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Permalink

Journal

ISSN

Authors

Otter, LB
Guenther, A
Greenberg, J

Publication Date

DOI

Copyright Information

Peer reviewed

Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands

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Abstract

Biogenic volatile organic carbon (BVOC) emissions are an important component of the global BVOC budget, contributing more than 90%. Emissions vary with species and vegetation type; therefore to produce accurate global budgets data is required from different vegetation types. This study investigates BVOC emissions from savannas, Kalahari woodlands, Kalahari open shrublands and Mopane woodlands in southern Africa. BVOC emission samples from individual species were collected using leaf cuvettes and the BVOC concentrations were determined by GC-FID/ MS. Ten of the 14 woodland species measured were high isoprene emitters, while two showed high monoterpene emission capacities. Landscape average isoprene emission capacities were estimated to be as high as 9, 8 and 1 mg $C\,m^{-2}\,h^{-1}$ for savannas, woodlands and shrub lands, respectively. The monoterpene emission capacity for Mopane woodlands were estimated at almost 3 mg $C\,m^{-2}\,h^{-1}$, while for other landscapes it varied between 0.04 and 3 mg $C\,m^{-2}\,h^{-1}$. Isoprene and monoterpene emissions at a savanna site in South Africa showed a seasonal variation, which is more pronounced for isoprene. During the winter (June–September) estimated emissions were <10 mg $C\,m^{-2}\,d^{-1}$, with peak emissions (ranging between 20 and 80 mg $C\,m^{-2}\,d^{-1}$) occurring during the summer months (December–March) when foliar density peaked. The total BVOC emission from southern African (south of the Equator) savannas was estimated to be in the range of 18–74 Tg $C\,yr^{-1}$.
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Keywords: BVOC; Isoprene; Monoterpenes; Savanna; Woodlands; Emission capacities; Seasonal variation

1. Introduction

Biogenic volatile organic carbons (BVOCs), through their influence on photochemical oxidant and aerosol formation, play an important role in the composition of the atmosphere and the global radiation budget. BVOCs react with the hydroxyl radical (OH), ozone (O_3) and nitrate (NO_3) leading to the formation of carbon monoxide, secondary chemicals, organic acids and ultimately secondary organic aerosols (Andreae and Crutzen, 1997; Atkinson, 2000; Calogirou et al., 1999; Fehsenfeld et al., 1992). The production or consumption of ozone depends on the ratio between VOCs and NO_x (Dodge, 1984; Liu et al., 1987; Bowman and Seinfeld, 1994; Diem, 2000) and regional ozone models have been shown to be very sensitive to isoprene emissions (Pierce et al., 1998).

Among the most abundant BVOCs emitted from vegetation are isoprene and monoterpenes, which are estimated to contribute 44% and 11%, respectively, to the global vegetation BVOC budget of 1150 Tg $C\,yr^{-1}$ (Guenther et al., 1995). BVOC emission rates are species specific, therefore, landscape emissions are dependent on the species composition and abundance in a landscape. Emission of isoprene and monoterpenes is influenced by temperature and, in some species, by light intensity (Ciccioli et al., 1997; Jobson et al., 1994; Kesselmeier et al., 1996; Lerdau and Keller, 1997; Lerdau et al., 1997;

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Monson et al., 1992). Tropical ecosystems have high temperatures and radiation fluxes and have therefore been identified as important sources of BVOCs.

Due to growing populations in the tropics each year 20–60 Mha of tropical land, mainly forest and savanna, are cleared and burned in preparation for shifting cultivation or permanent agricultural use (Crutzen and Andreae, 1990). Many plants are also harvested and used for food, medicine, domestic fires and other domestic purposes. These land use changes alter the specie composition and land cover in the tropics and influence the BVOC emissions (Guenther et al., 1999a; Klinger et al., 1998).

