Tree Physiology 16, 25–32

Effects of light, temperature and canopy position on net photosynthesis and isoprene emission from sweetgum (*Liquidambar styraciflua*) leaves

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Received March 16, 1995

Summary In June 1993, net photosynthetic rates, stomatal conductance and isoprene emission rates of sweetgum leaves (*Liquidambar styraciflua* L.) were measured at the top of the forest canopy (sun leaves) and within the canopy at a height of 8–10 m above ground level (shade leaves). Large differences in net photosynthetic rates and stomatal conductance were found between sun and shade leaves. Mean rates of isoprene emission, expressed on a leaf area basis, were significantly lower in shade leaves than in sun leaves (4.1 versus 17.1 nmol m^{-2} s^{-1}); however, because specific leaf area of sun leaves was lower than that of shade leaves (0.0121 versus 0.0334 m^2 g^{-1}), the difference between sun and shade leaves was less, though still significant, when isoprene emissions were expressed on a dry mass basis (45.5 versus 29.0 μg C g^{-1} h^{-1}). Saturation of both net photosynthesis and isoprene emission occurred at lower PPFDs in shade leaves than in sun leaves. The effect of leaf temperature on isoprene emissions also differed between sun and shade leaves. Sun leaves lost a significantly greater percentage of fixed carbon as isoprene than shade leaves. The leaf-level physiological measurements were used to derive parameters for a canopy-level isoprene flux model. The importance of incorporating differences between sun- and shade-leaf properties into existing models is discussed.

Keywords: canopy model, hydrocarbons, stomatal conductance.

Introduction

Forests and the atmosphere exchange large amounts of gaseous species. In addition to exchanges of CO_2 and H_2O vapor, many volatile organic compounds (VOCs) are emitted by vegetation. Although VOC fluxes may be several orders of magnitude less than those of CO_2 and H_2O, VOCs are of interest to atmospheric scientists because they play a crucial role in tropospheric chemistry.

The 10-carbon monoterpenes, such as the pinenes, play a biological role within the plant (Harborne 1988) and, in addition, a fraction of the monoterpenes escape to the atmosphere where they participate in a variety of chemical reactions. Isoprene (2-methyl-1,3-butadiene) is a 5-carbon molecule formed by the elimination of a phosphate group from dimethylallyl pyrophosphate (DMAPP), either in an acid-catalyzed (Deneris et al. 1985) or an enzyme-catalyzed reaction (Silver and Fall 1991). Although DMAPP and its isomer, isopentenyl pyrophosphate (IPP), are the basic building blocks of many so-called isoprenoid compounds, including sterols, monoterpenes and carotenoids, isoprene itself plays no known biological role in plants, although recent evidence suggests it may contribute to thermal protection at high temperatures (Sharkey and Singsaas 1995). Isoprene, unlike monoterpenes, is not stored within the leaf, but emitted through the stomata immediately upon its production (Sharkey et al. 1991*a*, Hewitt and Street 1992, Guenther et al. 1994). In areas of high emissions, it is a principal reactant in the formation of tropospheric ozone (Trainer et al. 1987, Chameides et al. 1988). Because of its high reactivity, the atmospheric lifetime of isoprene is short, about one hour, but some of its oxidation products are longer lived and may be capable of affecting the global atmosphere (Fehsenfeld et al. 1992). Approximately 90% of non-methane hydrocarbon emissions are biogenic in origin (Singh and Zimmerman 1992), and their oxidation may contribute as much as 25% of the global source of carbon monoxide (Seiler and Conrad 1987).

An increased understanding of the physiological and biochemical controls over isoprene emission at the leaf level is needed so that we can refine existing regional and global isoprene emission models and improve our ability to predict source strengths of this important tropospheric constituent. We have, therefore, conducted a physiological and micrometeorological study of isoprene fluxes in a temperate forest in Atlanta, GA, USA, described elsewhere in this volume (Guenther et al. 1996). In June 1993, we made leaf-level physiological measurements on sun and shade leaves of sweetgum (*Liquidambar styraciflua* L.) to compare rates of isoprene emission and net photosynthesis, to determine how incident photosynthetic photon flux density (PPFD) and leaf temperature affect isoprene emissions, and to derive parameters needed to drive a canopy-level isoprene flux model.

