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Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana

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[1] Biogenic volatile organic compound (BVOC) emissions were measured in a mopane woodland near Maun, Botswana in January–February 2001 as part of SAFARI 2000. This landscape is comprised of more than 95% of one woody plant species, *Colophospermum mopane* (Caesalpinaceae). Mopane woodlands extend over a broad area of southern Africa. A leaf cuvette technique was used to determine the emission capacities of the major vegetation and the temperature and light dependence of the emissions. In addition, relaxed eddy accumulation (REA) measurements of BVOC fluxes were made on a flux tower, where net CO_2 emissions were also measured simultaneously. Large light-dependent emissions of terpenes (mostly α-pinene and d-limonene) were observed from the mopane woodland. The diurnal BVOC emissions were integrated and compared with the CO_2 flux. Monoterpene flux exceeded 3000 μg C m^{-2} h^{-1} during the daytime period, comparable to isoprene fluxes and much higher than terpene fluxes measured in most areas. The terpene flux constituted approximately 25% of the diurnal net carbon exchange (CO_2) during the experimental period. Other BVOC emissions may also contribute to the carbon exchange. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0330 Atmospheric Composition and Structure: Geochemical cycles; 1615 Global Change: Biogeochemical processes (4805)

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1. Introduction

[2] Emissions from the biosphere account for approximately 90% of volatile organic compounds (VOCs) entering the atmosphere [*Singh and Zimmerman*, 1992]. The emissions are largely from terrestrial vegetation and include isoprene, monoterpenes, other reactive organic compounds, such as 2-methyl-3-buten-2-ol and hexenal, and other less reactive VOCs, such as methanol and acetone. Among the major environmental controls over these emissions are light, temperature, water stress, and phenology. The emissions are also vegetation species specific and, therefore, landscape-scale emissions are highly variable [*Guenther et al.*, 1995].

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[3] VOCs are key in determining the oxidative capacity of the atmosphere, and, therefore, influence the atmospheric concentrations of methane and carbon monoxide. Methane (an important greenhouse gas) and carbon monoxide control ozone levels in much of the atmosphere. VOCs, together with carbon dioxide (largely exchanged between the atmosphere and biosphere) influence the atmospheric radiative balance, temperature and precipitation patterns [*Granier et al.*, 1998].

[4] Woodland landscapes cover about one half of all land surfaces and may contribute 75% of global isoprene and terpene emissions and 66% of the emissions of other biogenic VOCs (BVOCs), which total approximately 1150 $\times$ 10^{12} g carbon annually from all sources [*Guenther et al.*, 1995]. BVOC emissions are dominated by fluxes from tropical rain forests, tropical seasonal forests, drought-deciduous woodlands, and savanna woodlands. While these

tropical wooded areas comprise only 15% of global land surfaces, they are estimated to contribute half the flux from all sources. However, there have been few reports of measurements of BVOC fluxes from these landscapes.

[5] Previous model estimates for Africa of BVOC emissions [*Guenther et al.*, 1999] have used land cover characteristics with the IGBP-Discover Seasonal Land Cover Regions database. The vegetation communities in the database are condensed into several general categories of tropical forest, savannas, and degraded landscapes and croplands. Non-species-specific emission capacities were assigned to most categories, since no detailed species descriptions or accompanying emission data were available. Recently, *Otter et al.* [2002] have presented a more detailed landscape characterization for southern Africa, along with emission capacity data measured for a number of important species.

[6] As part of the SAFARI 2000 experiment, we investigated BVOC emissions from a mopane woodland near Maun, Botswana, in January–February 2001. Woody plant vegetation was surveyed to determine emissions of isoprene and terpenes and the parameters that control these emissions. In combination with a biomass survey, landscape emissions of BVOCs were estimated. Additionally, relaxed eddy accumulation (REA) flux measurements of BVOCs were made from a tower located within this landscape; CO_2 emission fluxes were measured simultaneously on the same tower. BVOC emission fluxes from the REA technique were compared with those modeled with data from the vegetation survey. In addition, the BVOC flux was compared with the net flux of CO_2 during the same period to determine its importance to net ecosystem carbon exchange.

2. Experiment Description

2.1. Site Characterization

[7] The Harry Oppenheimer Okavango Research Center (HOORC) site is located in a broad-leaved *Colophospermum mopane* savanna woodland 20 km east of Maun, Botswana (23°33′E, 19°54′S). The long-term climate of this site is semiarid with a mean rainfall of 464 mm. There is a distinct dry season during the winter months May–September. Peak rainfall normally occurs between December and March. Intermittent dry spells during the rainy season are common; the present experiment was conducted near the end of a 2 month dry spell.

[8] A micrometeorological tower (height 13.5 m) was erected in the middle of a homogeneous, tall mopane stand (maximum canopy height 8 m); patches of short (shrub) mopane (maximum canopy height 2 m) were situated about 300 m to the NE and to the west of the tower. The tower has served as a platform for CO_2 flux measurements for approximately 3 years (E. M. Veenendaal et al., Seasonal variation in energy fluxes and carbon uptake in a broad-leaved semi-arid savanna in southern Africa, submitted to *Global Change Biology*, 2002, hereinafter referred to as Veenendaal et al., submitted manuscript, 2002).

