

## Seasonal course of isoprene emissions from a midlatitude deciduous forest

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**Abstract.** Continuous measurements of whole canopy isoprene emissions over an entire growing season are reported from Harvard Forest (42°32'N, 72°11'W). Emissions were calculated from the ratio of observed CO<sub>2</sub> flux and gradient multiplied by the observed hydrocarbon gradients. In summer 1995, 24-hour average emissions of isoprene from June 1 through October 31 were  $32.7 \times 10^{10}$  molecules cm<sup>-2</sup> s<sup>-1</sup> ( $\text{mg C m}^{-2} \text{ h}^{-1} = 2.8 \times 10^{11}$  molecules cm<sup>-2</sup> s<sup>-1</sup>), and the mean midday mixing ratio was 4.4 ppbv at 24 m. Isoprene emissions were zero at night, increased through the morning with increasing air temperature and light, reached a peak in the afternoon between the peaks in air temperature and light, and then declined with light. Isoprene emissions were observed over a shorter seasonal period than photosynthetic carbon uptake. Isoprene emission was not detected from young leaves and reached a peak rate (normalized for response to measured light and temperature conditions) 4 weeks after leaf out and 2 weeks after emissions began. The normalized emission rate remained constant for approximately 65 days, then decreased steadily through September and into October. Total isoprene emissions over the growing season (42 kg C ha<sup>-1</sup> yr<sup>-1</sup>) were equal to 2% of the annual net uptake of carbon by the forest. Measured isoprene emissions were higher than the Biogenic Emission Inventory System-II model by at least 40% at midday and showed distinctly different diurnal and seasonal emission patterns. Seasonal adjustment factors (in addition to the light and temperature factors) should be incorporated into future empirical models of isoprene emissions. Comparison of measured isoprene emissions with estimates of anthropogenic volatile organic compound emissions suggests that isoprene is more important for ozone production in much of Massachusetts on hot summer days when the highest ozone events occur.

### 1. Introduction

Emission of isoprene (2-methyl-1,3-butadiene) by terrestrial vegetation provides the dominant input of reactive non-methane hydrocarbons (NMHC) to the atmosphere and influences tropospheric chemistry on both regional and global scales [Zimmerman, 1979; Chameides *et al.*, 1988; Winer *et al.*, 1989; Singh and Zimmerman, 1992; Fehsenfeld *et al.*, 1992]. Isoprene is principally removed from the troposphere through oxidation by hydroxyl radicals, and in the presence of oxides of nitrogen (NO<sub>x</sub> = NO + NO<sub>2</sub>) is closely coupled to the photochemical production of ozone. Photochemical

modeling studies have shown that ozone production in the northeastern United States is quite sensitive to biogenic NMHC emissions [McKeen *et al.*, 1991; Roselle *et al.*, 1991; Sillman *et al.*, 1990] and that the uncertainty in those emissions introduces large uncertainty into predictions of reductions that could be achieved through NMHC or NO<sub>x</sub> emission control strategies. Hirsch *et al.* [1996] found that seasonality of ozone production efficiency per unit NO<sub>x</sub> determined from the Harvard Forest data was tightly coupled to seasonality of isoprene emissions. Furthermore, meteorological conditions that cause the highest isoprene mixing ratios (hot, sunny, and stable) also maximize ozone production.

Isoprene production is closely linked to photosynthetic processes [Sharkey *et al.*, 1991], and control over its production is coupled to isoprene synthase activity [Monson *et al.*, 1992]. Sharkey and Singaas [1995] have shown that isoprene emission increases the thermal tolerance of plants,

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and suggest that protection from heat may be the primary reason plants emit isoprene.

Isoprene emission from vegetation has been measured in natural environments using branch, leaf, and whole tree enclosure [Zimmerman, 1979; Lamb *et al.*, 1985; Lamb *et al.*, 1986; Khalil and Rasmussen, 1992; Monson *et al.*, 1994; Pier, 1995], tracer release [Lamb *et al.*, 1986], mixed layer and surface layer micrometeorological techniques [Knoerr and Mowry, 1981; Lamb *et al.*, 1985; Baldocchi *et al.*, 1995; Guenther *et al.*, 1996a, b, c], and in controlled laboratory settings [Sanadze, 1969; Tingey *et al.*, 1979; Monson and Fall, 1989; Guenther *et al.*, 1991]. Isoprene emission rates were observed to depend on both light and temperature and were zero at night. Studies of individual leaves showed isoprene emissions to be linearly dependent on the flux of photosynthetically active radiation (PAR) to a saturation point of approximately  $1000 \mu\text{E m}^{-2} \text{s}^{-1}$ , and exponentially dependent on temperature up to approximately  $35^\circ\text{C}$ , where emissions start to level off and eventually decline near  $40^\circ\text{C}$ . However, Sharkey *et al.* [1996] found that isoprene emission from oak trees is not fully light saturated at  $1000 \mu\text{E m}^{-2} \text{s}^{-1}$  under field conditions. Isoprene emission rates also depend on leaf age. Measurements on aspen leaves [Monson *et al.*, 1994] have shown that onset of emissions begins after a given number of growing days above  $5^\circ\text{C}$ , increases for approximately 3 weeks, holds steady for approximately 8-10 weeks, and decreases thereafter. Similar results were observed using leaf enclosures [Fuentes *et al.*, 1995] and whole tree enclosures [Pier, 1995].

Models of tropospheric chemistry and photochemical ozone production require accurate estimates of biogenic isoprene emissions. Currently, the U.S. Environmental Protection Agency uses inventories calculated from the Biogenic Emission Inventory System II (BEIS2) [Geron *et al.*, 1994]. These models calculate emissions using databases of forest type or species composition, biomass density, basal emission rate (species dependent), and the response of isoprene emission to temperature and PAR from Guenther *et al.* [1993]. Leaf temperature and PAR are derived from ambient conditions above the ecosystem, and a canopy model is used to estimate their distribution at five vertical levels in the canopy. Two scenarios are used: (1) leaf temperature is assumed to equal above canopy air temperature (BEIS2), (2) leaf temperature is estimated using the energy balance model of Lamb *et al.* [1993] (BEIS2E). The model is designed to simulate midsummer emissions and assumes that, for a given ecosystem, emission rates vary only with temperature and PAR. The model does not include diurnal or seasonal changes in the basal emission factors.

In order to quantify whole ecosystem isoprene emissions, determine the response to temperature, light, and phenology, assess regional significance, and test the accuracy of current biogenic emission models, we built and deployed an automated system to continuously measure isoprene fluxes and relevant environmental variables which control them. In this paper we present a nearly continuous record of whole canopy isoprene emissions over an entire growing season.

## 2. Experiment

### 2.1. Site

Harvard Forest is located in Petersham, Massachusetts ( $42^\circ32'\text{N}$ ,  $72^\circ11'\text{W}$ ; elevation 340 m), 100 km west of

Boston, Massachusetts, and 100 km northeast of Hartford, Connecticut. There is a highway  $\approx 5$  km to the north and a secondary road  $\approx 2$  km to the west. The site is accessible by a dirt road, which is closed to public vehicle traffic. Measurements were made from a 30 m tower, erected in May 1989, extending 7 m above the forest canopy. Instruments were housed in a temperature controlled shack located 15 m east of the tower.