Recent studies have provided information on BVOC emissions from vegetation of central African rainforests and savannas (Guenther et al., 1999b; Klinger et al., 1998) and southern African savannas (Guenther et al., 1996). Tropical forests and Sudanian woodlands are estimated to have isoprene emission rates of 1.9–3.4 mg $C m^{-2} h^{-1}$, which is lower than emission rates from central African savannas (2.4–4.9 mg $C m^{-2} h^{-1}$). Isoprene emissions from South African savannas have a much wider range (0.6–9 mg $C m^{-2} h^{-1}$) than central African savannas. Besides savannas there are other important landscapes in southern Africa, particularly in the region between South and Central Africa, which have not been investigated in terms of BVOC emissions. These are the Mopane woodlands, the Kalahari woodlands and shrub lands and the Miombo woodlands. Many of the species found in the Kalahari woodlands are also found in Miombo woodlands.

The objectives of this study are to: (a) determine the BVOC emission rates from dominant plant species in savannas, Mopane woodlands and Kalahari woodlands and shrublands in southern Africa; (b) estimate landscape average BVOC emission rates; and (c) to investigate seasonal BVOC emission patterns in savannas.

2. Field site descriptions

2.1. Savannas, SA

South African savanna emissions were studied at the Nylsvley Nature Reserve (24°39′S, 28°42′E), situated about 200 km north of Johannesburg. The Nylsvley site covers an area of about 30 km^2 that contains about 80% *Burkea africana* savanna (infertile, broad-leafed savanna) and 20% *Acacia tortilis* savanna (fertile, fine-leafed savanna) (Scholes and Walker, 1993). *B. africana* savannas consist of about 40% *B. africana*, 29% *Ochna pulchra* and 16% *Terminalia sericea*. *A. tortilis* savannas are comprised of about 71% *A. tortilis* and 29% *A. nilotica*.

2.2. Kalahari woodlands, Zambia

The Kalahari woodland sites in Zambia (Mongu and Senanga) are situated on Kalahari sands in southwestern Zambia. They are located on the Kalahari Transect, one of the IGBP mega transects (Scholes and Parsons, 1997), which spans an annual precipitation gradient of 200–1000 mm. The Kalahari is a sand-filled basin that occupies one-third of southern Africa. The weakly developed Kalahari sands are Aeolian and are low in nutrient availability and organic matter.

The woodland site at Mongu is situated in the Kataba Forest Reserve (15°44′S, 23°25′E) and consists of 52.1% *Brachystegia spiciformis*, 8% *B. africana*, 6.8% *Guibourtia coleosperma*, 5.9% *Brachestegia bakarana*, 4.3% *O. pulchra* and 3.5% *Baphia massaiensis* (Frost, 2000). The annual rainfall at Mongu is 950 mm. The foliar density of the woody component is calculated allometrically from measured biomass and LAI data to be 237 g m^{-2} (Otter et al., in press; Scholes et al., in press). All foliar density data, unless otherwise stated, is determined in this way.

Average annual rainfall at Senanga is about 900 mm with a mean annual daily temperature of 20.4°C. The woodland at Senanga (15°09′S, 23°16′E) consists of about 55% *B. spiciformis*, 13.5% *Erythrophleum africanum*, 10.8% *Diospyrus batacana*, 6% *Monotes glabra*, 4.5% *B. africana* and 3.7% *Pterocarpus angolensis*. The canopy is about 10 m high with ≈60% cover. No foliar density, biomass or LAI data has been collected at this site so it was assumed, due to its close proximity and similar rainfall, to be the same as at the Mongu site. Grass foliar densities at both sites range from 30 to 200 g m^{-2} with a typical value of 100 g m^{-2}.

2.3. Kalahari shrub land and Mopane woodland, Botswana

The Kalahari shrub land site at Okwa River Crossing, Botswana (22°41′S, 21°71′E) is located ≈80 km south of Ghanzi. The vegetation cover is an open shrub land dominated by *Acacia mellifera*, *T. sericea* and *Grewia flava* with scattered short trees. Woody foliar density is calculated to be 24 g m^{-2} (Otter et al., in press; Scholes et al., in press). Mean annual rainfall is 407 mm.