[9] *C. mopane* trees were often associated with *Ximenia americana*, a hemiparasitic shrub. The canopy cover of the mopane trees was 30–40%. Woody vegetation at the site is summarized in Table 1. The marginal understory consisted of grasses with a ground cover of less than 15%. Some herbs were also present. The soil slope in the area was <0.5%. The study area is under communal land use and has been primarily used for cattle grazing and firewood collection. During the period of this study, cattle were not present. *C. mopane* is a drought-deciduous tree with an almost total absence of leaves during the dry season. However, during the wet season (including the time of the study), maximum leaf area index for the stand varies from 0.9 and 1.3 (Mantlana et al., submitted to *Global Change Biology*, 2002, hereinafter referred to as Mantlana et al., submitted manuscript, 2002).

Table 1. Woody Vegetation at the Maun Tower Site [*Scholes et al.*, 2001]

Species	Leaf biomass[a] ($g\ m^{-2}$)	Emission capacity ($\mu g\ g^{-1}\ h^{-1}$)	
		Isoprene	Terpenes
Colophospermum mopane[b,c]	15.1	0	22
Acacia fleckii[d]	<0.3	0	0
Ximenia americana[b]	0.3	0	0
Acacia mellifera[c]	<0.3	6	0
Grewia flava[b]	<0.3	0	0
Acacia erioloba[b,c,e]	<0.3	0	8
Total all species on site	15.4		

[a]Mantlana et al. (submitted manuscript, 2002).
[b]This study.
[c]Both *C. mopane* and *A. erioloba* exhibited light-dependent terpene emissions.
[d]Inferred from measurements on several other *Acacia* spp. [*Harley et al.*, 2002].
[e]*Otter et al.* [2002].

2.2. Meteorology

[10] Wind speed, air temperature, water vapor pressure, and CO_2 concentration were measured with a closed-path eddy covariance system consisting of a Gill Sonic anemometer with an omnidirectional head (Solent R3, Gill Instruments, Lymington, UK) and a Licor 6262 closed path Infrared gas analyzer (LICOR Inc., Lincoln, NE, USA) installed at 12.6 m on the NE corner of the tower into the prevailing wind direction. The tower was also equipped with additional micrometeorological sensors that measured short and long wave radiation (CM3, Kipp & Zonen, Delft, NL), air temperature and humidity (HMP 45a Vaisala, Uppsala, Sweden) and photosynthetically active radiation (PAR) (LI-190 SA, LICOR Inc., Lincoln, NE, USA). These sensors were attached to 2 m long aluminum masts on the opposite side of the tower from the sonic anemometer. Rainfall, soil temperature and soil heat flux were measured to the east of the tower at a distance of approximately 20 m. Details of tower and CO_2 flux measurements are described elsewhere (Veenendaal et al., submitted manuscript, 2002).

2.3. Flux Platform: REA

[11] Air samples consisting of updrafts and downdrafts were collected separately into Teflon bags, using an REA system described by *Baker et al.* [1999] and shown in Figure 1. REA fluxes were estimated for 30 min periods, corresponding to sample collection times for statistically meaningful samples. Typically one 30 min sample pair was collected each hour. A three-dimensional sonic anemometer measured vertical wind speeds at 9 Hz at the end of a 2 m boom positioned at the top of the walk-up tower and

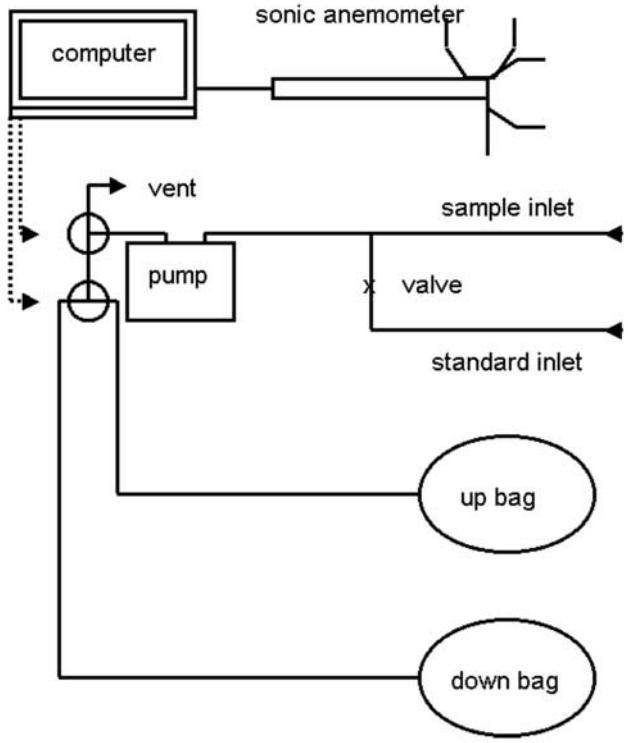

Figure 1. Schematic diagram of the REA system.

approximately 12 m above the ground and about 4 m above the top of the open canopy. The anemometer signal was sent to a laptop computer, which operated solenoid valves that sent samples to updraft and downdraft reservoirs. When vertical wind speeds were below a threshold value (±0.6 m s^{-1} σ_w, where σ_w is the standard deviation of the vertical wind speed, computed from the previous half hour period), sample air was not collected.