Materials and methods

Site description

Physiological and micrometeorological measurements were made in the Fernbank Forest, a 26-ha mixed hardwood–conifer woodland in northeast Atlanta, GA. The forest is representative of the eastern deciduous biome, and is dominated by tulip poplar (*Liriodendron tulipifera* L.), oaks (*Quercus* spp.), hickories (*Carya* spp.), loblolly pine (*Pinus taeda* L.) and sweetgum (*L. styraciflua*). The forest has been largely uncut since 1820 and represents a mature remnant stand of Georgia Piedmont forest. A 44-m walk-up tower provided access to sun leaves of sweetgum at the top of the canopy (about 22 m above ground) and shade leaves within the canopy at approximately 8–10 m above ground. Leaf area index, which was measured near the tower with a plant canopy analyzer (Model LAI-2000, Li-Cor, Inc., Lincoln, NE), averaged 4.8.

Experimental techniques

Leaves were collected from the top of the canopy (22 m) (sun leaves) and from within the canopy at a height of 8–10 m above ground (shade leaves). Leaf-level net photosynthetic rates, stomatal conductance and rates of isoprene emission were measured in an open-path gas exchange system (MPH-1000, Campbell Scientific, Logan, UT), consisting of a temperature-controlled cuvette connected to a measurement and control system. Air of specified water vapor and CO_2 concentration was generated by mass flow controllers (Model 825, Edwards High Vacuum International, Wilmington, MA) and passed to the cuvette. The flow rate of gas entering the cuvette was measured with a mass flow meter (Model 831, Edwards). The difference in water vapor content of the air entering and leaving the cuvette was measured with two dew point mirrors (General Eastern, Watertown, MA), and the difference in CO_2 concentration was determined by infrared gas analysis (Model 225 Mk3, Analytical Development Corp., Hoddesdon, UK). A portion of gas exiting the cuvette was diverted to a 2-ml sample loop of a portable, isothermal gas chromatograph, and isoprene was separated on a stainless steel column (1.3m long × 2mm id) packed with Unibeads 3S, 60–80 mesh (Alltech Assoc., Deerfield, IL). Isoprene eluting from the column was measured with a reduction gas detector (Model RGD2, Trace Analytical, Menlo Park, CA), and peak integration was accomplished by means of a commercial integrator (Model 3390, Hewlett-Packard, Avondale, PA). Details of this analytical system are given in Greenberg et al. (1993). The isoprene detection system was calibrated several times daily against a standard cylinder containing 70 ppbv isoprene, referenced to an NIST propane standard using GC/FID (Model 5880A, Hewlett-Packard).

Artificial light was provided by a portable system consisting of a quartz halogen lamp (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 a 45° angle to reflect visible light onto the cuvette. Neutral density filters of blackened window screen were inserted in the light path to vary the intensity.

When a new leaf was placed in the cuvette, a minimum of 30 min was allowed for equilibration, and all measurements were made after steady-state conditions were realized, as indicated by continuous real-time monitoring of CO_2 and H_2O fluxes. Isoprene fluxes are based on the average isoprene concentration calculated from the final two or three measurements made under a given set of environmental conditions. When PPFD was varied, an equilibration time of 15 to 20 min was required; when the cuvette temperature was varied, the equilibration time was about 30 min.

Tracings of the portion of a leaf that was inside the cuvette were measured with a leaf area meter (CID, Moscow, ID). All experimental leaves were oven-dried at 60 °C for 48 h and weighed. Dried samples were assayed for total Kjeldahl nitrogen (Jaeger and Monson 1992).

Results

Although leaf morphology and physiology change in a continuous manner as PPFD decreases with depth in a tree canopy, for simplicity, we have used the discrete terms "sun" and "shade" leaves to distinguish between leaves growing in more or less full sun at the top of the canopy and those found in deep shade within the canopy at a height of 10 m above ground. Rates of net photosynthesis and isoprene emission were higher in sun leaves than in shade leaves (Figure 1). The rates of both processes increased more or less linearly in the quantum yield region and leveled off as PPFD became saturating. The amount of PPFD required for rate saturation was substantially less for both processes in shade leaves than in sun leaves.