The Mopane woodland site is situated about 20 km northeast of Maun, Botswana (19°92′S, 23°59′E) in a woodland managed by the Harry Oppenheimer Okavango Research Centre (HOORC). The Mopane woodland forms large areas of monospecific stands of *Colophospermum mopane* (90% of the vegetation). The canopy height varies between 2 and 8 m. In some areas there are small patches of *T. sericea* thicket. The foliar density is determined to be 90 g m^{-2}. The mean annual rainfall in Maun is 460 mm (Otter et al., in press).

3. Materials and methods

3.1. Emission measurements

BVOC emission rates for individual leaves were collected during the summer months (February/March) at the various sites. Measurements were made between 7:30 and 11:30 a.m. and 14:30 and 16:30 p.m. Emission rates were estimated with a portable dynamic (open-flow), leaf cuvette (Fig. 1). The leaf chamber (0.5 l) was made of stainless steel with a glass lid. In the case of the *Acacia* species where the leaves are very small and the woody stems and thorns are large, a Delrin™ insert was used between the stainless steel base and glass lid that allowed for the insertion of thick branches. The cuvette system includes a flow sensor, a photosynthetically active radiation (PAR) sensor, a leaf thermocouple, humidity sensors upstream and downstream of the cuvette, and a data logger. The average relative humidity at the Nylsvley savanna, Kalahari woodland, Kalahari shrub land and Mopane sites were $44.3 \pm 18\%$, $50.31 \pm 2.3\%$, $41.23 \pm 12.2\%$ and $44.3 \pm 10.9\%$, respectively. Monitored flow rates through the leaf chamber were between 0.85 (± 0.04) l min^{-1} (Nylsvley samples) and 1 (± 0.07) l min^{-1} (all other samples) allowing for an exchange time of 30–40 s. Previous studies have used exchange rates of 20–60 s (Gabriel et al., 1999; Loreto et al., 1996; Singsaas and Sharkey, 2000). BVOCs in the air entering the cuvette were removed with an activated charcoal filter.
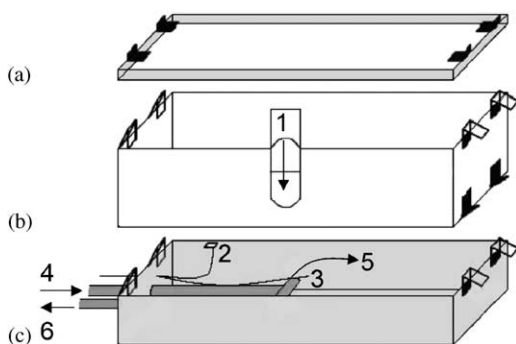

Fig. 1. Diagram of the leaf cuvette showing: (a) the glass lid with a stainless steel rim; (b) the Delrin™ insert for thick branches; and (c) the stainless steel base. The thick branches where placed in the slit in the side of the insert and a small slide piece (1) was pushed down to seal the chamber around the branch. If the leaves were large enough then section b was not used and the leaf was inserted directly into the chamber. There was a PAR sensor (2), a thermocouple (3), an inflow (4) carrying air into the chamber via a T-connection (5) to distribute air through the cuvette, and an outflow (6) tube in the base of the cuvette.

There was no specific control for temperature in the cuvette system, so temperatures did tend to increase slightly ($<3°C$) over the 30 min equilibrium period. Leaf temperature has a significant impact on emission rates (Loreto et al., 1996; Singsaas et al., 1997; Singsaas and Sharkey, 2000); therefore, this is a possible source of error ($3°C$ produces $\sim 5\%$ error) in the emission rates.

