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Authors

Otter, L
Guenther, A
Wiedinmyer, C
et al.

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Spatial and temporal variations in biogenic volatile organic compound emissions for Africa south of the equator

L. Otter,[1] A. Guenther,[2] C. Wiedinmyer,[2] G. Fleming,[3] P. Harley,[2] and J. Greenberg[2]

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[1] Improved vegetation distribution and emission data for Africa south of the equator were developed for the Southern African Regional Science Initiative (SAFARI 2000) and were combined with biogenic volatile organic compound (BVOC) emission measurements to estimate BVOC emissions for the southern African region. The BVOCs are estimated to total 80 Tg C yr^{-1} for the region, with isoprene and monoterpenes contributing 56 and 7 Tg C yr^{-1}, respectively. The large uncertainties, particularly in terms of basal emission capacity assignment, associated with these outputs are discussed. Woodlands are predicted to be the dominant vegetation type, covering 23% of southern Africa, and are the largest annual source of isoprene (20 Tg C), monoterpenes (3 Tg C), and other VOCs (4 Tg C). Mopane savannas and woodlands are predicted to contribute over 75% of all monoterpenes, primarily from light-dependent emission processes. Rain forests cover only 3.5% of the total area but have high annual emission rates (9.8 g C m^{-2} yr^{-1}). In the tropical regions with high rainfall, warm temperatures, and high plant productivity throughout the year, the seasonal variation in VOC emissions was small. In subtropical regions, dominated by highly seasonal savannas and grasslands, large variations were predicted, with emissions declining by up to 85% during dry winter periods (June–August) due to low leaf area index after leaf drop. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 3210 Mathematical Geophysics: Modeling; 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; 9305 Information Related to Geographic Region: Africa; *KEYWORDS:* biogenic VOC emissions, isoprene, monoterpenes, emission capacities, land cover, southern Africa, SAFARI 2000

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1. Introduction

[2] Volatile organic compounds (VOCs) consist of a wide variety of chemical species that can be emitted into the atmosphere, where they react with other compounds. These reactions have significant consequences for the chemical composition of the atmosphere. In the troposphere, VOC oxidation influences OH and ozone concentrations and leads to the formation CO, PAN and secondary organic aerosols [*Andreae and Crutzen*, 1997; *Atkinson*, 2000; *Calogirou et al.*, 1999; *Derwent*, 1999; *Grosjean*, 1995; *Seinfeld*, 1999]. It is through these pathways that VOCs play an important role in the global carbon budget and radiation balance, regional oxidant balance, and in the distribution of ozone and other reactive gases.

[3] VOCs are emitted into the atmosphere from both anthropogenic sources (fossil fuel burning, industrial processes, waste treatment and agricultural activities) and biogenic sources [*Friedrich and Obermeier*, 1999; *Muller*, 1992; *Piccot et al.*, 1992]. Biogenic volatile organic compound (BVOC) emissions are extremely important, with vegetation producing more than 90% of the total global VOC budget (1150 TgC yr^{-1}) [*Guenther et al.*, 1995]. Tropical regions, with their high temperatures and solar radiation (major factors in the control of BVOC emissions [*Lerdau and Keller*, 1997; *Lerdau et al.*, 1997]), are the largest contributors to the global VOC budget. It has been estimated that the tropical regions of Africa and South America contribute two-thirds of the global BVOC budget [*Guenther et al.*, 1995]. These estimates are dependent upon several factors, including climate, vegetative cover and the emission characteristics of individual species and vegetation types within the vegetation cover.

[4] In Africa, emission rates have previously been measured in shrublands and savannas [*Greenberg et al.*, 1999; *Guenther et al.*, 1996; *Otter et al.*, 2002a; *Harley et al.*, 2002], Kalahari woodlands [*Otter et al.*, 2002a], and forests [*Greenberg et al.*, 1999; *Klinger et al.*, 1998; *Serca et al.*,

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[1] Climatology Research Group, University of the Witwatersrand, Johannesburg, South Africa.

[2] National Center for Atmospheric Research, Boulder, Colorado, USA.

[3] Division of Water, Environment and Forestry Technology, Council for Scientific and Industrial Research, Pretoria, South Africa.

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2001]. During the Southern African Regional Science Initiative (SAFARI 2000) [*Otter et al.*, 2002a; *Swap et al.*, 2002a, 2002b] further emission data were collected from Mopane woodlands and vegetative species representative of the Kalahari and Miombo woodlands [*Greenberg et al.*, 2002; *Otter et al.*, 2002a]. Although some of these data were available prior to the SAFARI 2000 study, they have not been used to estimate biogenic emissions from all of southern Africa. The incorporation of detailed vegetation and climatic data into BVOC emission models, as well as these newly measured emission rates, will improve regional and global estimates of BVOC emissions.

[5] Reasonable estimates of BVOC from Africa are necessary for our improved understanding of global and regional atmospheric chemistry. This paper presents a detailed land cover data set for southern Africa, which has been developed for the specific purpose of modeling biogenic emissions. Canopy and leaf-level fluxes measured during SAFARI 2000 and past studies are interpolated to the regional scale in southern Africa. Combining detailed species composition and emissions data with climatic and leaf area index (LAI) data, new and more accurate regional BVOC emissions were estimated for the area of Africa south of the equator on a monthly basis over a one-year period. Seasonal variations in emissions across the region are investigated. The results of these emission simulations are compared with previous estimates and used to investigate seasonal variation of BVOC in southern Africa. Emissions can be compared at the landscape level, and the landscapes that contribute significantly to the regional BVOC budget can be identified. Understanding emissions at a landscape scale enables better predictions of future BVOC emissions as the land use in the region changes.

2. Methods

2.1. BVOC Model Description

[6] The vegetation characteristics data (LAI, specific leaf mass, emission capacity) were used with temperature and cloud cover data to estimate biogenic isoprene, monoterpene and other VOC emissions from southern Africa for the course of one year. The emissions were calculated using the algorithms described by *Guenther* [1999] and the following formula:

$$\text{emissions} = \varepsilon D \gamma_L \gamma_T \gamma_a, \qquad (1)$$

where ε is the basal emission capacity for a given species or land use classification (specified using the procedures described in section 2.2), D is the foliar density (based on an assigned specific leaf mass and the LAI derived from the procedures given in section 2.3), and γ_L, γ_T, and γ_a are emission activity factors that depend on light intensity, temperature, and leaf-age, respectively. The light-dependent emission algorithm of *Guenther et al.* [1993] and *Guenther* [1999] was used for describing the effects of light on isoprene emissions. Light-dependent monoterpene emissions have recently been shown to be important in southern Africa [*Greenberg et al.*, 2003]. Therefore the light-dependent emission algorithm was also used to describe the effects of light on those specific monoterpene emitters. The temperature-dependent emission algorithm of *Guenther et al.* [1993] and *Guenther* [1999] was used to describe the influence of temperature on emissions of isoprene, monoterpenes and OVOC.

