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Environmental controls over isoprene emission in deciduous oak canopies

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Summary In summer 1992, isoprene emission was measured on intact leaves and branches of *Quercus alba* (L.) at two heights in a forest canopy. Isoprene emission capacity (measured at 30 °C and a photosynthetic photon flux density of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$) was significantly higher in sun leaves than in shade leaves when expressed on a leaf area basis (51 versus 31 $\text{nmol m}^{-2} \text{s}^{-1}$; $P < 0.01$). Because leaf mass per unit area (LMA, g m^{-2}) was higher in sun leaves than in shade leaves, emissions of sun and shade leaves expressed on a dry mass basis did not differ significantly (99 versus 89 $\mu\text{g C g}_{\text{DW}}^{-1} \text{h}^{-1}$; $P = 0.05$). Similar measurements in 1995 were consistent with the 1992 data, but data from leaves in more shaded locations demonstrated that isoprene emission capacity decreased with decreasing growth irradiance, irrespective of units of expression. Isoprene emission capacity in leaves of *Q. coccinea* Muenchh. and *Q. velutina* Lam. also declined steeply with canopy depth. Emission capacity, on a dry mass basis, showed no obvious pattern with canopy position in *Q. prinus* L. There was no difference in the temperature response of sun versus shade leaves of *Q. alba*, but shade leaves exhibited a greater quantum efficiency and saturated at lower irradiance than sun leaves. Rates of isoprene emission measured on branches of *Q. alba* were approximately 60% of those measured on individual leaves, as a result of self-shading within branch enclosures. It is recommended that within-canopy variation in isoprene emission capacity be incorporated into regional emission models.

Keywords: canopy, Fagaceae, hydrocarbons, oaks, *Quercus alba*, *Quercus coccinea*, *Quercus prinus*, *Quercus velutina*, volatile organic compounds, white oak.

Introduction

Isoprene is emitted from leaves of numerous plant species, including many trees (Hewitt and Street 1992, Guenther et al. 1994) and when released at significant rates is a principal reactant in the formation of tropospheric ozone in both rural (Trainer et al. 1987) and urban landscapes (Chameides et al. 1988). It is highly reactive with the hydroxyl radical and other oxidizing species and plays an important role in determining the oxidative capacity of the troposphere (Thompson 1992).

Increased understanding of the physiological and biochemical controls over isoprene emission at the leaf level is necessary to improve our ability to predict source strengths for this important tropospheric constituent (Sharkey et al. 1991a, Monson et al. 1995). Isoprene emissions have long been known to respond to short-term changes in incident photosynthetic photon flux density (PPFD) (Sanadze and Kursanov 1966, Tingey et al. 1979, Monson and Fall 1989, Loreto and Sharkey 1990, Harley et al. 1996) and leaf temperature (Tingey et al. 1979, Tingey 1981, Monson and Fall 1989, Loreto and Sharkey 1990, Harley et al. 1996), and recent studies have demonstrated that the PPFD to which leaves are exposed during growth also affects their capacity to emit isoprene (Sharkey et al. 1991b, Harley et al. 1994, 1996, Litvak et al. 1996).

Because isoprene emissions are strongly dependent on incident PPFD, it is necessary to characterize the light environment within a forest canopy if one wishes to scale up from leaf-level measurements to regional estimates of isoprene emissions. In parameterizing a canopy emission model, it is also important to assess the amount of leaf to leaf variation in isoprene emission characteristics and to determine how leaf properties vary with canopy depth (Harley et al. 1996, Sharkey et al. 1996).

In July–August 1992 and in July 1995, we measured isoprene fluxes in a temperate, deciduous forest in Oak Ridge, TN. In this paper, we describe measurements made on individual leaves and intact branches at different canopy heights. Leaf measurements made under controlled conditions of light and temperature provided data for parameterizing a leaf-level isoprene emission model for sun-adapted leaves at the top of the canopy and increasingly shade-adapted leaves lower down. In companion studies (Baldocchi et al. 1995, Lamb et al. 1997), these leaf-level data are incorporated into a canopy model and our ability to scale isoprene fluxes from leaves to forest canopy is evaluated by comparing model predictions with canopy-scale micrometeorological measurements of isoprene flux (Guenther et al. 1996a). In conjunction with these measurements, fluxes of CO_2 and water vapor were measured in 1992 and modeled at both leaf and canopy scales (Baldocchi and Harley 1995, Harley and Baldocchi 1995).

Materials and methods

Site description

Measurements were made in a mixed deciduous forest dominated by oaks (*Quercus* spp.), hickories (*Carya* spp.) and maples (*Acer* spp.). The site is located on the United States Department of Energy reservation near Oak Ridge, TN (35°57'30" N; 84°17'15" W; elevation 365 m above sea level). Canopy height was approximately 30 m and a 44 m walk-up tower provided access to leaves of white oak (*Quercus alba* L.) at both canopy top and 3–5 m down in the canopy where leaves were shaded. In 1995, a vehicle with a platform on an extendable boom provided continuous access to the canopy to a height of about 20 m, sufficient to reach sun-adapted leaves of several oak species in canopy gaps.

