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Biogenic volatile organic compound emissions from a lowland tropical wet forest in Costa Rica

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Abstract

Twenty common plant species were screened for emissions of biogenic volatile organic compounds (BVOCs) at a lowland tropical wet forest site in Costa Rica. Ten of the species examined emitted substantial quantities of isoprene. These species accounted for 35–50% of the total basal area of old-growth forest on the major edaphic site types, indicating that a high proportion of the canopy leaf area is a source of isoprene. A limited number of canopy-level BVOC flux measurements were also collected by relaxed eddy accumulation (REA). These measurements verify that the forest canopy in this region is indeed a significant source of isoprene. In addition, REA fluxes of methanol and especially acetone were also significant, exceeding model estimates and warranting future investigation at this site. Leaf monoterpene emissions were non-detectable or very low from the species surveyed, and ambient concentrations and REA fluxes likewise were very low. Although the isoprene emission rates reported here are largely consistent with phylogenetic relations found in other studies (at the family, genus, and species levels), two species in the family *Mimosaceae*, a group previously found to consist largely of non-isoprene emitters, emitted significant quantities of isoprene. One of these, *Pentaclethra macroloba* (Willd.) *Kuntze*, is by far the most abundant canopy tree species in the forests of this area, composing 30–40% of the total basal area. The other, *Zygia longifolia* (*Humb. & Bonpl.*) *Britton & Rose* is a common riparian species. Our results suggest that the source strength of BVOCs is important not only to tropical atmospheric chemistry, but also may be important in determining net ecosystem carbon exchange. Published by Elsevier Science Ltd.

Keywords: Isoprene; Biogenic volatile organic compounds; Relaxed eddy accumulation; Pentaclethra macroloba; Palmae; La selva biological station

1. Introduction

Isoprene emission from vegetation is the world's largest known source of non-methane volatile organic compounds (NMVOCs). Its importance is further amplified by its high reactivity with the hydroxyl radical compared to other abundant atmospheric NMVOCs. It is estimated that over 90% of isoprene emission is from vegetation (Guenther et al., 1995). Modeling (Guenther et al., 1995) and limited measurement (Guenther et al., 1999, 1996) studies have suggested that at least 50% of the global annual isoprene flux is from tropical

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ecosystems, due to vast expanses of evergreen vegetation and warm climate throughout the year. Quantitative studies of tropical biogenic volatile organic compound (BVOC) emission at the plant level have been limited to isoprene in Puerto Rico (Lerdau and Keller, 1997) and Panama (Keller and Lerdau, 1999; Lerdau and Throop, 1999) and isoprene and monoterpenes in Central Africa (Klinger et al., 1998; Guenther et al., 1999) and South Africa (Guenther et al., 1996). Leaf-level emission rate measurements made under carefully controlled environments are needed to develop, parameterize, and test regional to global scale emission models (Lerdau and Throop, 1999; Geron et al., 2001). Here, we present leaf BVOC emissions from 20 of the most abundant plant species and a limited set of canopy-level relaxed eddy accumulation (REA) fluxes of isoprene, methanol, and acetone measured at the La Selva Biological Station in Costa Rica. Leaf BVOC emission rates (in $\mu g\, C\, g^{-1}\, h^{-1}$ or $nmol\, m^{-2}\, s^{-1}$) are measured at leaf temperatures of 30–39°C and photosynthetically active radiation (PAR) of $1000–2500\, \mu mol\, m^{-2}\, s^{-1}$. Canopy-level fluxes are determined over 30-min periods from morning to mid-afternoon.

2. Methods

Measurements were conducted at the La Selva Biological Station (10°26′N, 83°59′W) in the lowland [ca. 35 m above sea level (ASL)] tropical wet forests in the canton Sarapiqui, province of Heredia, Costa Rica. Annual rainfall is approximately 400 cm with wetter and drier seasons defined by the passing of the intercontinental tropical convergence zone. Typically, the annual distribution of rainfall is bimodal with a brief dry period, *verano,* in September or October, but with no month averaging $<10\, cm\, month^{-1}$. Average monthly temperature is 25.8°C, which differs little among months. Mean monthly minimum temperatures range from 19.8°C to 23.9°C, while monthly mean maximum temperatures range from 29.7°C to 31.1°C (Sanford et al., 1994). REA flux measurements were made 18–22 October 1999, primarily in the morning to mid-afternoon hours before mid-afternoon thunderstorm activity. Leaf-level measurements were taken from 21–23 October.

2.1. Leaf measurements

Hartshorn and Hammel (1994) and a current plot-level forest inventory database (Clark and Clark, 2000; D.A. Clark and D.B. Clark, unpublished data) summarize the importance of tree species (stems >10 cm in diameter) by basal area and abundance in primary forest types at La Selva. Forest basal area is dominated by the tree families Mimosaceae, Arecaceae (Palmae), Tiliaceae, Anacardiaceae, Burseraceae, and Papilionaceae, but many others are represented. We attempted to locate leaves on sunlit upper crowns of many of these species for emission sampling. However, in some cases only shaded foliage could be reached, and in others only foliage on cut branches could be analyzed. In the latter case, small branches were cut with a pole pruner and then re-cut while submerged in water to minimize air entry into the transpiration stream. The cut branch studies were usually performed indoors as afternoon thunderstorms approached. If photosynthesis was low following cutting ($<2\, \mu mol^{-2}\, s^{-1}$), results were discarded from further consideration in the analysis, since it was assumed that cutting had affected the gas exchange physiology of the foliage. This occurred on only 2 of 12 cut-branch samples, both of which had been cut several hours prior to sampling.