2.2. Species Composition Data

[7] A detailed vegetation mapping of land cover and vegetation distribution is necessary to accurately model the BVOC emissions in southern Africa. The vegetation species composition map used for this study was developed by the National Botanical Institute (NBI) in South Africa [*Rutherford et al.*, 2000]. This vegetation map consists of six independent subregional maps, namely *Low and Rebelo* [1998] (South Africa, Lesotho, Swaziland), *Giess* [1971] (Namibia), *Wild and Barbosa* [1968] (Botswana, Zimbabwe, Zambia, Malawi, Mozambique), *Barbosa* [1970] (Angola), *White* [1983] (Tanzania, Kenya, Uganda, Somalia), and *White* [1983] (Ruanda, Burundi, Congo, Gabon). Each base map consists of a wide variety of land cover categories (such as *Brachystegia* woodland, *Combretum* savanna, Miombo woodland, forest, desert) that differ from region to region and there are still vegetation discontinuities along some of the regional borders.

[8] The vegetation maps also contain a cross-referenced database of woody plant species lists. A plant species list is assigned to each land cover category and contains those species that, together, comprise at least 80% of the peak leaf area within each vegetation type. The database contains over 1100 species from 110 plant families. Species in the vegetation database were ranked according to their dominance in each landscape type. A percent cover for each of the listed species was estimated by using field composition and cover data from various sites in southern Africa (report located at http://modarch.gsfc.nasa.gov/MODIS/LAND/VAL/s2k_docs/Kataba_veg_survey1.doc) [*Scholes et al.*, 2001, 2002; R. J. Scholes, unpublished data, 2000; P. Frost, personal communication, 2000]. The species compositions of the grassland categories were excluded, since woody vegetation is considered to be the most important in terms of BVOC emissions, (although grasslands may contribute significantly to fluxes of oxygenated compounds) and very little information on BVOC emissions at the grass species level exists. The species distribution of the arid Fynbos in the Cape was not defined, since this land cover classification contains a large number of species located in that very small region, and there is a lack of emission data for the Fynbos species. These regions were given a general, default EC rather than species-specific ECs.

[9] The NBI species composition map defines only the vegetation of the region, and has very few nonwoody vegetation categories (such as urban and agriculture) identified. This mapping assumes the whole region is covered in vegetation. To create a more realistic mapping of the land cover, the NBI map was overlaid with the national land cover database of South Africa [*Fairbanks et al.*, 2000; *Thompson*, 1999]. This map of South Africa identifies the land cover and land use types in SA, including urban and agricultural areas. Due to lack of available data, urban and agricultural maps in other countries of the study domain were not included in this study. However, they will be incorporated in the future, as they are made available.

[10] The final land cover map consists of 262 land cover types, which includes 50 generic categories that do not have

Table 1. Annual Carbon Loss (GgC) and Average Emissions Rates (gC m^{-2} yr^{-1}) of Isoprene and Light-Dependent Monoterpenes (LDMT), Other Monoterpenes (OMT) and Other Volatile Organic Carbons (OVOCs) From the Various Land Cover Types in Southern Africa

		Carbon Loss Per Year, GgC				Average Emission Rate, gC m^{-2} yr^{-1}			
Land Cover Type	Area, km^2	Isoprene	LDMT	OMT	OVOC	Isoprene	LDMT	OMT	OVOC
Rain forest	290878	3119	0	401	1002	9.9	0.0	1.2	2.9
Rain forest/secondary grassland mosaic	460338	4460	0	638	1747	8.4	0.0	1.0	2.8
Swamp forest	198248	2593	0	315	787	9.0	0.0	1.0	2.5
Forest	377686	4181	37	549	1528	9.5	0.1	0.7	2.3
Forest/savanna	98695	1209	0	103	278	7.0	0.0	0.8	2.3
Coastal mosaic	59785	185	0	17	45	3.1	0.0	0.3	0.9
Montane	160407	694	0	56	187	4.7	0.0	0.4	1.2
Woodland	1934684	19508	96	734	3818	12.8	0.2	0.3	2.1
Miombo woodland	731757	5489	62	152	1385	7.5	0.0	0.2	2.1
Diplorhynchus woodland	269486	6697	1	84	634	23.4	0.2	0.3	2.3
Woodland/thicket	338	4	0	0	0	11.8	0.0	0.1	1.1
Woodland/savanna	293750	5318	0	113	631	13.2	0.0	0.5	2.1
Mopane veld (shrublands/savannas/woodlands)	355471	489	1769	73	525	1.6	5.0	0.2	1.5
Savanna	627963	4188	86	565	1598	4.2	0.3	0.4	1.4
Combretum savanna	91613	51	0	22	113	0.8	0.4	0.2	1.0
Acacia savanna	163891	902	68	50	208	6.7	0.2	0.4	1.4
Terminalia savanna	153533	2413	12	351	766	5.7	0.5	0.8	1.9
Savanna/grassland	32636	177	30	19	51	4.7	0.7	0.5	1.5
Savanna/thicket	88030	615	6	70	195	5.0	0.1	0.6	2.1
Thicket	47936	261	0	22	60	4.5	0.0	0.4	1.5
Bushveld	108451	311	7	48	147	3.2	0.2	0.3	1.2
Grassland	723111	683	17	95	1052	3.2	0.2	0.3	1.5
Desert/semidesert	1023	2	0	0	0	2.8	0.6	0.2	0.9
Crops[a]	963399	738	0	132	280	3.8	0.0	0.4	1.4
Degraded land[a]	306852	2009	0	142	363	4.3	0.0	0.3	1.2
Urban[a]	54764	193	0	18	71	5.0	0.0	0.4	1.2
Water	621574	2033	0	209	838	3.3	0.0	0.3	1.4
Other	595895	2722	1	331	1433	4.9	0.0	0.5	1.7
Average						6.3	0.3	0.5	1.7
Total	8401914	55692	2050	4620	17635				

[a] Only detailed land use maps for SA were incorporated into the model at this stage, therefore these values are underestimated for the southern African region.

species composition data (such as grasslands, desert, Fynbos, urban, crops). All 262 land cover categories were used in the emission calculations. However, for purposes of creating summary data tables in this presentation, some categories were combined using the actual species composition data to create 23 general land cover types (shown in Table 1).

2.3. Emission Capacities

[11] The EC (ε) is defined as the rate of emission under specific light and temperature conditions. For this study, the ECs used have been standardized for a light intensity of 1000 μmol m^{-2} s^{-1} and a leaf temperature of 30°C. Thus measured VOC emission rates from vegetation are corrected for light and temperature using the algorithms or activity factors (γ_L, γ_T) derived by *Guenther et al.* [1993].