The forest is 50 to 70 years old with a deciduous leaf area index of 3.5 (measured in 1994 by leaf litter collection by M. Goulden (unpublished data, 1994)). The tree species in descending order of abundance are oak (mostly red), red maple, red pine, hemlock, birch, white pine, and cherry with percent basal areas (stem cross-sectional area at 1.37 m determined from plot surveys (M. Goulden unpublished data, 1994) of 36.4, 21.8, 16.2, 15.6, 3.5, 2.9, and 2.3, respectively. The terrain is moderately hilly (relief  $\approx 30$  m), but there is no evidence of anomalous flow patterns that would make eddy-flux measurements at this site unrepresentative [Moore *et al.*, 1996], and measurements of the local energy budget are balanced to 20% [Goulden *et al.*, 1996a].

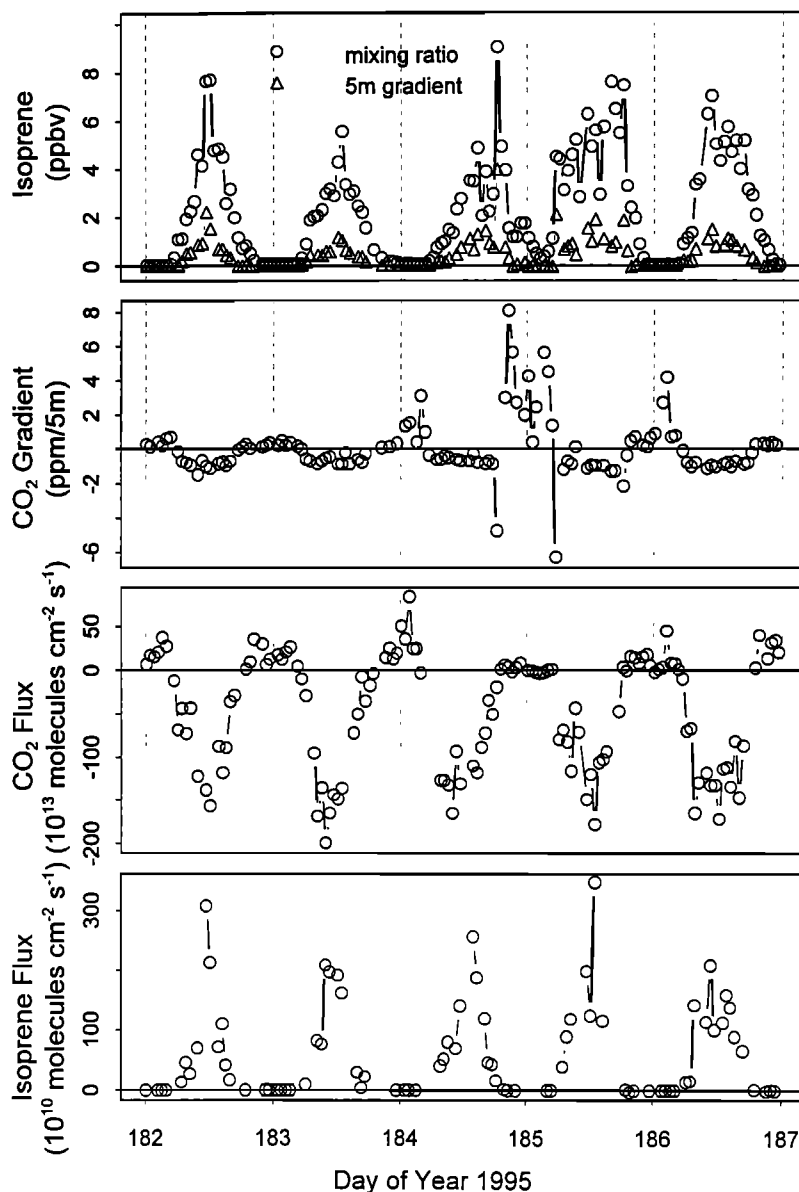
Measurements of  $\text{C}_2\text{-C}_6$  NMHCs were made in air sampled simultaneously from 2 and 7 m above the forest canopy every 45 min, commencing July 22, 1992 [Goldstein *et al.*, 1995a, b, 1996]. Other trace gas mixing ratios and meteorological conditions have been measured continuously at this site since 1990, including  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}_3$ ,  $\text{NO}_x$ ,  $\text{NO}_y$  ( $\text{NO} + \text{NO}_2 + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{HNO}_3 + \text{peroxyacetyl nitrate} + \text{other organic nitrates} + \text{organic aerosols}$ ),  $\text{H}_2\text{O}$ , rainfall, wind speed, wind direction, temperature, radiation, and eddy covariance fluxes of sensible heat, latent heat,  $\text{O}_3$ ,  $\text{NO}_y$ , and  $\text{CO}_2$  [Wofsy *et al.*, 1993; Munger *et al.*, 1996, 1998; Moore *et al.*, 1996; Goulden *et al.*, 1996a,b].

### 2.2. Flux-Gradient Similarity Calculation

We use a similarity approach for determining isoprene flux for a whole forest ecosystem, based on other quantities for which we have both mixing ratio data and direct measurements of flux [Goldstein *et al.*, 1996]. The trace gas flux ( $F$ ) is assumed to be proportional to the time-averaged mixing ratio gradient ( $dC/dz$ ) above the forest for intervals longer than the timescale for the slowest significant turbulent events (10 min):

$$F = K dC/dz, \quad (1)$$

where  $K$  is the exchange coefficient for the averaging interval. In 1993 we determined  $K$  simultaneously from fluxes and vertical gradients of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at this site [Goldstein *et al.*, 1996].  $\text{CO}_2$  has a source at the ground and a sink in the canopy, while  $\text{H}_2\text{O}$  and isoprene are both emitted from the canopy; thus  $\text{CO}_2$  is not strictly similar to these other scalars.  $K_{\text{CO}_2}$  was 20% lower than  $K_{\text{H}_2\text{O}}$  in the afternoon (1200-1800), and was 20% higher early in the day (0600 - 0900) and late in the day (1900-2100). Theoretical calculations suggest that  $K$  for isoprene and  $\text{H}_2\text{O}$  should be equal, but that  $K_{\text{CO}_2}$  should be 20% lower over a deciduous forest [Baldocchi *et al.*, 1995], in agreement with our afternoon values. In this study, we compute  $K$  using measurements of  $\text{CO}_2$  flux and gradient and take the product of this  $K$  with the isoprene gradient to determine the isoprene flux (Figure 1). We chose to use  $K_{\text{CO}_2}$  because we did not have routine measurements for  $\text{H}_2\text{O}$  or temperature gradients. Our choice of  $K$  may introduce a systematic underestimation of the



**Figure 1.** Isoprene mixing ratio at 24 m, isoprene gradient, CO<sub>2</sub> gradient, CO<sub>2</sub> flux, and isoprene flux (July 1 to 6, 1995).

isoprene flux in the afternoon of up to 20%; additionally, we may overestimate fluxes in the morning and evening by up to 20% though the fluxes are small at these times of day. The seasonal cycle of isoprene emissions is presented in this paper as midday mean flux values from 1000 to 1500, during which time the mean systematic underestimate of the flux may be roughly 12% based on comparison of  $K$  from H<sub>2</sub>O and CO<sub>2</sub> during this time of day. These systematic errors are smaller than the overall uncertainty in the individual hydrocarbon flux measurements and should not affect the long-term precision of the measurements or modify the observed seasonal cycle, which is the primary contribution of this study. The coefficient of variation (standard deviation/flux) for individual isoprene flux measurements during typical daytime summer conditions is 28% and is mostly due to uncertainties in quantifying the small gradients of CO<sub>2</sub> above the forest (for detailed discussion of the error analysis see Goldstein *et al.*, [1996]).