[12] Fluxes were calculated according to the relationship,

$$F = \beta \cdot \sigma_w \cdot (C_u - C_d), \quad (1)$$

where F is the flux of the trace gas of interest, β is a coefficient estimated by similarity with virtual temperature measured by the sonic anemometer [*Baker et al.*, 1999], σ_w is the standard deviation of the vertical wind during the time of sampling, and C_u and C_d represent the concentrations of the emitted gas determined from samples collected in the up and down Teflon sample reservoirs. After the sampling period, bags were removed and analyzed at the nearby HOORC laboratory within a few hours of collection.

2.4. Vegetation Leaf Enclosure Sampling

[13] BVOC emissions of *C. mopane* were studied from distinctly different soil profiles in two adjacent areas (300 m apart) in the tower footprint. These consisted of tall form of *C. mopane* (average tree height and crown diameter of 5.5 m), which was the dominant form represented, and a "Pan" form (averaging only 1.6 m in tree height and crown diameter), which grew where the soil profile is considerably shallower. The two stands were the same age. It was assumed that the macrometeorological conditions and rainfall at each were identical. An additional experiment on light dependence of VOC emissions from *C. mopane* was conducted on trees outside the nearby HOORC.

[14] Physiological measurements from leaves were made using a LI-6200 Portable Photosynthesis System (LICOR Inc., Lincoln, NE, USA), equipped with a 1 L leaf chamber, a thermocouple to monitor leaf temperature and a PAR sensor. Environmental parameters (PAR, temperature, relative humidity, and [CO_2]) were recorded, together with assimilation rate and stomatal conductance in the normal, closed-circuit configuration. BVOC emission samples were collected after photosynthesis and transpiration had reached a steady state. For BVOC emission sample collection, the chamber was then switched to an open-circuit configuration, where air was pumped into the chamber (through an activated charcoal filter to remove hydrocarbons). This permitted subsequent collection of BVOC emission samples and prevented depletion of CO_2 and static buildup of emitted VOC concentrations within the chamber. After a 30 min equilibration period, a sample of air exiting the chamber was collected into 2 or 5 L Teflon sample bags. Immediately following the VOC sample collection, the cuvette system was again converted to a closed-circuit path and a further record of physiological and environmental parameters was taken. The Teflon sample bags were sealed and stored in dark bags to prevent subsequent photochemical degradation of the samples prior to analysis, typically within 2 hours.

[15] For the light dependency experiment, VOC samples and physiological measurements were made on the same leaf throughout the day at the HOORC site. Light levels were artificially decreased from ambient levels by using cumulative filters to shade the chamber. The leaf was allowed to equilibrate for 30 min after each change of PAR, before emitted VOCs were sampled. Sampled leaf areas were recorded. Additional details are given by *James et al.* [2002].

2.5. Determination of VOC Concentrations

[16] Two gas chromatographs (GC), equipped with flame ionization detectors, were used in the HOORC laboratory for the determination of terpene concentrations (SRI Instruments Inc., Las Vegas, NV model 310; Shimadzu Inst., Kyoto, Japan, Model GC Mini2). The GCs used the same analytical chromatographic columns (MTX-624, 30 m × 0.25 mm internal diameter (i.d.), 1.4 μm film thickness, Restek Corp., Bellefonte, PA) and temperature program (initial temperature 40°C, 2 min hold, then 15°C min^{-1} to 150°C, then hold 5 min).

[17] The GCs were also instrumented with identical sample inlet systems. These allowed VOCs from ambient air samples to be preconcentrated for analysis and focused on the analytical column at the time of injection. Samples were first introduced to a first stage trap of Tenax TA (60–80 mesh, 2.2 mm i.d. × 100 mm length), cooled electrically to −10°C; this procedure trapped the VOCs of interest (isoprene, monoterpenes, calibration standards), but not nitrogen, oxygen, most of the water vapor, and other lighter weight VOCs. The concentrated sample was then heated and transferred (with helium flow of 10 cm^3 min^{-1} STP) to

the second stage cryofocusing trap (MTX-QPlot, Restek Corp., Bellefonte, PA, 0.53 mm i.d. × 500 mm long), cooled electrically to −30°C. Both the first and second stage traps were wrapped over their entire length with insulated nickel–chromium heating wire (0.25 mm diameter, 0.2Ω cm^{-1}), which allowed them to be heated for desorption of sample aliquots (to 150°C, slowly for first stage trap, but rapidly, in 10 seconds s, for the second stage, cryofocusing trap).

[18] The identification of isoprene and terpenes was made from the retention times compared to a mixture of isoprene and terpene analyzed repeatedly during the experiment. Quantification of concentrations was made with respect to a mixture of 2,2-dimethyl butane in nitrogen (Scott Specialty Gases, Plumsteadville, PA, 0.206 ppm), which had previously been intercompared with other standards [*Apel et al.*, 1994]. Sample volumes were typically 250–500 mL and were introduced directly from the Teflon bag samples collected from the REA or cuvette. Detection limits, for these sample volumes, were approximately 50 ppt, with the precision of the GC analysis computed from a propagation of errors of approximately 10% for α-pinene at 1000 ppt.