[12] VOC emissions from dominant African plant species have been measured during field studies in Africa over the past ten years using leaf-level and branch-level enclosure techniques [*Greenberg et al.*, 2003; *Guenther et al.*, 1996; *Harley et al.*, 2003; *Klinger et al.*, 1998; *Otter et al.*, 2002a; *Serca et al.*, 2001]. ECs for the species relevant to this study were estimated from these measurements. In addition to African field studies, field measurements on other continents and in greenhouses, have characterized emissions from additional important African genera. Approximately 400 species in Africa have been screened either for total VOC emissions using a branch enclosure and a photoionization detector, or for isoprene using a leaf chamber and Voyager portable GC with a photoionization detector. Quantitative ECs for isoprene and monoterpenes (including α- and β-pinene, camphene, myrcene, careen, cymene, d-limonene, and terpinolene) have been measured by means of gas chromatography for about 90 of these species. All of these measurement results are being compiled in a database that will be available online [*Wiedinmyer et al.*, 2003] (see http://bvoc.acd.ucar.edu). Even though the EC database used to estimate BVOC emissions for this study is much larger than any other used in past modeling studies of Africa, it still only provides information about a small portion of the total species in the region. Only about 10% of species- or genus-level ECs used in this study were assigned based on actual emission measurements.

[13] The commonly used approach for estimating BVOC emissions is to assign an EC to each species, and calculate an average EC for each land cover type within the study region based on the species composition data. However, it is an unrealistic task to obtain emission measurements for all species in southern Africa. Therefore a second approach is used for regions where species composition or EC data are lacking. Our methodology for assigning ECs to the land cover and vegetation mapping is described here. The first step was to assign ECs to those species for which emission data were available. The second step was the grouping of all

of the species assigned in the study region into their various genera. A taxonomic approach was then taken to assign ECs to the species within genera that had some emissions information. In the genera where some emission data are available, an average EC for each genus was calculated (using the available emission data of the species within that genera) and used as a default value for species in the genus that do not have measured ECs. If no data was available at the genus level then family level information was used, and if there was no data at all then a general EC was assigned as discussed in the next step. The third step involved the assignment of ECs to the generic land cover types, such as desert or plantations, where no species-level emissions information was available. In these cases, the assigned ECs for isoprene were 0.1, 1, 5, 25, 50, 75 or 100 μgC g^{-1} h^{-1}. The last category was incorporated based on the findings of *Geron et al.* [2001], which indicate that ECs are higher than previously suggested by *Guenther et al.* [1994]. Monoterpene emissions were divided into two categories: light-dependent monoterpene emissions and, what we have termed "stored" monoterpene emissions. The first monoterpene category consists of those emissions that are controlled by both light and temperature. These were assigned ECs of 0, 1, 5, 10 or 40 μgC g^{-1} h^{-1}. The second category ("stored" monoterpenes) is defined as monoterpene emissions from specialized storage structures within the plant; these emissions are controlled by temperature only, and were assigned ECs of 0.5, 0.15, 0.4, 0.8, 1.6, 2.4 or 3 μgC g^{-1} h^{-1}. A constant EC for other VOC (OVOC) (2 μgC g^{-1} h^{-1}) was used for all vegetation and landscapes. Very few measurements of OVOCs (compounds other than isoprene or monoterpenes) have been made in Africa. Thus the EC of this chemical class assigned to the land cover in this study is the best estimate of OVOC and was not determined by data collected from African vegetation. OVOCs are likely to be important, and their inclusion in this model serves as a placeholder for incorporating OVOC ECs as they become available.

2.4. Leaf Area Index (LAI) and Leaf Mass Density

[14] Monthly Leaf Area Index (LAI) and leaf mass density were estimated and assigned to each parcel in the study domain. LAI assignments can be obtained from satellite measurements. The MODIS 8-day LAI product is expected to have improved spatial and spectral resolution than past satellite measurements. However, after quality assurance procedures (filtering and masking for reflection from clouds, aerosols and deserts) and tree cover modifications (for separating the grass LAI from the woody LAI), the MODIS LAI data set for 2000 and 2001 was found to be missing data for a significant number of our mapping units. These data require further work before they can be applied in the presented BVOC emissions model. Therefore, for the purposes of calculating initial emission estimates, an older, LAI data set spanning two years (1987–88) from the ISCLCP LAI database was applied. These data have a 10 minute resolution and are described by *Sellers et al.* [1994]. Validation of the MODIS LAI data will continue, and the data will eventually be used to estimate BVOC emissions for the southern Africa domain. The modeling of BVOC emissions using the MODIS LAI will provide results for a comparison of emissions estimated using the 2 data sets. This type of sensitivity study will eventually allow for the investigation of the effects of changing LAI on BVOC emissions.

[15] LAI (m^2 leaf/m^2 ground) is combined with an estimate of specific leaf mass (SLM), in grams of leaf per m^2 of leaf area, to estimate the foliar density used in equation (1). Specific leaf mass and LAI data for various species have been collected in a number of field studies [*Harley et al.*, 2003; *Otter et al.*, 2002a; *Privette et al.*, 2002; *Scholes et al.*, 2001, 2002; R. J. Scholes, unpublished data, 2000]. The measured and estimated SLM values from these studies were used to calculate leaf mass density for as many vegetation species in our modeling domain as possible. An average of 130 g m^{-2} (estimated uncertainty of ±30%) was assigned to all other species. This value is higher than the previously suggested values of 100 g m^{-2} for broad-leafed species [*Geron et al.*, 2001], but is based on actual data and may need to be reviewed in future as more data for southern African species becomes available.

2.5. Cloud Cover and Temperature

[16] Photosynthetically active radiation (PAR) data are required for estimating light-dependent BVOC emissions. This information was estimated from available cloud cover data as described by *Guenther et al.* [1995]. Cloud cover fraction was obtained by extracting the cloud cover bitfield from the MODIS LAI QA product and coding this as either zero cloud, 50% cloud cover or 100% cloud cover for each pixel. The MODIS LAI data were not used for the LAI values since detailed pixel data were lacking (as discussed in previous section). However, the cloud cover data could be used because these data were integrated over large areas and were therefore applicable for identifying the fractional cloud cover. MODIS data are captured once a day, and as a result, cloud information at single pixels cannot be extrapolated or interpolated, but rather integrated over all the days in each month and over 100km square blocks (S. Platnick, NASA- GSFC, personal communication, 2000).

[17] Daily temperature data were obtained from the NOAA NCDC data set (http://www.ncdc.noaa.gov/cgi-bin/res40.pl?page = gsod.html) and joined with the temperature data from climate stations within the world climate station database. Daily maximum and minimum temperature surfaces (covering the SAFARI study region) were created using a kriging routine within ArcINFO. The monthly means of these surfaces were then calculated for a 1-year period. Hourly temperatures were calculated from the minimum and maximum temperature and solar elevation using the methods described by *Guenther et al.* [1999a].

[18] The temperature data described above are at a 20 km grid resolution and the cloud cover at 100km resolution. To obtain respective values for each parcel within the modeling domain (i.e., vegetation/land use polygon), these variables were integrated over each polygon in the land cover data set (described in section 2.2).

2.6. Model Uncertainties and Improvements

[19] As with all models, there is a degree of uncertainty associated with each input variable. Calculating an exact value for the uncertainty is extremely difficult, due mainly to limited data. Therefore error assessments for regional BVOC emissions are usually qualitative rather than quan-

titative. The uncertainty of regional BVOC emission models is often stated to be a factor of two to three, and the error in this study most likely is in this range. This section discusses the model weaknesses and possible causes of uncertainty at each level of the model. The improvements that this study has made to regional modeling of VOC, particularly in Africa, are also highlighted.