Measurements were taken from the blank cuvette system to ensure that the cuvette (a) was not releasing any hydrocarbons and (b) was sealing properly. CO_2 concentrations in the cuvette were not measured, however, a few separate measurements made with a Licor 6200 CO_2/H_2O analyzer (not presented) indicated that the plants were photosynthesizing during the time of the day that the hydrocarbon samples were collected. Both foliar area and leaf dry weight were determined after sampling so that the specific leaf area could be reported and emissions could be expressed on both a foliar area and an oven dried foliar mass basis.

After insertion the leaf was left to equilibrate for 30 min (approximate time required for photosynthesis to stabilize) before collecting a sample by pulling 0.5–2 l of the air exiting the enclosure through a multistage solid adsorbent cartridge (Carbotrap C, Carbotrap B and Carbosieve S-III) (Greenberg et al., 1999). Samples were typically collected at about 1000 μmol m^{-2} s^{-1} and $30°C$. To obtain these environmental conditions through the day shade screens were used over the chamber to attenuate incident radiation (and in some cases to cool the cuvette). After sample collection the adsorbent cartridges were stored in an ice chest and transported to the laboratory in Boulder, Colorado for analysis (samples stored at $-30°C$). Samples were thermally desorbed, cryogenically preconcentrated, injected onto a DB-1 column and separated by temperature pro-grammed GC-MS (Hewlett Packard 5890 (GC), 5972 (MSD), Palo Alto, CA). Isoprene and selected mono-terpenes (α-pinene, camphene, β-pinene, myrcene, carene, cymene, limonene) were analyzed by mass spectrometry with selected ion monitoring of masses specific for isoprene and terpenes (Greenberg et al., 1999). The detection limit for the GC-MS analysis was ≈ 1 ppt for isoprene, and uncertainty in the analysis, estimated from propagation of errors, was ≈ 0.05 ppb for a sample of 1 ppb.

3.2. Emission modeling

3.2.1. Species emissions and landscape emission capacities

Hydrocarbon emission estimates are calculated as described in Guenther et al. (1995) and Guenther (1999). The basic model for estimating the emission fluxes (F, μg m^{-2} h^{-1}) is

$$F = \varepsilon D \gamma \delta,$$

where ε is the landscape average emission capacity ($\mu g\,g^{-1}\,h^{-1}$), D is the foliar density ($g\,m^{-2}$), γ is an emission activity factor which accounts for light and temperature conditions (non-dimensional) and δ is an emission factor to account for longer term controls over emission variation (non-dimensional). Landscape emission capacities are determined as in Guenther et al. (1996). It is noted that the landscape emission rates do not specifically represent canopy fluxes (this would require tower or aircraft measurements); however, the landscape emission capacities give an indication of the ability of the various landscapes to produce BVOCs.

For the Nylsvley savanna an average species emission rate was calculated by using the emission data from this study as well as the emission rates from Guenther et al. (1996). The isoprene and monoterpene emission capacities for grasses were taken to be 5 and $0.2\,\mu g\,C\,g^{-1}\,h^{-1}$, respectively, and for other woody species the values of 16 and $0.8\,\mu g\,C\,g^{-1}\,h^{-1}$ were used (Guenther et al., 1995, 1996).

3.2.2. Seasonal BVOC emissions in savannas

The Nylsvley savanna site was used as a case study for investigating the seasonal variation in BVOCs. The landscape emission factor Nylsvley vegetation was combined with daily foliar density, light and temperature data for the year 1998. Emission capacities can vary from season to season, however, this change was not incorporated into the model as emission data was only available for the summer period.

There were no measured data on seasonal variation of foliar density for the study year at Nylsvley, therefore, it was calculated by means of satellite-derived normalized difference vegetation index (NDVI) and the derived global vegetation index (GVI) as described in Guenther et al. (1995) and summarized here. Monthly average foliar density was assumed to be negligible when the GVI was below 110 as savannas are woody, and increase exponentially if GVI was above 110:

$$F_m = F_p \exp[G_1(\mathrm{GVI} - 110)] - 1,$$

where F_m is the monthly average foliar density ($g\,m^{-2}$), G_1 is set at -72.5 (taken from Guenther et al., 1995) and F_p is the annual peak foliar density. The annual peak foliar density was calculated as the product of net primary production and an ecosystem dependent empirical coefficient (Guenther et al., 1995). NPP is either temperature or rainfall limited and can be estimated from empirical algorithms described by Lieth (1975). In this case, NPP is rainfall limited thus

$$\mathrm{NPP} = 3000(1 - \exp(-0.000664P)),$$

where P is the cumulative annual precipitation in mm. The ecosystem dependent empirical coefficient of 0.5 was taken from Guenther et al. (1995). Foliar density is seldom measured at sites and is often calculated from satellite data. Much of the uncertainty associated with BVOCs is associated with foliar density (Guenther et al., 1999a, b). This is, therefore, a potential source of uncertainty in this seasonal model and future efforts must be made to obtain field data.

BVOC emissions are influenced by light and temperature, indicating production without storage, or by temperature only, indicating volatilization of stored compounds. To include this variation the algorithms developed by Guenther et al. (1991, 1993) were used. Daily global radiation data for the Nylsvley region for the year 1998 were obtained from the South African Weather Bureau and used in the calculation of PAR, and direct and diffuse radiation (Harrison, 1984; Iqbal, 1983). The variation in solar radiation within a vegetation canopy was taken into account by incorporating a simple, one layer canopy model as described in Guenther et al. (1995). Daily leaf temperature was assumed to be the same as the average daytime ambient temperature as Harrison (1984) showed that there was no significant difference over the day. This assumption may lead to some error in the daily flux estimate, particularly since temperature influences emissions (Singsaas et al., 1997; Singsaas and Sharkey, 2000). The daily temperature and rainfall data for 1998 were collected at the Nylsvley Nature Reserve and compared with data collected at a nearby site by the South African Weather Bureau.

4. Results and discussion

4.1. Species emission rates

The emission rate of $56\,\mu g\,g^{-1}\,h^{-1}$ for *B. africana* at the Nylsvley savanna (Table 1) was higher than the previously measured rate of $36\,\mu g\,g^{-1}\,h^{-1}$ (Guenther et al., 1996), however, it is similar to the emission rate from *B. africana* in the Kalahari Woodland (Table 2). *T. sericea* had slightly lower monoterpene emissions in this study, whereas *Grewia flavescens* showed very low emissions in both cases. These differences could be due to seasonal or annual variation in environmental conditions, different measurements techniques, or genetic variability within a species. The major difference in measurement technique is that Guenther et al. (1996) used a branch enclosure technique rather than the leaf enclosure method. Guenther et al. (1994) report that leaf-level measurements of isoprene emission tend to be about 75% higher than branch-level measurements, for the same light and temperature conditions above the enclosure, due to self shading of leaves in a branch enclosure.

In this study additional emission rates at the Nylsvley site were measured for *Acacia nilotica*, *A. karroo* and *A. mellifera*. The former two species were shown to have

Table 1

Comparison of isoprene and monoterpene emission rate capacities[a] measured at Nylsvley during January 1998 by a leaf enclosure chamber and by Guenther et al. (1996) with a branch enclosure technique

Species	Total BVOC Guenther et al. (1996)	Isoprene ($\mu g\,g^{-1}\,h^{-1}$)		Monoterpene ($\mu g\,g^{-1}\,h^{-1}$)	
		Guenther et al. (1996)	This study	Guenther et al. (1996)	This study
Acacia nilotica	Low		<0.5		<0.5
Acacia karroo	Low		<0.5		<0.5
Acacia mellifera	High		5.7		<0.5
Burkea africana	High	36	56.1	<0.5	<0.5
Grewia flavescens	High	<0.5	<0.5	0.5	<0.5
Terminalia sericea	High	<0.5	<0.5	1.3	<0.5

[a] The emission rates were normalized using the temperature and light intensity dependent algorithms (Guenther et al., 1993) to estimate emissions representative of leaves at 30°C receiving a PAR of 1000 $\mu mol\,m^{-2}\,s^{-1}$.