Leaf gas exchange was monitored with a Li-Cor 6400 (Li-Cor, Inc., Lincoln, NE) gas exchange measurement system with a red/blue light source. This system measures water vapor (H_2O) and carbon dioxide (CO_2) exchange from leaf surfaces with infrared gas analyzers (IRGAs) and allows control of PAR, leaf and air temperature, humidity, CO_2 concentration, and air flow over a $6\, cm^2$ leaf area enclosed in the cuvette. Ambient purge air was drawn by the gas exchange system 2–3 m from the leaves being measured. This air was passed through a 2-l plastic mixing vessel at a flow rate of $300\, \mu mol\, s^{-1}$ (resulting in a mixing time of ca. 5 min) to help stabilize ambient concentrations of isoprene and CO_2.

A three-way Teflon valve was installed to direct exhaust air to either the LI-6400 reference and sample analyzers (for IRGA matching purposes) or to a Photovac Voyager portable gas chromatograph (GC) with a photoionization detector (PID, Perkin-Elmer, Norwalk, CT). A pump in the GC drew cuvette exhaust air at $200\, ml\, min^{-1}$ through a 0.5 ml sample loop for 10 s. Gas in the sample loop was injected onto a 0.53 mm i.d. CP-Sil-5 column 10 m in length. Column temperature was isothermal at 60°C. Zero (hydrocarbon-free) air was used as the carrier gas. The detector output was linear from 0 to 460 ppb (v/v) isoprene concentration with an intercept through zero. Ambient air samples were drawn through the gas exchange system prior to enclosing a leaf in the cuvette to determine ambient contributions to measured leaf isoprene emissions. Ambient isoprene concentrations were typically 0–5 ppb (v/v), although they reached 10 ppb on a few occasions.

The carrier gas flow through the column was reversed after the isoprene eluted. By backflushing the column, later eluting compounds were prevented from interfering with subsequent analyses. The system was calibrated against a standard containing 460 ± 2 ppb (v/v) isoprene in air (Scott Specialty Gases, Inc., Plumsteadville, PA).

The standard was referenced to the flame ionization detection (FID) response of a GC (Model HP5890, Hewlett Packard, Inc., Avondale, PA) which was calibrated to a National Institute of Standards and Technology (NIST) propane standard (SRM 1660a, 3 ppm propane in air, Rochester, NY). The Voyager portable GC/PID instrument was calibrated to concentrations of 4, 23, 46, 100, 230, and 460 ppb (v/v) using a dynamic gas calibration system (Model 146, Thermo Environmental Instruments, Inc., Franklin, MA). We estimate that both precision and accuracy were within 2–5% as determined by repeated measurements of the standard gas at these concentrations. The lower detection limit of our analytical system is approximately 2 ppb (v/v) for isoprene.

Leaf isoprene emission sampling was initiated after allowing leaf gas exchange (internal CO_2 concentration (C_{in}), photosynthesis (A), and stomatal conductance) to stabilize. This usually occurred within 10 min unless the leaf was from a deeply shaded environment. In most cases, at least three successive measurements at approximately 6-min intervals were performed on each leaf. At times it was necessary to maintain leaf temperatures at approximately 35°C to avoid condensation in the gas exchange system. Ambient isoprene samples were drawn from the sample line downstream from the mixing vessel before and after leaf measurements. Samples on intact foliage were taken between 900 and 1500 h, and foliage on cut branches were analyzed indoors during afternoon and evening thunderstorms that occurred throughout the period. Leaf mass per unit area was determined on the 6 cm^2 section of the enclosed leaves. These sections were dried at 80°C for 48 h and weighed.

Isoprene emission rate E ($nmol\,m^{-2}\,s^{-1}$) was calculated as

$$E = f(C_o - C_i)a^{-1}, \quad (1)$$

where f is the flow rate ($mol\,s^{-1}$) into the cuvette, C_o and C_i are the outlet (exhaust air) and inlet isoprene concentrations ($nmol\,mol^{-1}$), respectively, and a is the enclosed leaf area, which was typically 0.0006 m^2 (6 cm^2). Mass-based E ($\mu g\ C\,g^{-1}\,h^{-1}$) was calculated by substituting leaf dry weight for a in Eq. (1). As each isoprene emission sample was being drawn from the cuvette exhaust, leaf environment and gas exchange data were logged with the gas exchange system. Above-canopy meteorological data (30-min average measurements net radiation, air temperature, wind speed, and wind direction) were obtained from the CARBONO Project (S.F. Oberbauer, H. Loescher, D.B. Clark, D.A. Clark, and E. Veldkamp, unpublished data), where CO_2 and H_2O fluxes were also monitored above the forest canopy from a 42 m walkup tower in a primary forest within 2.5 km of the area where leaf measurements were made.

