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Biogenic isoprene emission: Model evaluation in a southeastern United States bottomland deciduous forest

Christopher D. Geron, Dalin Nie, Robert R. Arnts, Thomas D. Sharkey, Eric L. Singsaas, Peter J. Vanderveer, Alex Guenther, Joe E. Sickles, and Tad E. Kleindienst

Abstract. Isoprene is usually the dominant natural volatile organic compound emission from forest ecosystems, especially those with a major broadleaf deciduous component. Here we report isoprene emission model performance versus leaf and canopy level isoprene emission measurements made at the Duke University Research Forest near Chapel Hill, North Carolina. Emission factors, light and temperature response, canopy environment models, foliar mass, leaf area, and canopy level isoprene emission were evaluated in the field and compared with model estimates. Model components performed reasonably well and generally yielded estimates within 20% of values measured at the site. However, measured emission factors were much higher in early summer following an unusually dry spring. These decreased later in the summer but remained higher than values currently used in emission models. There was also a pronounced decline in basal emission rates in lower portions of the canopy which could not be entirely explained by decreasing specific leaf weight. Foliar biomass estimates by genera using basal area ratios adjusted for crown form were in excellent agreement with values measured by litterfall. Overall, the stand level isoprene emissions determined by relaxed eddy accumulation techniques agreed reasonably well with those predicted by the model, although there is some evidence for underprediction at ambient temperatures approaching 30°C, and overprediction during October as the canopy foliage senesced. A “Big Leaf” model considers the canopy as a single multispecies layer and expresses isoprene emission as a function of leaf area rather than mass. This simple model performs nearly as well as the other biomass-based models. We speculate that seasonal water balance may impact isoprene emission. Possible improvements to the canopy environment model and other components are discussed.

Introduction

Emissions of Biogenic Volatile Organic Compounds (BVOCs) are important inputs to atmospheric chemistry models at regional to global scales [Fehsenfeld et al., 1992; National Research Council, 1991]. Isoprene has been identified as the most abundant of BVOCs [Guenther et al., 1994, 1995; Geron et al., 1994] and has been a focus of air quality model analyses in many recent studies [Roselle, 1994; Sillman et al., 1995]. Geron et al. [1994] estimated BVOC emissions at landscape scales as functions of forest composition (genus level) and environmental factors. Here we test this model (hereafter referred to as BEIS2 to replace the original Biogenic Emission Inventory System of Pierce et al. [1990]) against isoprene emission, environmental, and biometrical measurements made in a bottomland deciduous forest in the lower piedmont of North Carolina during the summer and early fall of 1994. Our objectives were (1) to compare observed values of model components with values used in the model, (2) to compare stand level fluxes measured using the relaxed eddy accumulation system with leaf level measurements and isoprene emission estimated from BEIS2, and (3) to discuss probable sources of inaccuracy and areas for potential improvements to BEIS2.

Methods

Site Description

This study was conducted at the Duke University Research Forest (35°58'25"N latitude and 79°06'05"W longitude) near Chapel Hill, North Carolina. Soils are Iredell sandy loams with a water table which varies seasonally from the surface to roughly 1 m in depth. The forest is a mature second growth uneven-aged (oldest individuals exceed 180 years) bottomland deciduous hardwood mix, which has been undisturbed for at least the past 60 years. The stand is dominated by willow oak (Quercus phellos), swamp chestnut oak (Q. michauxii), white oak (Q. alba), delta post oak (Q. stellata), black oak (Q. velutina), northern red oak (Q. rubra), various hickories (Carya spp.), sweetgum (Liquidambar styraciflua), yellow poplar (Liriodendron tulipifera), and red maple (Acer rubrum). Canopy height is approximately 28 to 32 m. The terrain is very flat for approximately a kilometer in all directions, making it suitable
for micrometeorological experimentation. A 40 m walkup tower facilitates measurements within and above the forest canopy.

Forest Characterization

Since winds during most of the growing season tend to be dominated by southwesterly flow, 15 m radius fixed plots were sampled at 30 m intervals on transects extending out to 150 m due south, southwest, and west from the instrumented tower. To avoid plot overlap, only the southwest transect was sampled at 30 m from the tower. The genus, species, and diameter at breast height (DBH) (1.37 m) were recorded for all trees greater than 15 cm in diameter on each plot. Trees smaller than 15 cm were generally suppressed (received little direct light from above) and accounted for less than 2% of the basal area (total stem cross-sectional area at a height of 1.37 m) on each plot. These measurements were used to estimate foliar mass using the methods of Geron et al. [1994].

To assess the accuracy of the species composition and foliar mass estimates from the above methods, litterfall was collected from twenty-six 45 cm diameter litter traps that were placed 7.5 m from each plot center normal to the transect azimuth. Leaf litter was collected approximately every 2 weeks, dried to a constant weight, separated by species, and weighed.