### 3. Measurements

The analytical system for automated in situ measurements of hydrocarbon mixing ratios and gradients has been described in detail elsewhere [Goldstein *et al.*, 1995a]; thus only a brief description will be given here. Recovery of isoprene in the initial instrument configuration was low due to loss on the inner surfaces of stainless steel tubing. The loss of isoprene was eliminated in May 1995 by replacing all 1/16 inch stainless steel tubing in the sampling and preconcentration system with stainless steel tubing lined with fused silica (Silcosteel).

Air was drawn continuously from two inlets (24 and 29 m). Samples for analysis were extracted from the inlet lines and passed through glass cold traps at -20°C and Ascarite II (Thomas Scientific) traps to remove H<sub>2</sub>O, O<sub>3</sub>, and CO<sub>2</sub>. Samples were cryogenically preconcentrated on dual traps (40 mL min<sup>-1</sup> of air for 10 minutes onto fused silica lined 1/16

inch OD stainless steel tube, Silcosteel), and injected into a gas chromatograph with dual flame ionization detectors (Hewlett Packard 5890 series II). Chromatographic separation was accomplished using 30 m PLOT GS-Alumina Megabore capillary columns (J+W Scientific). Every fifth pair of samples was taken from the same altitude (29 m) by switching a valve near the inlet of the 24 m sampling line in order to determine the null for the observed mixing ratio gradient. The measurement system could operate continuously and unattended for 2 weeks, although data were normally downloaded at 6 day intervals. Mixing ratios for most hydrocarbons were determined using relative response factors [Ackman, 1964, 1968; Dietz, 1967] referenced to an internal neohexane standard (Scott-Marrin, National Institute of Standards and Technology (NIST) traceable  $\pm 2\%$ ) added to every sample near the sample inlet by dynamic dilution. Response factors for isoprene were determined from dynamic dilution of isoprene standards (Scott-Marrin, NIST traceable  $\pm 2\%$ ) added to ambient air samples near the sample inlet at the top of the tower and near the instrument at the bottom of the tower periodically from May to November 1995.

The analytical system was checked for contamination daily by running zero-air blanks. In addition, the Teflon sampling tubes were checked for contamination and memory effects by introducing zero-air at the sample inlets on top of the tower. No contamination or memory effects were detected for isoprene, and there was no detectable loss of isoprene in the Teflon sampling tubes.

The accuracy of the isoprene measurements was estimated to be  $\pm 8\%$ , based on the cumulative uncertainty of the isoprene standard, measurements of standard addition flows, and the integrity of isoprene in the sampling and analysis process. Measurement precision was approximately 3% at 1 ppbv, 5% at 0.5 ppbv, 10% at 0.2 ppbv, and 20% for mixing ratios less than 0.1 ppbv, as determined by the variance between measurements taken from the same level every fifth injection. The detection limit was approximately 0.01 ppbv.

Mixing ratio gradients of  $\text{CO}_2$  were measured simultaneously with the hydrocarbon gradients using a differential infrared gas analyzer (LICOR 6251), with air from 29 m passed through the reference cell and air from 24 m through the sample cell. Water vapor was removed from the air samples using nafion dryers, and the samples were assumed to be at a common temperature before analyzing for  $\text{CO}_2$ . The null gradient was measured after every sampling period by passing air from 29 meters through both cells. Instrument gain was determined by sequential standard addition of  $\text{CO}_2$  to the sample and then the reference air. The standard deviations of the zero gradient measurements were determined by comparing the null gradient measured every fifth sampling period (when hydrocarbon null gradients were determined) to the zero measurement directly following that period. The standard deviation in the zero measurements for  $\text{CO}_2$  (0.18 ppm) was  $\approx 20\%$  of the mean midday gradients (-0.9 ppm  $\text{CO}_2$ ). Flux determinations were not attempted when observed gradients were very small, i.e., within 1 standard deviation of zero. The  $\text{CO}_2$  fluxes and gradients, and all the NMHC measurements are reported as mole fractions relative to dry air at a common temperature, avoiding the need for density corrections due to gradients in temperature or  $\text{H}_2\text{O}$  [Webb *et al.*, 1980].