2.1.1. Canopy-scale measurement

Canopy-scale VOC emissions were measured using the REA system described by Baker et al. (2001). The system measures wind speed with a three-dimensional sonic anemometer (K-Probe, Applied Technologies, Boulder, CO) that was located 42 m above the ground, approximately 21 m above the zero-plane displacement. A controller operates a set of valves according to the vertical velocity signal and collects two air samples: one for updrafts and one for downdrafts. The valves were switched at 10 Hz. The flux is obtained from

$$F_i = \beta\sigma_w(C_u - C_d), \quad (2)$$

where F_i is isoprene (or other VOC) emission in mg-carbon $m^{-2}\,h^{-1}$, β is a proportionality constant, σ_w is the standard deviation of vertical wind speed, and C_u and C_d are mean concentrations of VOC collected from the updraft and downdraft air samples, respectively. A deadband was used (0.6 σ_w) in order to increase the difference between the up and down concentrations. If the vertical wind velocity did not exceed this value, sample air was routed back to the atmosphere rather than to the sample cartridges. This induces a bias which was corrected for in the calculation of fluxes. An adjusted β was calculated based on the measured sensible heat flux and the difference in temperature during updrafts and downdrafts. Testing of the REA system and adsorbent tubes (e.g., VOC breakthrough volume and recovery efficiency) is described by Baker et al. (2001). Their analysis indicates that the overall uncertainty in the flux measurements is roughly 10% for isoprene, 12% for acetone, and 25% for methanol. Additional details about the theory of the technique, design, and performance of the system are given by Baker et al. (2001).

The mean VOC concentrations of updrafts and downdrafts were determined by accumulating the samples in 0.25 × 3.5 in silco-steel tubes packed with 350 mg of Carbotrap followed by 180 mg of Carbosieve S-III. The tubes were returned to the laboratory where they were analyzed by thermal desorption/GC. The samples were analyzed using the GC/FID system described by Baker et al. (2001). The system was calibrated with NIST standards.

The operation of the REA system was also evaluated by calculating fluxes of several long-lived (years) anthropogenic trace gas compounds that have a negligible biogenic flux and can be analyzed using the same GC-mass spectroscopy (MS) analysis that was used for BVOC. The mean fluxes of carbon tetrachloride and the Freon compound, F-113, were determined to be near zero, indicating no significant bias in the REA system.

The long-term measurement systems of the CARBONO Project provided the ancillary data needed to initialize the emission model and determine energy balance closure at the site. The sensors included a net radiometer (model NR lite, Kipp and Zonen, Delft, Holland), PAR quantum sensor (Model Li-190sx, Li-Cor, Inc., Lincoln, NE) wet and dry bulb thermometers, soil heat flux, and fast response (10 Hz) H_2O and CO_2. Wind speed, wind direction, and CO_2 and H_2O concentrations were sampled and stored at 10 Hz. Net radiation, PAR, air temperature, and humidity were sampled at 0.1 Hz and stored as 30-min averages. Energy balance closure was within 10% of above-canopy net radiation flux during the measurement periods. The diffusor on the PAR sensor was sometimes disabled by algal accumulation if left unattended for periods of weeks. Therefore, PAR was calculated from a direct comparison between the net radiometer and Li-190 which yielded a relationship of PAR ($\mu mol\,m^{-2}\,s^{-1}$) = 6.5103 + 1.9972 (net radiation in $W\,m^{-2}$) with an R^2 of 0.991. The calculated PAR data were used for the BVOC model estimates discussed below.

Other ancillary measurements obtained for the REA flux study included occasional leaf temperature measurements performed using a hand-held infrared thermometer (Model 39800, Cole-Parmer Instrument Co.,Vernon Hills, IL). The primary fetch was considered to be south, southwest, and west of the tower. Winds from the northeast passed through the tower before reaching the REA inlet. Therefore, fluxes from this direction were deleted from the analysis. Additional samples were eliminated due to analytical difficulties and contamination's reducing the number of flux estimates to 6 for methanol, 8 for acetone, and 10 for isoprene.

2.1.2. BVOC emission model

Leaf-level VOC fluxes were extrapolated to the canopy scale for the La Selva forest in the proximity of the Proyecto CARBONO tower using modeling methods discussed by Guenther et al. (2000). The canopy foliar biomass density of 850 $g\,m^{-2}$ (dry weight) used here is from litterfall studies summarized by Parker (1994, p. 57 and Fig. 5.1). The forest cover is apportioned into species-level foliage quantities proportional to basal area by species determined using the plot-level forest inventory data (D.A. Clark and D.B. Clark, unpublished data). Basal isoprene emission rates for emitting species are 70 μg C (g-foliar dry mass)$^{-1}$ h^{-1} standardized for PAR values of 1000 $\mu mol\,m^{-2}\,s^{-1}$ and leaf temperatures of 30°C. This is equivalent to the basal rate measured for the canopy dominant *Pentaclethra macroloba* (Willd.) *Kuntze* in this study and is similar to that observed for other isoprene-emitting vegetation in this and other regions (Table 1). For other genera found at the site, a basal isoprene emission factor of 0.1 μg C $g^{-1}\,h^{-1}$ is applied (Guenther et al., 1994). Based on our emission measurements and the reported vegetation species composition for this site, we assumed that 50% (after subtracting 130 $g\,m^{-2}$ of estimated liana leaf biomass) of the plant species were isoprene emitters resulting in a site average basal emission rate of 35 μg C $g^{-1}\,h^{-1}$.