The rate of isoprene emission increased exponentially between 20 and 35 °C, reached an optimum above 40 °C and subsequently declined (Figure 2). On a leaf area basis, sun leaves had higher rates of isoprene emission than shade leaves;

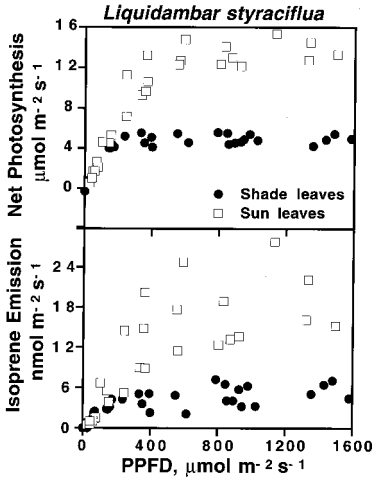

Figure 1. Effects of incident PPFD on net photosynthesis (top) and isoprene emission (bottom) in sun and shade leaves of sweetgum. Leaf temperature was 25 °C.

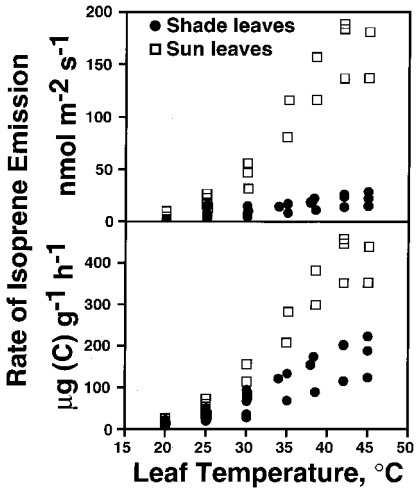

Figure 2. Effects of leaf temperature on isoprene emission by sun and shade leaves of sweetgum under saturating or near saturating PPFD. Rates are expressed on either a unit leaf area (top) or a unit dry mass (bottom) basis.

however, when isoprene emission rates were expressed on a leaf dry mass basis, differences between sun and shade leaves were reduced by about 60%, but sun leaves still emitted over 50% more isoprene than shade leaves ($P = 0.01$). This discrepancy was caused by the large differences in specific leaf area (SLA), which averaged 0.0121 $m^2\ g^{-1}$ (SD = 0.0010, $n = 20$) at the top of the canopy (22 m), 0.0239 $m^2\ g^{-1}$ (SD = 0.0025, $n = 5$) at 15 m and 0.0334 $m^2\ g^{-1}$ (SD = 0.0032, $n = 22$) at 8–10 m above ground.

Leaf nitrogen, expressed per unit leaf area, also varied more than twofold with canopy position, averaging 0.55 g m^{-2} (SD = 0.11, $n = 17$) for shade leaves and 1.26 g m^{-2} (SD = 0.20, $n = 15$) for sun leaves. However, because SLA increased with decreasing PPFD, shade leaves contained more nitrogen (18.3 mg g^{-1}, SD = 3.7) than sun leaves (15.2 mg g^{-1}, SD = 2.2) on a dry mass basis.

Mean net photosynthetic rates, stomatal conductance and isoprene emission rates expressed on a leaf area basis were all significantly higher for sun leaves than for shade leaves ($P = 0.01$) (Table 1). However, when these parameters were expressed on a dry mass basis, the differences between sun and shade leaves were reduced, and only isoprene emission rates remained significantly different (57% higher in sun leaves than in shade leaves). Rates of net photosynthesis and isoprene emission expressed per unit of leaf N were 29 and 83% greater, respectively, in sun leaves than in shade leaves ($P = 0.01$). The percentage of fixed carbon re-emitted as isoprene (assuming a loss of five carbon atoms for each molecule of isoprene emitted) was independent of the units of expression. At 25 °C, sun leaves lost an average of 53% more carbon than shade leaves ($P = 0.01$).