[20] The species composition data is a vast improvement on other southern African vegetation maps. Previously applied land cover maps had generic vegetation classifications that were not necessarily specific to the region, whereas the new map has associated databases describing the actual species composition within each vegetation type. The EC for each vegetation or landscape type can therefore be calculated based on actual species emission data instead of just assigning an average generic landscape value. There is some uncertainty associated with defining the boundaries between one vegetation type and another; however the effect of this uncertainty on regional emission modeling is small.

[21] A larger uncertainty is associated with the percent cover of each species in each landscape type. Since species-level aerial coverages were calculated from data collected in more wooded areas (e.g., savannas, woodlands, forests), the uncertainty in these areas is less (estimated at 10%) than that for the drier vegetation types, where the error is estimated to be as much as 30%. It should, however, be noted that in most of the drier vegetation types very little emission data was available; therefore in most of these cases a generic landscape EC was assigned to these vegetation types and the percent cover data was not used. An error of 10% in cover estimates leads to an uncertainty in the landscape EC of 10%.

[22] Variability in species emission rates is a larger source of uncertainty. Using field data to assign average emission rates to individual species is not an easy task. Uncertainty in this process arises from the within-species variability and the error associated with measurement and analysis of emission rates. *Isebrands et al.* [1999] report that genetic variability can lead to a change of up to 30% in isoprene emissions. Leaf age and the position of the leaf in the canopy can affect emission rates; emissions from leaves at the top of the canopy may be three- to fivefold greater than those from leaves at the bottom of the canopy [*Sharkey et al.*, 1996]. Other factors such as drought stress [*Fang et al.*, 1996; *Guenther et al.*, 1999b], humidity [*Dement et al.*, 1975; *Schade et al.*, 1999], foliar moisture [*Lamb et al.*, 1985; *Kim*, 2001], precipitation [*Helmig et al.*, 1998], leaf damage or wounding [*Litvak et al.*, 1999] and nutrient concentrations [*Harley et al.*, 1994] also contribute to variability in isoprene and monoterpene emission rates from species. These effects are not well characterized and have not been described quantitatively; therefore they are not yet incorporated into the model.

[23] An example of species variability can be demonstrated with oaks (*Quercus*). *Guenther et al.* [1994] initially assigned an isoprene emission value of 70 μg C g^{-1} h^{-1} to oaks of eastern North America, but *Benjamin et al.* [1996, 1997] reported ECs of between 3.4 and 76.6 μg C g^{-1} h^{-1} for various California oak species. *Geron et al.* [2001] re-examined a number of oak species, restricting their measurements to Sun-adapted leaves, and report ECs for oak trees of up to 158 μgC g^{-1} h^{-1}. They suggest that many of the lower EC values reported in the literature represent values from shade-adapted foliage, and suggest that the assigned EC for oaks (defined as the value for Sun-adapted leaves) be increased to either 90 or 100 μgC g^{-1} h^{-1}. In southern Africa, the measured emission rates for the species *Colophospermum mopane* varied considerably, with average reported monoterpene emission rates of 52, 16, 22 and 62 μg g^{-1} h^{-1} [*Guenther et al.*, 1996; *Otter et al.*, 2002b; *Greenberg et al.*, 2003; A. E. James et al., unpublished data, 2001]. Although this species has been well studied relative to other species in southern Africa, the uncertainty associated with its emission rate is calculated to be 47%. This suggests that the previously suggested uncertainty estimate of 50% in applied emission rates for this study is appropriate.

[24] The collection of more emissions data per species will not necessarily reduce the uncertainty associated with assigning average ECs to species. However, more data will allow for the quantification of the relationship between emissions and controlling factors. This information can be incorporated into emission models, thus accounting for a larger portion of the variability. For example, the repeated measurements of this study led to the identification of light-dependent monoterpene emitters that were subsequently modeled separately. Previous biogenic VOC modeling studies treat all monoterpene emissions in the same manner, including only a temperature dependency.

[25] The taxonomic approach of assigning isoprene ECs is estimated to have an uncertainty of one order of magnitude, but it is less for genera for which some information is available [*Karlik and Winer*, 2001]. For monoterpene emissions of this study, it is possible that the uncertainty is more than an order of magnitude due to the limited data on monoterpene emissions and the taxonomy of the emitting species. Despite the large uncertainties, the protocol for assigning ECs laid out in this manuscript represents an improvement over previous models where landscape scale default values were used due to a lack of measured data. An increase in data will assist in reducing uncertainty with respect to which species emit isoprene or monoterpenes, and aid in assignment of ECs to species, genera, families or generic landscapes. The advantage of this southern African data set is that there was an increase in data in terms of the number of species that were screened or analyzed for emissions. As more data becomes available, the framework discussed in this manuscript can be used to assign ECs and incorporate data with relative ease in order to reduce the uncertainty.

[26] A species emission rate varies throughout a day, mainly due to changes in light and temperature. The emission model incorporates light and temperature algorithms that account for most (>69%) of the diurnal variability in isoprene and monoterpene emissions [*Bertin et al.*, 1997; *Geron et al.*, 2000]. Furthermore, ECs are also standardized to a set light and temperature. This standardization process can introduce some uncertainty. The mean EC value for plants measured under basal conditions have been shown to differ from those measured under ambient conditions and adjusted [*Geron et al.*, 2000]. A number of recent studies have suggested that even this standardized EC for isoprene can vary diurnally [*Geron et*

al., 2000; *Xiaoshan et al.*, 2000; *Goldstein et al.*, 1998; *Geron et al.*, 2001]; however, incorporating this small-scale variation into regional models would be difficult and would probably not have a significant effect on annual estimates.

[27] ECs have been shown to vary as a function of season, in some cases by an order of magnitude [*Boissard et al.*, 2001]. In this study, one value was assigned for the entire year. A single EC, which is usually based on summertime values, can therefore lead to an overestimation of the average monthly wintertime emissions (can be by a factor of 50). A single EC was used in this study as applying ECs for each season may lead to increased uncertainty for two reasons: (1) there is virtually no data on wintertime fluxes in the region, and (2) it would need to be determined for each landscape or region exactly when summer and winter started and ended, and thus when to switch from the one EC to the other. Furthermore, seasonal variations in tropical and subtropical regions, such as southern Africa, are not considered to be as significant as in northern temperate zones where winter temperatures are really low.

[28] Temperature and light variables need to be based on reliable data. Uncertainty in these variables can lead to large (>50%) error in the final emission estimates. *Guenther et al.* [2000] indicated that the error in environmental variables has a small impact on seasonal and annual estimates, but could be important for site-specific scenarios. For example, *Guenther et al.* [1999b] predicted that an increase in ambient temperature of 6°C could produce a twofold increase in biogenic VOC emissions. Cloud cover, precipitation and relative humidity have some effect on emissions but their influence is highly variable and therefore difficult to quantify. Each monthly value has an uncertainty associated with the variability in environmental condition during each month and this error will differ across the region.