Emission factors for acetone (0.09 μg C $g^{-1}\,h^{-1}$) and methanol (0.6 μg C $g^{-1}\,h^{-1}$) are derived from Guenther et al. (2000) and are applied to all species. Emissions of these compounds are highly uncertain and may be strongly influenced by factors such as stress, herbivory, or mechanical disturbance. They are thought to be especially influenced by phenological stage, with highest emissions from young expanding foliage (Guenther et al., 2000). Emission of methanol is assumed to be influenced by PAR in a manner similar to isoprene, while acetone emission is allowed to increase exponentially with increasing leaf temperature (Guenther et al., 1993, Eq. (5)).

The empirical algorithms of Guenther et al. (1993) were used to adjust emission rates to ambient PAR and temperature conditions. The PAR correction factor changes vertically through the canopy in the manner illustrated in Fig. 1 of Guenther et al. (2000). Direct beam and diffuse fractions of measured total above-canopy PAR and sunlit/shaded fractions of leaf area were estimated using the techniques described in Guenther et al. (1995). Exponential decay algorithms are applied to reduce diffuse PAR and specific leaf weight (SLW, or leaf mass per unit area, one-sided) at lower levels within forest canopies (Geron et al., 1994). A leaf area index (LAI, m^2 one-sided leaf area per m^2 ground area) value of 8.0 was used in the model simulations, which is consistent with the high foliar biomass density in the region and previous estimates of LAI from wet tropical evergreen broadleaf forests (Box, 1981). However, reliable LAI measurements specific to La Selva are currently unavailable. Isoprene and methanol emission rates are not highly sensitive to variability in LAI values above ca. 3 since these compounds are emitted as a function of PAR, most of which is intercepted in the upper canopy. Model estimates are sensitive to specific leaf weight, which was allowed to vary from 60 $g\,m^{-2}$ for sun leaves to 40 $g\,m^{-2}$ for shaded leaves lower in the canopy. The sun leaf value is 20% higher than that measured for the canopy dominant *P. macroloba* and is the mean value for isoprene emitters we found in this region (Table 1). Leaf temperatures were calculated from above-canopy radiation, temperature, relative humidity, and wind speed values using iterative methods described in Goudriaan and van Laar (1994). Calculated leaf temperatures were typically within 1.5°C of ambient air temperatures. The leaf age activity factors, ratio of current to peak foliar density, and escape efficiency factors described in Guenther et al. (2000) are incorporated here. These factors probably have minimal effect on net estimated flux (ca. 5–10%) since leaf senescence

Table 1
Summary of isoprene emission rates adjusted to leaf temperature of 30°C and PAR of 1000 μmol m^{-2} s^{-1} using algorithms of Guenther et al. (1993)

Family	Species	SLM	E	C	L,P	DW	LA	LA^{OTH}
Arecaceae	*Euterpe precatoria* Mart.^{V1}	52	L	I	2,1	41(14)	10	
Arecaceae	*Prestoea decurrens* (H. Wendl. ex Burret) H.E. Moore	65	H	I	4,1	0	0	
Arecaceae	*Socratea exorrhiza* (Mart.) H. Wendl.	69	H/L	I	2,2	80(23)	26	15^{L} (*exorrhiza*)
Arecaceae	*Welfia regia* H. Wendl. ex André	67	L	I	2,1	33(5)	10	
Boraginaceae	*Cordia alliodora* (Ruiz & Pav.) Oken	67	H	C	2,1	0	0	0^{K,L} (*alliodora,bicolor*)
Burseraceae	*Protium pittieri* (Rose) Engl.	67	H	I	2,2	76 (9)	24	46^{L} (*panamense*)
Cecropiaceae	*Pourouma bicolor* Mart.^{V2}	35	H*	I	1,1	0	0	
Euphorbiaceae	*Alchornea costaricensis* Pax & K. Hoffm.	58	H	I	2,1	0	0	0^{J} (*cordifolia*)
Melastomataceae	*Miconia impetiolaris* (Sw.) D. Don ex DC.	39	H	I	2,2	0	0	0^{L} (*spp.*)
Menispermaceae	*Cissampelos* spp	50	L	I	1,1	0	0	28^{K} (*pareira*)
Mimosaceae	*Pentaclethra macroloba* (Willd.) Kuntze	50	H/L	I	3,2	69(15)	16	0^{J} (*macrophylla*)
Mimosaceae	*Stryphnodendron microstachyum* Poepp. & Endl.	125	H	I	2,1	0	0	
Mimosaceae	*Zygia longifolia* (Humb. & Bonpl.) Britton & Rose	96	H	C	2,2	106(24)	47	0^{R} (*spp.*)
Musaceae	*Musa acuminata* Colla	39	H	I	1,1	0	0	0^{J} (*sapientum*)
Myristicaceae	*Virola sebifera* Aubl.	54	L	I	2,2	10(1)	2	13^{L} (*spp.*)
Papilionaceae	*Dipteryx panamensis* (Pittier) Record & Mell	66	L	C	2,2	43(2)	13	
Papilionaceae	*Pterocarpus officinalis* Jacq.	43	H	I	2,2	126(12)	25	3–20^{J} (*luscens*, *soyauxii*)
Poaceae	*Bambusa vulgaris* Schrad. Ex J.C. Wendl.	47	L	C	2,2	12(2)	3	Low^{J} (*vulgaris*)
Rubiaceae	*Warszewiczia coccinea* (Vahl) Klotzsch	68	H	I	2,1	0	0	
Sapindaceae	*Nephelium ramboutan-ake* (Labill.) Leenh.	64	L	C	2,2	0	0	

