Micrometeorological and leaf-level measurements of isoprene emissions from a southern African savanna

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Received 30 May 2002; revised 24 July 2002; accepted 1 August 2002; published 12 February 2003.

[1] In February 2001, as part of the Southern African Regional Science Initiative (SAFARI 2000), isoprene fluxes were measured for 8 days using the relaxed eddy accumulation technique from a 21-m tower in a Combretum-Acacia savanna in Kruger National Park, 13 km from Skukuza, RSA. Despite warm and sunny conditions, midday isoprene concentrations were low, averaging 0.39 nL/L. Fluxes of isoprene increased through the morning hours, with midday fluxes averaging 0.34 mg m⁻² h⁻¹ and a maximum measured flux of approximately 1.0 mg m⁻² h⁻¹. Consistent with these low fluxes, leaf enclosure measurements of woody species within the tower footprint determined that only one isoprene-emitting species, Acacia nigrescens, was present in significant numbers, comprising less than 10% of the woody biomass. Combining enclosure data with species composition and leaf area index data from the site, we estimated that the isoprene emission capacity of the vegetation within the vicinity of the tower was very low, approximately 0.47 mg m⁻² h⁻¹, and patchy. Under these circumstances, low and variable fluxes are expected. Additional leaf enclosure measurements, for a total of 121 species, were made at other locations, and approximately 35% of the species was found to emit significant amounts of isoprene. Important isoprene emitting plant families included Caesalpinaceae, Mimosaceae, Papilionaceae, Euphorbiaceae, Moraceae, and Myrtaceae. Twelve members of the important savanna genus Acacia were measured, of which five species, all belonging in Subgenus Aculeiferum, Section Aculeiferum, were found to emit significant amounts of isoprene. In contrast, the plant family, Combretaceae, dominant in many savanna ecosystems, was found to contain no species which emit isoprene. INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere-composition and chemistry; 1615 Global Change: Biogeochemical processes (4805)

Citation: Harley, P., L. Otter, A. Guenther, and J. Greenberg, Micrometeorological and leaf-level measurements of isoprene emissions from a southern African savanna, *J. Geophys. Res.*, *108*(D13), 8468, doi:10.1029/2002JD002592, 2003.

1. Introduction

[2] Emissions of reactive trace gases from the biosphere significantly influence the oxidative photochemistry of the lower troposphere [*Fehsenfeld et al.*, 1992; *Monson and Holland*, 2001]. In particular, emissions of biogenic volatile organic compounds (BVOC) affect the tropospheric distribution of ozone, hydroxyl radicals, reactive nitrogen species and carbon monoxide. Improved quantification of the biospheric source strength of these compounds is crucial to understanding tropospheric chemistry at regional and global scales. The global model of *Guenther et al.* [1995] provided a useful framework for modeling BVOC emissions by combining a vegetation classification scheme, aboveground biomass estimates, species level BVOC emission estimates, and

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algorithms describing physiological controls over emission. Similar efforts using higher resolution data and more detailed inventories have resulted in regional scale models for North America [*Guenther et al.*, 2000] and Europe [*Simpson et al.*, 1999], but efforts elsewhere have lagged behind. This and two companions papers [*Greenberg et al.*, 2003; *Otter et al.*, 2003] describing research on BVOC emmissions conducted as part of the Southern African Regional Science Initiative (SAFARI 2000) represent attempts to apply these methods to develop a regional scale BVOC emmission model for southern Africa.

[3] The SAFARI 2000 experiment was an international science initiative to investigate interactions between the land surface and the atmosphere in southern Africa [*Swap et al.*, 2002]. An important research goal was improved understanding of the relationship between biogenic, pyrogenic and anthropogenic emissions/deposition and the biogeochemical systems of southern Africa. Approximately 35% of South Africa is covered by savanna, broadly defined as a tropical mixed tree-grass community [*Scholes and Walker*, 1993]. Savannas generally occupy the vast region separating the equatorial forest from midlatitude deserts, and represent a

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major vegetation classification, comprising approx. 20% of the global land surface, and about 40% of the total land surface in Africa. Savanna regions in Africa are under increasing population pressure, and are undergoing rapid land use change. Improved understanding of the magnitude and potential importance of emissions of BVOC in southern Africa will require characterization of a number of different savanna ecosystems in terms of their species composition, biomass and BVOC emission characteristics. Data presented here represent an attempt to characterize BVOC emissions from one widespread savanna type in southern Africa.

[4] As part of SAFARI 2000, land-atmosphere fluxes of CO_2 , water vapor and energy were continuously monitored from flux towers in two distinct savanna vegetation types [Otter et al., 2002b], for which little information exists concerning the potential emissions of BVOC. In the southern hemisphere summer of 2001, these two towers were therefore selected as sites at which to measure emissions of BVOC and screen local vegetation species for their potential to emit these compounds. This manuscript treats isoprene emissions from a previously unstudied but widespread savanna type in the lowveld of South Africa, dominated by trees in the genera Combretum and Acacia. Fluxes of isoprene were measured above the savanna canopy using the Relaxed Eddy Accumulation (REA) technique. In addition, tree species in the footprint of the measurement tower were screened for their ability to emit isoprene. This information, combined with site-specific species composition and biomass data [Scholes et al., 2001] was used to make predictions of isoprene emissions from this landscape, which were then compared with tower flux measurements. We also took advantage of the wide variety of easily accessible plant specimens growing in a nearby nursery to screen an additional 95 species of South African plants for the ability to emit isoprene, providing species level isoprene emission information which can be used to further initial estimates of isoprene emissions from additional ecosystems of southern Africa [Otter et al., 2002a]. A companion paper [Greenberg et al., 2003] investigates the unusually high emissions of monoterpenes from a mopane (Colophospermum mopane) woodland near Maun, Botswana.