Experimental methods

Two sampling schemes were employed in 1992, one for assessing isoprene fluxes from individual leaves of *Q. alba*, and one for measuring branch-level emissions. To determine mean leaf-level emission rates and to establish the effects of varying light and temperature on isoprene emissions, an open-path gas exchange system (MPH-1000, Campbell Scientific, Logan, UT) was employed. Air of specified water vapor and CO₂ concentration was generated by mass flow controllers (Type 825, Edwards High Vacuum International, Wilmington, MA), and passed to a temperature-controlled cuvette. The flow rate of gas entering the cuvette was measured with a mass flow meter (Type 821, Edwards High Vacuum International). Except when natural light was used, light was provided by a quartz halogen bulb (ELH 120V-300W, General Electric, Cleveland, OH) mounted in a slide projector lamp holder and directed at a Tempax cold mirror (Optical Coating Labs, Inc., Santa Rosa, CA) mounted at 45° to reflect visible light onto the cuvette. Blackened window screens were inserted in the light path to vary the intensity. To follow the diurnal pattern of isoprene emission under natural conditions, we modified the Campbell MPH-1000 to control cuvette temperature at the external air temperature, measured with a shielded thermistor (YSI, Yellow Springs, OH). Air exiting the cuvette was collected in 10-ml glass syringes (Dynatech, Baton Rouge, LA) and analyzed by gas chromatography.

In 1995, we used a portable photosynthesis system (LI-6400, Li-Cor, Inc., Lincoln, NE) to measure leaves of *Q. alba* growing in a wide range of light environments, as well as leaves from three additional oak species, *Q. prinus* L., *Q. coccinea* Muenchh. and *Q. velutina* Lam. Measurements were made from the tower, from the ground and from the platform of an extendable 20-m boom. An accessory LED light source (LI-6400-02, Li-Cor, Inc.) was employed. The cuvette was modified slightly by inserting a T-junction in the air line exiting the cuvette, thus directing air from the cuvette to the sample loop of a gas chromatograph located adjacent to the photosynthesis system.

Branch-level isoprene emission rates were also measured in 1992 with a 24-l flow-through branch enclosure, consisting of 5-mil Teflon film placed over a stainless steel wire support

frame. Ambient air was pumped through the enclosure at a rate of approximately 9 l min⁻¹. Leaf and air temperatures inside the enclosures were measured with shielded thermistors (YSI) and incident PPFD was measured with a quantum sensor (LI-190SA, Li-Cor, Inc.) mounted next to the enclosure. Samples of air entering and leaving the enclosure were collected in 10-ml glass syringes and isoprene concentration was determined by gas chromatography.

Leaf area was measured for all experimental leaves (CI-201, CID, Inc., Moscow, ID) which were subsequently oven-dried at 60 °C for 48 h and weighed. Total leaf N content was determined for 1992 leaves with a carbon–nitrogen analyzer (Model NA 1500, Carlo Erba Instruments, Saddle Brook, NJ).

In 1992, all samples were collected in glass syringes and injected into the 2-ml sample loop of a portable, isothermal gas chromatograph within 10 min. In 1995, air exiting the cuvette was drawn directly through the sample loop of the gas chromatograph. Isoprene was separated on a stainless steel column (1.3 m long × 2 mm i.d.) packed with Unibeads 3S, 60/80 mesh (Alltech Assoc., Deerfield, IL) and measured with a reduction gas detector (RGD2, Trace Analytical, Menlo Park, CA). Peak integration was accomplished with a commercial integrator (Model 3390, Hewlett-Packard, Avondale, PA). Details of this analytical system may be found in Greenberg et al. (1993). The system was calibrated several times daily against a standard cylinder containing 71 ppb (v/v) isoprene, referenced to a National Institute of Standards and Technology propane standard (SRM 1660a; 1 ppm propane in N₂, Rochester, NY).

Results

Within a tree canopy, leaf morphology and physiology change continuously with reductions in solar irradiance (Sellers et al. 1992). In 1992, because we were restricted to making measurements at two heights on the tower, we compared isoprene emission rates of leaves growing in full sun at the top of the canopy with those growing in a more shaded environment, 3–5 m within the canopy. The two groups of leaves differed morphologically, as evidenced by large differences in leaf mass per unit area (LMA, g m⁻²) (Table 1). In addition, the amount of N per unit leaf area was significantly higher in leaves at the top of the canopy than in shaded leaves; however,

Table 1. Mean values (± SE) of leaf mass per unit area (LMA) and leaf nitrogen content (N) for sun leaves of white oak at the top of the canopy and shade leaves 3–5 m down. Leaf nitrogen is expressed on both a leaf area and leaf mass basis. Mean values of LMA and N (g N m⁻²) for sun and shade leaves are significantly different at *P* = 0.01. Data are from 1992 only.

	Sun leaves (top of canopy) (<i>n</i> = 7)	Shade leaves (3–5 m down) (<i>n</i> = 10)
LMA (g m ⁻²)	111.5 ± 5.9	75.4 ± 7.0
N (g N m ⁻²)	2.10 ± 0.04	1.38 ± 0.05
N (mg N g ⁻¹)	18.9 ± 0.1	18.6 ± 0.4

leaf N concentration expressed on a leaf dry mass basis was similar in the sun and shade leaves (Table 1).