SLM is mean (S.D. was $<5\%$) specific leaf mass in g m^{-2}, E is light environment of sample leaf (H = High light or sun leaf, L = Low light or shade leaf, * this was an expanding leaf from a stump sprout) for species for which both sun and shade leaf emissions were measured, sun leaf emission rates (and SLM) are reported, C is the condition of sample leaf (C = Cut branch, I = Intact plant), L,P is the number of individual leaves and plants sampled, respectively, DW is the emission factor in μg C g^{-1} h^{-1} (standard deviation in parentheses), LA is the emission factor in nmol m^{-2} s^{-1}, and LA^{OTH} is the isoprene emission rate in nmol (isoprene) m^{-2} s^{-1} for species in the same genus determined by Klinger^{J} et al. (1998), Keller and Lerdau^{K} (1999), Lerdau and Throop^{L} (1999), Rasmussen^{R} (1978). ^{V1}var. longevaginata (Mart.) Andrew Hend. ^{V2} subsp. scobina (Benoist) C.C. Berg & Heusden minor Benoist.

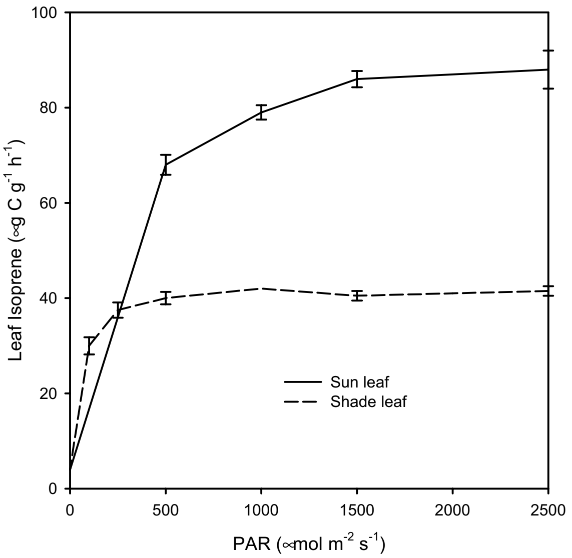

Fig. 1. Response of *S. exorrhiza* sun (solid line) and shade (dashed line) leaf isoprene to changing PAR within the leaf cuvette. Leaf temperature was held constant at 35°C. Error bars denote ±1 standard deviation about the mean of duplicate isoprene emission measurements at each PAR level for each leaf.

and litterfall appear to be fairly uniformly distributed throughout the year in the forests of this region (Parker, 1994).

Above-canopy PAR, temperature, wind speed, and relative humidity measurements at the CARBONO tower were used as model inputs to estimate hourly BVOC emissions. These emissions were compared with flux measurements of corresponding compounds made from the tower above the canopy.

3. Results and discussion

3.1. Leaf-scale BVOC emissions

Isoprene emission rates were measured at leaf temperatures of 30–35°C, although emission rates were examined at temperatures as high as 39°C during temperature response experiments. Light levels were held either at 1000 or 1500 μmol m^{-2} s^{-1}, except during light response experiments. Emission rates were adjusted to standard conditions ($T_L = 30°C$ and PAR of 1000 μmol m^{-2} s^{-1} in this study) based on the PAR and leaf temperature algorithms of Guenther et al. (1993). Temperature response of *Dipteryx panamensis* (Pittier) Record & Mell (Papilionaceae) and *Bambusa vulgaris* Schrad. ex J.C. Wendl. (Poaceae) was examined by measuring isoprene emission as T_L was increased in 3°C increments from 30°C to 39°C. After A and C_{in} were allowed to stabilize at each new T_L level, which occurred by 10–15 min, isoprene emission was measured 3 times at 6 min intervals. Coefficients of variation in isoprene emission measured at each T_L level ranged from 1–4%. The temperature correction algorithm of Guenther et al. (1993) worked very well for these species, as adjusted rates measured at T_L ranging from 33°C to 39°C were within a few percent of the rates measured at 30°C. Response of isoprene emission from *P. macroloba* and *Socratea exorrhiza* (Mart.) H. Wendl. to changing PAR was examined by measuring emission as PAR was decreased from 2500 to 0 μmol m^{-2} s^{-1} in 500 μmol m^{-2} s^{-1} increments. Emissions from shade leaves were also measured at 250 and 100 μmol m^{-2} s^{-1}. After A and C_{in} were allowed to stabilize at each new PAR level, which occurred by 8–12 min, isoprene emission was measured 2 times at 6 min intervals. Fig. 1 shows that isoprene emission from *S. exorrhiza* shade leaves saturated at much lower (ca. 500 μmol m^{-2} s^{-1}) light levels (and at least 50% lower isoprene emission rates) than the sun leaves, consistent with findings from temperate (Harley et al., 1996, 1997) as well as tropical sites (Keller and Lerdau, 1999; Lerdau and Throop, 1999). The light correction factor of Guenther et al. (1993) underestimated sun leaf response to PAR above 1000 μmol m^{-2} s^{-1} by 2–10%. Standard rates were corrected for these biases. Somewhat larger increases in isoprene emission with increasing PAR above 1000 μmol m^{-2} s^{-1} were reported by in Panama by Keller and Lerdau (1999) and in Tennessee by Harley et al. (1997). The fact that we started with high (near ambient) PAR and gradually reduced it to zero may have affected this comparison, since light response curves developed in the past typically started at low values and increased to a maximum PAR.