2. Methods

2.1. Site Description

[5] The field flux study was carried out in February 2001 at a savanna flux measurement site in Kruger National Park, Republic of South Africa, described previously [Scholes et al., 2001]. The site, located 13 km WSW of Skukuza, is an intensive study site of the SAFARI 2000 campaign, and meteorological parameters as well as exchanges of energy, CO₂ and H₂O, measured using eddy covariance, have been measured continuously since April 2000. The 21-m walk-up flux tower (25°01.184'S; 31°29.813'E; 365 m above sea level) is situated at the top of a gentle slope and straddles the ecotone between two distinct savanna types. The top of the slope is characterized by sandy soil and a broad-leaved savanna dominated by members of the Combretaceae. This Combretum dominated savanna is replaced by a fine-leafed Acacia savanna on clayey soils as one moves downslope. This is a characteristic and repeated catenal pattern throughout the undulating topography of the region [Chappell,

1992], and savannas of these types cover a wide area of the broad coastal plain, or "lowveld", at altitudes of about 300 m above sea level. As discussed by *Scholes et al.* [2001], the vegetation, with about 32% tree plus shrub cover, may be classified as a wooded grassland or open savanna. About two-thirds of the site, occupying the ridge top, is broad-leaved wooded grassland, dominated by *Combretum apiculatum* and *Sclerocarya birrea*, while the remaining third, occupying the midslope, is fine-leaved wooded grassland, dominated by *Acacia nilotica, A. nigrescens*, and *S. birrea*. Another 22 woody species were encountered within the tower footprint, totaling only about one eighth of the woody biomass. Tree density data, utilized below to estimate isoprene-emitting biomass within the tower footprint, is also presented by *Scholes et al.* [2001].

[6] The climate is semiarid subtropical, annual rainfall at Skukuza averaging 55 cm, with hot, wet summers and warm, dry winters. On average, January and February are the wettest months, each averaging about 9 cm, but January 2001 was abnormally dry (2.8 cm), and the grass component of the system was almost entirely senescent at the time of measurements. Long-term climate statistics may be found in the work of *Scholes et al.* [2001].

2.2. Tower Flux Measurements

[7] The relaxed eddy accumulation (REA) technique estimates a flux by rapidly partitioning air parcels in upward or downward moving eddies into separate reservoirs. Samples are collected over a half-hour time period to allow for a statistically significant sampling of eddies of various size, and for collection of air samples large enough for accurate analysis. In this study, air samples corresponding to updrafts and downdrafts were collected separately into 3-1 Teflon bags, using a valve switching system similar to that described by Baker et al. [1999]. Improvements incorporated into the present system include modified plumbing to allow sample reservoirs to be evacuated without removal from the system, and inclusion of two up and two down reservoirs. Thus, one pair of Teflon bags can be sampled and evacuated while the second pair is filling, allowing continuous sampling. A 3-dimensional sonic anemometer (ATI, Boulder, CO), positioned at the end of a 2 m boom near the top of a walk-up tower approximately 21 m above the ground, measured vertical wind speed and direction at 9 Hz. Air was drawn continuously (approx. 100 $\text{cm}^3 \text{min}^{-1}$) through an inlet located approx. 5 cm from the anemometer and fitted with an ozone trap consisting of filter paper impregnated with potassium iodide. Vertical wind data were sent from the anemometer to a laptop computer, which operated fast-switching solenoid valves that directed air to either the updraft or downdraft reservoir. A complete technical description of the REA system, including LabView programming used to control valves and collect data, is available from the corresponding author. If vertical wind speed was below a threshold value ($\pm 0.6 \sigma_w$ computed from the previous half hour period, where σ_w is the standard deviation of the vertical wind speed), sample air was not collected. Samples were collected over 30 minute periods, and calculated fluxes represent half-hour averages. Immediately following collection, a sample of air from each reservoir was collected onto 2-stage solid absorbent cartridges, consisting of 200 mg Tenax or 200 mg Carbotrap B,

followed by 200 mg Carbosieve (all from Supelco Inc., Bellefonte, PA), by pumping sample air for 5 min directly through the cartridge, using a controlled-flow pump (AirPro Surveyor, AFC Intl., DeMotte, IN) located downstream from the cartridge. The flow rate of air through the cartridges was nominally 300 cm³ min⁻¹, but varied slightly since each cartridge offered a different flow resistance. Actual flows were measured using a portable primary flow calibrator (BIOS Dry-Cal DC-Lite, AFC Intl.), and the total volume collected onto the cartridges varied from 1250 cm³ to 1680 cm³. Cartridges were stored under refrigeration at approximately 0°C and subsequently analyzed in the laboratory at the National Center for Atmospheric Research (Boulder, CO) using gas chromatography-mass spectroscopy (GC-MS; HP5890 with HP5972 detector, Hewlett-Packard) in selected ion mode. Details of cartridge construction, cartridge storage tests, sample inlet system and GC-MS analysis have been described previously [Greenberg et al., 1999]. The detection limit for the GC-MS analysis was approximately 1 ppty for isoprene, and uncertainty in the analysis, estimated from propagation of errors, was approximately 0.05 nL/L for a sample of 1 nL/L.

[8] Fluxes were calculated according to the relationship, $F = \beta * \sigma_w^* (C_u - C_d)$, where *F* is the flux of the trace gas of interest (µg m⁻² h⁻¹), β is a unitless coefficient estimated by similarity with virtual temperature as measured by the sonic anemometer [*Businger and Oncley*, 1990; *Bowling et al.*, 1998], σ_w is the standard deviation of the vertical wind speed (m h⁻¹) during the 30 min of sampling, and C_u and C_d represent the concentrations of the VOC of interest (µg m⁻³), determined from samples collected in the up and down Teflon sample reservoirs. Reliable wind and cartridge concentration data were obtained from a total of 15 half-hour measurement periods, from which isoprene fluxes were estimated.