3. Results and Discussion

[29] A region-specific land cover mapping of southern Africa (south of the equator) was created for the purpose of estimating BVOC emissions. This map includes detailed vegetation species information that has not been used in prior estimates of biogenic emissions from this region. Recent observations of ECs for African vegetation were applied to model these emissions. Monthly estimates of isoprene, "stored" and light-dependent monoterpenes and other VOCs have been calculated. The first regional estimates of light-dependent monoterpenes within southern Africa are presented, and the magnitude of these emissions demonstrates their importance. The results presented here enable an evaluation of the seasonal and spatial variability in the BVOC emissions throughout southern Africa.

3.1. Spatial Variations

[30] The species composition map describes over 250 land cover types in southern Africa, and is more detailed than land use information used in previous estimates of BVOC emissions from Africa. Monthly averaged emission rates of BVOCs were estimated for each land cover type in southern Africa (Table 1). Woodlands cover the largest area (23%) of the southern African land surface, followed by cultivated land (11.5%), grasslands (8.6%) and savannas (7.5%). The areas classified as woodlands produce the largest amount of isoprene per year, not only because they cover the largest area in the domain, but also because they have the second highest (after woodland/savanna transitions) annual average EC (12.8 g C m^{-2} yr^{-1}). Woodlands consist of a wide variety of species and thus several types of woodland classes have been specified. In Table 1, two specific woodlands classifications are explicitly shown: Miombo Woodlands and *Diplorhynchus condylocarpon* Woodlands. These two land use classifications have interesting species distributions and ECs that are worth noting. The Miombo Woodlands land cover classification is the most dominant of the woodland types, constituting 37% of the woodland area, and has a moderate annual average isoprene emission of 7.5 g C m^{-2} yr^{-1} (Table 1). Miombo woodlands are characterized by species from the genera *Brachystegia*, *Julbernardia* and *Isoberlinia*. The Kalahari Woodlands is included in this category since they are also dominated by these species. The woodlands dominated by *Diplorhynchus condylocarpon* have a very high average annual isoprene EC of 23.4 g C m^{-2} yr^{-1}, making their emissions very distinct from those of other woodlands. The *Diplorhynchus condylocarpon* woodlands also contain some light-dependent monoterpene emitters.

[31] The other land cover type that is presented explicitly in Table 1 is savanna. Savanna regions of Africa are often divided into broad-leafed, nutrient poor savannas and fine-leafed, nutrient-rich savannas. The former is often dominated by *Combretum* species, which have very low isoprene emissions, or *Burkea africana*, which have high emission rates. The latter is dominated by *Acacia,* a genus that contains both isoprene-emitting and nonemitting species, as well as light-dependent monoterpene emitters. *Terminalia sericea* is the most widely distributed woody species in southern Africa and it is the primary species in savannas along seep lines and at the bottom of catenas (hillslopes). This species emits stored monoterpenes. Because of their widely varied species compositions, each of the savanna types has very different ECs and therefore a very different emission pattern.

[32] Several species across the world have been identified as light-dependent monoterpene emitters [*Kesselmeier et al.*, 1996; *Owen et al.*, 2002; *Simon et al.*, 1994; *Staudt and Seufert*, 1995; A. E. James, personal communication, 2002], in which monoterpenes are emitted at much higher rates than for those species in which monoterpenes are emitted from stored pools. This manuscript is the first to separate out emission estimates of light-dependent monoterpenes in an attempt to quantify the contribution that these emissions make to the total southern African BVOC budget. In southern Africa, the species *Colophospermum mopane*, *Acacia tortilis*, *A. mellifera*, and *A. erioloba* are reported to have high monoterpene emissions [*Greenberg et al.*, 2003; *Guenther et al.*, 1996; *Otter et al.*, 2002a], and these emissions are suggested to be light-dependent. A recent study (A. E. James et al., unpublished data, 2001) confirms that the emissions from *Colophospermum mopane* are light-dependent. This study has provided a better understanding of the controls and emission rates of light-dependent monoterpene emissions from *Colophospermum mopane*. Few data describing the monoterpene emissions of African *Acacia* species have been collected, and there is a need to investigate these emissions in more detail to confirm their

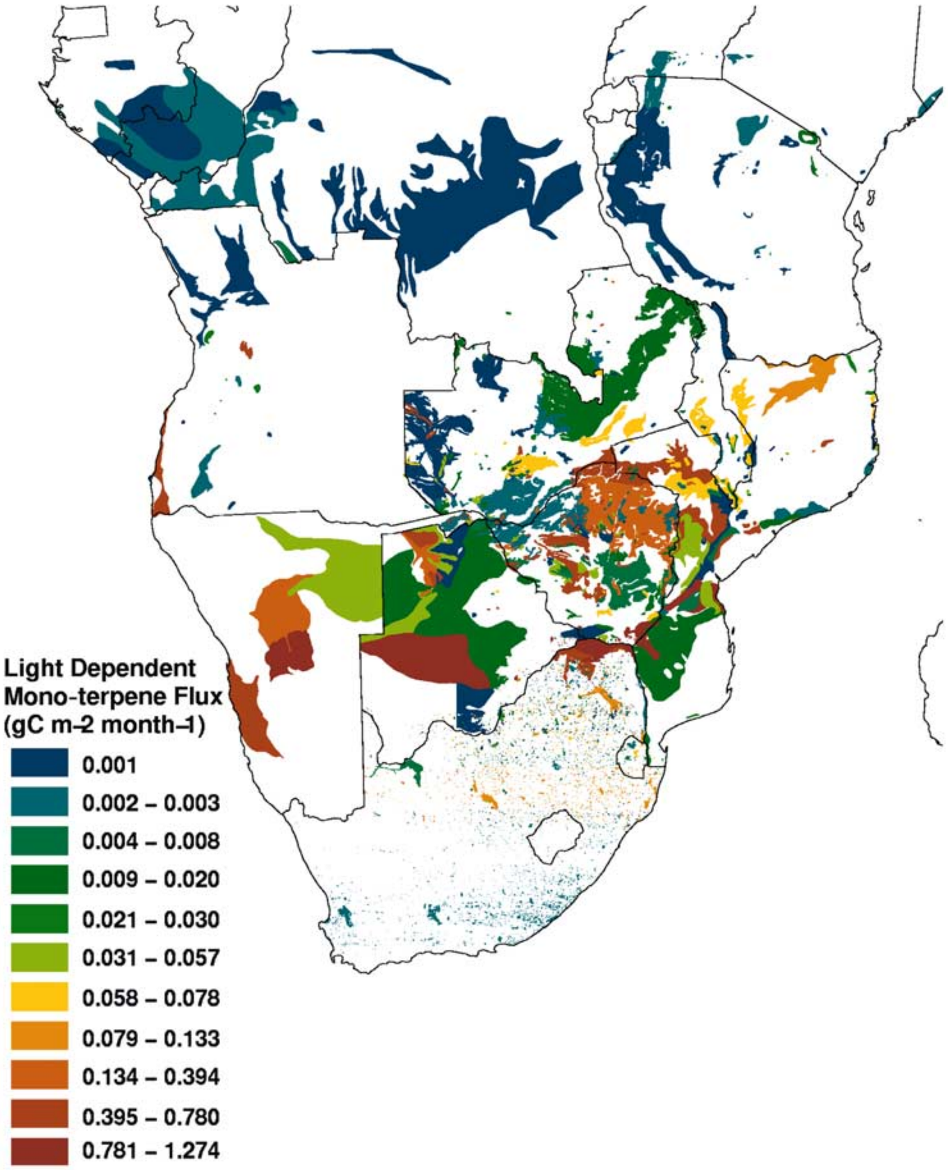

Figure 1. Distribution of light-dependent monoterpene emissions across southern Africa during January (gC m^{-2} $month^{-1}$). White areas indicate no emissions.

light-dependent behavior. Based on preliminary measurements, the *Acacia* species mentioned above were assumed to have light-dependent monoterpene emissions for this study.