Table 2

Measured isoprene and monoterpene emission rates for the various species

Species	Family/sub family	Form	n	Specific leaf area ($cm^2\,g^{-1}$)	Isoprene ($\mu g\,g^{-1}\,h^{-1}$)	Monoterpenes ($\mu g\,g^{-1}\,h^{-1}$)
Acacia erioloba	Mimosoideae	Tree/shrub	4	95	0	9
Baikiaea plurijuga	Caesalpinioideae	Tree	2	85	36	0
Baphia massaiensis	Papilionoideae	Shrub	4	104	97	0
Bauhinia petersiana	Caesalpinioideae	Shrub	2	95	34	0
Brachystegia spiciformis	Caesalpinioideae	Tree	4	107	0	0
Burkea africana	Caesalpinioideae	Tree	3	78	62	0
Colophospermum mopane	Caesalpinioideae	Tree/shrub	7	85	0	16
Cryptosepalum exfoliatum	Caesalpinioideae	Tree	4	76	17	0
Diallium engleranum	Caesalpinioideae	Tree	3	96	21	0
Diplorhynchus condylocarpon	Apocynaceae	Tree/shrub	3	102	25	0
Erythrophleum africanum	Caesalpinioideae	Tree	4	99	0	0
Guibourtia coleosperma	Caesalpinioideae	Tree	2	101	23	0
Julbernardia paniculata	Caesalpinioideae	Tree	4	95	34	0
Pterocarpus angolensis	Papilionoideae	Tree	4	116	44	0

very low emissions whereas *A. mellifera* was shown to be an isoprene emitter (Table 1). *Acacia erioloba*, from the woodland site, is shown to be a monoterpene emitter, similar to *A. tortilis*. Data from this study, Guenther et al. (1996) and unpublished data (Harley, P.) shows that 50% of the measured southern African *Acacia* species (16 species) emit isoprene, 12.5% emit monoterpenes and 37.5% show very low or no detectable emissions. Such variability has also been seen amongst the *Quercus* species (Csiky and Seufert, 1999) where isoprene emissions vary between 0.1 and 59 $\mu g\,g^{-1}\,h^{-1}$ and monoterpenes from 0 to 20.5 $\mu g\,g^{-1}\,h^{-1}$. In the case of *Acacias* isoprene emissions vary from 0.5 to 110 $\mu g\,g^{-1}\,h^{-1}$, and monoterpene emissions only going as high as 10 $\mu g\,g^{-1}\,h^{-1}$. It is suggested that the emission patterns in *Quercus* species could be related to the taxonomy of the genus. This should be investigated in the *Acacia* species as gaining insight into the taxonomic relationship may assist with BVOC scaling up efforts in the future.

Table 2 shows the isoprene and monoterpene emission rates for 14 species in the Kalahari Woodland. The monoterpene emission rate of 16 $\mu g\,g^{-1}\,h^{-1}$ for *C. mopane* is three times less than the estimate of Guenther et al. (1996). They did, however, note that the high monoterpene emission rate for *C. mopane* might have been due to disturbance of secretary cells. Alternatively, the difference in emission rates could be due to seasonal and environmental (such as soil type, soil nutrients) differences, since the *C. mopane* measured in the two sites were from different regions of southern Africa.

Ten of the 14 Kalahari woodland species measured have high isoprene emissions, however, the two most dominant species (*B. spiciformis* and *E. africanum*) did not show any emissions. *A. erioloba* and *C. mopane*, have high monoterpene emissions. *A. erioloba* is one of the dominant species of the southern and central Kalahari savanna and shrub land that is found in Botswana, while *C. mopane* is particularly important as it can form large areas of monospecific stands and therefore its emissions will dominate in that region. Several species with high monoterpene emissions have been recorded and data indicates that these emissions are light dependant (Simon et al., 1994; Staudt and Seufert, 1995). Unpublished data collected during the field campaigns suggests that emissions from *A. erioloba* and *C. mopane* are light dependant.