2.3. Enclosure Sampling for Isoprene Emissions

[9] All woody species found at the Skukuza tower site were screened for the ability to produce and emit isoprene in significant amounts. In addition, over 100 species of plants growing either naturally or in pots at a tree nursery operated by volunteers of Kruger National Park in Skukuza were sampled. Intact leaves were carefully inserted into the standard 6-cm² leaf cuvette of an LI-6400 Portable Photosynthesis System (Li-Cor, Lincoln, NE) and physiological activity verified by measuring positive rates of net photosynthesis and transpiration. The LI-6400 red light LED light source was used to illuminate leaves (1000 µmol photons $m^{-2} s^{-1}$), and leaf temperature was controlled to as near 30°C as possible, although with the high air temperatures and high solar irradiances encountered, temperatures frequently exceeded 30°C. Using the sample pump of a Voyager Portable Gas Chromatograph (Photovac Int'l., Inc., Deer Park, NY), air exiting the cuvette was pulled through Teflon tubing into the sample loop and analyzed using the built-in photoionization detector. Chromatograms were stored digitally and hand-integrated. The Voyager was calibrated daily using a gas-phase isoprene standard (31.3 nL/L isoprene in air) verified against a 201 nL/L neohexane standard (Scott Specialty Gases, Plumsteadville, PA, USA). Measurement precision was assessed based on repeated measurements of the standard (n = 11), in which the standard deviation was 4% of the mean concentration. Repeated samples drawn from the empty cuvette consistently evidenced a small unidentified peak which would interfere with isoprene; this peak, if treated as isoprene, averaged 0.9 nL/L; this value was subtracted from isoprene concentrations for all leaf samples. Given this interference and a variable baseline, we assign a lower detection limit of 1 nL/L isoprene. Experimental leaves were harvested, oven-dried at 70°C and subsequently weighed. The dry mass of leaf tissue inside the cuvette during each measurement was calculated, and specific leaf mass (SLM, g m⁻²) determined for all leaves. Isoprene emission rates are expressed as μg Carbon g^{-1} dry mass h^{-1} . For the flow rates used in this experiment (540 cm³ min⁻¹) and a typical amount of leaf biomass (60 mg), the isoprene emission calculated at the detection limit (1 nL/L isoprene) gives an emission rate of $1.2 \ \mu g \ C \ g^{-1} \ h^{-1}$.

[10] In a few cases, where leaf-level measurements were ambiguous (i.e., a very small isoprene peak was evident), branches with several leaves were enclosed in a static enclosure consisting of a 3-1 Teflon bag. After approx. 10 min in the sun, air from the bag was sampled for isoprene concentration.

3. Results

3.1. Meteorology

[11] In general, weather during the period of tower flux measurements was sunny, warm to hot, and dry. Mean diurnal fluctuations in air temperature and incoming shortwave radiation (W m⁻²) for the 7 days of data collection are depicted in Figure 1. Daytime temperature maximum averaged 28.5°C over the experimental period, but exceeded 35°C on two days. Midday relative humidity values varied between 30 and 70%. Nighttime temperatures were mild, falling below 20°C on only one night. Solar irradiance was variable, but incoming shortwave radiation always exceeded 475 W m⁻² during midday and exceeded 1000 W m⁻² on four of the measurement days. Rain totaling 37 mm fell during two nights.

3.2. Tower Flux Measurements

[12] A total of 15 up-down paired samples were considered valid samples for isoprene flux estimation. All measured isoprene concentrations, from both up and down reservoirs, and including data from periods when fluxes were not calculated, are plotted in Figure 2a as a function of time of day. Concentrations were generally low, the maximum concentration measured being 0.86 nL/L. The midday (0900-1300 UT) mean concentration was 0.39 nL/L (s.e. = 0.03; n = 52) and the mean difference in isoprene concentration between up and down bags was only 0.14 nL/L (s.e. = 0.04). Given an estimated uncertainty level associated with the GC-MS analysis of 0.05 nL/L in each reservoir, it is clear that that the REA technique is operating near the limits of its usefulness in this low isoprene environment. All isoprene flux estimates obtained from the REA technique are plotted as a function of time of day in Figure 2c. Early morning fluxes were very low, and though variable, fluxes generally increased until midday, reaching a maximum of 1.0 mg m⁻² h⁻¹. The average midday (0900-1300 UT) flux, based on 12 samples, was $0.34 \text{ mg m}^{-2} \text{ h}^{-1}$ (s.e. = 0.11). The magnitude of the



Figure 1. Average weather conditions at the Skukuza tower site for the duration of the tower flux study. Points are hourly means of incoming short wave radiation (W m⁻²; top panel) and air temperature (°C; bottom panel) for period between 1 February and 8 February 2001. Lines represent one standard error.

isoprene fluxes did not appear to be correlated with wind direction (Figure 2d).

3.3. Screening for Isoprene Emission With Enclosure Measurements

[13] Scholes et al. [2000] list 19 species (Table 1) that dominate the woody biomass within a circle 800 m in radius, centered on the flux tower. Leaves from all of these species were sampled in this study either at the tower site or elsewhere, and their measured emissions appear in Table 2. In addition to these 19 species, we measured leaves from an additional 8 species of trees and shrubs (Table 1) that, although present at the site, constitute less than 1% of the biomass. Of the 7 species which dominate the landscape, only Acacia nigrescens emits significant amounts of isoprene. Although 5 of the remaining 20 species appear to be isoprene emitters, their contribution to the landscape scale isoprene flux is expected to be very small, due to their minor presence in the tower footprint.

[14] In addition to those woody species growing at the flux tower site, 95 additional species were screened, repre-

senting 41 plant families, growing either at the Skukuza researchers' lodging compound or at the Skukuza tree nursery (Table 2).

[15] Given a detection limit of 1 nL/L isoprene and typical leaf biomass and flow rate, the lowest isoprene emission rate which can be measured with confidence is $1.2 \ \mu g \ C \ g^{-1} \ h^{-1}$ and all measurements below that value are assigned to the category of nonisoprene emitters. Using this criterion, 52 of the 123 species measured may be classified as emitters, and 18 of the 41 plant families contained at least one emitting species. If we adopt a slightly less conservative criterion of 3 $\mu g C g^{-1} h^{-1}$, only 43 species are classified as emitters, from 15 different families. Since results for those 9 species with emission capacities between 1.2 and 3 μ g C g⁻¹ h⁻¹ are somewhat ambiguous, they will be examined on a case by case basis below, and assigned to one category or the other based on additional information, where available. It is clear from Table 2 however, that several families of flowering plants commonly occurring in southern Africa contain a significant percentage of isoprene emitting species, including the three legume families, Caesalpinaceae, Mimosaceae and Papilionaceae, as well as Burseraceae, Euphorbiaceae, Flacourtiaceae, Moraceae and Myrtaceae.

4. Discussion

[16] Results from the tower REA flux measurements and the screening of tree species at the tower site are consistent, both indicating that this savanna landscape represents a relatively minor source of isoprene to the atmosphere.

4.1. Measured and Estimated Isoprene Fluxes

[17] Given the inherent sources of error associated with the REA technique [Bowling et al., 1998] and the small differences in measured isoprene concentrations in up versus down reservoirs relative to the uncertainty of the analytical technique, each individual REA flux should be regarded as highly uncertain. Taken as a whole, however, the data in Figure 2 indicate that the vegetation within the flux footprint is a small but significant source of isoprene. Given the lack of a significant nearby homogeneous source of isoprene, considerable variability in both isoprene concentration and flux is not surprising. Given an extremely patchy and heterogeneous source region (see below), the concentration of isoprene in air masses reaching the REA inlet will vary continuously depending on wind speed and direction, as will the measured flux.