Short-term controls over isoprene emission: temperature and PPFD

Figure 1 shows the temperature response of isoprene emission at the two canopy positions, expressed both on a leaf area basis ($\text{nmol isoprene m}^{-2} \text{s}^{-1}$) and leaf dry mass basis ($\mu\text{g C g}_{\text{DW}}^{-1} \text{h}^{-1}$). Leaves growing in full sun had much higher rates of isoprene emission than shaded leaves when expressed on a leaf area basis (Figure 1A). However, because of systematic variation in LMA (Table 1), these differences were substantially reduced when isoprene emission rates were expressed on a leaf dry mass basis (Figure 1B).

To compare the shape of the temperature responses of isoprene emission of sun and shade leaves, we normalized the data in Figure 1 by assigning a value of 1.0 to the emission rate at 30 °C, and scaling other data proportionately (Figure 2), thereby generating a temperature scaling factor, C_T (Guenther et al. 1991, 1993). We used nonlinear least squares regression (Systat, Evanston, IL) to fit the response of C_T to the temperature algorithm developed by Guenther et al. (1991, 1993). Because there was no apparent difference between sun and shade leaf responses to temperature, the data were pooled. For the fit shown in Figure 2, C_{T1} and C_{T2} , the activation energy and energy of deactivation, respectively, were assigned values of 78,000 and 379,800 J mol^{-1} . The empirical coefficient T_M was assigned a value of 315.8 K.

The effect of varying incident PPFD on isoprene emission rate was determined at four leaf temperatures for leaves grow-

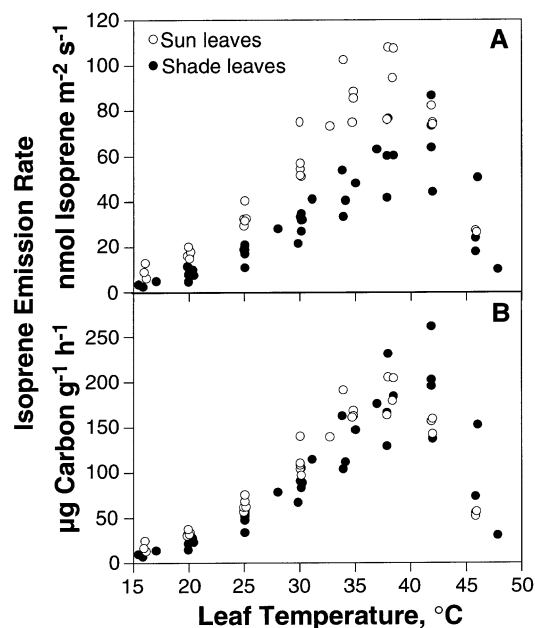


Figure 1. Rates of isoprene emission from sun and shade leaves of white oak as a function of leaf temperature. Rates are expressed on a leaf area basis (A) and a leaf dry mass basis (B).

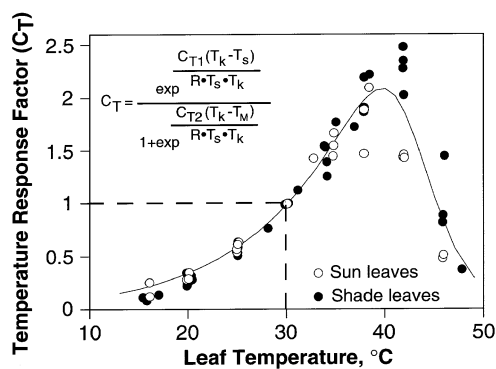


Figure 2. The temperature response factor (C_T) as a function of leaf temperature for leaves of white oak. Emission data are normalized to a value of 1.0 at a leaf temperature of 30 °C. Data from sun and shade leaves were pooled. Solid line is a fit to the data using the temperature algorithm of Guenther et al. (1993) with model parameters determined from these data.

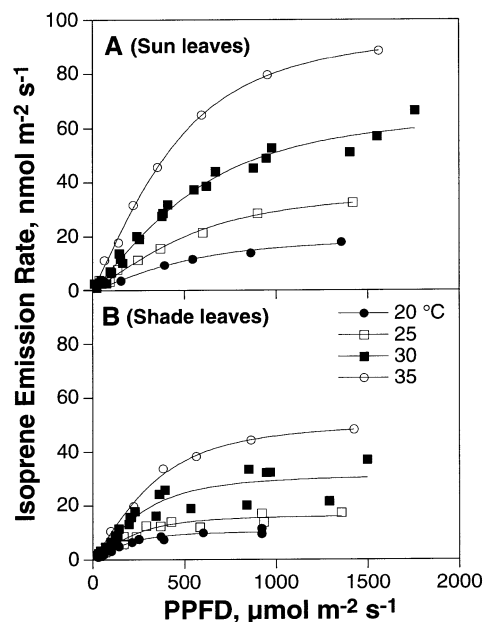


Figure 3. Rates of isoprene emission from sun (A) and shade leaves (B) of white oak as a function of incident PPFD at four leaf temperatures. Solid lines are independent fits to Equation 1 at each leaf temperature, based on the parameter values in Table 2.

ing in full sun at the top of the canopy (Figure 3A) and shaded leaves below (Figure 3B). Both the initial slope of the response and the light-saturated rate of isoprene emission increased with increasing leaf temperature. Isoprene emission of shade-grown leaves reached saturation at lower irradiances than that of sun leaves.