Modeling PPFD and leaf temperature effects on isoprene emission

Because the algorithms developed by Guenther et al. (1991, 1993) closely mimic the effects of PPFD and leaf temperature on isoprene emissions, we have used these functions to model our data. Before attempting to model the PPFD response of isoprene emission, Guenther et al. (1993) removed much of the leaf to leaf variation by normalizing their data, i.e., by assigning a value of 1.0 to the measured rate at PPFD = 1000 µmol $m^{-2}\ s^{-1}$ and then adjusting the rest of the data proportionately, as we have done in Figure 3 using the raw data from Figure 1. Guenther et al. (1993) developed the following function to describe a light scaling factor, CL, which assumes a value of 1.0 at PPFD = 1000 µmol $m^{-2}\ s^{-1}$:

$$CL = \frac{\alpha\ CL_1\ PPFD}{\sqrt{1 + \alpha^2\ PPFD^2}}, \qquad (1)$$

Table 1. Comparison of net photosynthesis, stomatal conductance and isoprene emission measured at 25 °C and PPFD of 1000 µmol $m^{-2}\ s^{-1}$ for sun and shade leaves of sweetgum. Data are expressed on a leaf area, a leaf dry mass, or a leaf nitrogen basis. The percentage of fixed carbon emitted as isoprene, which is independent of the units of expression, is also shown. Values are means ± SD. Different letters following the means indicate significant differences ($P = 0.01$). Sample size was 15–17.

		Leaf area		Leaf dry mass		Leaf nitrogen	
		Shade	Sun	Shade	Sun	Shade	Sun
Net photosynthesis	Units	µmol CO_2 $m^{-2}\ s^{-1}$		µmol CO_2 g^{-1} (DM) s^{-1}		µmol CO_2 g^{-1} (N) s^{-1}	
	Mean	4.53 ± 1.16a	13.44 ± 1.39b	539 ± 123a	590 ± 97a	8.52 ± 2.73a	10.98 ± 2.35b
	Ratio (sun/shade)	2.97		1.09		1.29	
Stomatal conductance	Units	mmol H_2O $m^{-2}\ s^{-1}$		mmol H_2O g^{-1} (DM) s^{-1}			
	Mean	93 ± 30a	239 ± 43b	3.08 ± 0.95a	2.91 ± 0.62a	–	–
	Ratio (sun/shade)	2.57		0.94		–	
Isoprene emission	Units	nmol Isoprene $m^{-2}\ s^{-1}$		µg C $g^{-1}\ s^{-1}$	nmol Isoprene g^{-1} (N) s^{-1}		
	Mean	4.11 ± 2.52a	17.13 ± 3.85b	29.0 ± 16.5a	45.5 ± 13.9b	7.64 ± 4.79a	13.97 ± 4.04b
	Ratio (sun/shade)	4.17		1.57		1.83	
% C lost as isoprene	Mean	0.42 ± 0.18a	0.64 ± 0.12b	–	–	–	–
	Ratio (sun/shade)	1.53		–		–	

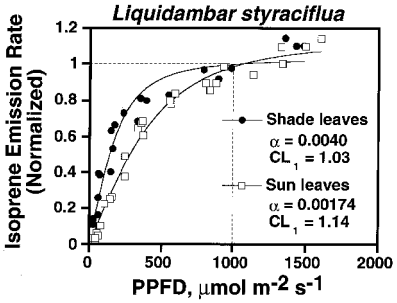

Figure 3. Effects of incident PPFD on isoprene emission in sun and shade leaves of sweetgum. Emission rates have been normalized to a value of 1.0 at a PPFD of 1000 μmol m^{-2} s^{-1}. Leaf temperature was 25 °C. The solid lines were fitted with Equation 1, using the parameter values shown.

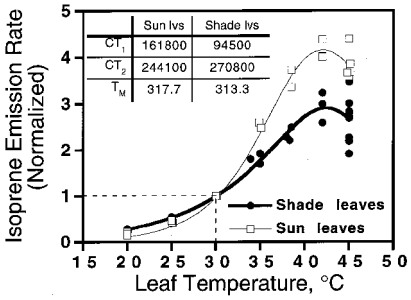

Figure 4. Effects of leaf temperature on isoprene emission by sun and shade leaves of sweetgum under saturating, or near saturating, PPFD. Emission rates have been normalized to a value of 1.0 at 30 °C. The solid lines were fitted with Equation 2, using the parameter values shown.

where α determines the initial slope of the normalized response, and CL_1 is the predicted normalized rate of emission as PPFD → ∞. We used non-linear least squares regression to arrive at best fit values of α and CL_1. When this function was fitted to the normalized data for sun and shade leaves, we obtained the model fits shown in Figure 3.

