity rates (s^{-2}) as a percentage of the total for isoprene (a), and MT, SQT (b). Each vertical gridline represents midnight.

July 2001) a direct comparison is possible. Using these values, we estimated OH reactivity with respect to isoprene to be $\sim 0.01-1.0\,s^{-1}$ at night and $\sim 10\,s^{-1}$ during the day. These values agree favorably with the results of Di Carlo et al. (2004) who calculated reactivities (with respect to isoprene) between ~ 0.5 and $5.5\,s^{-1}$ for the temperature range of $9-27\,°C$. Di Carlo et al. (2004) estimated that it would be necessary to have mixing ratios of highly reactive compounds (such as terpinolene) of $\sim 500\,pptv$ in order to account for the missing OH reactivity. Resulting ambient concentrations depend on production as well as loss rates. Using the 2001 measured ambient isoprene mixing ratios and assuming that MT would scale directly to the measured emission rates of the individual BVOC, we estimate maximum midday MT mixing ratios between 150 and 300 pptv for the time period shown in Fig. 7. The total MT mixing ratio is approximately 5% of isoprene, and is composed predominately of *trans*-ocimene. Because *trans*-ocimene is considerably more reactive than isoprene (see Table S1), actual ambient MT mixing ratios are expected to be considerably less than this. Based on OH reactivity alone, the ambient MT mixing ratio

would be expected to $\sim\frac{1}{3}$ of these values (i.e. 50–100 pptv). The estimated ambient MT mixing ratios from this modeling study are of the same order of magnitude measured by Di Carlo et al. (2004). However, these inferred levels are a factor of 2–10 smaller than what would be necessary to account for the missing OH reactivity. Faloona et al. (2001) reported ambient nighttime mixing ratios of the sum of MT of $\sim 55\,pptv$, which is consistent with our nighttime estimates. However, in order to account for anomalously high OH concentrations, they estimated that a production rate of a highly reactive terpene (such as terpinolene or ocimene) of $360\,\mu g\,C\,m^{-2}\,h^{-1}$ would be necessary. This value is over 2 times the maximum fluxes estimated at this site ($150-180\,\mu g\,C\,m^{-2}\,h^{-1}$; see Fig. 5).

The inclusion of previously unaccounted-for MT and highly reactive SQT (such as β-caryophyllene, α-farnesene, and α-humulene) in the present study increases the level of known reactive biogenic compounds over previous estimates. However, they are still considerably less than what would be required to account for either the anomalously high nighttime OH levels from terpene ozonolysis suggested by Faloona et al. (2001) or the missing OH

reactivity reported by Di Carlo et al. (2004). This holds true even considering the uncertainty of the flux estimates reported here (approximately ±27% for MT and ±50% for SQT).

There are a number of uncertainties and potential biases in our comparison that cannot be overcome due to limitations in the current knowledge of the BVOC oxidation chemistry and due to limitations in available data. As mentioned above, because of the larger molecule size and carbon number, OH reactivities on a per-molecule basis are potentially larger for MT and SQT than for isoprene. On the other side, there is ample evidence that much larger fractions of MT and SQT oxidation products partition into the aerosol phase, which will remove a proportionally higher fraction of the reaction products from participation in gas-phase chemistry.

Each of these studies (including the current report) utilizes estimates or measurements of concentrations obtained during different times of the year and during different years. Because of the expected variability of seasonal and interannual variations in emission rates and ambient concentrations, comparisons of data sets from different measurement periods will always be problematic. Other BVOC that were not considered in our measurements (e.g. oxygenated BVOC) have been shown to be emitted from vegetation at this site (Karl et al., 2003). However, their ambient concentrations are lower than for isoprene (typically less than 1 ppbv), and these compounds are less reactive towards atmospheric oxidants than terpenoid compounds. For example, acetone has an estimated lifetime with respect to OH of 61 days while isoprene, MT, and SQT have lifetimes ranging from minutes to hours (Atkinson and Arey, 2003 and references therein). Consequently, oxygenated compounds, which were not included in these modeling results, are not expected to significantly affect the total OH reactivity.

4. Conclusions

Branch-level measurements of all terpenoid species (isoprene, MT, and SQT) were taken from the biomass representing the footprint of the UMBS-flux tower and were used to model whole-canopy BVOC fluxes and OH reactivity rates from this forest site. The isoprene emission rates in conjunction with a canopy model demonstrated that the isoprene daily and seasonal fluxes compared favorably with the directly measured values. Modeled results best represented EC fluxes when the upper estimates of basal emission rates were used. The dominant MT (*trans*-ocimene) had a strong light dependence. Light-dependent MT accounted for the majority of the total terpenoid fluxes. SQT fluxes contributed less than a percent to the total. Since the modeled isoprene fluxes were well within the uncertainties of the measured canopy fluxes, we believe that extending this technique to estimate MT and SQT fluxes is appropriate. Karl et al. (2003) reported seasonal fluxes of primarily oxygenated BVOC, but the emissions presented here provide the first estimates of total terpenoid fluxes from this site. These terpenoid fluxes were then used to estimate their influence on OH reactivity from this canopy. Since ambient measurements of SQT and many MT were not available or even feasible, a new parameter (reactivity rate) was defined, which is representative of the BVOC + OH reaction potentials. Reactivity rates are based on fluxes rather than ambient concentrations. This approach could be more relevant since it utilizes dynamic properties that are coupled to the emission source, in contrast to determining OH reactivity, which requires the assumption of nearly steady-state BVOC concentrations. Ambient concentrations are dependent on local emissions, as well as chemical reactions and mixing within the canopy. As expected, isoprene was the dominant contributor to the BVOC + OH reactivity rate. The maximum contribution to total reactivity rate from the other terpenoid compounds is estimated to be on the order of 10% during the day and can comprise the majority of the reactivity rate at night. However, the total reactivity rate decreases by over two orders of magnitude from day to night. Our flux estimates of MT and SQT are the first to be reported from this site and include highly reactive BVOC that have not been previously considered. However, the estimated fluxes of these compounds are still insufficient to affect observed oxidant levels to the degree suggested by other recent reports. Better characterization of the BVOC + oxidant interactions will ultimately require kinetic and product studies of the newly identified BVOC, as well as concurrent measurements of ambient OH and BVOC concentrations and BVOC emission rates.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at 10.1016/j.atmosenv.2006.12.033.

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