Isoprene Emission Measurements

Leaf level measurements. Leaf level isoprene emission and physiological measurements were made using a portable gas exchange system with a light and temperature controlled cuvette and portable gas chromatograph [Sharkey et al., 1996]. Measurements were made on June 23–25, 1994, following an unusually warm and dry spring, and again on August 20–22, 1994, following a wet period. These latter measurements were taken while the relaxed eddy accumulation (REA) system was in operation. Measurements were made at three vertical levels on leaves of a white oak. Hickory, yellow poplar, and northern red oak leaf emissions were also measured from branches which were cut from the upper canopy. The branches were recovered after cutting and cut again while the branch end was submerged in water. Isoprene emission from foliage on the cut branch was then measured immediately to avoid physiological disturbance to the leaves. Leaf disks were removed from all foliage sampled to determine specific leaf weight and xanthophyll and chlorophyll content. Since leaf temperature is an important influence on isoprene emission, a handheld infrared thermometer (Everest Interscience, Inc., Justin, California) was also used to assess temperature variation of shaded and illuminated leaves vertically through the canopy. These readings were made at approximately the same time and canopy position as the leaf-level isoprene emission measurements.

Canopy level measurement. Canopy level isoprene emission measurements were made using an REA system. Details about the theory of the technique and the design and performance of the system can be found elsewhere [Nie et al., 1995]. Briefly, the system measures wind speed with a three-dimensional sonic anemometer (Applied Technology, Inc., Boulder, Colorado) and collects two air samples: one for rising air (updrafts) and one for downdrafts. The flux of isoprene \( F_i \) is obtained from

\[
F_i = \beta \sigma_{uw} (C_u - C_d)
\]

where \( F_i \) is isoprene emission in \( \text{mg carbon m}^{-2} \text{h}^{-1} \), \( \beta \) is a proportionality constant, \( \sigma_{uw} \) is the standard deviation of vertical wind speed, and \( C_u \) and \( C_d \) are mean concentrations of isoprene collected from the updraft and downdraft air samples, respectively.

The mean concentrations of isoprene in the updrafts and downdrafts were determined by accumulating the samples in tubes packed with adsorbents (carbon molecular sieve and graphitized carbon black). The tubes were returned to the laboratory where they were analyzed by thermal desorption/gas chromatography with flame ionization detection (GC/FID). A complete description of isoprene recovery efficiency testing and analytical procedures is given by Arnits et al. [1995]. The GC/FID was calibrated to a National Institute of Standards and Technology (NIST) propane standard, while the adsorbent tubes were analyzed for isoprene breakthrough volume and recovery efficiency by using a laboratory standards dilution system [Arnits et al., 1995]. The GC/argon ionization detector used to analyze the leaf isoprene samples was calibrated using 256 parts per billion by volume (ppbv) isoprene standards formulated in the field using both nitrogen and ambient air [Sharkey et al., 1996].

Uncertainty associated with REA flux measurements is estimated to be of the order of 20 to 25%. Of this, 10 to 15% is associated with the micrometeorological methodology, while approximately 10% uncertainty is attributed to the isoprene analytical technique. At switching frequencies greater than 1 Hz it was found that a 120 torr pressure differential across the zero gas and sample gas sides of the sampling valves could cause fluxes to be underestimated by approximately 8% (R. R. Arnits et al., manuscript in preparation, 1997). However, analysis of recent fast response isoprene, temperature, \( \text{CO}_2 \), and \( \text{H}_2\text{O} \) vapor data collected at this site shows that at least 90% of the flux during a given 0.5 hour sample period is contained in large eddies with a turnover time of 10 s or greater (D. Nie et al., Development of a relaxed eddy accumulation system for the measurements of nonmethane volatile organic chemical fluxes, submitted to Journal of Geophysical Research, 1996). Therefore, the lack of response to switching between 1 to 10 Hz would be expected to have a minor impact on flux estimates. Furthermore, we note that the isoprene flux measurements were performed in the roughness sublayer (\( z/h = 1.2 \)) of the canopy and not the atmospheric surface layer (ASL). As discussed by Raupach [1988] and Kana et al. [1996], the main contributing eddies to the turbulent scalar transport in this layer are of the order of \( h \) (vis-a-vis \( z \) in the ASL, where \( z \) is the height from the zero-plane displacement and \( h \) is the canopy height). Hence, with a mean \( (U) = 1 \text{ m s}^{-1} \) (where \( (U) \) is the mean horizontal wind speed) and \( h = 32 \text{ m} \), the eddy timescale is of the order of 0.03 Hz, which is in agreement with our frequency range findings from this recent analysis. Hence the 1 Hz response frequency of the REA is sufficient to resolve all flux-contributing eddies. It is worth noting that this and other sources of potential error in the REA system itself (e.g., those due to inaccurately timed valve switching and longitudinal mixing in the sample line) and the analytical technique (e.g., isoprene breaking through the adsorbent cartridge, or less than 100% isoprene recovery efficiency during sample desorption) would tend to cause systematic underestimates of the actual isoprene flux.