[18] Based on the measured emissions of species within the footprint of the tower, and the published species composition and biomass data of *Scholes et al.* [2001], we derived a landscape-scale isoprene emission capacity (μ g C m⁻² ground area h⁻¹), as follows (Table 1). *Scholes et al.* [2001] estimated tree basal area surrounding the tower site to a distance of 600 m (Table 1). Based on these data, and assuming that tree cover is proportional to tree basal area, the percent cover of each species was calculated. This value multiplied by the woody plant leaf area index (LAI, m² of leaf area per m² of ground area), averaged over the site, provides an estimate of the total leaf area of each species per unit ground area (not shown), which when multiplied by the specific leaf mass of leaves of each species (SLM, g m⁻²) yields foliar density (g of leaf per m² of ground). Foliar



Figure 2. Summary of isoprene concentrations and fluxes measured at the Skukuza tower site between 1 February and 8 February 2001. Top panels represent isoprene concentrations (nL/L) measured at 19 m as a function of time of day (A) and wind direction (B). Bottom panels depict measured isoprene fluxes (mg C $m^{-2} h^{-1}$) as a function of time of day (C) and wind direction (D).

	Basal A	Area	LAI,	SLM, g m ⁻²	Foliar Density, g m ⁻²	Leaf-Level Emission Capacity,	Area-Averaged Emission Capacity,
Species	$m^2 ha^{-1}$	%	$m^{2} m^{-2}$	(Leaf)	(Ground)	$\mu g C g^{-1} h^{-1}$	μ g C m ⁻² h ⁻¹
Combretum apiculatum	1.55	29.6	0.67	117	23.2	0.2	4.6
Sclerocarya birrea	1.73	33.1		154	34.1	0.2	6.8
Acacia nigrescens	0.69	13.2		82	7.2	50	360
Acacia nilotica	0.22	4.2		145	4.1	0.2	0.8
Ziziphus mucronata	0.31	5.9		86	3.4	0.2	0.7
Grewia bicolor	0.14	2.7		104	1.9	0.2	0.4
Lannea schweinfurthii	0.12	2.3		99	1.5	0.5	0.8
Acacia tortilis	0.02	0.4		100	0.3	0.2	0.1
Balanites maughamii	0.06	1.1		92	0.7	1.7	1.2
Peltophorum africanum	0.02	0.4		100	0.3	0.2	0.1
Spirostachys africana	0.08	1.5		101	1.0	68	68
Dichrostachys cinerea	0.12	2.3		120	1.8	0.2	0.4
Euclea natalensis	0.02	0.4		202	0.5	0.2	0.1
Diospyros mespiliformis	0.02	0.4		82	0.2	0.2	0.1
Grewia hexamita	0.02	0.4		106	0.3	0.2	0.1
Schotia brachypetala	0.04	0.8		126	0.6	0.2	0.1
Lonchocarpus capassa	0.06	1.1		148	1.1	24	26
Terminalia sericea	0.01	0.2		159	0.2	0.3	0.1
Carissa edulis	0	0.0		57	0.0	0.2	0.0
	Species Below	Not Listed	in Scholes et	al. [2001] but	Measured at the Tow	ver Site in This Study	
Rhus lancea						53	
Combretum imberbe						0.2	
Combretum hereroense						0.4	
Combretum zeyheri						0.2	
Bolusanthus speciosus						40	
Dalbergia melanoxylon						39	
Pterocarpus rotundifolius						57	
Grewia flavescens						0.2	
Total	5.23						471

Table 1. Data Used to Estimate Area-Averaged Emission Rates for Isoprene^a

Basal area data and site-specific leaf area index (LAI) are from Scholes et al. [2001]. Specific Leaf Mass (SLM) and isoprene emission capacities are estimated in this paper (species designated as "below detection limit" in Table 2 are assigned a value of $0.2 \ \mu g$ C g⁻¹ h⁻¹). Area-averaged emission capacity (by species) is determined as [% of total basal area/100] × [LAI] × [SLM] × [Emission Capacity]. ^aEmission rates for isoprene are expressed as $\mu g \ C \ m^{-2} \ h^{-1}$.