Substantial quantities of isoprene were emitted by 10 of the 20 species surveyed (Table 1). All emission measurements were made on mature, fully expanded leaves with the exception of a single *Pourouma bicolor* leaf and possibly a leaf from the genus *Cissampelos* as well. Emission rates at standard conditions were similar to leaf measurements at temperate (Geron et al., 2001) and tropical (Lerdau and Keller, 1999; Keller and Lerdau, 1999; Lerdau and Throop, 1999) sites. Harley et al. (1999) found that only 2 of 29 species (and 2 of 13 genera) in the family Mimosaceae emitted isoprene. These species were *Acacia nigrescens* in Africa (Guenther et al., 1996) and *Inga spectabilis* in South America (Rasmussen, 1978). Here, however, we found that both *P. macroloba* and *Zygia longifolia* (Humb. & Bonpl.) Britton & Rose (previously: *Pithecellobium longifolium*) emitted substantial quantities of isoprene. Other species in these same genera have previously been reported to be non-isoprene emitters in Africa by Klinger et al. (1998) and Rasmussen (1978), respectively (Table 1). Continental divergence in isoprene emission potential has been observed within the spruce (*Picea*) and oak (*Quercus*) genera (Harley et al., 1999). Our results here support conclusions by Harley et al. (1999) that studies are needed to better understand phylogenetic patterns in isoprene emission characteristics within the families Mimosaceae and Leguminosae. The high leaf-level isoprene emission rates from *P. macroloba* and *Z. longifolia* reported here also represent a significant finding when one considers that the former species is the dominant canopy tree species in the La Selva old-growth forest, accounting for 32–35% of basal area (Clark and Clark, 2000). The 10 emitting species account for at least 35–50% of the total basal area of old-growth forest on the two main edaphic site types.

Three of four palms emitted significant amounts of isoprene. The high emission rate we report for *S. exorrhiza* (Palmae) sun and shade leaves is in good agreement with the isoprene emission capacity recently observed for this species by Lerdau and Throop (1999) in Panama. Foliage of the palms *Euterpe precatoria* Mart. var. longevaginata (Mart.) Andrew Hend. and *Welfia regia* H. Wendl. ex André could be reached only in fully shaded environments, and emission capacities were equivalent to those of *S. exorrhiza* shade leaves. However, emissions continued to increase over time as the enclosed foliage was exposed to high temperature and PAR conditions, which was consistent with observations elsewhere (Guenther et al., 1999). Since shade leaf emission rates were similar to those of *S. exorrhiza*, we suspect that sun leaves of *E. precatoria* and *W. regia* were similarly higher. The shade/sun leaf emission ratios observed here were similar to those observed in temperate species (Harley et al., 1997; Sharkey et al., 1996). Several leaves of a *Prestoea decurrens* (H. Wendl. ex Burret) H.E. Moore palm specimen exposed to full late-morning sun failed to emit detectable amounts of isoprene.

Two lower canopy leaves of the species *Virola sebifera* Aubl. (Myristicaceae) emitted at modest rates. Lerdau and Throop (1999) also found that this species emitted at rates lower than other species studies in Panama. Shaded foliage of *B. vulgaris* Schrad. ex J.C. Wendl. (Poaceae) also emitted at similar low rates (Table 1).

Emissions from a single leaf of a woody liana (vine) in the genus *Cissampelos* (family Menispermaceae) were measured in a deeply shaded environment. This leaf did not emit isoprene even when cuvette conditions were elevated to T_L of 35°C and PAR of $2500\,\mu\mathrm{mol\,m^{-2}\,s^{-1}}$. However, this may have been an expanding, immature leaf. Canopy foliage of *Cissampelos pareira* in Panama was found to emit at $28\,\mathrm{nmol\,m^{-2}\,s^{-1}}$ under standard conditions (Keller and Lerdau, 1999), and these authors found 7 of 21 vines screened to be isoprene emitters. Nineteen distinct vine genera were identified and sampled by Keller and Lerdau (1999). Four (*Cissampelos, Dioclea, Doliocarpus,* and *Stigmaphyllon*) of the six identified isoprene-emitting vine genera are also found at La Selva. Nine (*Arrabidaea, Cissus, Combretum, Gouania, Gurania, Mikania, Serjania, Trichostigma,* and *Vitis*) of the thirteen non-isoprene-emitting vine genera are also found at La Selva. Lianas can account for a substantial fraction of canopy foliage in tropical forests (cf. Avalos, 1999) and should be examined further in this biome.