## 4. Effects of Isoprene Source Spatial Heterogeneity

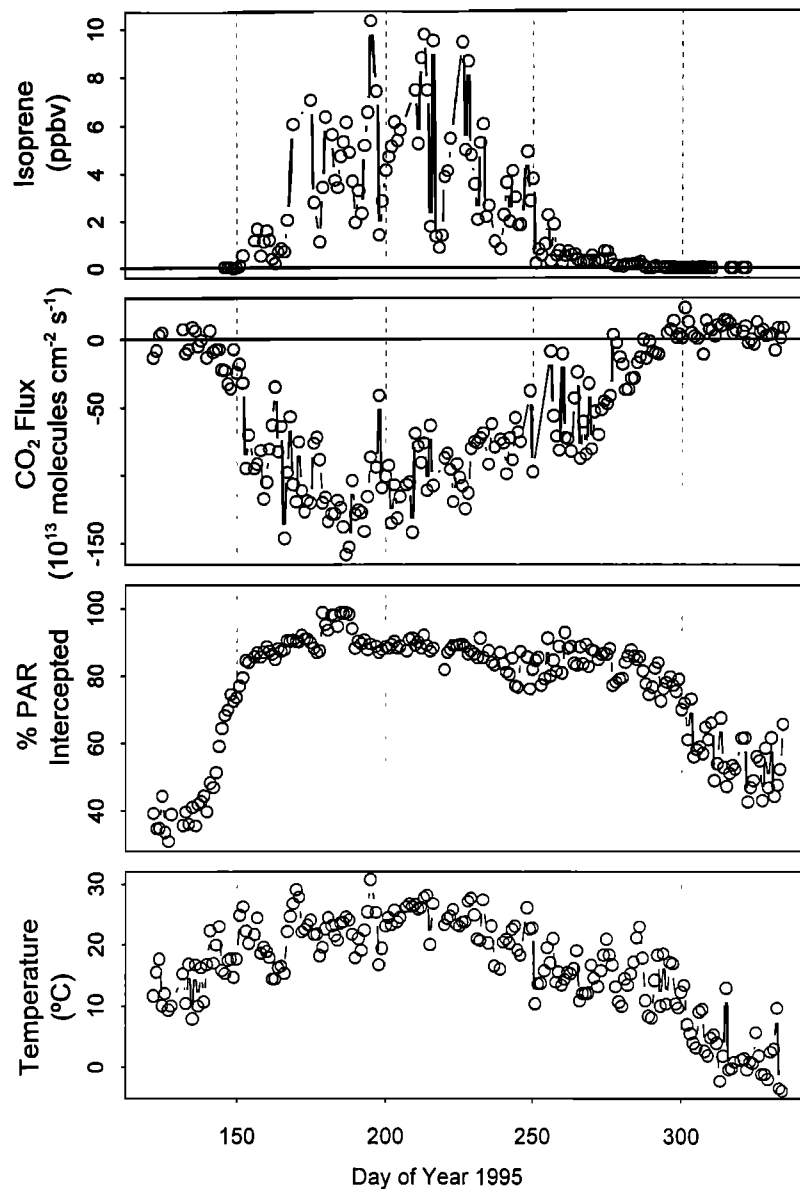
An inherent weakness in the gradient approach for quantifying isoprene fluxes is that the lower sampling intake has a different effective footprint than the upper sampling intake. If the isoprene source from the forest canopy is heterogeneous, this difference in footprints for the sample intakes could bias the measured fluxes. To determine whether isoprene emission was heterogeneous, we examined whether fluxes varied with wind direction from the tower. We calculated a normalized emission rate as measured/(modeled using BEIS2E), effectively removing the influence of light and temperature from the emission measurements, as represented by the model. Data were parsed into four wind quadrants ( $0^\circ$ - $90^\circ$  (NE),  $90^\circ$ - $180^\circ$  (SE),  $180^\circ$ - $270^\circ$  (SW), and  $270^\circ$ - $360^\circ$  (NW)) and the mean normalized emission rates were compared. The mean midday (1000 - 1500 EST, June 15 to August 31) measured flux was 35% higher than the model. The mean normalized flux from the SW, NW, and NE wind quadrants agreed within  $\pm 6\%$ . The SE wind quadrant was 20% lower than the mean of the other three wind quadrants (NE 1.29, SE 1.16, SW 1.39, NW 1.42). The percentage of data from each quadrant was 10%, 18%, 45%, and 28%, respectively. This comparison of normalized flux by wind quadrant suggests that systematic isoprene flux errors due to spatial heterogeneity of isoprene sources at our site are unlikely to be higher than 20% and are probably less than 10%.

## 5. Results and Discussion

### 5.1. Isoprene Ambient Mixing Ratios

Isoprene mixing ratios had a diurnal cycle with maximum mixing ratios in the afternoon, and minimum mixing ratios at night (Figure 1). The mean summer daytime mixing ratio at 24 m was 4.4 ppbv (averaged from 1200 to 1600 EST, days 170-250); midday mixing ratios exceeded 15 ppbv on 3 days. The daytime isoprene mixing ratio at 29 m was typically 25% lower than the 24 m mixing ratio. Summer daytime null gradient measurements showed excellent agreement between the parallel measurement channels with a mean ratio of  $1.007 \pm 0.023$  (standard deviation). Nighttime mixing ratios varied with atmospheric stability and the previous day's emissions. On windy nights isoprene mixing ratios were usually below the instrument detection limit ( $< 10$  pptv). On stable nights that followed days with significant emissions, mixing ratios were typically between 0.1 and 2 ppbv and decreased slowly until isoprene emissions resumed in the morning. There was no observable gradient from 24 to 29 m during the stable nights (e.g. night of day 184-185), indicating that nighttime isoprene loss was due mainly to chemical reactions (probably with ozone or nitrate) rather than direct deposition to the forest.

The seasonal courses of isoprene mixing ratio (24 m), carbon dioxide flux, percent PAR intercepted by the canopy (measured from fixed platforms at 30 and 15 m, above and below the canopy), and air temperature are shown in Figure 2 as midday mean values (1000 to 1500 EST). Percent of PAR intercepted indicates the change in leaf density in the forest, and increased from less than 40% as the leaves began to emerge (day 140) to 90% when the canopy was fully



**Figure 2.** Isoprene mixing ratio at 24 m, CO<sub>2</sub> flux, percent photosynthetically active radiation (PAR) intercepted by the canopy, and air temperature at 29 m (May to November 1995, midday means from 1000 to 1500 EST).

developed (approximately day 160). It remained constant through the summer until the leaves began to senesce around day 240, and continued to decline slowly as the leaves fell off the trees. CO<sub>2</sub> uptake followed a similar pattern in the spring beginning about day 140 and reached a maximum rate after day 160. Photosynthetic uptake decreased after day 230 as the leaves began to senesce, and shut off completely around day 290. The first isoprene emissions of the growing season were detected on day 152, when air temperature exceeded 25°C after two nights in a row with temperatures remaining above 13°C. Isoprene emissions did not begin until the forest canopy had reached a mature state, 2 weeks after leaves began to emerge and photosynthesis had begun. The seasonal change in isoprene emission is not a function of temperature and light alone. The processes that control isoprene emission from oaks are apparently not active in young leaves and

decrease as the leaves age, similar to observations of aspen leaves by *Monson et al.* [1994]. Isoprene mixing ratios decreased rapidly after day 250, coinciding with decreased air temperature, nighttime temperatures falling below 10 °C regularly, photosynthetic uptake by the canopy declining, and leaf senescence beginning.

## 5.2. Isoprene Emission Rates

Plate 1 shows isoprene emission rates during midsummer (days 165-230) as a function of both light and temperature measured above the canopy at 29 m. Isoprene emissions were not detected during periods with low light (PAR < 300  $\mu\text{E m}^{-2} \text{s}^{-1}$ ) or air temperature below approximately 13 °C. Emission rates increased exponentially with temperature and linearly with PAR up to a saturation point of approximately 1000  $\mu\text{E m}^{-2} \text{s}^{-1}$ , as has been observed in other studies. However,