To obtain a quantitative assessment of these differences, we fit the data obtained at each temperature to the following equation, which has been used to model the effects of light on

Table 2. Values for quantum yield (QY) and maximum rate of isoprene emission (I_{\max}) providing the best least squares fit to Equation 1, based on data collected at each leaf temperature in Figure 3.

	Quantum yield				I_{\max}			
	$\mu\text{mol mol}^{-1}$				$\text{nmol m}^{-2} \text{s}^{-1}$			
Leaf temperature ($^{\circ}\text{C}$)	20	25	30	35	20	25	30	35
Sun leaves (top of canopy)	27	48	81	148	19.6	37.1	66.1	96.3
Shade leaves (3–5 m down)	42	52	82	107	10.7	16.6	31.5	50.9

CO_2 -saturated rates of photosynthesis (Smith 1937, Harley et al. 1992),

$$I = \frac{\text{QY PPFD}}{\sqrt{1 + \frac{\text{QY}^2 \text{PPFD}^2}{(I_{\max})^2}}}, \tag{1}$$

where I is isoprene emission rate, QY is quantum yield (μmol isoprene per mol of incident photons) and I_{\max} is the predicted rate of emission as $\text{PPFD} \rightarrow \infty$. The resulting fits (Figure 3) were obtained using the values of QY and I_{\max} in Table 2. There were large differences in I_{\max} between sun and shade leaves at a given temperature. Quantum yield clearly increased with leaf temperature, but there was no consistent difference in QY between sun and shade leaves.

There were strong interactions between PPFD and leaf temperature. However, when a light response factor, C_L , was generated by normalizing the data to a value of 1.0 at $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, the effects of leaf temperature on isoprene emission rate were eliminated (Figure 4). The initial slope of the C_L response was significantly higher for shade leaves than for sun leaves. This is a result of the normalization procedure, in which emission rates of sun leaves, which have a higher emission rate than shade leaves at $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, are divided by a larger number, thereby depressing the initial slope of the normalized response. Normalized data obtained over a range of leaf temperatures were fit to an algorithm describing C_L developed by Guenther et al. (1993). The resulting fits are shown in Figure 4, where C_{L1} is the value of C_L as $\text{PPFD} \rightarrow \infty$ and α is an empirical fitting factor.

If we define isoprene emission capacity (I_S) as the rate of isoprene emission when $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and leaf temperature = 30°C , then the effects of light and temperature on isoprene emission rate (I) may be combined in a single expression:

$$I = I_S C_T C_L. \tag{2}$$

In Figure 3, each set of light curves obtained at a different temperature was fit independently to Equation 1. Figure 5 depicts a simulation of the same data (expressed on a leaf dry mass basis) using Equation 2. Values of C_T were obtained from

fits to data in Figure 2 (sun and shade leaf data pooled) and values of C_L were obtained from fits to data in Figure 4 (sun and shade leaves treated separately). The values of I_S used for sun and shade leaf simulations were 98.9 and $88.7 \mu\text{g C g}^{-1} \text{h}^{-1}$, respectively, the mean values for all measured leaves (Table 3).

Diurnal patterns of isoprene emission, measured approximately every 15 min, are shown for a leaf growing at the top of the canopy (Figure 6A) and a leaf within the canopy (Figure 6B). Both PPFD and leaf temperature were measured concurrently (Figures 6C and 6D). The measured values of I_S for the sun and shade leaves were 95.7 and $68.0 \mu\text{g C g}^{-1} \text{h}^{-1}$, respectively. Equation 2 was used to predict isoprene emission rates as PPFD and leaf temperature varied through the day, using values of C_T and C_L obtained from fits to data in Figures

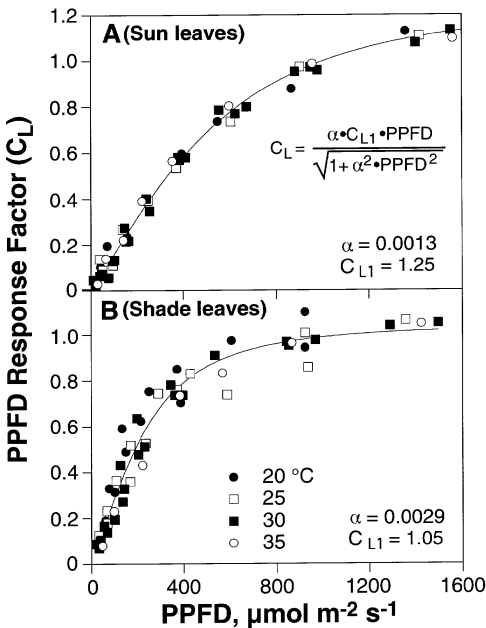


Figure 4. The light response factor (C_L) as a function of incident PPFD for sun (A) and shade leaves (B) of white oak. All data from Figure 2 have been normalized such that the emission rate equals 1.0 when $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. Solid lines are fits to the light algorithm of Guenther et al. (1993), based on parameter values shown.