[33] The amount of light-dependent monoterpenes emitted from Mopane savannas and woodlands is at least an order of magnitude higher that those emissions produced by any other land cover type located in southern Africa (1770 Gg C yr^{-1}) (Table 1). The average annual emission rate of these monoterpenes is higher than the calculated isoprene emission rates in savannas. Other landscapes that produce light-dependent monoterpene emissions are forests, woodlands, savannas and the bushveld. The majority of these monoterpene-emitting landscapes lie within a narrow band through the middle of southern Africa, extending through Namibia, Botswana, Zimbabwe, Zambia, Malawi and Mozambique (Figure 1). "Stored" monoterpenes (those emitted only as a function of temperature, not light) are also emitted from Mopane woodlands and savannas, but in much smaller amounts (73 Gg C yr^{-1}). It is the rain forests (located primarily in the northwest of the modeled region) and other forested regions that are important emitters of stored monoterpenes. These areas have estimated monoterpene emission rates between 0.7 and 1.2 g C m^{-2} yr^{-1}. Little is known about the prevalence of stored versus light-dependent monoterpene emissions, and the results of this modeling exercise demonstrate the potential magnitude and importance of these emissions in southern Africa. The further study of light-dependent monoterpene emissions is necessary for the better understanding of BVOC emissions in southern Africa.

[34] The major uncertainties associated with these results include those associated with the estimates of ECs and foliar densities. A number of dominant species have been

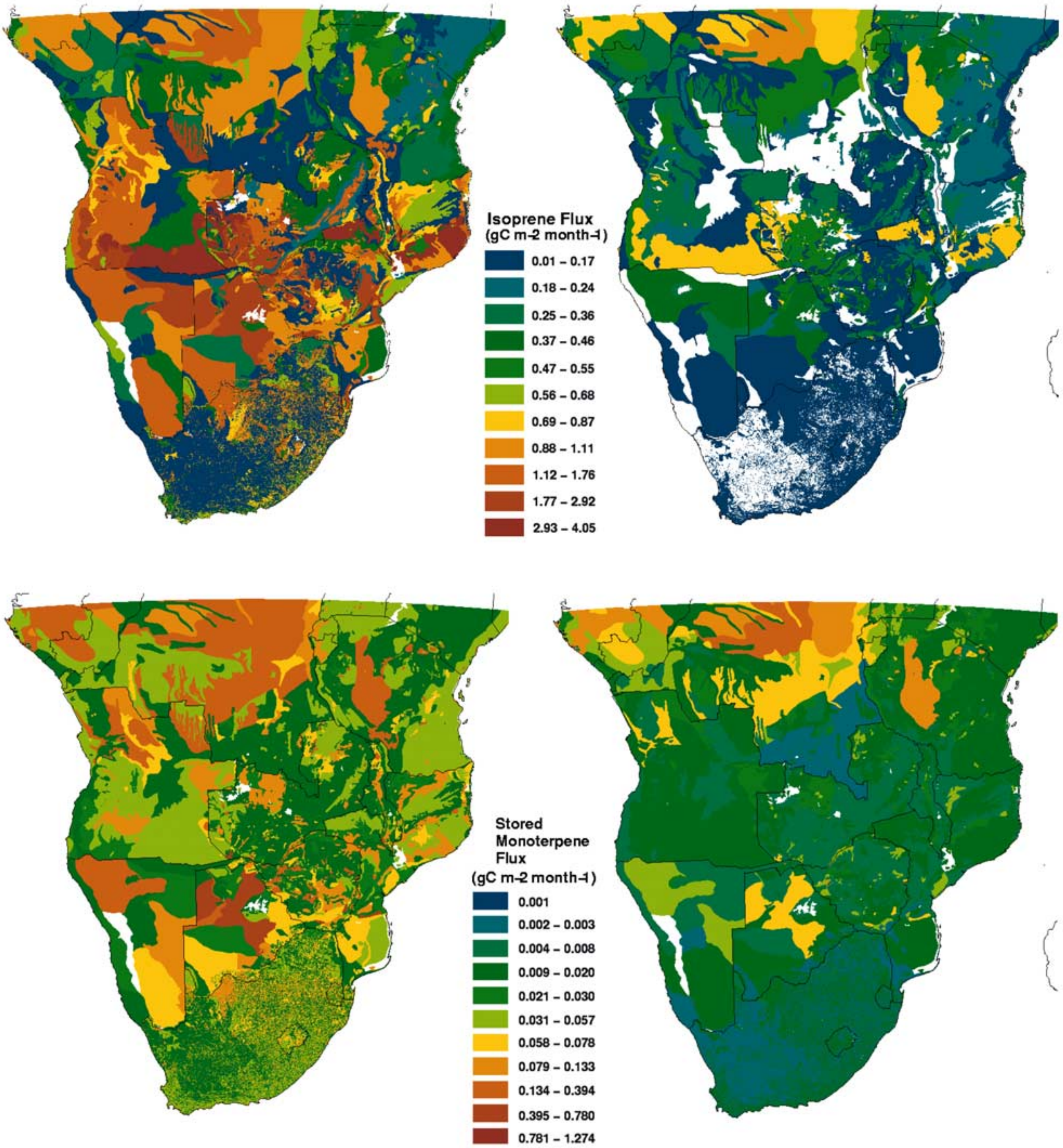

Figure 2. Average monthly isoprene emissions (top) and "stored" monoterpene emissions (bottom) (gC m^{-2} $month^{-1}$) over southern Africa decline from January (left) to July (right), particularly in the southern parts as July is very dry. White areas on the map indicate land areas that do not show any emissions.

assigned to the different land cover classifications within the southern African map. But, these species distributions are uncertain and need better characterization in terms of ECs in order to improve regional BVOC estimates. Species of *Brachystegia,Diplorhynchus*, *Julbernardia* and *Isoberlinia* are dominant across the modeled region, but there are few reported emission measurements from these plants. There may be several other species present in the region, other than those reported here, that emit light-dependent monoterpenes. A lack of these measurements may have prevented the identification of these emitters and more measurements are needed to characterize these species and incorporate the results into BVOC emission models for the region.