		Photosynthesis,		Isoprene,	Isoprene,			
		μmol		$\mu g C g^{-1} h^{-1}$	nL/L			Isoprene
Plant Family	Plant Species	$m^{-2} s^{-1}$	$T_{\text{leaf}}, ^{\circ}\text{C}$	(LI-6400)	(Branch)	Site	Miscellaneous	Emitter
Acanthaceae	Mackaya bella	9.8	30.1	BDL		nursery	pot	No
Anacardiaceae	Lannea schweinfurthii	1.3	27.1	BDL		tower	-	No
	Rhus gueinzii	9.9	30.2	40.5		nursery	pot	Yes
	Rhus lancea	10.3	30.7	23.9		nursery	pot	Yes
	Rhus lancea	4.9	31.7	72.7		tower		Yes
	Rhus pyroides	0.2	20.0	BDI		nursery	pot	No
Annonacease	Scierocarya birrea Haralobus monopatalus	0.5	30.0	BDL		lower	not	No
Aniaceae	Steganotaenia araliacea	4.5	50.1	BDL		nursery	pot	No
Apocvnaceae	Adenium multiflorum			BDL		nurserv	pot	No
r J	Carissa edulis	9.0	32.5	BDL		nursery	pot	No
	Diplorhynchus condylocarpon	10.1	29.4	72.7		nursery	pot	Yes
	Tabernaemontana elegans	13.4	28.7	BDL		nursery	pot	No
Araliaceae	Cussonia zuluensis	6.4	30.1	BDL		camp		No
Arecaceae	Borassus aethiopium	7.0	30.0	18.5		nursery		Yes
	Phoenix reclinata	2.7	30.1	1.9		camp		?Yes
Asteraceae	Vernonia colorata	0.0	21.4	BDL		nursery	pot	No
Balanitaceae	Balanites maughamii	9.8	31.4	1.7		nursery	pot	?No
Bignoniaceae	Kigelia africana	3.0	40.3	BDL		camp		NO No
	Kigella africana Markhamia zanzibarica	14.2	30.0 20.6	BDL		nursery	pot	No
Bombacaceae	Adansonia digitata	0.0 16 3	29.0	BDL		nursery	pot	No
Boraginaceae	Cordia ovalis	83	30.1	BDL		camn	por	No
Boluginaceae	Ehretia obtusifolia	9.1	30.0	2.8		nurserv	pot	2No
Burseraceae	Commiphora mollis	0.3	30.1	40.6		nurserv	pot	Yes
	Commiphora schimperi	16.8	30.1	18.6		nursery	pot	Yes
	Commiphora pyracanthoides	15.6	29.4	51.9		nursery	pot	Yes
Caesalpinaceae	Afzelia quanzensis	14.3	29.9	BDL		nursery	pot	No
-	Bauhinia galpinii	11.6	30.8	56.4		camp	-	Yes
	Bauhinia galpinii			87.9		nursery	pot	Yes
	Bauhinia thonningii	14.6	29.5	BDL		nursery	pot	No
	Bauhinia tomentosa	14.5	30.3	148.6		nursery	pot	Yes
	Cassia abbreviata	6.5	34.4	BDL		camp		No
	Colophospermum mopane	9.3	34.6	BDL	0.5	nursery	pot	NO
	Colophospermum mopane				8.5	nursery	branch	N0 Vac
	Guidourtia conjugata Sebetia brachumetala	11.2	20 7	PDI	65	tower	branch	Yes
	Schotia capitata	12.1	20.7	1.2		camp		2No
Canellaceae	Warburgia salutaris	12.1	50.1	BDL		nurserv	not	No
Celastraceae	Cassine aethiopica	7.2	30.1	BDL		nurserv	pot	No
	Catha edulis	6.3	30.1	BDL		nurserv	pot	No
	Maytenus undata			BDL		nursery	pot	No
Combretaceae	Combretum apiculatum	6.7	30.5	BDL		tower	1	No
	Combretum hereroense	9.1	30.0	BDL		tower		No
	Combretum imberbe	0.7	33.0	BDL		tower		No
	Combretum zeyheri	6.9	32.3	BDL		tower		No
	Terminalia prunoides	2.5	39.6	BDL		camp		No
	Terminalia prunoides	15.0	29.1	BDL		nursery	pot	No
Ehamaaaaa	Terminalia sericea	13.0	30.0	BDL		tower	te of	N0 No
Ebenaceae	Evolog evigna	15.5	20.0	BDL		nursery	pot	No
	Euclea natalensis	17.3	30.8	BDL		tower	por	No
Funhorbiaceae	Androstachys johnsonii	5.8	30.4	29.6		nursery	not	Ves
Euphorotaceae	Antidesma venosum	5.0	50.7	BDL		nurserv	pot	No
	Bridelia micrantha	11.7	30.1	BDL		nursery	pot	No
	Croton megalobotrys	14.4	28.9	BDL		nursery	pot	No
	Pseudolachnostylis maprouneifolia	11.0	29.0	73.9		nursery	pot	Yes
	Securinega virosa	11.6	28.0	51.4		nursery	pot	Yes
	Spirostachys africana	11.6	29.2	67.5		nursery	pot	Yes
Flacourtiaceae	Dovyalis caffra	10.3	33.2	101.3		nursery	pot	Yes
	Homalium dentatum	8.8	31.1	83.3		nursery	pot	Yes
	Oncoba spinosa	16.8	29.4	60.0		nursery	pot	Yes
Lecythidaceae	Barringtonia racemosa	3.2	30.1	BDL		nursery	pot	No
Loganiaceae	Strychnos spinosa	2.6	34.9	BDL		nursery	pot	No
Lythraceae	Gaipinia transvaalica	9.1	50.1 20.1	BDL		nursery	pot	INO No
wienaceae	Exedergia capensis Trichilia amotica	0.5	32.6	BDL		camp	por	INO No
Mimosaceae	Acacia borlege	3.7 10 1	30.1	BDL		nursers	not	No
minosaceae	Acacia horleae	17.1	50.1	DDL	54	nuiserv	branch	No
	Acacia hurkei	8.9	29.8	22.6	0. r	nurserv	pot	Yes
	Acacia erioloba			- 64	4.5	nursery	branch	No

Table 2. Results of Enclosure Screening for the Presence of Significant Isoprene Emissions

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Table 2. (continued)