[19] Samples were also collected from the cuvette onto solid adsorbents and returned to the NCAR Boulder laboratory for analysis by GC with mass spectrometry (GC-MS). The procedures for these analyses and details of the solid absorbent cartridges have been described previously [*Greenberg et al.*, 1999a, 1999b]. Absorbent cartridges were kept at approximately −20°C during storage and 0°C during transport, but were filled at ambient temperatures. Sample volumes for cartridges were typically 500–1000 ml. The GC-MS analysis allowed for the positive identification of terpenes sampled. The GC-MS results were used for the GC-FID identifications. Detection limits for the GC-MS analyses were lower, approximately 1 ppt for isoprene and terpenes, and uncertainties in the GC-MS analysis were estimated from propagation of errors to be approximately 50 ppt for α-pinene at 1000 ppt.

2.6. Leaf-Level Emission Rate Calculation

[20] Emission rates (E) are expressed as μg (carbon) per g leaf dry weight per hour (μg (C) g^{-1} dw h^{-1}), and were calculated using the expression:

$$E = F \cdot C \cdot (1 - MFw_b)/\{(1 - Mfw_a) \cdot W\} \quad (2)$$

where F = airflow rate through cuvette, C = concentration of emitted compound in cuvette, Mfw_b = mole fraction of water in air entering cuvette, Mfw_a = mole fraction of water in air leaving cuvette, W = dry leaf biomass.

[21] The BVOC emission algorithm of *Guenther et al.* [1995], developed for isoprene, was used to model the terpene data. In this algorithm, emission rates are described by the equation:

$$E = E_S \cdot C_{PAR} \cdot C_T \quad (3)$$

where E is the emission rate (μg C g^{-1} dw h^{-1}) predicted at temperature T (K) and PAR (μmol m^{-2} s^{-1}), and E_S is the base emission capacity (the emission rate at standard conditions of 1000 μmol m^{-2} s^{-1} and 30°C).The two variables C_{PAR} and C_T are light and temperature coefficients derived from experimental measurements on eucalyptus, sweet gum, aspen and velvet bean. These factors are defined by:

$$C_{PAR} = (\alpha \cdot C_{PAR1} \cdot PAR) \cdot \left(1 + \alpha^2 \cdot PAR^2\right)^{-0.5} \quad (4)$$

$$CT = \left\{\exp\left[C_{T1}(T - T_s) \cdot (R \cdot T_s \cdot T)^{-1}\right]\right\} \cdot \left\{1 + \exp\left[C_{T2}(T - Tm) \cdot (R \cdot T_s \cdot T)^{-1}\right]\right\}^{-1} \quad (5)$$

where α = 0.0027 m^2 s μmol^{-1}, C_{PAR1} = 1.066 μmol m^{-2} s^{-1}, C_{T1} = 95 000 J mol^{-1}, C_{T2} = 230 000 J mol^{-1}, Tm = 312.5 K and R = 8.314 J K^{-1} mol^{-1} are empirically derived constants [*Guenther et al.*, 1995]. At standard conditions for PAR and temperature, 1000 μmol m^{-2} s^{-1} and 303 K, respectively, $(C_{PAR} \cdot C_T)_{std} = 1$.

2.7. Landscape Emission Model

[22] Emissions of biogenic VOCs were estimated using the Global Biogenic Emissions and Interactions System (GLOBEIS) [*Guenther et al.*, 1999]. GLOBEIS estimates foliar emissions as:

$$\text{Emission} = [\varepsilon]\left[D_p\ D_f\right]\left[\gamma_p\ \gamma_T\ \gamma_A\right][\rho], \quad (6)$$

where ε is a landscape average emission capacity, D_p is the annual peak foliar density, D_f is the fraction of vegetation of foliage present at a particular time of year, the emission activity factors γ_p, γ_T, and γ_A account for the influence of PAR, temperature, and leaf age, respectively, and ρ is an escape efficiency that represents the fraction of the BVOC emitted by the canopy that is released into the above-canopy atmosphere. Tower measurements of PAR and air temperature were used to calculate the parameters γ_p and γ_T.

3. Experimental Results

3.1. Meteorological Observations

[23] Average daily temperatures and PAR measured at approximately 5 m above the canopy on the tower are shown in Figure 2. Daily tower-top temperatures ranged, on average, from 28°C in the afternoon to 22°C at night. Temperature at the top of the canopy was likely higher (soil temperatures at times exceeded 60°C); canopy leaf temperature was not measured but were expected to be higher than air temperature above the canopy during mostly sunny midday hours. PAR consistently reached a maximum of 1800–2000 μmol m^{-2} s^{-1} and the sky was normally cloudless. Rain occurred only on 8 February; a short, intense downpour (1 mm) occurred at approximately 11 AM, with a more prolonged rainy period (12 mm) later in the evening, after the experiment ended. Relative humidity ranged from approximately 90% at night to 30% during the day.