[35] Figure 2 shows the spatial distribution of estimated isoprene and "stored" monoterpene fluxes in southern Africa. South Africa has relatively low isoprene emissions,

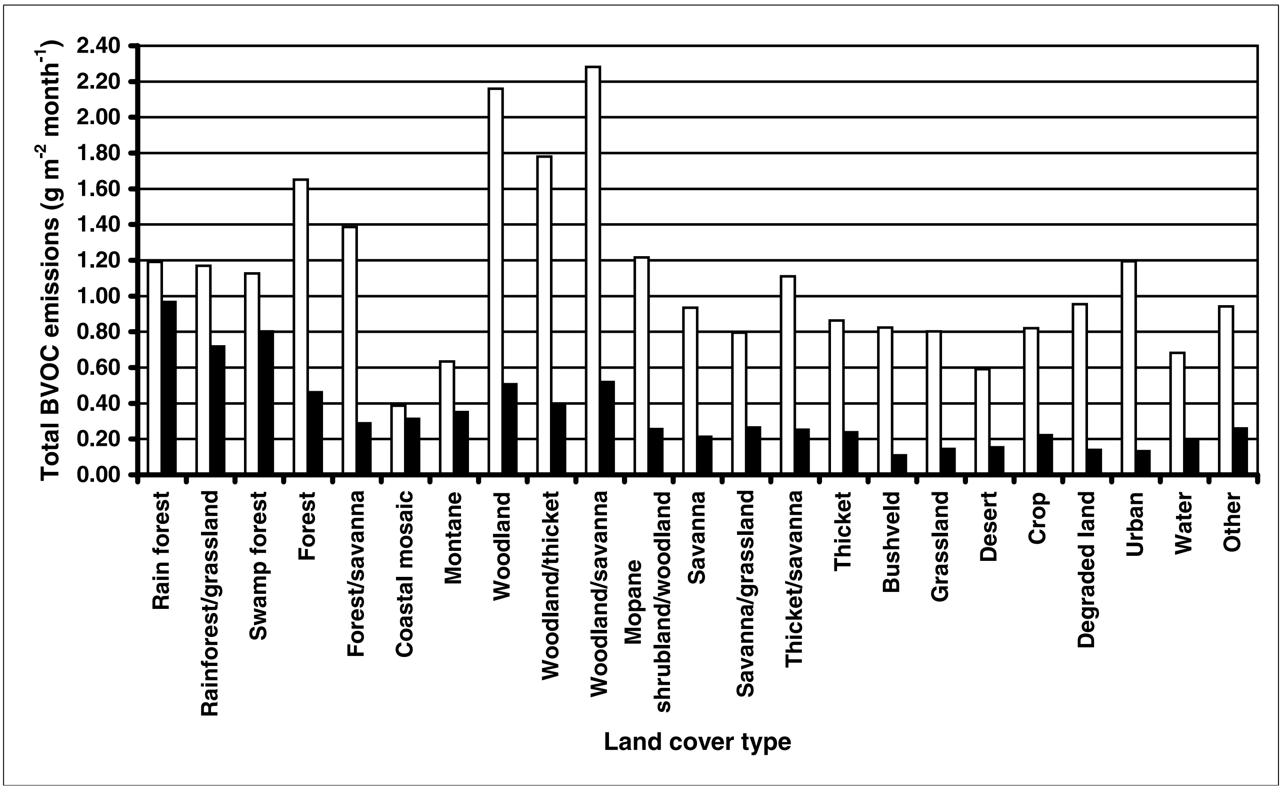

Figure 3. Total BVOC emissions (gC m^{-2} $month^{-1}$) during January (open bars) and July (black bars) for the various land cover types.

which is to be expected considering the low ECs assigned to the dominant species and small biomass density of the vegetation within this region. The higher isoprene emissions appear to be located in the western side of southern Africa. This area tends to have higher average temperatures than other areas in the study domain, which could partly explain the higher emissions in that area.

[36] Namibia appears to have unusually high BVOC emissions, considering that this region generally has low vegetation cover and consists mainly of desert and scrublands. This region experiences high temperatures, which could lead to the increased emissions in this region. On the other hand there are alternative explanations for these high emissions. First, the percent cover calculation for this region, particularly for the scrubland areas along the west coast, could be overestimated, due to the fact that these estimates were based on data from more wooded regions where vegetation density is higher. Secondly, the assigned ECs for the vegetation of this subregion have very high associated uncertainties and may be overestimated. Very few data are available from scrublands and desert species. The BVOC emissions of Namibia, (and a few other such regions), need to be investigated in more detail to determine the accuracy of the emission model results.

3.2. Temporal Variations

[37] Regional and local BVOC emissions fluctuate greatly due to variations in climate and leaf biomass. BVOC fluxes vary seasonally because of the influence of ecological factors such as light, temperature, and rainfall, which in turn affect vegetation biomass. In the humid tropical regions of central Africa, rainfall and plant productivity are high year-round. As a result, seasonal variations are small. As one moves further south, rainfall decreases during winter months (June–August), leading to distinct wet and dry seasons. BVOC emissions in these subtropical regions (woodlands and savannas) and more arid grasslands, show a strong seasonal pattern with very low BVOC emissions during winter (Figures 2 and 3), compared with the higher emissions during the summer months. Emissions of isoprene and monoterpenes are predicted to decrease by 17–37% and 21–43%, respectively, from January (summer) to July (winter) in tropical rain forest areas, whereas in savanna and grassland regions, emissions decrease as much as 85% in the winter.

[38] As expected, LAI, temperature and cloud density (and therefore light) appear to be the primary factors controlling the seasonal variability observed in the predicted BVOC emissions (Figure 4). Average BVOC emissions for the whole of southern Africa decline from a maximum in January to a minimum in July/August. Temperatures are shown to initially decrease, reaching the lowest values during July, whereas LAI continues to decline through August. The rains start in September, and the LAI begins to increase. It should be noted that the monthly BVOC emission values are an average value for the entire southern Africa domain and does not necessarily imply that all areas within southern Africa will have the same seasonal pattern. For example, the rainfall and foliar density in Central African savannas peak in September and decline to a minimum in February [*Guenther et al.*, 1999b]; whereas the rainfall and foliar density in South African savannas

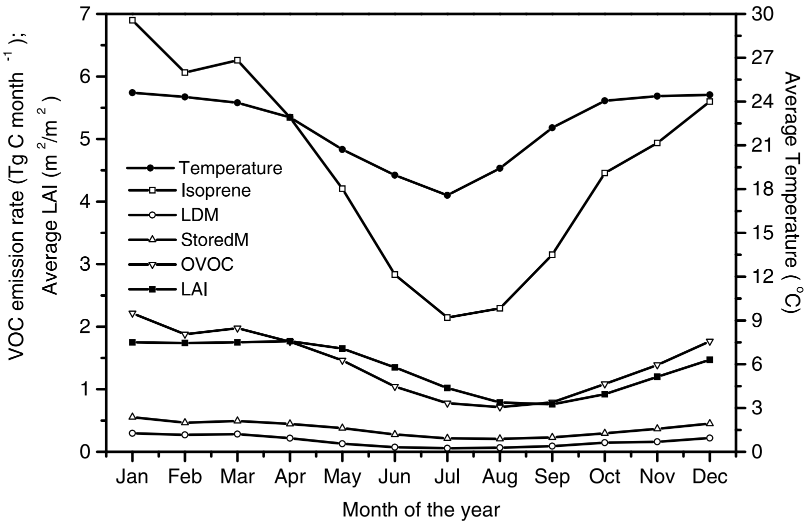

Figure 4. Monthly carbon loss (in TgC) as isoprene, light-dependent monoterpenes (LDM), "stored" monoterpenes (StoredM) and OVOC in Africa south of the equator. Seasonal variations in BVOCs are influenced by changes in air temperature and LAI.

peak in January and are at the lowest in July when rainfall is very low and the majority of the woody vegetation drops their leaves.