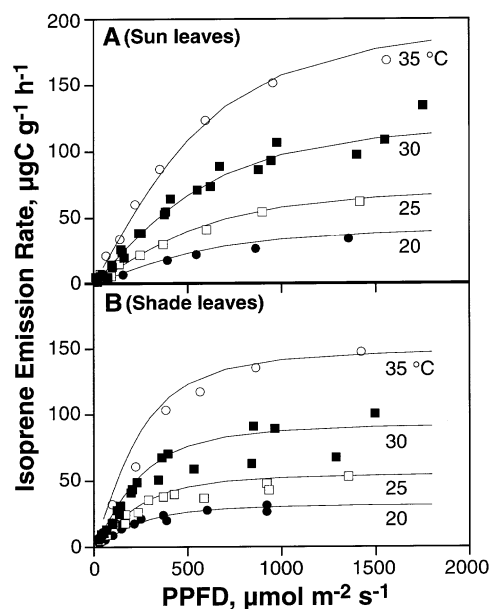


Figure 5. Isoprene emission, on a leaf dry mass basis, as a function of incident PPFD for sun (A) and shade leaves (B) of white oak, determined at four leaf temperatures. Solid lines are model simulations using Equation 2 and parameter values given in the text for sun and shade leaves, respectively.

2 and 4. Correspondence between measured and modeled isoprene emissions was good for the sun leaf, but isoprene emissions for the shade leaf were underestimated in the afternoon.

Long-term controls over isoprene emission capacity: canopy position

We used the 1992 cuvette data collected at 30 °C and PPFD = 1000 µmol m⁻² s⁻¹ to calculate mean values of isoprene emission capacity (I_S) for sun leaves at the top of the canopy and shade leaves growing 3–5 m within the canopy (Table 3). On a leaf area basis, the mean emission capacity of leaves growing

within the canopy was 40% less than that of sun leaves at the canopy top ($P < 0.01$). On a dry mass basis, emission rates from sun leaves were 11% higher on average than emission rates from shade leaves, but the difference was not significant ($P > 0.10$).

In 1995, measurements on white oak were extended to include leaves from a wide range of growth light environments, including leaves of seedlings, saplings, and leaves at lower canopy positions than in 1992. We did not characterize the light environment for each leaf measured, but made the assumption that LMA was directly related to growth irradiance. When I_S was plotted versus LMA, using data from both 1992 and 1995 (Figure 7), I_S increased with increasing LMA, and the correlation was stronger on a leaf area basis (Figure 7A; $r^2 = 0.80$) than on a dry mass basis (Figure 7B; $r^2 = 0.30$). Isoprene emission rates expressed per unit area varied sixfold within the canopy, whereas rates on a dry mass basis varied two- to threefold.

In many earlier studies, isoprene emission rates were determined using branch enclosures. In 1992, we compared isoprene emission rates obtained using individual leaf enclosures with those obtained using a branch enclosure. Numerous measurements were made from a branch enclosure at the top of the canopy and a shaded branch enclosure within the canopy. Because these enclosures lacked environmental control, incident PPFD and leaf temperature varied widely. To facilitate comparisons between these measured rates and rates determined using the controlled cuvette systems, values of C_T and C_L were calculated for sun and shade leaves, using the values of PPFD and leaf temperature at the time of each measurement. We then inverted Equation 2 and solved for I_S , given the measured values of isoprene emission. As PPFD decreased to low values or leaf temperature increased above the temperature optimum, the values of C_L and C_T declined; as either value became very small, the calculation of I_S became increasingly prone to large errors. Consequently, data collected at PPFDs below 100 µmol m⁻² s⁻¹ or at temperatures exceeding 39 °C were eliminated from our analysis. Pooling the results from all other measurements, we arrived at mean estimates of I_S for branches at two canopy levels (Table 3).

Table 3. Summary of measurements made in 1992 on sunlit and shaded leaves and branches of white oak. Isoprene emission capacity (PPFD = 1000 µmol m⁻² s⁻¹ and leaf temperature of 30 °C) is given in two sets of units. For uncontrolled branch enclosures, only data collected when PPFD > 100 µmol m⁻² s⁻¹ and leaf temperature < 39 °C were used in the analysis.

Type of measurement	Height in canopy (m)	I_S (µg C g⁻¹ h⁻¹)	I_S (nmol m⁻² s⁻¹)
Leaf cuvette with environmental control	Sun leaves at top of canopy ($n = 8$)	98.9 ± 4.6 ($n = 8$)	50.8 ± 2.7 ($n = 8$)
	Shade leaves 3–5 m down ($n = 8$)	88.7 ± 4.2 ($n = 8$)	30.5 ± 1.8 ($n = 8$)
Branch enclosure without environmental control	Branch at top of canopy ($n = 1$)	58.5 ± 13.5 ($n = 7$)	24.5 ± 5.7 ($n = 7$)
	Branch 3 m down ($n = 1$)	49.7 ± 26.8 ($n = 27$)	17.5 ± 9.4 ($n = 27$)