Although the normalization procedure reduces variation in the PPFD-saturated rates of isoprene emission, it introduces a systematic difference in the initial slope of the normalized response. This is because the raw emission rates of sun leaves, which on average have a higher rate of emission at PPFD = 1000 μmol m^{-2} s^{-1} than shade leaves, are divided by a larger number than that used for the shade leaf data, and this depresses the initial slope of the normalized response in Figure 3. Therefore, the apparent difference in initial slope should not be taken as evidence of a difference in the quantum use efficiency of isoprene production between sun and shade leaves.

To compare the temperature response of sun leaves versus shade leaves, we normalized the data in Figure 2, following Guenther et al. (1991). For each curve obtained from a given leaf, we assigned a value of 1.0 to the measured value at 30 °C and PPFD = 1000 μmol m^{-2} s^{-1}, and scaled other data proportionately. These normalized data (Figure 4) revealed large differences in the shape of the temperature responses of sun and shade leaves. By means of non-linear least squares regression, we fitted the normalized temperature data for sun and shade leaves to the temperature algorithm developed by Guenther et al. (1991, 1993), which defines a temperature scaling factor (CT) and assumes a value of 1.0 at temperature T_s (30 °C):

$$CT = \frac{e^{\frac{CT_1(T_k - T_s)}{R\,T_s\,T_k}}}{1 + e^{\frac{CT_2(T_k - T_M)}{R\,T_s\,T_k}}}, \quad (2)$$

where T_k is leaf temperature (K), T_s is the leaf temperature to which raw data are normalized (303.2 K), R is the gas constant (8.314 J K^{-1} mol^{-1}), CT_1 and CT_2 are the activation energy and energy of deactivation, respectively (J mol^{-1}), and T_M is an empirical coefficient (K). The solid lines in Figure 4 represent fits of this function to the data based on the normalized parameter values. We used these functions to calculate the Q_{10} for isoprene emission. Between 15 and 25 °C, the Q_{10} values for sun and shade leaves were 9.6 and 3.7, respectively, and between 25 and 35 °C, the values were 7.0 and 3.3, respectively. The lower Q_{10} values for shade leaves agree well with the values reported by Guenther et al. (1993) based on measurements from a variety of species, including sweetgum, although the temperature optimum in the current study was several degrees higher. However, the Q_{10} values for sun leaves were much higher than the values reported by Guenther et al. (1993), possibly because all the leaves used in their analysis were from plants grown in a growth chamber or greenhouse where light intensities were low relative to the full sun conditions experienced by the sun leaves in our study. The Q_{10} values for sweetgum sun leaves were more similar to the high Q_{10} values obtained by Sharkey and Loreto (1993) for isoprene emission in leaves of kudzu (*Pueraria lobata* C.K. Schneid.).

Discussion

Variation between sun and shade leaves

Sun leaves had higher rates of physiological activity than shade leaves when activity was expressed on a leaf area basis (Figures 1 and 2, Table 1). Net photosynthetic rates, stomatal conductance and rates of isoprene emission were all greater in sun leaves than in shade leaves by a factor of about 3, 2.5 and 4, respectively. Similar results have been reported for aspen (*Populus tremuloides* Michx.) and red oak (*Quercus rubra* L.) (Sharkey et al. 1991*b*). However, the differences between sun and shade leaves were greatly reduced when values were expressed on a leaf dry mass basis, because SLA increased with depth in the canopy (Table 1), reflecting leaf acclimation to reduced irradiance (Boardman 1977).

Differences between sun and shade leaves in leaf area based rates of photosynthesis and isoprene emission may be partially explained by the higher unit area N content of sun leaves than of shade leaves. However, N allocation alone cannot explain these differences, because isoprene emission rates expressed on a unit N basis were 80% higher in sun leaves than in shade

leaves (14.0 versus 7.6 nmol g^{-1} N s^{-1}). To the extent that isoprene emission rate is controlled by the activity of isoprene synthase, this result suggests that leaves growing in high light devote a higher proportion of their leaf N to isoprene synthase. This is consistent with the finding that, in velvet beans, for a given light treatment, isoprene emission showed a strong positive correlation with percent leaf N (Harley et al. 1994).