The REA system was placed in the walkup tower about 10 m above the canopy. Micrometeorological sensors (net radiometer, photosynthetically active radiation (PAR) meter, wet and dry bulb thermometers, soil heat flux, and fast response (10 Hz) water vapor (\( \text{H}_2\text{O} \)) and carbon dioxide (\( \text{CO}_2 \))) were also
Placed at the top of the tower in order to verify closure of the energy balance during measurement periods and to collect data needed for emission model comparison. Wind speed, wind direction, and CO$_2$ and H$_2$O concentrations were sampled and stored at 10 Hz. Net radiation, PAR, air temperature, and humidity were sampled at 0.1 Hz and stored as 30 min averages. The REA and micrometeorological system were operated and monitored by a common data acquisition system. A handheld infrared thermometer was used to measure upper canopy surface temperature from the top of the tower during each flux measurement. Measurements were made between the hours of 1100 and 1500 LT from August 20 to October 12, 1994, intermittently during fair weather conditions with winds predominantly from south to westerly directions where the best fetch was provided. Occasionally, fluxes were measured when winds were from the northwest or southeast (reference arrows on Plate 1). A large gap (15–20 m in diameter) is present in the canopy immediately northwest of the tower, while winds from the northeast of the tower must pass through the tower itself. Therefore fluxes from these directions must be interpreted cautiously. The primary fetch is considered to be south, southwest, and west of the tower. Volumetric soil water content (cm$^3$ water cm$^{-3}$ soil) of the soil surface layer (top 30 cm) was also determined using time domain reflectometry.
where \( \text{crnwd} \) is crown width (meters) and DBH is tree stem diameter (centimeters). If total crown area exceeds ground area, crown area is adjusted so that they are equal, avoiding overestimation of foliar mass. Foliar mass is then assumed to be equivalent to ambient air temperatures above the forest canopy. Since leaf temperatures can differ substantially from surrounding air temperature [Knoerr, 1966], the leaf temperature energy balance of Gates and PapJan [1971] used by Lamb et al. [1993] was also examined to determine (1) if the model could account for observed differences between canopy surface and air temperatures and (2) impacts on isoprene emission estimation. This model is of the form

\[
Q_{\text{abs}} = \varepsilon \sigma T^4 + k_1 \left( \frac{V}{D} \right)^{0.5} (T - T_a) + L \left[ \frac{S \sigma(T) - RH[S \sigma(T_a)]}{r_1 + k_2(W^0.7D^{0.9})/V^{0.5}} \right]
\]

where

- \( Q_{\text{abs}} \) total radiation absorbed (cal cm\(^{-2}\) min\(^{-1}\));
- \( \varepsilon \) leaf emissivity, equal to 0.95;
- \( \sigma \) Stefan-Boltzman constant, equal to 8.132 x 10\(^{-11}\) cal cm\(^{-2}\) min\(^{-1}\) K\(^{-4}\);
- \( T \) leaf temperature (K);
- \( k_1 \) empirical constant relating to heat transfer, equal to 0.0162 cal cm\(^{-2}\) min\(^{-1}\) K\(^{-1}\);
- \( V \) wind speed (cm s\(^{-1}\));
- \( D \) leaf dimension parallel to wind direction, equal to 10 cm;
- \( T_a \) air temperature (K);
- \( L \) latent heat of vaporization (cal g\(^{-1}\));
- \( S \sigma(T) \) saturation vapor density at leaf temperature (g cm\(^{-3}\));
- \( RH \) relative humidity;
- \( S \sigma(T_a) \) saturation vapor density at air temperature (g cm\(^{-3}\));
- \( r_1 \) leaf resistances varies with time of day between 0.0083 and 0.0333 min cm\(^{-1}\) for a deciduous leaf and between 0.0167 and 0.0833 min cm\(^{-1}\) for a coniferous needle (min cm\(^{-1}\));
- \( k_2 \) empirical leaf boundary layer resistance coefficient, equal to 0.026 min cm\(^{-1}\);
- \( W \) leaf dimension perpendicular to wind direction, equal to 5 cm, deciduous, and 1 cm, coniferous.

Equation (4) is solved iteratively to converge to a leaf temperature where the energy budget is approximately balanced between the leaf absorption (\( Q_{\text{abs}} \)) and the sum of radiative, convective, and latent terms. Vertical gradients of humidity, wind speed, solar radiation, and air temperature were estimated from measurements taken at 10 m above the forest canopy by assuming profiles similar to those of Lamb et al. [1993]. These meteorological data allow us to make isoprene emission (mg carbon m\(^{-2}\) h\(^{-1}\)) estimates based on the measured tree species composition, BEIS2, and (4) as described above. REA-derived isoprene emissions are then compared with model estimates for the corresponding time periods.

### Results and Discussion

#### Forest Characterization

The estimated percentage of foliar mass by genus derived from the Blackwood Forest mensurational (forest survey) data using (2) and (3) is shown as CRWNAREA in the histogram of...
leaves were measured to determine leaf to leaf variability. Standard errors for leaf area index (LAI) and specific leaf weight (SLW) at each level values were found in a study at Oak Ridge, Tennessee [Harley et al., 1997]. Since the BEIS2 SLW equation was developed specifically for oak leaves, it was determined on the white oak adjacent to the tower. Trends mensurational standards and likewise yields peak foliar mass are approximately 5%.

Plate 1. The forest is fully stocked (i.e., closed canopy) by species from a subsample of litterfall and multiplying by the specific leaf weight (g m⁻²) for those species [Vose et al., 1995]. This method yielded a mean footprint total LAI of 5.2 m² m⁻² for the forest fetch. This is in agreement with LAI measurements of 4.4 to 5.8 made in using the LAI 2000 during the late summer of 1995 on the plots where the litterfall was collected. Overall, the foliage characteristics measured at the site agree quite well with those used in BEIS2.