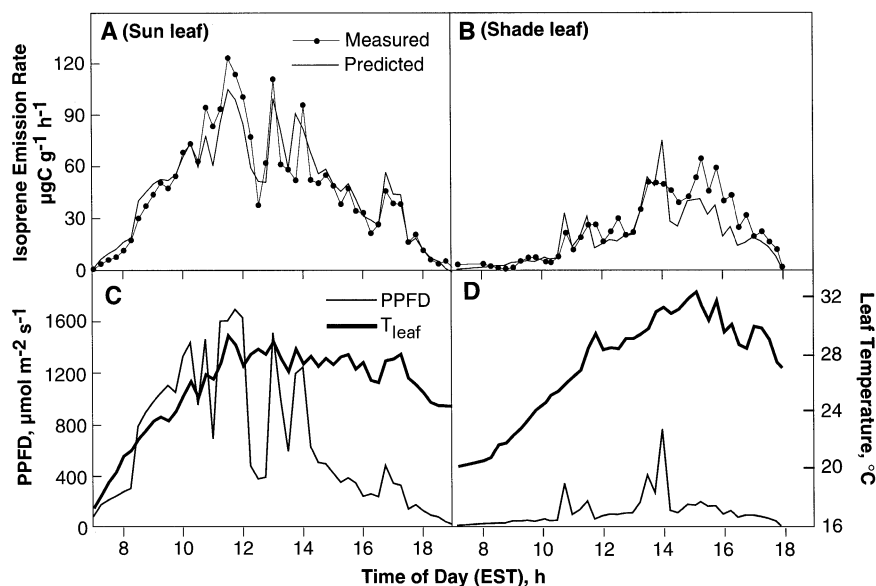


Figure 6. The diurnal course of isoprene emission measured at approximately 15-min intervals, for a sun leaf (A) and shade leaf (B) of white oak. The predicted data are model simulations of isoprene emission, based on Equation 2, with the light and temperature data in (C) and (D) as inputs.

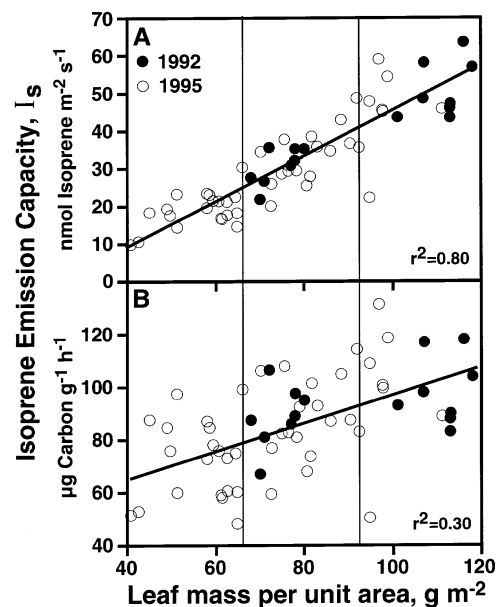


Figure 7. Isoprene emission capacity of leaves at various heights in a *Quercus alba* canopy as a function of leaf mass per unit area. Data from both 1992 and 1995 are shown, and emission capacity (emission rate at 30°C and $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) is expressed on both a leaf area basis (A) and a dry mass basis (B). The data are divided into three compartments, representing the three layers used in a canopy radiation transfer model.

In 1995, isoprene emission data were collected on three other oak species and related to LMA (Figure 8). The range of variation in emission capacity in leaves of *Q. coccinea* was similar to that of *Q. alba* (Figure 7), and I_s increased with increasing LMA. There was only a two- to two and a half-fold variation in emission rates of *Q. velutina* ($n = 11$) and *Q. prinus*

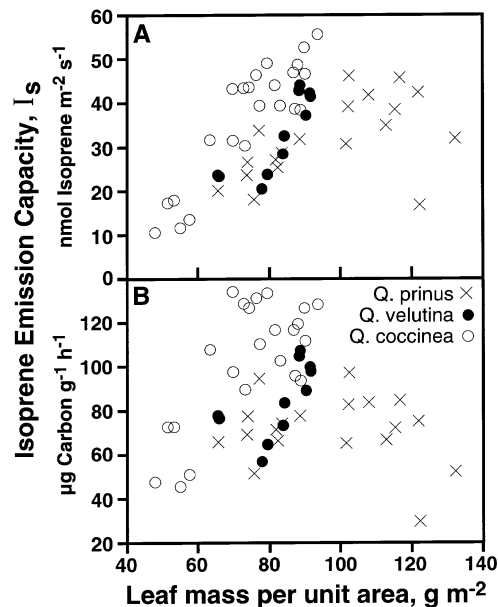


Figure 8. Isoprene emission capacity of leaves of three oak species at various heights in a canopy as a function of leaf mass per unit area. Emission capacity (emission rate at 30°C and $\text{PPFD} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) is expressed on both a leaf area basis (A) and a dry mass basis (B).

($n = 19$) irrespective of how rates were expressed, although it should be noted that the sample size was less than for either *Q. alba* ($n = 60$) or *Q. coccinea* ($n = 23$). The range of variation in LMA was also much less in *Q. velutina*, perhaps because fully sun-adapted leaves were not accessible. When expressed on a dry mass basis, I_s appeared to be independent of LMA and, presumably, canopy position for leaves of *Q. prinus*.

Discussion

Short-term controls over isoprene emission: temperature and PPFD

Variations in PPFD and leaf temperature constitute the primary short-term controls over isoprene emission (Monson et al. 1995). In common with other studies (Tingey 1981, Monson and Fall 1989, Loreto and Sharkey 1990, Guenther et al. 1991, Harley et al. 1996), isoprene emission rates were strongly temperature dependent (Figure 1), increasing exponentially to an optimum between 38 and 40 °C. In this study, the Q_{10} for isoprene emission exceeded 3.5 between 15 and 30 °C. Above the optimum temperature, emission rates declined sharply, and above approximately 40 °C, it was impossible to obtain steady-state rates. The algorithm developed by Guenther et al. (1991) to model the temperature response of isoprene emission adequately described our data. In contrast to the findings reported for sweetgum (*Liquidambar styraciflua* L.) (Harley et al. 1996), there was no apparent difference in the temperature dependency for sun and shade leaves of white oak.