The percentage of carbon fixed in photosynthesis and immediately re-emitted as isoprene was 53% greater in sun leaves than in shade leaves at 25 °C (Table 1). The percentage of carbon lost as isoprene increased with temperature for both sun and shade leaves (Figure 5); however, the disparity between sun and shade leaves increased with increasing temperature (Figure 4).

Modeling at different scales

At the individual leaf scale, isoprene emission responds to variation in PPFD and temperature in a well characterized and easily modeled fashion; however, our ability to model isoprene emission from forest stands is limited primarily by our ability to model the light and temperature environment to which leaves are exposed, and our ability to determine the distribution of isoprene emitting biomass within a forest stand. Light interception in canopy models is best handled on a leaf area basis. If we express isoprene emission on a leaf-area basis, we need to incorporate the fourfold difference in emission rate between leaves at the top and at the bottom of the canopy into a multilayer canopy-level model. Alternatively, if we express isoprene emission rates per unit dry mass, the difference in isoprene emission rate between sun and shade leaves is reduced to less than a factor of two; however, we then need to incorporate systematic changes in SLA within the canopy into the model to allow conversion from mass-based leaf-scale emissions to ground-area-based canopy flux predictions. We investigated the potential significance of variations in both SLA and isoprene emission characteristics with depth in the canopy using a simple three-layer, canopy light interception model.

Early estimates of regional-scale isoprene fluxes did not take account of canopy light interception processes; instead light-dependent processes were driven by incident PPFD (Zimmerman 1979). However, it was soon realized that to model strongly light-dependent processes such as isoprene emission, it is necessary to take account of canopy light interception processes to avoid overestimation of fluxes. Accordingly, models were developed that incorporated multilayer canopy models, which calculated light extinction, and use calculated PPFD values to drive isoprene emission at different canopy depths (Pierce et al. 1991, Lamb et al. 1993). Geron et al. (1994) investigated the effects of leaf biomass distribution within a given canopy on model flux estimates and found that, given a typical distribution of SLA for deciduous forest canopies (Jurik 1986), a disproportionate share of isoprene emitting biomass occurs in the upper canopy layers where PPFD is higher. As a result, model flux estimates increased by about 10% if SLA was allowed to vary in a realistic fashion.

We tested the effects of varying leaf biomass within a sweetgum canopy on model estimates of isoprene flux. We used the canopy radiation transfer model developed by Norman (1982), as modified by Guenther et al. (1995), to estimate global emissions of natural VOCs. Leaf area index was assumed to be 6, 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 average leaf angle of 60°, and the average PPFD incident on sunlit and shaded leaves in each layer was also calculated (Guenther et al. 1995).

Initially, leaves in the top, middle and bottom canopy layers were assigned SLA values of 0.012, 0.024 and 0.033 m^2 g^{-1}, respectively. Total leaf biomass was thus 312 g m^{-2} ground area (LAI = 6 and three canopy layers). We assigned a base isoprene emission rate (at 30 °C and PPFD = 1000 μmol m^{-2} s^{-1}) to the top (109 μg C g^{-1} h^{-1}) and bottom canopy layers (56 μg C g^{-1} h^{-1}), and a value of 82 μg C g^{-1} h^{-1} to the middle layer. Assuming PPFD = 2000 μmol m^{-2} s^{-1} above the canopy

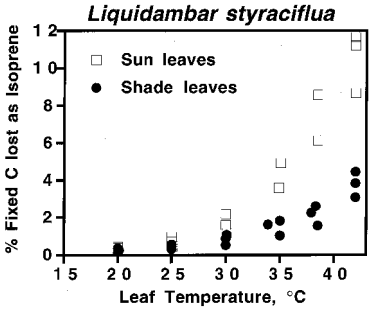

Figure 5. The percentage of fixed carbon lost immediately as isoprene by sun and shade leaves of sweetgum as a function of leaf temperature. Values were calculated on the assumption that five carbon atoms are lost per isoprene molecule emitted.