3.2. Leaf-Level Emissions

[24] Leaf-level measurements were made for the major woody plant species in the tower footprint. The woody

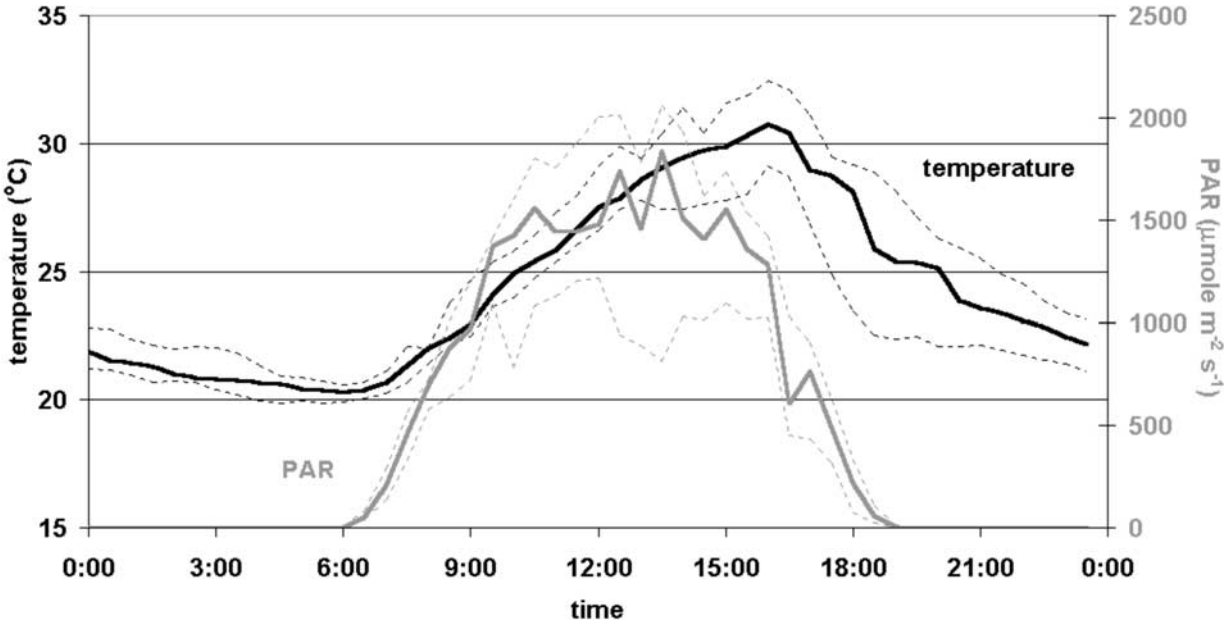

Figure 2. Tower measurements of temperature and PAR during the 1–8 February 2001 experimental period. Mean values (solid curve) and 1σ range (dotted curves).

plants consisted primarily of *C. mopane* (approximately 95% of biomass). Table 1 lists the species in the footprint of the tower, their percent coverage, and emission capacities. Since the mopane represented such a large fraction of the coverage, its measurements will be discussed in detail, although similar measurements were made of other species.

[25] The enclosure system used in the leaf-level emission measurements lacked temperature control; it was, therefore, not possible to generate curves independently describing the PAR and leaf temperature dependencies of α-pinene emission. The leaf-level emissions of α-pinene were parameterized using the algorithms in equations (4) and (5). The data for α-pinene emissions in Figure 3 was collected on a single leaf growing on the edge of the tree canopy exposed to nearly full Sun for much of the day, artificially shaded using screen mesh. Assuming that the cumulative LAI above the measured leaves was only 0.5 (i.e., nearly full-Sun leaf) light algorithm coefficients (equation (4)) were determined: $\alpha = 0.00142$; $C_L = 1.22$. Figure 3 displays the fit obtained for the data. The average α-pinene emission capacity observed in a survey of over 30 leaves from mopane trees in the study area was (42 ±1 4 μg C g^{-1} h^{-1}) [*James et al.*, 2002].

3.3. BVOC Ambient Concentrations and Emission Fluxes

[26] REA experiments were made from 1 to 8 February. Flux samples were collected between 6 AM (dawn) through late afternoon (6 PM). A total of 28 up/down pairs, representing 1/2 hour average sampling periods, were collected and analyzed at the HOORC laboratory in Maun. Monoterpenes were the major BVOC emission determined from the GC analysis; isoprene was observed at much lower concentrations, consistent with the observation of few isoprene emitting species in the landscape. The BVOC flux of terpenes was more than 60% α-pinene; limonene and β-pinene contributed almost all of the remainder. Ambient concentrations of terpenes were lowest early in the morning (<1 ppb α-pinene) and increased linearly (up to 2 ppb α-pinene) by midafternoon (Figure 4). Fluxes of α-pinene were also low in the early morning (~0.6 mg C m^{-2} h^{-1}) and increased until midafternoon (more than 3 mg C m^{-2} h^{-1}) (Figure 5).

4. Discussion

[27] The low concentrations of α-pinene and other terpenes at dawn (Figure 4) are most likely a combination of early daytime emissions and the residuals of the previous day's emissions, but not nighttime emissions. Nighttime emissions of terpenes into the shallow nocturnal boundary layer would result in higher surface concentrations than in daytime, when mixing through a deeper boundary layer and chemical losses would decrease ambient concentrations. This is consistent with the report by *Guenther et al.* [1996], suggesting a light-dependent terpene emission behavior for *C. mopane*.

[28] Leaf-level data in Figure 3 include parameterization of α-pinene emissions that are dependent on light, as well as temperature; although temperature generally increased through the day, fluctuations in monoterpene emission clearly parallel changes in PAR. The monoterpenes light algorithm coefficients derived here for *C. mopane* are remarkably similar to those derived for sunlit leaves of isoprene emitting woody plants [*Guenther et al.*, 1999]. The PAR and leaf temperature algorithm derived from isoprene emitting vegetation (equation (3)) has been used to model light-dependent monoterpenes emissions [*Ciccioli et al.*, 1997; *Bertin et al.*, 1997] and also light-dependent emissions of 2-methyl-3-buten-2-ol from certain species of pine [*Baker et al.*, 1999].