**Leaf Isoprene Emission**

The light- and temperature-controlled cuvette system and portable GC were deployed at three levels to measure the isoprene emission and physiological function of white oak leaves. Foliage at the upper- and midcanopy levels was sampled from the tower, while scaffolding provided access to shade leaves lower in the canopy. Using the LAI 2000, LAI above each sample level was determined to be 0.3, 1.1, and 3.0 (standard deviation ±10%). The number of leaves sampled and replicate measurements of isoprene emission under controlled light and leaf temperature conditions varied between the June and August sampling periods and are shown in Table 2. During the June measurement period, upper level isoprene emission rates measured at standard conditions (PAR equal to 1000 μmol m⁻² s⁻¹ and leaf temperature of 30°C) were higher than the current standardized emission rates of 70 μg C (g foliar dry mass)⁻¹ h⁻¹ ± 50% used in BEIS2. These measurements followed an abnormally dry spring in the area. Sharkey et al. [1992] also observed high isoprene emissions by kudzu following exposure to drought and rewatering. However, leaf level isoprene emissions were lower at the middle and lower canopy levels. This difference could not be entirely explained by the specific leaf weight gradient as shown in Table 2, since isoprene emissions expressed on a dry weight basis (μg C g⁻¹ h⁻¹) were still 25 to 50% higher at the top of the canopy than at the bottom.

The period between the leaf level measurements featured frequent thunderstorm activity. We speculate that this may have had an impact on the lower isoprene emission rates observed during the August measurement period, when rates at the top of the canopy more closely approximated the value of 70 μg C g⁻¹ h⁻¹ used in BEIS2. The gradient between vertical levels remained, however.

### Table 2. Leaf Level Isoprene Emission Rates ExpRESSED on a Leaf Area and Dry Weight Basis

<table>
<thead>
<tr>
<th></th>
<th>June, August</th>
<th>June, August</th>
<th>June, August</th>
<th>June, August</th>
<th>August</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Top of Canopy, LAI = 0.3, SLW = 133 g m⁻²</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAR/temperature</td>
<td>1000/35</td>
<td>1000/35</td>
<td>2000/35</td>
<td>2000/35</td>
<td>2000/40</td>
</tr>
<tr>
<td>Isoprene, nmol m⁻² s⁻¹</td>
<td>87 ± 9, 65 ± 3</td>
<td>135 ± 8, 107 ± 5</td>
<td>108 ± 8, 76 ± 5</td>
<td>155 ± 12, 126 ± 7</td>
<td>180 ± 10</td>
</tr>
<tr>
<td>Isoprene, μg C g⁻¹ h⁻¹</td>
<td>142 ± 11, 106 ± 5</td>
<td>219 ± 10, 174 ± 8</td>
<td>176 ± 12, 123 ± 8</td>
<td>263 ± 13, 205 ± 11</td>
<td>292 ± 16</td>
</tr>
<tr>
<td><strong>Middle of Canopy, LAI = 2.1, SLW = 110 g m⁻²</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAR/temperature</td>
<td>1000/35</td>
<td>1000/35</td>
<td>2000/35</td>
<td>2000/35</td>
<td>2000/40</td>
</tr>
<tr>
<td>Isoprene, nmol m⁻² s⁻¹</td>
<td>65 ± 6, 47 ± 2</td>
<td>98 ± 10, 69 ± 2</td>
<td>80 ± 7, 53 ± 3</td>
<td>108 ± 11, 81 ± 3</td>
<td>NA</td>
</tr>
<tr>
<td>Isoprene, μg C g⁻¹ h⁻¹</td>
<td>128 ± 10, 92 ± 4</td>
<td>193 ± 16, 135 ± 4</td>
<td>157 ± 6, 104 ± 6</td>
<td>212 ± 22, 159 ± 6</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Bottom of Canopy, LAI = 3.0, SLW = 52 g m⁻²</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>PAR/temperature</td>
<td>1000/35</td>
<td>1000/35</td>
<td>2000/35</td>
<td>2000/35</td>
<td>2000/40</td>
</tr>
<tr>
<td>Isoprene, nmol m⁻² s⁻¹</td>
<td>21 ± 1.9, 19 ± 1</td>
<td>24 ± 2.2, 22 ± 2</td>
<td>NA, 21 ± 2</td>
<td>28 ± 1.7, 21 ± 1</td>
<td>NA</td>
</tr>
<tr>
<td>Isoprene, μg C g⁻¹ h⁻¹</td>
<td>87 ± 5, 79 ± 3</td>
<td>100 ± 7, 91 ± 4</td>
<td>NA, 87 ± 3</td>
<td>115 ± 6, 112 ± 17</td>
<td>NA</td>
</tr>
</tbody>
</table>