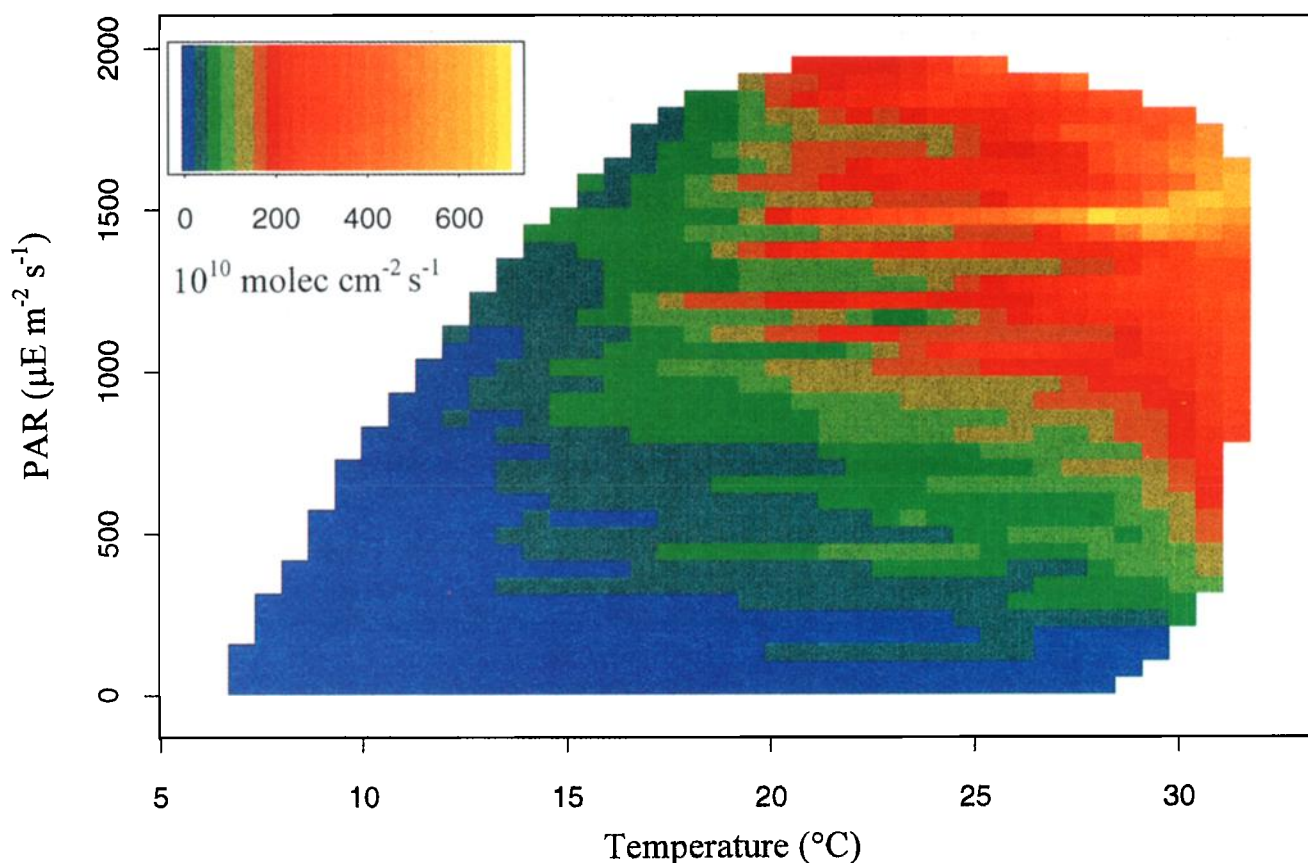


Plate 1. Isoprene flux as a function of light and temperature (June 14 to August 18, 1995).

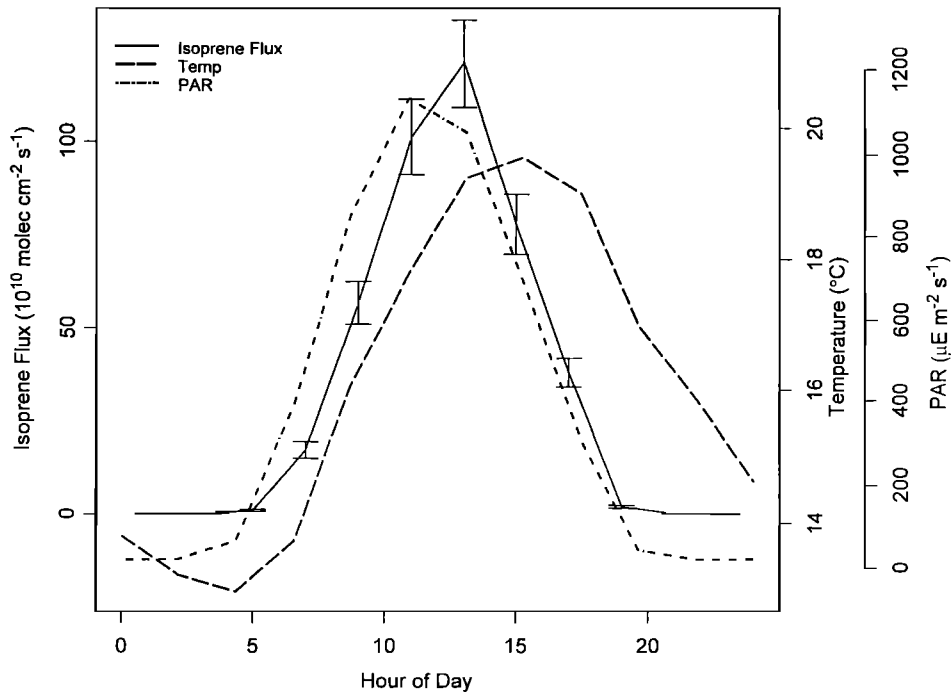
maximum emissions did not necessarily occur simultaneously with maximum temperature or maximum PAR. On average, isoprene emissions were zero at night, began after sunrise, increased through the morning with increasing air temperature and PAR, reached a peak in the afternoon between the maxima in air temperature and PAR, and declined with decreasing PAR toward the end of the day (Figure 3). The mean isoprene emission over the whole growing season (24 hour mean from June to October 1995, calculated by integrating the mean diurnal flux (Figure 3)) was  $32.7 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , giving an annual emission rate of 48 kg isoprene  $\text{ha}^{-1} \text{yr}^{-1}$ , with emissions occurring mainly from mid-June through mid-September.

Previous above canopy isoprene flux studies from a wide variety of ecosystems in the United States yield estimates ranging from 30 to  $300 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  when standardized to air temperatures of  $30^\circ\text{C}$  and above canopy PAR of  $1000 \mu\text{E m}^{-2} \text{s}^{-1}$  [Guenther *et al.*, 1996 a,b,c; Lamb *et al.*, 1985; Baldocchi *et al.*, 1995; summarized in Geron *et al.*, 1997]. Our measurements are near the high end of these values ( $307 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at  $30 \pm 2^\circ\text{C}$  with PAR  $> 1000 \mu\text{E m}^{-2} \text{s}^{-1}$ ) and are in reasonable agreement with those at sites with similar oak abundance.