		Photosynthesis,		Isoprene, $C a^{-1} b^{-1}$	Isoprene,			Iconrono
Plant Family	Plant Species	$m^{-2} s^{-1}$	T_{leaf} °C	μg C g n (LI-6400)	(Branch)	Site	Miscellaneous	Emitter
	Acacia galpinii	17.6	28.4	22.1		nursery	pot	Yes
	Acacia galpinii	27.6	30.2	12.1		nursery	pot	Yes
	Acacia nigrescens	13.7	30.1	4.0		nursery	pot	Yes
	Acacia nigrescens			20.0	260	nursery	pot	Yes
	Acacia nilotica	11.5	30.1	BDI	200	tower	Dialicii	No
	Acacia nilotica	2.9	36.4	BDL		camp		No
	Acacia nilotica	2.9	50.1	DDL	5.4	nurserv	branch	No
	Acacia polyacantha	19.6	30.1	7.2		nursery	pot	Yes
	Acacia polyacantha	20.0	30.2	8.0		nursery	pot	Yes
	Acacia polyacantha				>1500	nursery	branch	Yes
	Acacia robusta			1.2		nursery	pot	?No
	Acacia robusta	0.7	25.5	50.1	1.8	nursery	branch	No
	Acacia senegal	8.7	35.7	50.1 PDI		nursery	pot	Yes
	Acacia tortilis	0.5	27.7	BDL		tower	pot	No
	Acacia tortilis	12.0	20.0	DDL	4.6	nurserv	branch	No
	Acacia xanthoploea	18.8	30.2	BDL	4.0	nurserv	pot	No
	Albizia adianthifolia	8.5	33.1	4.9		nurserv	pot	Yes
	Albizia amara	6.8	31.3	BDL		nursery	pot	No
	Albizia forbesii			12.5		nursery	pot	Yes
	Albizia harveyi	7.9	30.1	1.2		nursery	pot	?No
	Albizia harveyi				5.9	nursery	branch	No
	Albizia versicolor	18.9	28.9	105.0		nursery	pot	Yes
	Dichrostachys cinerea	8.3	30.2	BDL		tower		No
	Elephantorrhiza burkei	13.8	26.6	BDL		nursery	pot	No
	Faidherbia albida	0.0	22.0	BDL		nursery	pot	No
Манадаад	<i>Xylia torreana</i>	8.0	32.8	BDL 74.4		nursery	pot	N0 Vac
Moraceae	Ficus ingens	27	20.0	/4.4		nursery	pot	Yes
	Ficus stuhlmannii	0.4	37.3	31.9		nurserv	not	Ves
	Ficus sycamorus	93	30.1	23.0		camp	por	Yes
Mvrtaceae	Heteropyxis natalensis	710	2011	BDL		nurserv	pot	No
5	Syzygium cordatum	8.7	28.4	7.8		nursery	pot	Yes
	Syzygium sp.	10.5	30.0	16.4		nursery	pot	Yes
Ochnaceae	Ochna natalita	7.9	31.2	69.3		nursery	pot	Yes
Papilionaceae	Baphia massaiensis	4.0	29.8	113.9		nursery	pot	Yes
	Bolusanthus speciosus	8.3	27.9	30.6		tower		Yes
	Bolusanthus speciosus	12.1	31.4	48.7		nursery	pot	Yes
	Calpurnia aurea	4.9	29.9	2.8		nursery	pot	?Yes
	Corayla africana	3.0	30.0	80.4		tower	pot	Yes
	Dalbergia melanoxylon	5.4	27.0	38.0 40.1		nursery	not	Ves
	Frythring hysistemon	7.2	35.1	1.6		camp	por	2No
	Lonchocarpus capassa	17.2	30.0	22.6		tower		Yes
	Lonchocarpus capassa	10.5	29.9	24.1		nursery	pot	Yes
	Mundulea sericea	17.2	30.2	98.3		nursery	pot	Yes
	Mundulea sericea	6.5	36.5	179.8		nursery	pot	Yes
	Ormocarpum trichocarpum	13.6	29.2	10.1		nursery	pot	Yes
	Ormocarpum trichocarpum				834	nursery	branch	Yes
	Peltophorum africanum		20.0	BDL		camp		No
	Pterocarpus rotundifolius	14.1	30.8	56.7		tower		Yes
	Vigna sp. Vanthoomia zambosiana	0.3	33.3 20.1	BDL 57.6		tower	not	INO Vac
Doncene	Auninocercis zambesiaca Phraomitos australis	14.0	28.0	3/.0		nursery	pot	Vec
Rhamnaceae	Rerchemia zevheri	10.8	32.3	70.9		camp		Ves
Tellallinaceae	Ziziphus mucronata	5.2	34.9	BDL		camp		No
	Ziziphus rivularis	10.1	29.5	BDL		nurserv	pot	No
Rubiaceae	Breonadia salicina	14.1	30.4	BDL		nursery	pot	No
	Pachystigma macrocalyx	13.8	27.2	BDL		nursery	pot	No
Salvadoraceae	Salvadora angustifolia	2.5	30.2	5.5		nursery	pot	Yes
	Salvadora persica	12.3	33.6	52.8		nursery	pot	Yes
Sapindaceae	Pappea capensis	6.5	30.1	BDL		nursery	pot	No
Sapotaceae	Manilkara mochisia		a a a	BDL		nursery	pot	No
Simaroubaceae	Kirkia acuminata	3.6	30.0	BDL		nursery	pot	No
Sterculiaceae	Dombeya rotundifolia	12.3	32.7	BDL		camp		No
Tiliagass	Sterculia murex	8.9	28.8	BDL		nursery	cut	INO NI-
maceae	Grewia Dicolor Grewia devoceore	12.2	54.0 41.1	BDL		tower		INO No
	Grewia flavescens	1./	+1.1 20.6	RDI		nursery	not	No
	Grewia hexamita	6.7	34.0	BDL		tower	por	No
	Grewia hexamita	2.3	39.9	BDL		camp		No
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Plant Family	Plant Species	Photosynthesis, $\mu mol m^{-2} s^{-1}$	T_{leaf} °C	Isoprene, μ g C g ⁻¹ h ⁻¹ (LI-6400)	Isoprene, nL/L (Branch)	Site	Miscellaneous	Isoprene Emitter
Ulmaceae	Celtis africanus	14.4	30.1	1.2		nursery	pot	?No
	Trema orientalis	6.9	38.1	BDL		camp	*	No
Verbenaceae	Vitex sp.	-4.9	30.3	BDL		tower		No
Vitaceae	Cissus cornifolia	1.4	32.3	BDL		tower		No

 Table 2. (continued)

Species are arranged alphabetically by plant family. Photosynthetically active radiation was 1000 μ mol m⁻² s⁻¹ for LI-6400 measurements, and above that value for branch enclosures. Leaf temperature during measurement and rates of net photosynthesis measured simultaneously are given. Leaf level measurements in which less than 1 nL/L isoprene was measured are designated as below detection limit (BDL). For those taxa with isoprene emission rates less than 3 μ g C g⁻¹ h⁻¹ (designated with a "?" in the final column), justification for inclusion in a given category is provided in the text.

density multiplied by the species-specific emission capacity for isoprene (μ g C g⁻¹ h⁻¹) gives the area-averaged emission capacity for that species (μ g C m⁻² h⁻¹). Summing these values for all species provides the isoprene emission capacity averaged over the entire site (0.47 mg C m⁻² h⁻¹). Thus, the combination of low tree cover (approx. 30% [*Scholes et al.*, 2001]) and biomass and the small percentage of isoprene emitting species within the tower footprint results in low emissions, as reflected in the tower flux measurements.