*Miconia (*family Melastomataceae) is a common and widespread neotropical genus of shrubs and small trees. We found no isoprene emission from intact sun leaves of *Miconia impetiolaris* (Sw.) D. Don ex DC. A *Miconia* species in Panama was also found to be a non-emitter (Lerdau and Throop, 1999).

We found that isoprene was emitted from intact isoprene-emitting sun leaves (all emitting species combined) at 2–3.5% (on a carbon basis) of measured CO_2 assimilation (A) rates. Rates from intact shade leaves ranged between 1% and 2% of A, while leaves from cut branches or those elevated to extremely high temperature ($T_L > 38°C$) emitted high amounts of isoprene (8–25%) relative to A. However, most leaves emitting high percentages of fixed carbon as isoprene also featured declining A and C_{in} values due to stresses induced from high temperature and/or cutting. We also screened the leaf samples for monoterpene emissions by drawing 1.5 L of cuvette exhaust air through the adsorbent cartridges described above. GC/MS analysis was performed on these samples as described in Baker et al. (2001). Monoterpene emissions were non-detectable or very low ($<0.1\,\mu\mathrm{g\,C\,g^{-1}\,h^{-1}}$) from the species surveyed, and ambient concentrations and REA fluxes likewise were very low.

3.2. Canopy-scale BVOC emissions

The mean REA-measured isoprene flux was $2.2\,\mathrm{mg\,C\,m^{-2}\,h^{-1}}$ ($n = 10$), and these measurements were made under cloudy conditions (mean temperature = 27.6 C, PAR = $1100\,\mathrm{mol\,m^{-2}\,s^{-1}}$, sensible heat flux = $135\,\mathrm{W\,m^{-2}}$). Overall, the mean scaled model predictions ($2.8\,\mathrm{mg\ C\,m^{-2}\,h^{-1}}$) agreed reasonably well with the mean REA measured fluxes. These model estimates agreed well with two fluxes measured during warm, sunny periods, but substantially underestimated (by ca. factor of 2) the highest flux measured under similar conditions. Model predictions were somewhat higher than observed fluxes for cloudy, cooler periods (Fig. 2). More data are needed to better understand isoprene and oxygenated VOC exchange from forests in this region during conditions of partial cloudiness. Given the rapidly changing light environment under such conditions, eddy correlation techniques such as those applied by Guenther and Hills (1998) may be more suitable for determining trace gas exchange at such sites. The observed fluxes were within the lower end of the range of isoprene fluxes reported for similar environmental

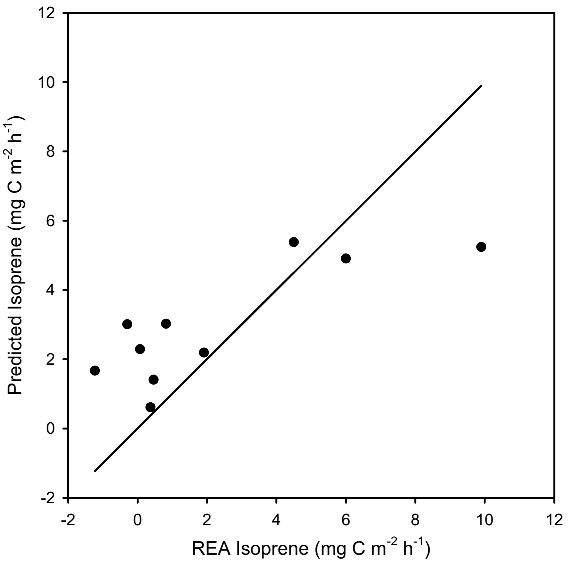

Fig. 2. REA derived flux estimates versus model estimates for corresponding time periods at the La Selva forest. The solid line denotes 1:1 agreement.

conditions at temperate forest sites in the eastern United States (e.g., Guenther et al., 2000; Geron et al., 1997). It should be noted that other variables affecting model versus flux comparisons such as LAI, foliar biomass density, leaf longevity, seasonal litterfall patterns, and fraction of liana coverage are not well characterized at this site or in tropical forests in general.

The mean REA fluxes for acetone (1.4 mg C m^{-2} h^{-1}, $n = 8$) and methanol (0.53 mg C m^{-2} h^{-1}, $n = 6$) were measured under slightly shadier and cooler conditions than the mean isoprene flux. We assumed these emissions increased exponentially with temperature as recommended for oxygenated VOC by Guenther et al. (1995). Temperature correction resulted in a methanol emission factor of 1 μg C g^{-1} h^{-1} which is ca. 67% higher than the average methanol emission factor (0.6 μg C g^{-1} h^{-1}) given by Guenther et al. (2000). The acetone emission factor derived from these measurements (2.5 μg C g^{-1} h^{-1}) was much greater than the average value (0.09 μg C g^{-1} h^{-1}) of Guenther et al. (2000). In addition to direct emissions from physiologically active foliage, possible sources of acetone and methanol fluxes include abiotic decay of dead plant material discussed by Warneke et al. (1999). This source could be especially significant at this site considering the high biomass turnover rates in wet tropical forests. However, even at the upper limit of methanol and acetone production rates discussed by Warneke et al. (1999), abiotic decay can explain only a relatively small fraction of the canopy-scale fluxes estimated from the REA measurements. Poschl et al. (2001) also reported high (over 8 ppb) acetone concentrations over the tropical forests of Surinam. These authors suggested that large emissions of acetone and/or acetone precursors, such as possibly 2-propanol, from living plants or decaying litter in the rainforest may be largely responsible for these high concentrations. Other recent studies have reported above-canopy measurements of acetone and methanol fluxes from a sub-alpine conifer forest (Baker et al., 2001) and a pine plantation (Schade and Goldstein, 2001) that exceed the fluxes observed at this tropical forest site. Midday fluxes of ca. 2.5 mg C m^{-2} h^{-1} of acetone and ca. 1 mg C m^{-2} h^{-1} of methanol were associated with the relatively cool conditions at the sub-alpine site (Baker et al., 2001) while even higher fluxes were reported for the pine plantation (Schade and Goldstein, 2001). Singh et al. (2001) report evidence of large global sources of oxygenated compounds from measurements in the troposphere over the Pacific Ocean. The REA fluxes of methanol and especially acetone reported here are evidence that these compounds may be emitted directly from tropical forests in quantities that are underestimated by current BVOC emission models. These emissions may at least partially account for the large unknown source discussed by Singh et al. (2001).