### 5.3. Regional Significance of Isoprene Emissions

Red oak is the dominant isoprene-emitting plant at Harvard Forest and in Massachusetts. If we assume that all of

Massachusetts has a similar composition to Harvard Forest (80% is probably more accurate, based on oak tree distributions in the database of Geron *et al.* [1994]), our results suggest that  $10^5$  metric tons  $\text{yr}^{-1}$  of isoprene are emitted from Massachusetts forests. The National Acid Precipitation Assessment Program (NAPAP)[1985] estimates that  $1.1 \times 10^5$  metric tons of volatile organic carbon (VOC) are emitted from anthropogenic sources during the summer in Massachusetts. Thus, on the average day from June through October, biogenic isoprene emissions are approximately equal to total anthropogenic VOC emissions; however, on hot summer afternoons when the highest ozone episodes occur, isoprene emissions increase dramatically. For example, mean isoprene emissions around midday (PAR  $> 1000 \mu\text{E m}^{-2} \text{s}^{-1}$ ) were 89, 176, and  $307 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  at 20, 25, and  $30 \pm 2^\circ\text{C}$ , respectively. At  $30^\circ\text{C}$ , isoprene emission rates are approximately 9 times the 24 hour average summertime emission rate. In addition, isoprene is estimated to be 2.5 times as effective for photochemical ozone production per atom of carbon as the typical mix of VOCs found in urban air [National Research Council (NRC), 1991]. Assuming that anthropogenic VOC emissions are substantially less temperature dependent than biogenic isoprene emissions, our measurements suggest that isoprene is more important than anthropogenic VOCs for photochemical ozone production on hot summer days in much of Massachusetts (outside of the largest urban areas).



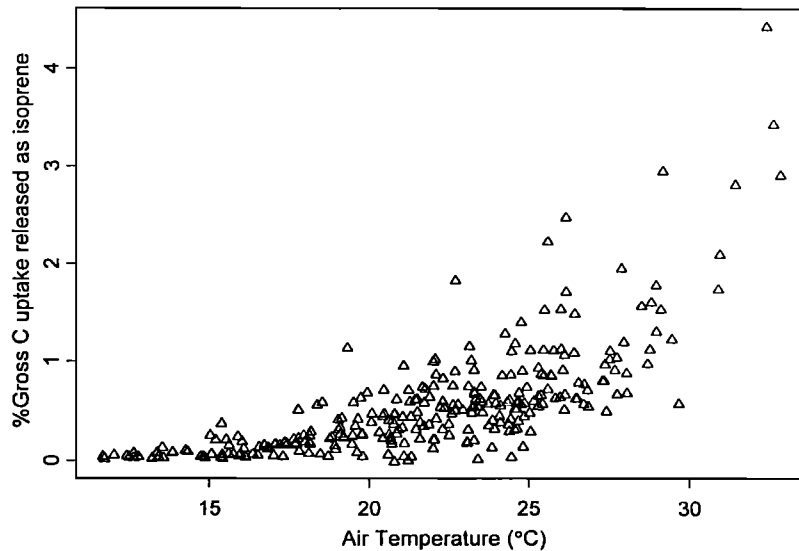
**Figure 3.** Mean diurnal cycle of isoprene flux ( $\pm$  standard error) along with temperature at 29 m and incident photosynthetically active radiation (PAR) (June 1 to October 31, 1995). Data were parsed into 2-hour time windows.

**6. Comparison to Net Ecosystem Production**

The percent of gross carbon uptake returned to the atmosphere as isoprene is strongly temperature dependent (Figure 4, calculated as isoprene flux divided by gross ecosystem production during summer midday periods). In Harvard Forest, approximately 1% of the gross carbon uptake is released as isoprene at 25°C, and the percentage increases with temperature. These measurements reflect the uptake of

carbon by a mixture of plants that do not all release isoprene, and this fraction is certainly higher for plants that emit isoprene.

Annual isoprene emissions ( $42 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ ) equal 2% of the net carbon uptake at Harvard Forest ( $2200 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ , five year mean value [Goulden *et al.*, 1996b]). The percentage of photosynthesized carbon that is released as isoprene has been reported in many studies to be between 0.1 and 3%, and occasionally higher for leaf level measurements [Sharkey *et*



**Figure 4.** Percent gross carbon uptake released as isoprene as a function of air temperature.



*al.*, 1996]. Isoprene emissions do not represent a major carbon loss from this ecosystem but are potentially significant on a shorter time scale during hot summer days.

### 6.1. Isoprene Emission Model Scenarios

The isoprene emission model used is BEIS2 as described by *Geron et al.* [1994]. Isoprene emission rates are assumed to be  $70 \mu\text{gC (g-foliar dry mass)}^{-1} \text{h}^{-1}$  standardized for PAR values of  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$  and  $30^\circ\text{C}$  for the oaks, and  $0.1 \mu\text{gC (g-foliar dry mass)}^{-1} \text{h}^{-1}$  for the other species. This forest average basal emission factor (EF) was determined by multiplying the fraction of oak and non-oak basal areas by their corresponding EFs, yielding an average EF of  $25 \mu\text{gC (g-foliar dry mass)}^{-1} \text{h}^{-1}$ . Since oaks have greater crown area in proportion to basal area compared to other genera (e.g., birch, pine) this likely represents an underestimate of oak foliage on the order of 5% [*Geron et al.*, 1997].

The empirical algorithms of *Guenther et al.* [1993] were used to adjust emission rates to ambient PAR and temperature conditions. Exponential decay algorithms are applied to reduce PAR and specific leaf weight at lower levels within forest canopies [*Geron et al.*, 1994]. The measured LAI of 3.5 was used in the model simulations.

This model assumes that leaf temperatures are equivalent to ambient air temperatures above the forest canopy. Since leaf temperatures can differ substantially from surrounding air temperature (especially in the upper canopy), the leaf temperature energy balance of *Gates and Papian* [1971] used by *Lamb et al.* [1993] and *Geron et al.* [1997] was also used to estimate leaf temperature in scenario BEIS2E. Vertical gradients of humidity, wind speed, solar radiation, and air temperature were estimated from measurements taken above the canopy by applying the profiles of *Lamb et al.* [1993].

### 6.2. Comparison With Models

Measured isoprene emissions were 40% higher than the BEIS2E model and 100% higher than the BEIS2 model at midday and showed distinctly different diurnal and seasonal emission patterns. The current oak basal emission factor of  $70 \mu\text{gC g}^{-1} \text{h}^{-1}$  has an estimated uncertainty of  $\pm 50\%$ . However, recent scaling studies at other sites have suggested that rates of  $100 \mu\text{gC g}^{-1} \text{h}^{-1}$  or more may be more realistic [*Guenther et al.*, 1996c; *Lamb et al.*, 1996; *Geron et al.*, 1997]. Indeed, at Harvard Forest, researchers using environmentally controlled leaf cuvette systems (for methods, see *Harley et al.* [1997] and *Sharkey et al.* [1996]) measured rates during July 1995 and 1996 ranging from approximately 70 to over  $160 \mu\text{gC g}^{-1} \text{h}^{-1}$  (C.D. *Geron et al.*, manuscript in preparation, 1998). Taken together, these results suggest that a peak summer oak basal emission rate of  $100 \mu\text{gC g}^{-1} \text{h}^{-1} \pm 50\%$  would be more appropriate for the model. These higher basal emission rates could account for the difference between the measured and modeled isoprene fluxes.