[19] Guenther et al. [1996] estimated landscape average emission capacities for a variety of savanna types in southern Africa, and reported values ranging from 0.60 to 0.90 mg C $m^{-2} h^{-1}$ for isoprene. Our estimate therefore falls slightly below their low estimate. Their value for Combretum apicu*latum* savanna was $0.97 \text{ mg Cm}^{-2} \text{ h}^{-1}$, approximately twice our estimate from a similar savanna in this study. This discrepancy results largely from two factors. Guenther et al. [1996] used an emission capacity for A. nigrescens of 110 µg $C g^{-1} h^{-1}$, while we measured much lower rates, averaging only 20 μ g C g⁻¹ h⁻¹. For the purpose of estimating the landscape average emission capacity of the tower site, we adopted an intermediate emission capacity for A. nigrescens of $50 \ \mu g \ C \ g^{-1} \ h^{-1}$. If the higher value of 110 were used in our area-averaged emission capacity calculations, the estimate would increase to 0.90 mg C m^{-2} h^{-1} . Only additional measurements can resolve this discrepancy in species emission capacity, although our measurements were carried out on leaves growing on low, shaded branches or on saplings growing in the shade at the Skukuza nursery, and might therefore be expected to underestimate emission rates from the upper canopy of field-grown trees. A second reason why our fluxes were lower than expected is the species composition at the study site. Generally speaking, this savanna type consists of a repeating sequence of sandy, infertile upland sites dominated by nonemitting members of the Combretaceae and sites lower on the slope on more fertile clayey soils, dominated by fine-leafed Acacia spp. Although on the regional scale, this community is dominated by the isoprene-emitting A. nigrescens, the 300×300 m sample area around the tower, and the flux footprint in general, is dominated by the nonemitting A. nilotica [Scholes et al., 2001]. A. nigrescens comprises only about 10% of the leaf biomass, confined to the area southeast of, and a considerable distance from, the flux tower. Thus, the low isoprene fluxes measured in this study may underestimate the fluxes expected from the widespread Combretum-Acacia savanna of the "low-veld". In any case, isoprene emissions from this savanna type

would be expected to be generally low, but with significant patchy source areas dominated by *A. nigrescens*.

4.2. Screening of Vegetation for Isoprene Emission

[20] Two published studies report results of previous attempts to screen savanna vegetation of southern Africa for BVOC emissions [*Guenther et al.*, 1996; *Otter et al.*, 2002a], and a third similar study was carried out in central Africa [*Klinger et al.*, 1998]. The screening during this study of over 120 species, many of which had not been measured previously, for the presence of significant isoprene emissions adds considerably to the emissions database for southern Africa.

[21] The capacity for isoprene emission from leaves of different species varies over several orders of magnitude [Harley et al., 2000]. All leaves produce the immediate precursor of isoprene, dimethylallyl pyrophosphate (DMAPP), in the light, and it is likely that most or possibly all leaves can produce very small amounts of isoprene (i.e., <1 μ g C g⁻¹ h⁻¹), perhaps by a nonenzymatic, acid catalyzed reaction [Deneris et al., 1985]. A significant fraction of tree species (and a few herbaceous species) are capable of producing and emitting much larger amounts of isoprene (up to at least 200 μ g C g⁻¹ h⁻¹ under high light and optimal temperature) in a reaction catalyzed by the enzyme isoprene synthase [Silver and Fall, 1991]. These enzyme-catalyzed rates of production vary widely across and within species, depending on, among other things, light and temperature during measurement, leaf age, canopy position, and light and temperature conditions experienced by the leaves in the days prior to measurement [Geron et al., 2000; Harley et al., 2000; Petron et al., 2001; Sharkey et al., 1999]. In this screening study, each determination is based on a single measurement (or few), and frequently measurements were made on young plants with leaves growing in relatively low light environments at the Skukuza nursery. These measurements may be expected to underestimate the true emission capacity for these species. We report results of all measurements in Table 2, but these values were used only to identify isoprene emitting taxa, rather than to assign definitive isoprene emission capacities to each species.

[22] Most of the measurements allow an unambiguous determination of whether or not a given species is capable of emitting significant amounts of isoprene, and all species for which we measured an emission rate greater than 3 μ g C g⁻² h⁻¹ are designated as isoprene emitters in Table 2. Similarly, those with measured rates less than 1.2 μ g C g⁻² h⁻¹

(designated as "below detection limit" [BDL] in Table 2) are classified as nonemitters.

[23] Nine measurements gave readings between 1.2 and $3 \ \mu g \ C \ g^{-2} \ h^{-1}$ and assigning these taxa to one or the other category is somewhat problematic. Because the initial measurements were very close to our detection limit, Acacia robusta and Albizia harvevi were resampled using static branch enclosures; isoprene concentrations in the enclosures after 10 min in the sun were sufficiently low (1.8 and 5.9 nL/L, respectively) that they may both be safely regarded as nonemitters. Celtis, Ehretia and Balanites may all be tentatively classified as nonemitters, based on the very low values reported here and their taxonomic position vis-à-vis known isoprene emitting species. Several species of Celtis (Ulmaceae) have been measured previously (the reader is referred to the isoprene emission database maintained at an NCAR web site (http://www.acd.ucar.edu:8080/voc/vocIndex.jsp) for these supporting data and references), and none was reported to emit isoprene; indeed, no members of the Ulmaceae have been shown to emit. *Ehretia* (Boraginaceae) has not been measured previously, but no emitting members of the Boraginaceae have been reported. Only one other species of Balanites has been sampled, and isoprene emission was not detected. Phoenix reticulata is a palm (Arecaceae), many but not all of which are isoprene emitters. Indeed, both emitting and nonemitting members of the genus *Phoenix* have been reported, as has a report of low emissions in P. reticulata. Although we suspect it is an isoprene emitter, this characterization remains unclear. Calpurnea and Erythrina (Papilionaceae) and Schotia (Caesalpinaceae) are all members of the legume family, characterized by many isoprene emitting taxa. However, three species of Erythrina, including E. lysistemon, have been previously found not to emit isoprene, as has a closely related species of Schotia. Calpurnea, which has not been measured previously, belongs to Papilionaceae, subfamily Sophoreae, which is dominated by isoprene emitting species, and is likely to emit, but we cannot assign it to that category with confidence.

[24] A comparison of the results in Table 2 with published isoprene emission studies [*Guenther et al.*, 1996; *Otter et al.*, 2002a; available at http://www.acd.ucar.edu:8080/voc/ vocIndex.jsp] reveals that our findings are generally consistent with previous data. The importance of a number of tropical plant families for isoprene emission is confirmed here, including Caesalpinaceae, Euphorbiaceae, Flacourtiaceae, Mimosaceae, Myrtaceae and Papilionaceae. Similarly, the general absence of isoprene emitting species in such important and widespread families as Bignoniaceae, Combretaceae, Ebenaceae, Meliaceae, Rubiaceae and Tiliaceae is confirmed. The high rates of isoprene emission observed in *Diplorhynchus* was somewhat surprising (though confirming a previous determination of *Guenther et al.* [1996]) since the Apocynaceae contains very few emitting species.