Values are means plus or minus standard errors for three leaves measured at each canopy level with the cuvette system under the controlled PAR (μmol m⁻² s⁻¹) and leaf temperatures (degrees Celsius) shown, except at the top of the canopy during June, when emissions from five leaves were measured to determine leaf to leaf variability. Standard errors for leaf area index (LAI) and specific leaf weight (SLW) at each level are approximately 5%.
During the August leaf-level isoprene emission measurements, isoprene emissions were measured at leaf temperatures exceeding 40°C with the light- and temperature-controlled cuvette system. Emission rates from leaves on cut branches of Quercus alba, Q. rubra, and intact foliage of Q. alba in the upper canopy peaked at leaf temperatures between 40°C and 44°C and then declined (data not shown). These trends are consistent with BEIS2 and observations by Guenther et al. [1991, 1993]. It is not currently known if leaf isoprene emission rates are affected by branch removal. Temperature response from the intact leaves over the range 30° to 40°C was also similar to that observed by Guenther et al. [1991, 1993], although some increase was observed at PAR intensities greater than 1000 μmol m⁻² s⁻¹.

Basal isoprene emission factors (determined at a leaf temperature of 30°C and a PAR of 1000 μmol m⁻² s⁻¹) from the foliage of the cut branches were largely in agreement with current rates used in BEIS2. Red oak (Q. rubra) emitted at approximately 60 μg C g⁻¹ h⁻¹, while hickory (Carya tomentosa) and yellow poplar (Liriodendron tulipifera) emitted less than 1 μg C g⁻¹ h⁻¹ from branches cut from the upper canopy. Note, however, that many oak species in the fetch could not be sampled. Quercus michauxii (swamp chestnut oak) has never been studied to our knowledge, while Q. phellos (willow oak) has been shown to emit at rates similar to those measured here [Meeks et al., 1992]. These two species compose a large portion of the stand (see Table 1). The substantial difference in isoprene emission rate between the red and white oaks suggests that interspecific variability within the Quercus genus may indeed be significant. Since leaf-level isoprene emission rates from only one white oak were examined, we also cannot rule out substantial intraspecific variability. However, intraspecific variation in white oak itself probably is not a significant factor at this particular site since other oak species were more abundant in the primary fetch. Also, the leaf-level rates reported here are similar to those reported by Guenther et al. [1996c]. Nonetheless, intraspecific variability may still be important at regional scales.

Canopy Level Isoprene Emission

Canopy level isoprene fluxes measured using the REA system varied from 0.11 to 13.35 mg C m⁻² h⁻¹. Emissions initially ranged from 2 to 7 mg C m⁻² h⁻¹ (mean PAR, temperature equal to 1408, 27.2, N = 13) until mid-September, when much higher (8 to 13.35 mg C m⁻² h⁻¹, mean PAR, temperature equal to 1574, 28.9, N = 6) values were measured (Figure 2). Following this warm period, fluxes decreased to previous levels (mean PAR, temperature equal to 1422, 24.3, N = 6), and then fell below 2 mg C m⁻² h⁻¹ (mean PAR, temperature
Figure 2. Isoprene emission rates observed using the REA system, model predictions, and temperature (degrees Celsius) and PAR (μmol m⁻² s⁻¹) data during the study period. Data were collected between 11 am and 3 pm on the dates shown. Unlabeled tick marks indicate measurements made sequentially during the previously labeled day. Stars denote fluxes (REA) from the south to the west of the tower (primary fetch), while circles denote suspect measurements (REAo) made when winds were from the northwest or southeast. Model simulations are CNTYB2: BEIS2 is used assuming that the forest composition is identical to that of Orange County, North Carolina, as determined by the database of Hansen et al. [1992]; SITEB2: BEIS2 is applied to the average forest composition determined from the 13 fixed radius plots in the forest fetch; WISCEB applies the vertical gradient in emission factors measured at the site, the leaf energy balance model, and distance-weighted biomass calculated from the fixed radius plots corresponding to the observed mean horizontal wind direction; BGLEAF applies the mean leaf-level isoprene emission rate (50 nmol m⁻² s⁻¹) observed at the canopy top during August to the estimated horizontal area occupied by Quercus and Liquidambar. The leaf energy balance model and distance-weighted wind direction specific transect data are also used in estimating emissions. Only one canopy layer is assumed, however. The PAR and leaf temperature response algorithms are those of Guenther et al. [1993] in all four cases.

equal to 1173, 20.0, N = 14) as the foliage senesced in October. These fluxes are compared to emissions predicted from four configurations of BEIS2 using the meteorological conditions observed during each flux measurement. These four configurations are described below.

Model CNTYB2 is the simple configuration of BEIS2 used with a forest composition similar to that of Orange County, North Carolina, as determined by the database of Hansen et al. [1992]. This is a reasonable assumption for a larger forest fetch extending in all directions from the tower, since a larger component of pine is present to the northwest and several hundred meters to the south and west. Model SITEB2 is BEIS2 applied to the average forest composition, foliar mass, and leaf area determined from the 13 fixed radius plots in the primary forest fetch (Plate 1).