The diurnal and seasonal cycles of the isoprene emission rate are examined by normalizing the measured isoprene emissions to those calculated with the BEIS2 models (as described above). This normalized emission rate removes the effects of temperature and PAR as represented by the model. If the normalized emission rate equals 1 then the measurements and model are in perfect agreement. Deviations from 1 indicate changes in the basal EF or

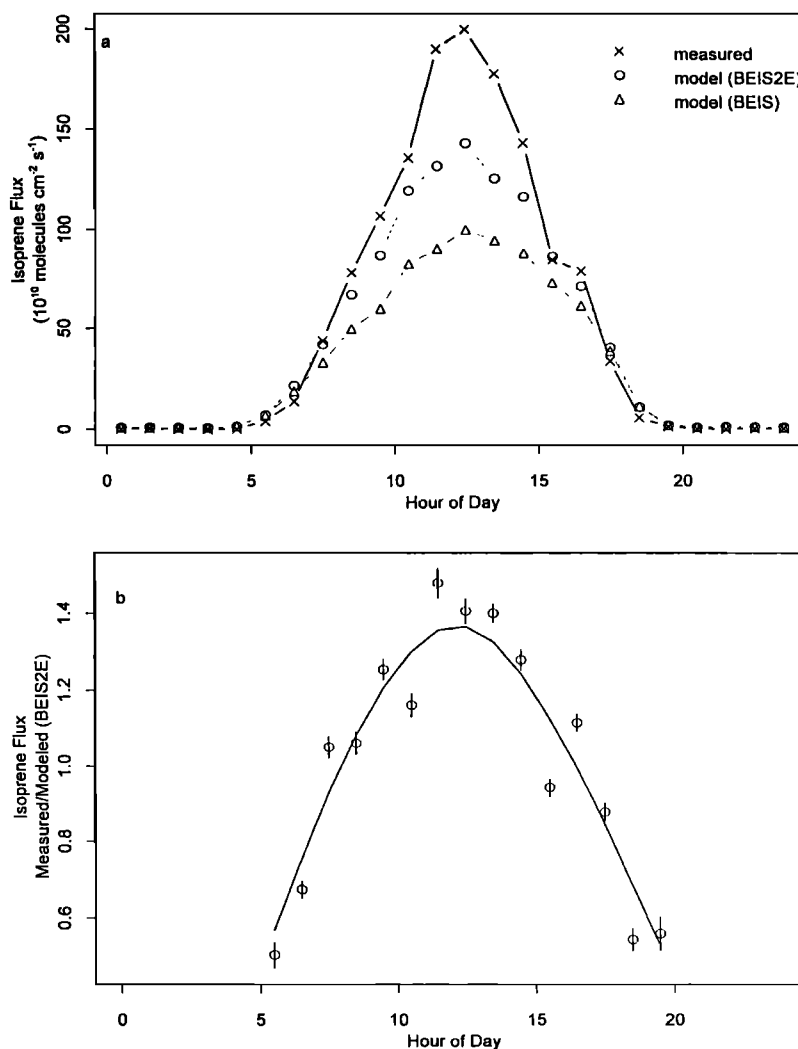
responses to the environment that are not captured by the model.

Figure 5a shows an hourly mean of the measurements and the model results for both model scenarios (BEIS2 and BEIS2E), and 5b shows the normalized emission rate (using BEIS2E) for summer 1995 (90% confidence intervals are indicated). A diurnal course of the normalized emission rate is apparent, increasing in the morning, maximizing around noon, and decreasing in the afternoon (the normalized rates at night, 2000 - 0500 hours, are not included in the figure because fluxes are zero for both the measurements and the model). Most likely, this apparent diurnal course is due to underestimating leaf temperature at high values of solar input using the energy balance model [see *Geron et al.*, 1997]. This would result in the observed pattern for diurnal changes in the normalized emission rate and possibly accounts for the BEIS2E model underestimates of midday fluxes. Alternatively, the isoprene emitting plants could have additional physiological functions related to their diurnal cycle or incoming PAR that are not represented by the model, or the gradient flux method could be underestimating fluxes during the more stable periods in the morning and late afternoon. It is most important for the models to accurately predict isoprene emissions during midday, when rates are highest; thus the rest of our discussion will focus on comparing midday emission rates (1000-1500).

Figures 6a and 6b show the seasonal course of the measured and modeled isoprene emission rates, and the normalized midday emission rate (1000-1500 EST, weekly mean values with 90% confidence intervals). The seasonal course of the normalized emission rate reached its peak 4 weeks after leaf out and 2 weeks after emissions began. From day 165 to 230 the normalized rate remained relatively constant. The normalized rate decreased steadily after day 230 as the leaves senesced, and essentially went to zero by day 300. The forest was at its maximum isoprene emission potential for approximately 65 days. The seasonal reduction in normalized isoprene emission after day 230 coincided with seasonally decreasing air temperature and nighttime temperatures falling below  $10^\circ\text{C}$ . The current model underpredicts emissions during most of the summer and overpredicts emissions in the spring and fall. These predictions could lead to significant errors in modeling photochemical  $\text{O}_3$  production and in assessing the need for legislation to regulate anthropogenic VOC emissions. The seasonal duration of strong isoprene emission lasted only 100 days with much lower rates continuing for approximately 30 days, similar to the  $\text{CO}_2$  uptake pattern of the oaks [*Bassow*, 1995], and shorter than the approximately 150 days of active  $\text{CO}_2$  uptake by the whole ecosystem. This seasonal emission cycle needs to be included in isoprene emission models to accurately simulate emission rates.

Figure 6b compares the seasonal changes in normalized midday emission rate to an estimate of the leaf area index (LAI) at Harvard Forest (estimated from PAR measured above the canopy and at midcanopy, then scaled to summer maximum LAI measured by leaf litter collection), and the normalized difference vegetation index (NDVI, biweekly composites with 1.1 km resolution, data for Harvard Forest extracted by K. Moore from U.S. Geological Survey National Mapping Division EROS data center). The NDVI composites can be used to estimate seasonal variation in leaf area index,