[29] Light-dependent terpene emissions have been reported for the group of oaks in subgenus Cerris [*Staudt*

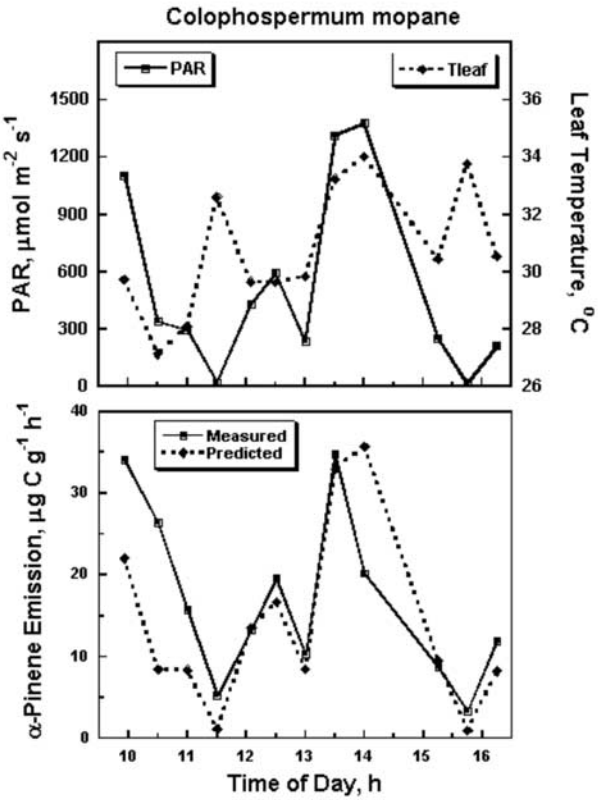

Figure 3. Comparison of leaf-level emission algorithm calculation. The top figure illustrates the behavior of emissions at various light and temperature conditions. The lower figure compares the emission rates observed with those computed from equations (4) and (5) using both temperature and light controls.

and Seufert, 1995; *Kesselmeier et al.*, 1996] and for a canopy tree of the neotropics, *Apeiba tibourbou* (Tiliaceae) [*Kesselmeier et al.*, 2000]. The rates of emission from *C. mopane* exceed by at least an order of magnitude those reported for undamaged leaves of species, such as conifers or eucalypts, which store monoterpenes in specialized structures, and are comparable to those of the light-dependent emissions from oaks in the Cerris subgenus.

[30] REA emission measurements were compared with those computed from equation (6), which was constrained by temperature and light conditions measured at the time of the REA sample. An average leaf area index of 1.3 for the mopane woodland was used to compute foliar density. Figure 5 bins the median and interquartile ranges of REA data and model results into three daytime periods over the 8 day experiment. This was considered a reasonable assumption, since meteorological conditions did not vary greatly during this period (Figure 2) in a way that would significantly alter modeled results. PAR was almost always above saturation levels (800 $\mu E\ m^{-2}\ s^{-1}$) after 9 AM and temperatures were also constrained within a narrow range. Measured emissions of α-pinene appear to be slightly lower in the later afternoon compared to modeled results. This may be attributed to uncertainty in the emission capacity used in the model calculation, which may be higher than the average emission capacity of the mopane landscape. The temperature dependence of monoterpene emissions from *C. mopane* was not measured explicitly in this experiment; instead, the temperature dependence of isoprene emissions was used [*Guenther et al.*, 1995]. Alternatively, emissions may actually be lower in the later afternoon, due to a factor not included in the model parameterization. High afternoon temperatures may result in higher leaf temperatures exceeding the temperature maximum for emissions.

[31] Fluxes of BVOC measured over evergreen forest and wooded savanna of central Africa near the beginning of the dry season using an aircraft REA technique were reported to be approximately 890 and 570 $\mu g\ m^{-2}\ h^{-1}$ for isoprene and 110 and 90 $\mu g\ m^{-2}\ h^{-1}$ for α-pinene for evergreen forest and wooded savannas, respectively [*Greenberg et al.*, 1999b]. Tower-based REA flux measurements of isoprene [*Serca et al.*, 2001] were made