Since there is some variability in base emission rates between transects, we compared the REA fluxes with model estimates derived from the transect mean and weighted mean (1/D², where D is the plot center distance from the tower) associated with each REA measurement. In other words, if a flux was measured while the winds were predominantly from the west, the model estimate was derived using the canopy cover data from the transect oriented toward the west from the tower. Arrows on Plate 1 indicate the mean horizontal wind
Table 3. Statistics for Isoprene Flux Measurements and Model Simulations at the Blackwood Site

<table>
<thead>
<tr>
<th>Fluxes Measured Using REA System</th>
<th>Pre-October Fluxes</th>
<th>Pre-October, Primary Fetch Fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>39</td>
<td>25</td>
</tr>
<tr>
<td>Mean</td>
<td>3.78</td>
<td>5.74</td>
</tr>
<tr>
<td>Range</td>
<td>0.11–13.35</td>
<td>1.1–13.35</td>
</tr>
</tbody>
</table>

**Model CNTYB2**

| Mean                             | 2.66               | 3.40                            | 3.00                            |
| Range                            | 0.51–5.35          | 2.24–5.35                       | 2.22–4.95                       |
| RSD                              | 0.96               | 0.71                            | 0.71                            |
| NMSE                             | 1.06               | 0.84                            | 0.96                            |

**Model SITEB2**

| Mean                             | 4.70               | 5.99                            | 5.30                            |
| Range                            | 0.91–9.47          | 3.92–9.47                       | 3.92–8.77                       |
| RSD                              | 0.64               | 0.44                            | 0.43                            |
| NMSE                             | 0.33               | 0.19                            | 0.21                            |

**Model WISCEB**

| Mean                             | 7.96               | 10.18                           | 8.11                            |
| RSD                              | 0.89               | 0.56                            | 0.57                            |
| NMSE                             | 0.37               | 0.18                            | 0.23                            |

**Model BGLEAF**

| Mean                             | 5.27 (24.39)       | 6.61 (30.61)                    | 5.40 (25.00)                    |
| Range                            | 1.04–12.32 (4.82–57.06) | 1.24–12.32 (5.74–57.06)   | 3.84–8.88 (17.77–41.09)        |
| RSD                              | 0.64               | 0.48                            | 0.48                            |
| NMSE                             | 0.35               | 0.20                            | 0.25                            |

Units are mg C g⁻¹ h⁻¹ and also nmol m⁻² s⁻¹ for the big leaf model. RSD is the root mean square of model deviations divided by the mean of the REA fluxes (in mg C g⁻¹ h⁻¹). NMSE is the normalized mean square error as discussed in the text. Pre-October fluxes are measured before October 1. Primary fetch fluxes are measurements made while winds were from the south, southwest, and west.

Directions observed during each of the REA flux measurements. Average emission factors (EFs) and weighted EFs were estimated to be 38 (32), 32 (30), and 43 (45) µg C g⁻¹ h⁻¹ for the south, southwest, and west transects, respectively. This simple "footprint" adjustment accounted for modest additional variability (3 to 5%) in the REA flux data. A large improvement is not expected, considering the relatively low variability in abundance of the high isoprene emitting crown area between plots and transects measured. Lamb et al. [1996, p. 22, 791] conclude that isoprene flux footprint estimates in a study with similar instrument displacement height and meteorology (convective conditions) "were sharply peaked within 50 meters of the tower with 70% of the total flux within 100 m of the tower. At 300 meters upwind, the cumulative flux is predicted to equal 95% of the total flux." Similar estimates at this site (C.-I. Hsieh and G. Katul, unpublished data, 1997) yield very similar source flux footprint estimates. The forest structure and composition of the primary fetch beyond 150 m from the tower appear not to change appreciably at the Blackwood site. In addition, the fixed radius plots at the Blackwood site do not exhibit the extreme variability in composition of isoprene emitting biomass that is present in the Oak Ridge, Tennessee, study of Lamb et al. [1996].

Model WISCEB applies the vertical gradient in emission factors measured at the site (Table 2), the leaf energy balance model of Lamb et al. [1993], and the distance-weighted, wind-direction-specific transect data discussed above. Model BGLEAF applies the mean leaf level isoprene emission rate (65 nmol m⁻² s⁻¹ at PAR equal to 1000 µmol m⁻² s⁻¹ and leaf temperature equal to 30°C) observed at the canopy top during August (since the canopy level measurements also began on August 20) to the estimated horizontal area occupied by Quercus and Liquidambar. The leaf energy balance model and distance-weighted, wind-direction-specific transect data are also used in estimating emissions. Only one canopy layer is assumed, however. Since most of the direct beam PAR is intercepted by the upper foliage, where observed basal emission factors were the highest, emissions from lower levels were assumed to be negligible in this simulation. The PAR and leaf temperature response algorithms are those of Guenther et al. [1993] in all four cases.

Figure 2 shows the model results compared to the REA fluxes. Model CNTYB2 substantially underpredicts most of the REA fluxes, especially those from the primary fetch during August and September (Figure 2). This is expected, since the primary fetch contains a higher percentage of isoprene emitters than forests in Orange County (which are composed of approximately one-third pine) as a whole. Overall, Model SITEB2 performs better than CNTYB2 in terms of agreement with REA fluxes. Of the August and September simulations, 21 of the 25 were within 50% of the REA flux values. Mean predictions by SITEB2 of 5.99 mg C g⁻¹ h⁻¹ over this period also compared favorably with the mean REA flux values of 5.74 (see Table 3 for complete model comparison). Over the observed ambient temperature and solar radiation ranges the relative patterns of the BEIS2 models are very similar to the REA fluxes, indicating that the PAR and temperature algorithms developed by Guenther et al. [1993] do seem to extrapolate well to the canopy level.