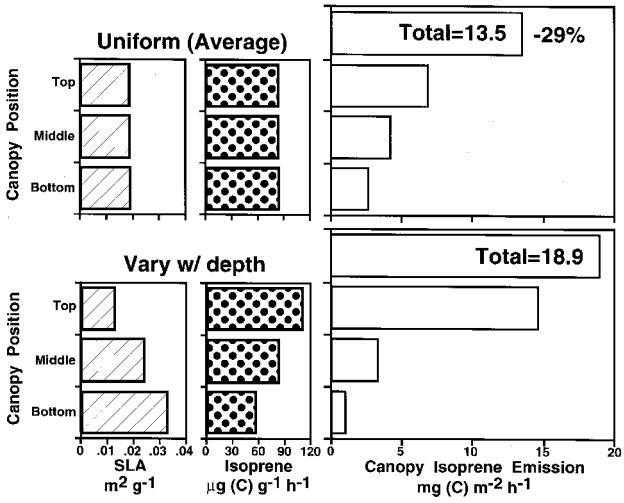

Figure 6. Total canopy isoprene emission predicted by a simple three-layer canopy model. Results show the effect of varying SLA and isoprene emission in a realistic way with canopy depth (bottom) rather than assuming that both are uniform throughout the canopy (top). The emissions from each canopy layer, as well as total canopy emission, are shown.

and a uniform leaf temperature of 30 °C, the model, incorporating the light algorithms in Figure 3, predicted a canopy flux of 18.9 mg C m^{-2} h^{-1}, with over 75% of the emissions originating in the top third of the canopy (Figure 6, bottom). When we replaced the measured values of SLA and isoprene emission characteristics with average values of 0.019 m^2 g^{-1} and 82 μg C g^{-1} h^{-1}, respectively, isoprene emissions were more evenly distributed through the canopy (Figure 6, top) and overall emissions declined by 29%. If SLA was held constant while isoprene emission potential was allowed to vary, canopy emissions were reduced by 21%, whereas if isoprene emission potential was held constant while SLA was allowed to vary, canopy emissions were reduced by 17% (Table 2).

Our canopy model does not incorporate an energy budget routine to calculate leaf temperature, but assumes that leaf and air temperatures are equal. However, given the strong temperature dependency of isoprene emission, especially for sun leaves, and the likelihood that leaf temperature may differ from air temperature by several degrees (Gates 1968), it may be important to calculate average leaf temperatures for sun and shade leaves in each canopy layer.

Potential carbon losses due to isoprene emission

Sharkey et al. (1991*a*) used $^{13}CO_2$ to demonstrate that isoprene is produced from recently fixed carbon, and that the isoprene precursor pool is small and is flushed within 10 min in oak leaves. Thus, some fraction of fixed carbon is lost almost immediately in isoprene-emitting species. In the short term, the percentage of carbon lost varies from near zero to over 20% (Sharkey et al. 1991*a*), depending on environmental conditions. In sweetgum, the average loss of carbon at 25 °C and high PPFD was about 0.5% (Table 1), which is probably not of great significance to the plant (Lambers and Poorter 1992). However, as a result of the large differences in the temperature dependences of net photosynthesis and isoprene emission, the percentage of fixed carbon lost due to isoprene emissions increased dramatically with increasing leaf temperature (Figure 5). Thus, during midsummer when leaf temperatures reach 35 °C, losses may reach 1–2% for shade leaves and 3–5% for sun leaves.

Table 2. Predictions of isoprene emissions from a sweetgum canopy according to a three-layer canopy model, assuming an LAI of 6, leaf biomass of 312 g m^{-2} (ground area), leaf temperature of 30 °C and PPFD of 2000 μmol m^{-2} s^{-1}. The model assesses the consequences for canopy isoprene emission of assuming constant or variable SLA (0.012, 0.024 and 0.033 m^2 g_{DW}^{-1} for the top, middle and bottom of the canopy, respectively), and constant or variable isoprene emission rates (109, 82 and 56 μg C g^{-1} h^{-1} for the top, middle and bottom of the canopy, respectively).