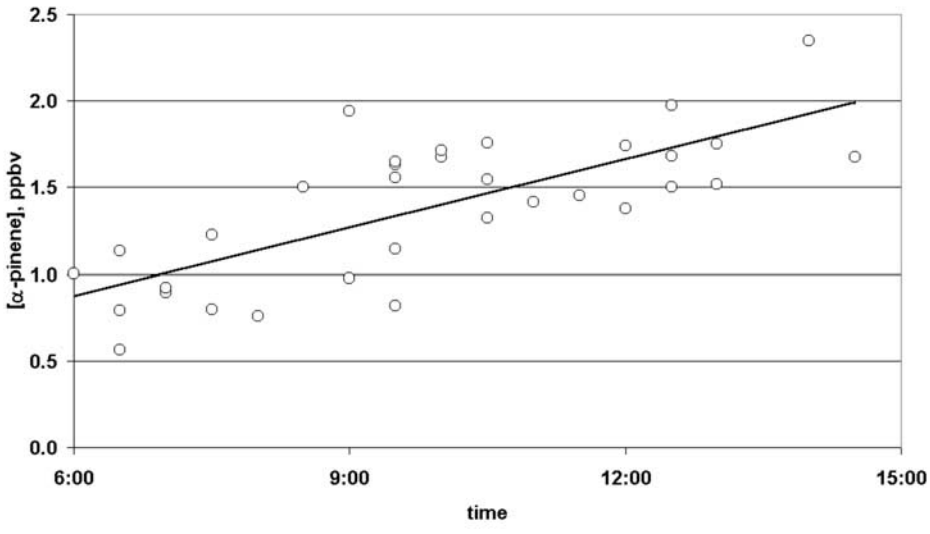

Figure 4. Ambient concentration of α-pinene measured at the tower, 1–8 February.

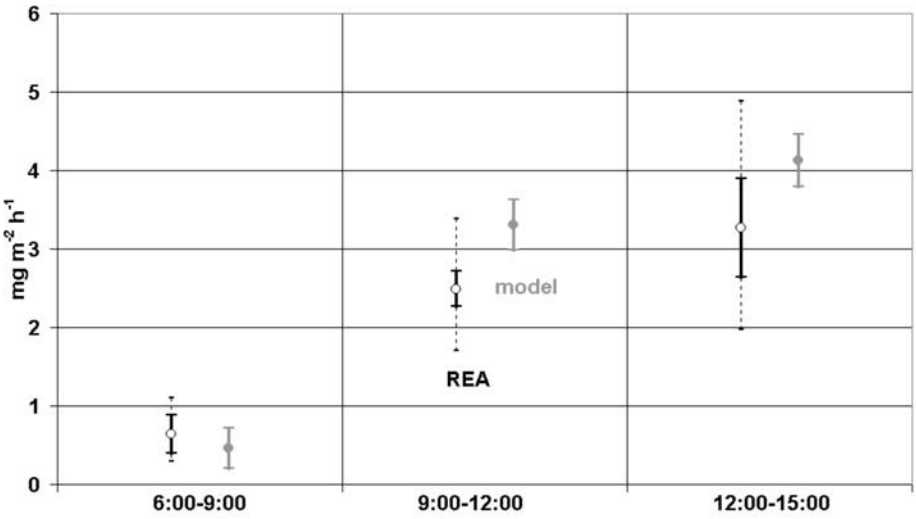

Figure 5. REA (measured) and GLOBEIS (modeled) results are compared for three daytime periods. Included are the median REA values (circles), central 50% of REA measurements in the time interval (solid vertical bars), and uncertainty of the median flux (dotted vertical bar, from propagation of errors).

approximately 100 km SE during the same experimental period and also during the wet season (1100 and 500 μg isoprene m^{-2} h^{-1} during the wet and dry seasons, respectively). However, the species distribution in the central African landscapes, as well as climatological factors, are quite different from the mopane woodland studied here. The only other previous estimates of terpene emissions from mopane woodlands have been made from model extrapolations based upon leaf-level emission measurements. *Guenther et al.* [1996] reported a terpene emission capacity of 3.0 mg C m^{-2} h^{-1} for different mopane woodland (using an emission capacity of 52 μg g^{-1} h^{-1}, an LAI of 0.8, and specific leaf mass of 80 g m^{-2}); *Otter et al.* [2002] report a terpene emission capacity of 2.4 mg C m^{-2} h^{-1} for the same landscape as this study (using an emission capacity of 16 μg g^{-1} h^{-1}, an LAI of 1.5, and specific leaf mass of 100 g m^{-2}). The landscape average emission capacity derived in this study (equation (6)) is 5.4 mg C m^{-2} h^{-1} (using a higher leaf-level emission capacity of 42 μg g^{-1} h^{-1}, an area averaged LAI of 1.3, and specific leaf mass of 100 g m^{-2}), almost a factor of 2 higher than previous estimates. An important difference in the emission estimates reported here is related to the emission capacity of *C. mopane*, which in the previous studies was averaged from a much smaller number of leaves than in this study.

[32] Emissions of terpenes over a day were integrated from equation (6) (Figure 5), assuming that emissions were 60% α-pinene. For the 8 day experiment, an average of 63 mg C m^{-2} d^{-1} was computed for terpene emissions. The emission of terpenes was compared with the CO_2 emissions measured simultaneously on the tower (Figure 6). The morning peak in CO_2 uptake, followed by continuous decline in the afternoon is consistent with stomatal closure induced by high leaf temperatures or water stress. Although decreasing stomatal conductance restricts CO_2 uptake, it does not affect isoprene emissions [*Fall and Monson*, 1992] and may not affect the light-dependent monoterpene emissions. The integrated CO_2 flux for the same experimental period averaged a net release of 255 mg C (CO_2) m^{-2} d^{-1}. The net release of CO_2 may be attributable to the drought conditions of the landscape (soil respiration and litter decomposition were not measured separately). During this time, however, terpene emissions contributed an additional 25% to the net ecosystem exchange of carbon (NEE) not measured in the CO_2 flux. In wetter periods, net CO_2 flux may be expected to be negative (storage of carbon in the system); terpene emissions during these times would reduce the NEE measured by CO_2 flux techniques. While the emissions of BVOCs may represent only a few percent of net primary productivity, they may, nonetheless, be very significant to NEE.