Models WISCEB and BGLEAF somewhat overpredict most
emission rates, except at the higher temperatures encountered during September 14 and 16 when all models seem to underpredict measured isoprene fluxes. The leaf energy balance correction for leaf temperature used in WISCEB and BGLEAF appears to account partially for this, although underprediction still occurs. It is possible that the leaf level emission rates may have changed from August (late August and early September were also dry periods as indicated by the declining soil water content in Figure 3), or that REA sampling may have been subject to source variability in the footprint or "organized elements" discussed by Gao et al. [1993]. At this point our database is inadequate to address these factors.

The effects of the leaf energy balance model are observed in more detail in Figure 3. Here BEIS2 (SITEB2) is compared with BEIS2 using the energy balance model (BEIS2eb). Resulting leaf temperatures in the upper canopy simulated by BEIS2eb were 1°C to 3°C higher than air temperatures. In contrast, individual leaves, oriented toward the Sun and fully exposed, were up to 10°C warmer than the surrounding air. Leaves oriented away from the Sun exhibited much lower or no increases. This is in agreement with observations made by Knoerr [1966]. The energy balance model is more conservative in this increase because it considers a mean leaf-Sun angle which is less than 90°. Use of the energy balance model did improve model (WISCEB and BGLEAF in Figure 2, BEIS2eb in Figure 3) agreement with some of the flux estimates, although not substantially, since the increase in calculated leaf temperatures at the canopy top was small. Figure 3 shows the effect of applying the leaf energy balance model to BEIS2. It improves model agreement with 9 of the 25 pre-October REA measurements, especially those of mid-September. The largest increase in canopy temperature over air temperature was also observed during this period (September 14 and 16) as shown in Figure 3. The mid-September period was the only time when measured canopy surface temperature exceeded air temperature by more than 2°C. It is possible that the declining soil moisture, combined with high temperature and radiation levels, may have decreased the capacity of the forest canopy to dissipate heat through transpiration. During other periods, measured canopy temperature was usually within 1°C of air temperature and occasionally was 1°C-2°C lower.

It is interesting that the single layer BGLEAF model per-
formed nearly as well as the others in terms of agreement with the REA flux data (Figure 2, Table 3). This model offers the advantage of being computationally more efficient, since multiple levels of leaf area, biomass, and environmental variables need not be accounted for. In addition, relating leaf area emissions to surface fluxes is much simpler and not subject to uncertainties involved in extrapolating mass-based emissions to areal fluxes. The mean of pre-October isoprene fluxes from the REA data was 5.74 mg C m \(^{-2}\) hr \(^{-1}\) compared to 6.61 (30.61 nmol m \(^{-2}\) s \(^{-1}\)) for the BGLEAF model estimates for Northern WI. This study found isoprene emissions to be unrelated to stomatal aperture [Mortson et al., 1989].

Overall, model scores of Table 3 indicate that the simulations are in reasonable agreement with fluxes. Following the criteria of Lamb et al. [1996], the normalized mean square error (NMSE) is used to evaluate model performance. NMSE is given as

\[
NMSE = \frac{(O_i - P_i)^2}{PO}
\]

where \(O_i\) are the observed or REA-estimated fluxes and \(P_i\) are the model predictions. NMSE scores less than 0.4 are generally considered to be satisfactory [Lamb et al., 1996]. Fluxes observed after September 28 (Figures 2 and 3) seem to be lower than pre-October fluxes measured during similar temperature and radiation conditions, indicating a probable seasonal decline in isoprene emission potential. Model agreement is improved considerably when only the earlier measurements are considered. Deleting fluxes from the northwest and the southeast ("off-fetch") did not substantially improve overall model agreement. When wind speeds were less than 1.4 m s \(^{-1}\) (as was the case with the off-fetch REA fluxes measured during September 1 and 8), REA fluxes were also lower than model estimates (Figure 2). This would be expected considering the lack of high isoprene emitters near the tower in these directions. It should also be noted that REA measurements are probably less reliable at very low wind speeds. The two off-fetch measurements made during September 14 featured higher wind speeds (greater than 2 m s \(^{-1}\)) from the northwest, when fluxes somewhat higher than expected were measured.

Model scores using the site specific fetch data indicated good agreement with observed values, especially when only pre-October values were considered (Table 3). Each model component was within 20% of the values assumed in BEIS2, although June emission rates at the leaf level were much higher than expected. We suspect that these high values, and a reduction in the capacity of the canopy to cool by transpiration, resulted in a higher net isoprene flux, and/or (3) a reduction in the capacity of the canopy to cool by transpiration, leading to leaf temperatures which are substantially higher than surrounding air. Although stomatal conductance may be reduced during dry periods, isoprene emission has been found to be unrelated to stomatal apertures [Monson et al., 1995].
Considering the uncertainties associated with the flux measurement technique, small sample size, limited leaf level measurements, crude footprint model, and other factors, it is difficult to determine if any one configuration of BEIS2 performs appreciably better than the others. However, the overall agreement of BEIS2 with the fluxes measured at the Blackwood site is very encouraging. A comparison of BEIS2 estimates with other above-canopy (mixed-deciduous forests) isoprene flux studies in the United States is presented in Table 4. BEIS2 estimates are taken directly from the references listed in Table 4 or are calculated from meteorological and forest survey data collected during the studies. Surface layer measurements employ micrometeorological techniques to estimate fluxes directly from forest canopies over areas of roughly a few hectares. Mixed layer flux estimates are based on isoprene concentration gradients (or mixed-layer mean concentrations) at heights of roughly 50 m to over 1 km. Source regions for fluxes determined using these techniques range from approximately 5 to several thousand square kilometers. See Guenther et al. [1996a, b, c] and Lamb et al. [1985, 1996] for further details on these techniques.