3.3. Annual and Regional Totals

[39] Annual isoprene emission rates (<27.5 g C m^{-2} yr^{-1}) estimated for land use classifications assigned to Central Africa are in the same range as those estimated by *Guenther et al.* [1999b] (<22 g C m^{-2} yr^{-1}). *Guenther et al.* [1999b] estimated that much of the region showed annual isoprene emissions of between 5 and 13 g C m^{-2} yr^{-1}, and the results of this study lie similarly between 8 and 12 g C m^{-2} yr^{-1}. Comparisons of hourly landscape isoprene emissions rates from various studies indicate that the values in this study are approximately 15% higher than those estimated by *Guenther et al.* [1995] and are, in general, 45% higher than the *Guenther et al.* [1999c] model (Table 2). It was noted by *Guenther et al.* [1999b] that their model may have over predicted the isoprene flux in Central Africa at the end of the wet season.

[40] It is difficult to make direct comparisons between the model results and previous field observations, as each field study is for a specific site, month and year; Therefore the environmental conditions are not necessarily similar to those used for the modeling exercise. Furthermore, differences in modeled emission estimates (between this and previous studies) may also occur from the use of different vegetation map or land cover classification system. The use of inconsistent classification schemes makes direct comparisons between the different model results difficult.

[41] The summer time emission estimates of stored monoterpenes calculated as part of this study are below 0.3 mg C m^{-2} hr^{-1} (predominantly between 0.1 and 0.26 mg C m^{-2} hr^{-1}), which is in the same range (0.04–0.2 mg C m^{-2} hr^{-1}) as previous estimates [*Guenther et al.*, 1996; *Otter et al.*, 2002a]. However, the Mopane woodland

Table 2. Comparison of Isoprene Emission Potentials for Various Landscapes

	Landscape Average Isoprene Emission Rate, mgC m^{-2} h^{-1}						
	Guenther et al. [1996b][a]	*Klinger et al.* [1998][b]	*Guenther et al.* [1995][c]	*Guenther et al.* [1999b][d,e]	*Otter et al.* [2002b][f]	This Study[f]	
Land Cover Type						July	Jan.
Rain forests		0.8–2.0	1.9	3.3		1.8	2.2
Forests			2.9	2.2		0.9	3.3
Woodlands			3.4	3.1		1.1	4.8
Isoberlinia forests		3.0				0.7	2.8
Brachystegia woodlands					3.6–8.2	0.7	2.8
Savanna/woodlands			4.9	2.4		1.2	5.1
Savannas	0.6–9.0	0.4–0.95			3.1	0.4	1.7
Combretum savannas	1.0					0.1	0.3
Acacia savannas	8.7				0.7	0.5	2.8
Degraded land			1.6	0.8		0.1	2.0

[a] Field-based study conducted in December.
[b] Field-based study.
[c] Modeling experiment.
[d] Modeling experiment [*Guenther et al.*, 1999b], and the given estimates are for November/December.
[e] Emission rates are daytime emission rates, as this is when the other field-based studies were conducted.
[f] Field-based study conducted mainly in February.

light-dependent monoterpene emission estimate of 2.0 mg C m^{-2} hr^{-1} is slightly lower than that reported by *Guenther et al.* [1996] and *Otter et al.* [2002a] (2.4–3 mg C m^{-2} hr^{-1}). The use of the updated EC for light-dependent monoterpenes obtained for *Colophospermum mopane* in this study may be the primary cause for this difference.

[42] The model estimates that the total annual BVOC emissions from southern Africa amount to 80 Tg C yr^{-1}. This total consists of 70% isoprene, 22% OVOCs, 6% stored monoterpenes and 3% from light-dependent monoterpenes. The model described by *Guenther et al.* [1995] predicts that the annual southern African emissions include 59 Tg C of isoprene, 11.8 Tg C as monoterpenes, and 23.4 Tg C of other VOC. The isoprene emission estimates between the two modeling studies are quite similar. However, the total monoterpene emissions estimated in this study are almost half the amount estimated by *Guenther et al.* [1995]. The inclusion of light-dependent monoterpene emissions in this model and improved EC data could explain the large differences in the two monoterpene emission estimates. Improved vegetation and emission data does not appear to have a large impact on annual isoprene emission estimates, but does significantly impact estimates of monoterpene emissions. Future research needs to be focused on the emissions of monoterpenes, and the factors controlling these emissions, as well as identifying other species that show light-dependent monoterpene emissions.

4. Summary and Conclusions

[43] A detailed land cover and species mapping of southern Africa was compiled and used to estimate BVOC emissions. Recent measurements of EC from African vegetation were applied in this modeling exercise. The BVOC emissions for the African region south of the equator were estimated to total 80 Tg C yr^{-1}, with isoprene and monoterpenes contributing 56 and 7 Tg C yr^{-1}, respectively. In the tropical regions the seasonal variation in VOC emissions was small, whereas in the more subtropical regions, dominated by highly seasonal savannas and grasslands, large variations were observed with emissions declining by up to 85% during dry, winter periods.

[44] The major advances in the emission modeling procedures described in this manuscript are improved spatial and temporal distributions that result from better vegetation distributions, EC data, and light and temperature estimates. This larger database allowed for the taxonomic assignment of ECs, which is vast improvement on previous studies that just used landscape level ECs. Even though significant advances have been made, the results have uncertainties and so this continues to be a work in progress. The model presented provides a framework for the incorporation of new data as it becomes available, particularly improved emissions factors and LAI estimates. In addition to the advancement of the BVOC emissions model, this is the first attempt to predict the African distribution of light-dependent monoterpene emissions, which we estimate contribute about 30% of the total monoterpene flux.

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G. Fleming, Division of Water, Environment and Forestry Technology, CSIR, P.O. Box 395, 0001 Pretoria, South Africa. (gfleming@csir.co.za)

J. Greenberg, A. Guenther, P. Harley, and C. Wiedinmyer, National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80303, USA. (greenber@ucar.edu; guenther@ucar.edu; harley@ucar.edu)

L. Otter, Climatology Research Group, University of the Witwatersrand, P.Bag 3, WITS 2050 Johannesburg, South Africa. (luanne@crg.bpb.wits.ac.za)