Our results (Figure 3, Table 2) on the interactive effects of light and temperature on isoprene emission extend the measurements made on velvet bean by Monson et al. (1992), in which both the initial slope of the light response and the light-saturated emission rate increased between 26 and 34 °C. Although the light response of isoprene emission is superficially similar to that of net photosynthesis, the interaction between light and temperature for isoprene synthesis differs from that for photosynthesis. If photorespiration is eliminated by measuring under conditions of high CO₂ or low O₂, quantum yield of photosynthesis becomes independent of temperature (Ehleringer and Björkman 1977). The finding that both the initial slope and the maximum rate of isoprene emission increase with increasing temperature supports the suggestion of Monson et al. (1992) that isoprene emission is controlled primarily by isoprene synthase activity. Even under low light conditions, isoprene synthase activity, rather than products of the light reactions, appears to limit isoprene production. Nevertheless, isoprene production increases with increasing light, suggesting that enzyme activation is controlled, directly or indirectly, by PPFD.

Tingey (1981) concluded that light and temperature effects on isoprene emission were independent and could not be modeled by a single expression. However, Equation 2 described the measured responses to PPFD and temperature and their interactions extremely well (Figure 5), and simulated the measured diurnal pattern of isoprene emission in Figure 6.

Long-term effects of growth light environment and canopy position

In the 1992 study, sun leaves had significantly higher rates of isoprene emission than shade leaves when isoprene emission was expressed on a leaf area basis (Figure 1A, Table 3). However, because sun leaves had significantly higher LMA than leaves lower in the canopy (Table 1), when rates were converted to a leaf dry mass basis, the difference between the two groups of leaves was not significant. It is possible that the

differences in leaf-area-based emission rates between sun and shade leaves in 1992 resulted from significantly different amounts of N per unit leaf area (Table 1). However, differences in N content also resulted from differences in leaf morphology, because mean N concentrations of sun and shade leaves were identical when N was expressed per unit mass (Table 1).

In 1995, we did not characterize the light environment in which each experimental leaf was growing, but assumed that LMA decreased with depth in canopy, as indicated by the 1992 data. When plotted against LMA, the 1992 and 1995 white oak data were indistinguishable (Figure 7). Furthermore, the 1995 data confirmed the roles of canopy position and light environment on isoprene emission capacity indicated by the 1992 data. There was as much as a sixfold increase in isoprene emission capacity, expressed per unit leaf area, with increasing LMA, and LMA and I_s were highly correlated ($r^2 = 0.80$). The effect of canopy position on isoprene emission capacity in leaves of *Q. coccinea* and *Q. velutina* (Figure 8) was similar to that of white oak, but canopy position exerted less control in leaves of *Q. prinus*.

When expressed on a leaf mass basis, the range of variation in I_s in white oak leaves was reduced to two- to threefold. Although there was a positive relationship between I_s and LMA, the relationship was weak ($r^2 = 0.30$). The range of variation in I_s was similarly reduced in leaves of *Q. coccinea* and *Q. velutina*. When expressed on a leaf mass basis, I_s in *Q. prinus* was independent of canopy position, i.e., variation in I_s , expressed per unit leaf area, was fully explained by variation in LMA.

Differences in the capacity for isoprene emission on a leaf area basis were largely, but not entirely, the result of changes in LMA with depth in canopy. The observed reductions in LMA are an expected result of acclimation to reduced growth irradiance (cf. Boardman 1977, Jurik 1986); Geron et al. (1994) assumed a 37% decrease in LMA between the top and bottom of a deciduous canopy. Such changes will always tend to increase the rates of physiological processes of shade-adapted leaves versus sun-adapted leaves, when rates are converted from an area to a mass basis. Thus, within a sugar maple (*Acer saccharum* L.) canopy, Ellsworth and Reich (1993) found that twofold reductions in net photosynthesis and nitrogen concentration, both expressed on a per unit area basis, were almost completely explained by a parallel decrease in LMA, and similar results were found in a *Nothofagus fusca* (Hook. f.) Ørst. canopy (Hollinger 1996). Photosynthetic rates in white oak followed a similar pattern (Harley and Baldocchi 1995).

Similar effects of growth light environment on isoprene emission capacity have been observed in other studies. Harley et al. (1994) grew velvet beans (*Mucuna* sp.) under two light regimes, and found that significant differences in isoprene emission rate on a leaf area basis were eliminated when rates were expressed on a dry mass basis. Sharkey et al. (1996) reported average emission capacities of 65 and 19 nmol m⁻² s⁻¹ for white oak leaves at the top and bottom of the canopy, respectively. They also reported a two and a half-fold decrease in LMA through the canopy. Thus, differences in emission

capacity within the canopy are sharply reduced, but not eliminated, when expressed per unit dry mass. Harley et al. (1996) found that isoprene emission capacity declined significantly with depth in a sweetgum canopy, even when rates were expressed on a dry mass basis. Litvak et al. (1996) found that isoprene emission rates were significantly lower in saplings of white oak and aspen (*Populus tremuloides* Michx.) grown in reduced light, although the percentage reduction was substantially less if rates were expressed on a dry mass rather than a leaf area basis.