SLA	Isoprene emission	Canopy isoprene emission mg C m^{-2} h^{-1}
Variable	Variable	18.94
Uniform	Variable	14.90
Variable	Uniform	15.79
Uniform	Uniform	13.47

In addition to the short-term effects of leaf temperature, the percentage of carbon lost also varies over time, because the capacity for photosynthesis and isoprene production follow different developmental paths. Early in the growing season, the onset of isoprene production lags behind photosynthesis in leaves of velvet bean (Grinspoon et al. 1991), *Eucalyptus globulus* Labill. (Guenther et al. 1991) and aspen (*Populus tremuloides* Michx.) (Monson et al. 1994), and during this growth phase, volatile carbon losses are very small. In mature leaves, isoprene production may remain high after photosynthetic competence has begun to decline with leaf aging (unpublished data of Jaeger and Monson, cited in Fehsenfeld et al. 1992), resulting in increased carbon losses (as a percentage of carbon fixed) during senescense. We have preliminary evidence that, in *Quercus stellata* Wangenh., *Mahonia trifoliata* Moric. and *Condalia obovata* Hook., photosynthesis is more sensitive than isoprene production to increasing water stress (authors' unpublished observations). Similar findings have been reported for container-grown sweetgum subjected to repeated cycles of short-term drought (C. Fang, R.K. Monson and E.B. Cowling, unpublished observations). Although stomatal closure has little direct effect on isoprene emission rates (Fall and Monson 1992), drought-induced stomatal closure could have a large indirect effect on isoprene emission rates by increasing leaf temperature.

Thus, instantaneous losses of fixed C due to isoprene emission may exceed 10–20% under conditions of high temperature or drought. Integrated over the longer term, however, losses will be much less. In the most recent estimate of annual global scale isoprene and monoterpene emissions, isoprene volatilization is equivalent to about 1.3% of annual net primary productivity (NPP) (Guenther et al. 1995). Furthermore, if other less reactive compounds volatilized from leaves, such as methanol (MacDonald and Fall 1992, Nemecek-Marshall et al. 1995), and other alcohols and aldehydes are included in the global estimates, total global carbon losses may be as great as 2.4% of NPP (Guenther et al. 1995), and for ecosystems in warm, highly productive regions, such as tropical forests, the predicted losses exceed 4% of NPP. These estimates assume that only about 25% of the tree biomass in a given region is composed of species with high isoprene emission rates. In monospecific stands of forest plantation species which are known to be high emitters of isoprene, such as *Populus* and *Eucalyptus* spp., predicted losses exceed 8–10% of NPP.

All of the above calculations are based on the assumption that the carbon cost of producing and emitting a single molecule of isoprene (C_5H_8) is five; however, Sharkey et al. (1991*a*) have pointed out that an additional CO_2 molecule is lost in the production of each of the three molecules of acetyl CoA necessary for the formation of IPP, the precursor of isoprene and the monoterpenes, and a fourth CO_2 molecule is lost in the final conversion of mevalonic acid to IPP, bringing the total carbon cost to nine for each isoprene produced. In determining the true carbon cost to the plant of VOC emissions, therefore, these hidden carbon costs must be taken into account.

In summary, despite large uncertainties in current estimates, it appears that losses of volatile carbon may be significant for

species with inherently high rates of VOC emissions, and in areas experiencing warm growing seasons. Although experimental evidence is lacking, Field et al. (1992) suggest that projected increases in CO_2 may lead to increased production and presumably emission of carbon-based secondary compounds such as monoterpenes. Furthermore, if average temperatures in a region increase, or if a region is subject to higher temperature extremes, rates of volatilization of isoprene, monoterpenes and presumably other VOCs are likely to increase in parallel.

Acknowledgments

The authors thank Dr. Russ Monson for analyzing leaf nitrogen samples, Dr. Lee Klinger for LAI measurements, Dr. Jim Greenberg for analytical support, and all for helpful comments on the manuscript. This research was supported in part by the U.S. Environmental Protection Agency (Interagency Agreement DW49935389-01-0), and the Southern Oxidants Study (Southern Oxidants Research Program on Emissions and Effects). The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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