[25] It is often assumed that all members of a given genus are either isoprene emitters or nonemitters. The presence of several genera in this study with both emitting and nonemitting species is worth noting, therefore, complicating as it does attempts to assign emission rates to unmeasured species based on rates measured on other members of the same genus [*Benjamin et al.*, 1996; *Karlik and Winer*, 2001]. Both emitting and nonemitting members of *Rhus* have been previously reported, and the same is true for Albizia and Bauhinia (http://www.acd.ucar.edu:8080/voc/ vocIndex.jsp). The report that Acacia nigrescens emitted isoprene [Guenther et al., 1996], in contrast to other species of the genus, was confirmed in this study, and four additional emitting species of Acacia were discovered. A careful look at the subgeneric classification of the very large genus Acacia (\approx 1250 spp.) [Miller and Bayer, 2001; Robinson and Harris, 2000] reveals that all these emitting species are restricted to Subgenus Aculeiferum, Section Aculeiferum, a relatively small group of perhaps 100 spp., restricted to Africa and Asia. Additional reports of isoprene emission from A. mellifera in southern Africa [Guenther et al., 1996] and A. catechu (Asia), A. caffra (southern Africa) and A. modesta (India) (Rasmussen, personal communication), all of which are also found in Subgenus Aculeiferum, Section Aculeiferum, lends support to the notion that isoprene emission in the genus Acacia is restricted to that subgroup. Three additional Indian species, A. ferruginea, A. lenticularis and A. sinuate are also reported to emit isoprene (Rasmussen, personal communication) but we have been unable to determine the subgeneric classification of these species. The large subgenus Phyllodineae (>950 spp.), largely confined to Australia, although not well sampled, has not produced any isoprene emitting species. Although fewer than 50 of the over 1250 species within the genus Acacia have been sampled for VOC emissions, this apparent sharp dichotomy in the emissions characteristics of a single taxonomic subgroup is reminiscent (though opposite) of the situation in the large genus *Quercus* (oaks), where all species have been found to emit isoprene except those in a relatively small Subgroup, Section Cerris, many of which emit large amounts of monoterpenes in a light-dependent fashion [Loreto et al., 1998; Csiky and Seufert, 1999]. It is interesting to note in this context that two species of Acacia, A. tortilis [Guenther et al., 1996] and A. erioloba [Greenberg] et al., 2003] have also been reported to emit light-dependent monoterpenes.

5. Summary and Conclusions

[26] Field campaigns during SAFARI 2000 have characterized biogenic VOC emissions from two distinct savanna types, both of which are widespread in southern Africa. Combretum-Acacia savanna (sensu latu), investigated in the current study, has generally low amounts of woody biomass, which is dominated by nonisoprene emitting tree species. It is therefore expected to be a relatively small source of biogenic VOC. Although the REA tower flux estimates reported here exhibit considerable scatter and are based on relatively few sampling periods, the generally low fluxes of isoprene measured from the Skukuza tower confirm this prediction. However, within this broad savanna classification, there are areas with greater abundance of isopreneemitting Acacia species (especially A. nigrescens) which will emit significant amounts of isoprene to the atmosphere. Thus, the lowveld is expected to be a patchy mosaic of landscapes, some areas of very low isoprene emissions and others of moderate to high emissions, depending on species composition and biomass density, which are dependent in turn on soil properties [Chappell, 1992]. Mopane woodlands, on the other hand, dominated by Colophospermum

mopane (Caesalpinaceae) have among the largest emissions of monoterpenes (primarily α -pinene and d-limonene) of any ecosystem yet investigated [Greenberg et al., 2003] and are widespread in southern Africa, with implications for regional tropospheric chemistry and aerosol formation and growth. A third major savanna type of south central Africa, the moist broad-leafed miombo woodlands, distinctly different from that discussed here, is dominated by members of the Caesalpinaceae, including Brachystegia (miombo), Julbernardia and Isoberlinia, the latter two of which are known to be isoprene emitters [Guenther et al., 2000; Klinger et al., 1998]. Miombo woodland is the dominant vegetation type of the Central African plateau, extending from Tanzania and the Democratic Republic of Congo south through Zambia, Malawi and eastern Angola, to Zimbabwe and Mozambique. Based on species composition and biomass estimates and enclosure measurements on dominant vegetation [Otter et al., 2002a], miombo woodland is expected to represent a much stronger isoprene source than Combretum-Acacia savanna, though this has not yet been verified through field investigations of above canopy fluxes.

[27] Emission potential of other types of savanna, and other forested ecosystems of southern Africa, in which BVOC emissions have not been directly measured, may be inferred by combining estimates of species composition and biomass with BVOC enclosure data. Since actual measurements of isoprene emission from many of these species are lacking, estimates of emission capacity must frequently depend on the emission characteristics of taxonomically closely related species (see, e.g., Benjamin et al. [1996], who developed a similar strategy in California). Enclosure measurements reported here, in conjunction with other measurements found in the literature, confirm that several plant families frequently represented in African savanna landscapes have a high proportion of isopreneemitting genera and species. These include two families of legumes, Caesalpinaceae and Papilionaceae, and Euphorbiaceae. Although the third legume family, Mimosaceae, generally contains fewer isoprene emitting taxa, the confirmation of isoprene emission from several members of the genus Acacia, widespread in savanna ecosystems, is important to understanding BVOC fluxes in southern Africa. Equally important is data indicating the general lack of isoprene emissions from dominant savanna plant families such as Combretaceae.

[28] Attempts to integrate species composition and leaf biomass data with species level estimates of BVOC emission characteristics were initiated with the global model of *Guenther et al.* [1995] and elaborated by *Guenther et al.* [1996]. Coupling a detailed and updated vegetation classification scheme with ground and satellite-based estimates of LAI and leaf biomass, and species-level BVOC emission data, *Otter et al.* [2003] have developed a highly resolved biogenic VOC emission model for southern Africa, the most detailed such scheme outside North America and Europe. Additional regional BVOC flux studies will be needed to validate predictions of such models, which will provide important VOC source information for use in regional tropospheric chemistry and air quality models.

[29] Acknowledgments. This study was part of the SAFARI 2000 Southern African Research Initiative. The authors wish to thank Bob and Mary Scholes for inviting us to participate, as well as for logistic support and species identification. Chris Geron (U.S. Environmental Protection Agency) provided the Voyager gas chromatograph. The authors wish to thank Ona Davies, Director of the Skukuza Nursery, and her staff for opening their facility to us and providing us with assistance and afternoon tea. Andrew Woghiren provided valuable logistic support in the field. The National Center for Atmospheric Research is supported by the National Science Foundation, and Luanne Otter was supported by the Department of Arts, Culture, Science and Technology in South Africa.

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