5. Conclusions

[33] Emissions of BVOCs were measured by a REA technique in a mopane woodland near Maun, Botswana in January–February 2001. *C. mopane* dominated the landscape (~95% of the standing biomass). Mopane emitted large quantities of monoterpenes (approximately 42 μg g^{-1} h^{-1} measured from a leaf cuvette and over 3 mg m^{-2} h^{-1} from tower flux measurements). The emissions consisted of α-pinene (62%) and limonene (33%); β-pinene represented most of the remainder. These emissions were light and temperature dependent. Ambient concentrations and emissions of terpenes increased during the day from sunrise until late in the afternoon. There was no apparent increase of terpene concentrations in the shallow nocturnal boundary layer that is typical of terpene emissions from temperate conifer forests.

[34] The measured emissions of terpenes are much higher than those observed from most terpene emitting species previously studied, which consisted almost exclusively of woody plant species from temperate areas. Because of the lack of direct species information and

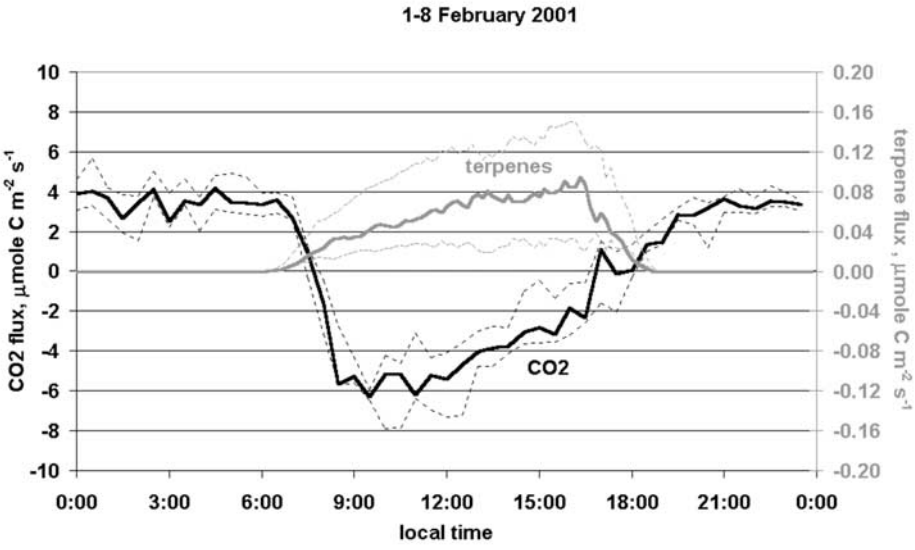

Figure 6. Comparison of REA fluxes of terpenes with the eddy covariance measurements of CO_2 for the experimental period. Included are the median (solid) and interquartile ranges (dotted) of CO_2 (data) and terpene (model from REA data) fluxes for the 1–8 February experimental period.

accurate landscape characterization, previous model estimates of landscape level emissions for southern Africa have assigned the same area emission factors for most wooded savanna areas. Emission capacities for savanna and for drought deciduous forests were assigned at 45 and 0.8 $\mu g\ g^{-1}\ h^{-1}$ and 45 and 1.2 $\mu g\ g^{-1}\ h^{-1}$ for isoprene and terpenes, respectively. The mopane woodland studied here is very different in species composition from other savannas in southern Africa. In a similar study simultaneously conducted in a *Combretum*/*Acacia* savanna near Skukuza, Republic of South Africa [*Harley et al.*, 2002], landscape emissions of isoprene (less than 0.4 $\mu g\ g^{-1}\ h^{-1}$) and terpenes (not detectable) were considerably lower and were consistent with the emissions modeled from a detailed biomass and species emission survey of the site. Consequently, significant revisions within the existing biogenic emission models for African savannas is required. This revision may be accomplished in a straightforward manner. A more detailed, species-specific landscape characterization has become available. Using this landscape characterization and leaf-level emissions capacities of over 100 southern African woody plant species, *Otter et al.* [2002] have revised landscape level emission estimates for many landscapes in southern Africa.

[35] The contribution of BVOC emissions to NEE of carbon is of additional interest. In the present study (restricted to an 8 day period), terpene emissions from mopane woodland contributed an additional 25% of carbon to the net CO_2 flux out of the ecosystem. This result is not expected throughout the year or necessarily a yearly average. Both BVOC and CO_2 emission fluxes may differ over longer timescales. The area studied was under significant drought conditions at the time (the effect of drought is not presently included in the model), even though this period is usually considered the rainy season (Veenendaal et al., submitted manuscript, 2002). However, during wetter periods, when net uptake of CO_2 may be expected, terpene emissions will continue to contribute a flux of carbon out of the ecosystem, which to some extent should offset the net CO_2 flux into the system.

[36] We have only measured the flux of 2 classes of BVOC fluxes here, isoprene and terpenes. Other BVOC fluxes certainly occur. Of particular interest is methanol, produced by all plants in the demethylation of pectins, during periods of rapid growth and decay. The flux of methanol may be as high as 40 $\mu g\ g^{-1}\ h^{-1}$ during certain growth stages [*Fall*, 1999]. In addition, BVOC emissions from vegetation should exhibit significant seasonality, which has not been studied for the mopane woodland.

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