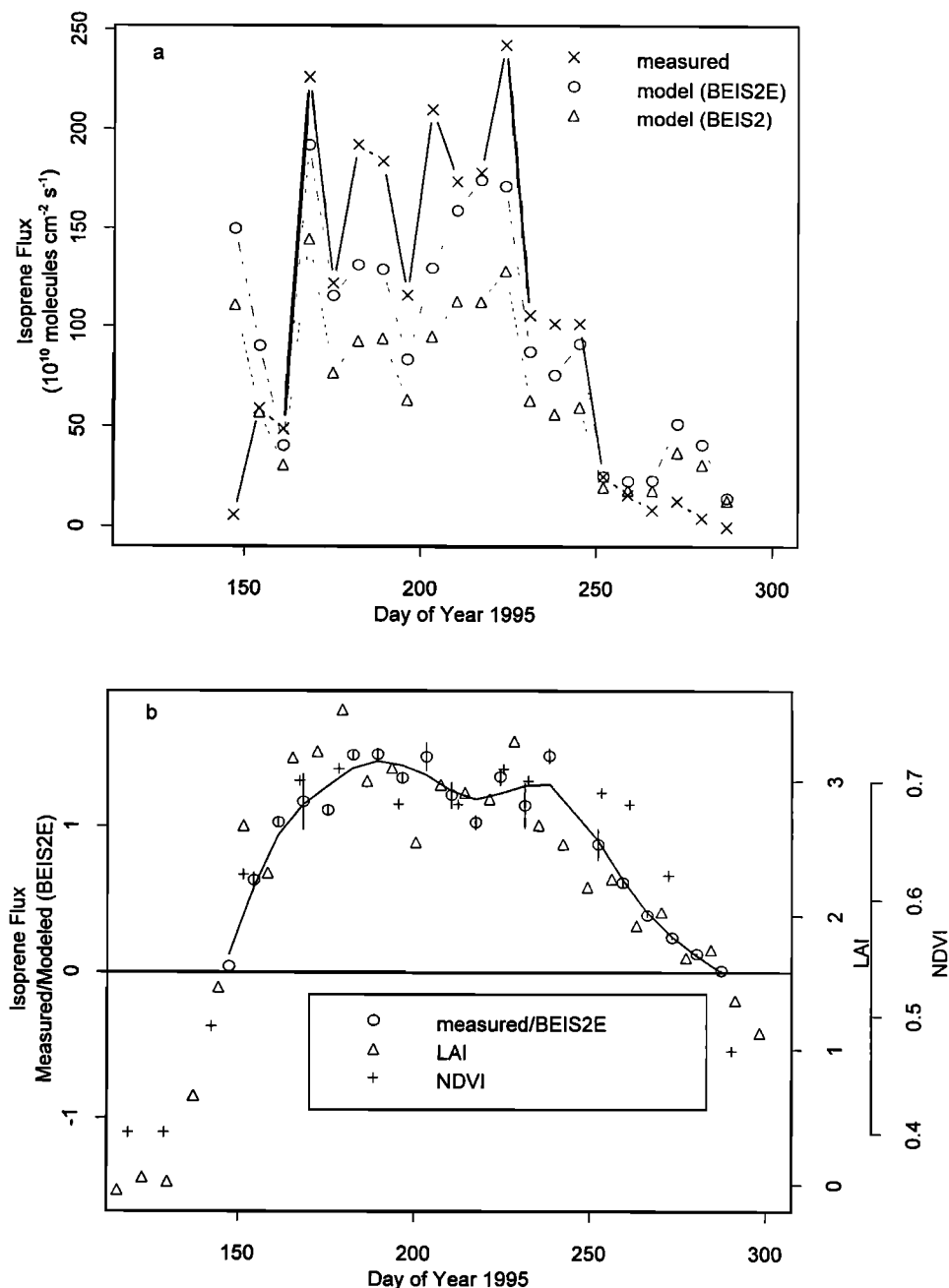
**Figure 5.** Diurnal pattern of (a) measured and modeled (BEIS2 and BEIS2E; see text for model descriptions) isoprene emissions, and (b) normalized (measured/modeled (BEIS2E)) isoprene emissions (June 24 to August 28, 1995, hourly mean values with 90% confidence intervals).

chlorophyll content, and biomass [Moore *et al.*, 1996]. The LAI and NDVI data have a seasonal pattern that is notably consistent with the normalized midday emission rate. Isoprene is not emitted for the first few weeks after leafout ( $\text{LAI} < 1.5$ ), then increases with increasing LAI and NDVI. Isoprene emissions diminish in the fall in a manner consistent with decreasing LAI and NDVI, but isoprene emissions end before the leaves have fallen from the trees ( $\text{LAI} < 1.5$ ) and before photosynthesis has ceased. Our findings suggest that seasonal changes in isoprene emissions could be modeled using NDVI data, or possibly by finer scale multispectral/temporal imagery, with minor adjustments for emission initiation in the spring and cessation in the fall. Such metrics should be incorporated into future empirical models of isoprene emission.

## 7. Conclusions

Whole canopy isoprene emissions were measured from Harvard Forest over the entire 1995 growing season. The

seasonal duration of isoprene emissions was substantially shorter than net photosynthetic uptake. Comparison of the measurements with the EPA BEIS2E model gave a clear definition of temporal changes in the emission rate which are not captured by the model, and could be used to improve future models. Young leaves did not emit isoprene for 2 weeks and did not reach their maximum normalized emission rate for another 2 weeks. The normalized emission rate remained constant for approximately 2 months, then decreased steadily through September and October before emissions ceased. These seasonal changes in isoprene emission rates are important for two major reasons: (1) they dramatically affect the regional ozone production efficiency per  $\text{NO}_x$  [see Hirsch *et al.*, 1996] and are thus crucial for the development of air quality control strategies, and (2) they provide constraints for understanding the physiological mechanism of isoprene production. Current EPA models underestimate isoprene emissions at Harvard Forest in midsummer and overestimate in spring and fall. The model underestimates in midsummer are likely due to an



**Figure 6.** Seasonal course of (a) measured and modeled (BEIS2 and BEIS2E; see text for model descriptions) midday isoprene emissions (1000 to 1500 EST, weekly mean values), and (b) normalized (measured/modeled (BEIS2E)) midday isoprene emissions (with 90% confidence intervals), and an index of LAI and measurements of NDVI.

underestimate in the basal emission rate. Future empirical models of isoprene emission should incorporate seasonal adjustment factors.

The relative magnitude of anthropogenic and biogenic VOC emissions must be determined accurately to develop useful clean air legislation for reducing tropospheric ozone. In this study, isoprene emissions from Massachusetts forests were estimated to be  $10^5$  metric tons  $\text{yr}^{-1}$ , with emissions occurring mainly from mid-June through mid-September. This is equivalent to the total summertime VOC emissions

from anthropogenic sources in Massachusetts according to the NAPAP [1985] emission inventory ( $1.1 \times 10^5$  metric tons). Moreover, the importance of biogenic isoprene emissions increases dramatically on hot summer afternoons, coincident with periods of peak photochemical activity. In addition, isoprene is approximately 2.5 times as effective for photochemical ozone production per atom of carbon as the typical mix of VOCs found in urban air. Assuming that anthropogenic VOC emissions are substantially less temperature dependent than biogenic isoprene emissions, our

results indicate that isoprene is more important than anthropogenic VOCs for photochemical ozone production on hot summer days in much of Massachusetts.

**Acknowledgments.** This work was supported by grants to Harvard University from the U.S. Department of Energy's (DOE) National Institute for Global Environmental Change (NIGEC) through the NIGEC Northeast Regional Center at Harvard University (DOE Cooperative Agreement DE-FC03-90ER61010), by the National Aeronautics and Space Administration (NAGW-3082), the National Science Foundation (BSR-89-19300), the Long Term Ecological Research program at the Harvard Forest funded by the National Science Foundation (BSR-88-11764), and by Harvard University (Harvard Forest and Division of Applied Sciences). The authors wish to thank David Fitzjarrald and Kathleen Moore of the Atmospheric Sciences Research Center at the State University of New York at Albany for helpful discussions and for providing NDVI data.

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(Received October 10, 1997; revised May 15, 1998; accepted May 21, 1998.)