On modeling canopy emissions

We are confident in our ability to predict leaf-level behavior if leaf temperature, PPFD and emission capacity are known (Figure 6; see also Guenther et al. (1996b)). In a whole-canopy context, therefore, it is critical to characterize accurately changes in PPFD and leaf temperature with depth in the canopy, and to determine the impact of within-canopy variation in isoprene emission capacity.

Because of the strong PPFD dependency of isoprene emission, Pierce and Waldruff (1991) and Lamb et al. (1993) developed multiple-layer canopy light-extinction models to calculate PPFD values used to drive isoprene emission at different canopy depths. They did not incorporate within-canopy variation in leaf morphology or isoprene emission capacity. Geron et al. (1994) investigated the importance of leaf biomass distribution within a canopy, and found that a disproportionate share of isoprene emitting biomass typically occurs in the upper canopy layers where PPFD is higher. As a result, model flux estimates increased by about 10% if LMA was allowed to vary realistically. Harley et al. (1996) used a radiation transfer model to estimate the effects on canopy isoprene flux of including realistic variations in both leaf morphology and isoprene emission capacity within a sweetgum canopy.

Although the range of variation in both isoprene emission capacity and LMA is less for white oak than for sweetgum, a similar exercise using the canopy radiation transfer model of Norman (1982) and our white oak data confirms this conclusion. Leaf area index (LAI) was assumed to be 4.5, and the canopy was divided into three layers of equal LAI. The sunlit and shaded leaf fraction in each layer was calculated, assuming a solar elevation of 60° and a realistic average leaf angle of 60°, and the mean PPFD incident on sunlit and shaded leaves in each layer was calculated. Isoprene emission capacities were assigned to each layer based on data in Figure 7. Leaves with LMA above 92.2 g m⁻² were assigned to the top layer, those between 92.2 and 66.5 to the middle layer, and those below 66.5 to the bottom layer. Mean values of isoprene emission capacity for leaves in each layer were then assigned to the entire layer (top: 47.6; middle: 32.2; bottom: 18.9 nmol isoprene m⁻² s⁻¹). Assuming full sunlight above the canopy and uniform leaf temperatures of 30 °C, the model predicts a canopy scale emission rate of 21.8 mg C m⁻² (ground) h⁻¹. Sixty percent of the total flux originated from the top canopy layer (28 and 12% from the middle and bottom layers, respectively). However, if values for sun leaves were assigned to all leaves in the canopy, the simulated canopy flux was overesti-

mated by 31%. Although these values will change depending on leaf angle distribution, total LAI, solar angle, and other factors, they demonstrate that models should incorporate within-canopy variation in isoprene emission capacity. The range of variation depends on the units of expression, because over half the variation in rates expressed on a leaf area basis results from parallel changes in LMA. Whichever units are employed, it is important to present LMA data to allow conversion between units.

Guenther et al. (1994) assigned to oaks an isoprene emission capacity of 70 ± 35 µg C g⁻¹ h⁻¹. The rates of isoprene emission capacity for sun leaves of three of the four oak species in our study were at the upper end of that range (mean ± SE): *Q. alba* = 99.3 ± 5.0 (n = 15); *Q. coccinea* = 114.5 ± 4.5 (n = 10); *Q. prinus* = 70.7 ± 6.4 (n = 10); and *Q. velutina* = 97.0 ± 4.1 µg C g⁻¹ h⁻¹ (n = 6). This represents the largest data set of isoprene emission by oaks under controlled conditions, and justifies raising the emission capacity of these trees to at least 90 µg C g⁻¹ h⁻¹ (cf. Sharkey et al. 1996).

Although current emission models (Geron et al. 1994, Baldocchi et al. 1995, Guenther et al. 1995, Lamb et al. 1997) are parameterized using leaf-level data, many earlier measurements of isoprene emission were obtained using branch enclosures, in which self-shading occurs (Guenther et al. 1994). Thus, rates determined for branches tend to be considerably lower than rates determined on individual leaves (Table 3). If branch-level data are used to parameterize emission models, therefore, rates need to be adjusted upward to compensate for the shading effect. For our data, the ratio of leaf to branch emission capacities is 1.69 for sun leaves and 1.78 for shade leaves, bracketing the value of 1.75 used by Guenther et al. (1994) to convert from branch to leaf estimates.

In addition to variation in the capacity for isoprene emission, there are more subtle physiological differences between sun and shade leaves. Shade leaves produce and emit isoprene more efficiently at low light, but saturate at much lower PPFD (Figure 3). Although these factors result in relatively small changes in overall model behavior, these physiological differences could be easily incorporated into emission models. Nevertheless, it is clear from Figure 6 that changes in daily rates of isoprene emission with depth in a white oak canopy are driven more by prevailing light than by subtle changes in leaf physiological properties. Guenther et al. (1995) currently employ a three-layer canopy model, which we feel predicts well the extinction of PPFD with canopy depth and represents a reasonable compromise between physiological/micrometeorological reality and model complexity/CPU time. For simplicity, this canopy model does not incorporate an energy budget routine to calculate leaf temperature, but assumes that leaf and air temperature are equal. Given the strong temperature dependency of isoprene emission and the likelihood that leaf temperature may differ from air temperature by several degrees (Gates 1968), it may also be important to calculate leaf temperatures for each canopy layer.

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