With one exception, mean BEIS2 estimates are within 50% of measured flux estimates presented in Table 4. Daytime average flux estimates range from roughly 1 to 10 mg C m⁻² h⁻¹. The one exception is from the southern Pennsylvania data of Lamb et al. [1985] where several of the fluxes were measured during relatively low temperature conditions (approximately 20°C). When these measurements were eliminated from the comparison (i.e., measurements compared when ambient air temperatures were between 25° and 35°C), the flux data from
this site also compare favorably with BEIS2 estimates (Figure 4). Variation in flux estimates from these studies can be largely explained by the percentage of high isoprene emitting leaf area (primarily oaks, sweetgum, and aspen) in the source region of each study. This is illustrated in Figure 4, where above-canopy emissions from the studies listed in Table 4 are standardized to air temperatures of 30°C and an above-canopy PAR of 1000 μmol m⁻² s⁻¹ and plotted against the estimated fraction of the respective source region occupied by the high isoprene emitting leaf area. This is estimated from forest survey and/or remote sensing data compiled during each study. To minimize potential errors due to standardizing [Guenther et al., 1993], only those emissions measured when ambient temperature was between 25°C and 35°C and PAR > 400 μmol m⁻² s⁻¹ are included in this plot.

Guenther et al. [1996c] and Lamb et al. [1996] describe results from the study near Oak Ridge, Tennessee, where isoprene emissions were measured at leaf, branch, canopy, and landscape scales. Canopy level fluxes using gradient profile and REA techniques during similar meteorological conditions were very similar to those presented here (Table 4). Biomass density of high isoprene emitters (predominantly oaks) ranged from 110 to 220 g m⁻² [Lamb et al., 1996], also similar to the range estimated from the fixed radius plots at Blackwood (150 to 200 g m⁻²). Guenther et al. [1996c] show that emission rates are compatible at all scales, again lending confidence to current isoprene emission schemes. However, these authors, Guenther et al. [1996b, c] and Sharkey et al. [1996], recommend that leaf-level isoprene emission rates of 100 μg C g⁻¹ h⁻¹ for the genera Quercus and Populus be used in modeling compared to 70 μg C g⁻¹ h⁻¹ currently used in BEIS2.

Recommendations

Results presented in this paper indicate that current BVOC emission models agree reasonably well with the limited data collected at the Blackwood site during 1994. More detailed leaf microenvironment models may be needed to explain model deviations from observed isoprene emission rates, especially those observed during warm, dry periods. The simple leaf energy balance model examined in this study appears to yield reasonable estimates of canopy surface temperature. However, Fuentes et al. [1992] found that this model underestimated leaf temperature at lower levels within an aspen canopy by as much as 10°C. It may also be necessary to consider the developmental climate [Monson et al., 1994] of forest canopies over a growing season in more detail to further improve the accuracy of isoprene emission models such as BEIS2. We plan to make REA VOC measurements over the course of at least two growing seasons to examine these effects. Determinations of transpiration at leaf, tree, and canopy scales will also be made to aid in understanding moisture effects on isoprene emissions. It is our hope that simultaneous comparisons of leaf and stand level emissions over multiple growing seasons will aid in developing relationships between seasonality, drought events, and isoprene emission. Foliage angle distributions and optical properties will also be studied to examine the validity of current canopy environment models.

To test scaling assumptions, leaf-level emission rates from other species in the fetch, especially the oaks, will also be measured several times during the year. Leaf-level isoprene emission measurements reported at this site thus far are primarily from a white oak near the tower. The predominant oaks in the footprint, however, are Quercus michauxii (swamp chestnut oak) and Q. phellos (willow oak), with each accounting for approximately 15% of the leaf area (or foliage biomass) in the footprint. Similar efforts are needed at other sites in order to derive robust emission factors for high isoprene emitting genera and to characterize interspecific and intraspecific variability within genera, particularly the oaks (Quercus spp.). Such variability has been found to be significant for Picea (spruce) in the work of Kempf et al. [1996] and should be incorporated into models such as BEIS2 when appropriate.

Simple "footprint" analyses also seem to explain some variability in observed fluxes. More detailed models such as those used over more uniform fetches [Leclerc and Thurtell, 1990; Horst and Weil, 1992] may perhaps be adapted to forest stands to further examine footprint effects on measured and modeled fluxes. This will likely require a more complete classification of the canopy surrounding the tower, possibly from aerial photographs or other remotely sensed information such as Landsat imagery [Guenther et al., 1996c].

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