The global BVOC emission model described by Guenther et al. (1995) estimated isoprene fluxes in the Costa Rica region of ca. 0.4–0.5 g C m^{-2} month^{-1} for both July and January with predicted daytime average fluxes of ca. 1.5 mg C m^{-2} h^{-1}. This is ca. 30% lower than the estimate derived by extrapolating leaf-level measurements using the modeling approach described above. This difference is probably due to the larger fraction of isoprene-emitting biomass observed at La Selva compared to that assumed in the global model. However, these estimates were well within the uncertainties (which are a factor of 2–3) of the opposing models, and the REA measured fluxes appear to fall between the two model estimates.

Analysis of the 1998–2000 CARBONO meteorological data as well as the long-term monthly average meteorological data for La Selva (Sanford et al., 1994) shows that monthly isoprene emission estimates exhibited substantial variation, largely due to variability in cloud cover in this region. Seasonal patterns of isoprene emission based on the model described above and meteorological inputs for 1998–2000 are shown in Fig. 3. Seasonal peaks in the spring and fall are due to high PAR during the dryer months, while summer and winter emissions were suppressed due to frequent afternoon cloud cover and rainfall. The period of higher mean PAR values extended well into June, in 1999, accounting for the higher isoprene flux estimates in the summer of that year. Our total annual isoprene emission estimate ranges from 7.8 to 8.3 g C m^{-2} yr^{-1} for the 3 years 1998–2000. Mean daytime (7 AM–5 PM) above-canopy temperatures during 1999 (26.5°C) was about

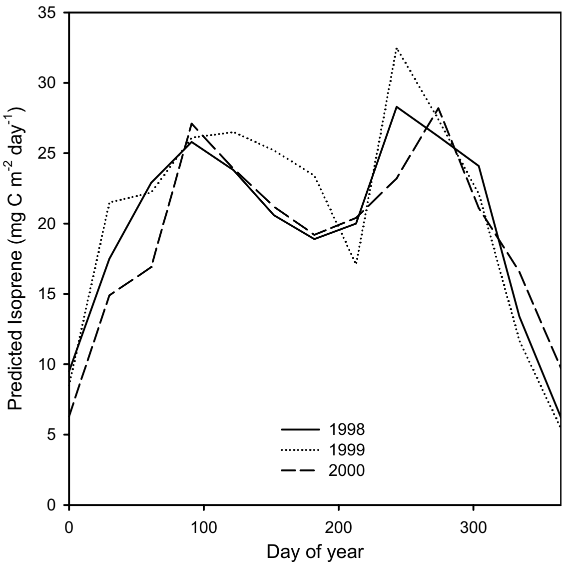

Fig. 3. Model estimates of monthly predicted isoprene fluxes from the La Selva forest using CARBONO meteorological inputs for the years 1998–2000.

equal to that of 2000 (26.4°C) but somewhat cooler than 1998 (27.2°C). However, daytime mean PAR values were 10–20% higher in 1999 (889 μmol $m^{-2}s^{-1}$) than in 1998 (738 μmol $m^{-2}s^{-1}$) and 2000 (816 μmol $m^{-2}s^{-1}$). This resulted in somewhat higher annual fluxes (ca. 8.3 g C $m^{-2}yr^{-1}$) in 1999 compared to the cloudier years of 1998 and 2000.

The Guenther et al. (1995) estimate of the total annual flux of all biogenic VOCs other than isoprene (e.g., methanol, acetone, and others) is ca. 10 g C m^{-2} and is similar to our estimate of the annual flux of acetone and methanol alone if the observed above-canopy fluxes are representative of year-round rates. The upper range of annual CO_2 flux estimates (H. Loescher and S. Oberbauer, unpublished data) from 1999 suggests that the La Selva forest was a sink for ca. 205 g of carbon as CO_2 $m^{-2}yr^{-1}$. This is in reasonable agreement with other recent estimates for moist tropical forests in the Amazon basin (Grace et al., 1995; Kuck et al., 2000) but is ca. a factor of 3 lower than the annual net flux found by Malhi et al. (1998). These initial measurements indicate that BVOC emissions might offset 10% or more of the net ecosystem exchange of CO_2 carbon at this site.

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