In Zambia, large areas of Kalahari woodland are cleared for rotation with cassava plantations, as this is an important source of food in the region. *B. massaiensis* is a pioneer species and once a patch is cleared it is one of the first plants to appear in the region. Table 2 shows that *B. massaiensis* has a very high isoprene emission rate and, due to all the land use change occurring in the region, could therefore be important in future landscape emissions when taking into account the effects of land use change.

4.2. Landscape emission rates and capacities

The landscape average emission capacity for the *B. africana* and *A. tortilis* savannas of Nylsvley reported in Guenther et al. (1996) were updated using the additional species emission data collected in this study. The landscape average isoprene emission capacity for the *B. africana* savanna was calculated to be 5.5 mg $C m^{-2} h^{-1}$. This is slightly higher than the emission capacity of 4.7 mg $C m^{-2} h^{-1}$ given in Guenther et al. (1996) due to the higher *B. africana* emission rate. The isoprene landscape emission capacity for the *A. tortilis* savanna is 0.7 mg $C m^{-2} h^{-1}$, which is much lower than that reported in Guenther et al. (1996). In this study the measured emission rate of $<0.5 \mu g\, g^{-1} h^{-1}$ was used for *A. nilotica* whereas the estimated average woody species emission rate of 16 $\mu g\, g^{-1} h^{-1}$ was used in Guenther et al. (1996). This has a large effect on the landscape emission capacity because *A. nilotica* is one of the dominant species in the savanna. In this study it is estimated to contribute only 3% to the landscape average emission capacity as compared to the 80% previously shown. The monoterpene emission capacity in the *B. africana* and *A. tortilis* savannas were 0.05 and 3 mg $C m^{-2} h^{-1}$, respectively, which are similar to previous reports.

Isoprene and monoterpene emission capacities for the entire Nylsvley savanna were calculated to be 16.2 and 2.3 $\mu g\ C g^{-1} h^{-1}$, respectively. The overall savanna emission capacity is calculated from the emission capacities of both the landscapes types and the percentage area of the total savanna that each landscape covers. Even though the isoprene emission capacity for the *A. tortilis* savanna is substantially lower than previously recorded it only occupies 20% of the total savanna. The effect, therefore, on the overall savanna emission capacity is minimal. Furthermore, the slightly higher isoprene emission from the *B. africana* savanna compensates for the small reduction in the *A. tortilis* savanna emissions.

Savanna isoprene emission estimates in this study are within the range found by Guenther et al. (1996), however, they are much higher than those reported for grassland and woodland savannas of Central Africa (Klinger et al., 1998). This is most likely due to the variation in species composition and foliar density. An average emission capacity for savannas in general will therefore need to be estimated or calculated from the emission factors measured at numerous savanna sites across the world. The Senanga site, classified as Kalahari woodland, has an emission capacity of 3.6 mg $C m^{-2} h^{-1}$ for isoprene and 0.2 mg $C m^{-2} h^{-1}$ for monoterpenes (Table 3). Klinger et al. (1998) estimated that *Isoberlinia* forests in Central Africa, which are often considered as Miombo woodlands, have landscape emissions rates of 3.0 and about 0.5 mg $C m^{-2} h^{-1}$ for isoprene and monoterpenes, respectively. These values compare well with those estimated for Senanga. The isoprene emission capacity at Senanga is within the range found for savannas (0.6–8.7 mg $C m^{-2} h^{-1}$), as is the case for the monoterpenes. The isoprene emission capacity is half, while the monoterpene emission capacity is double that found at the woodland site at Mongu. The Mopane savannas and woodlands in SA and Botswana have very similar emission capacities with isoprene emissions being less than a quarter of the monoterpene emissions, as is the case in the *A. tortilis* savannas.

Results indicate that savannas whose dominant species are isoprene emitters have emission capacities of 1–8.7 mg $C m^{-2} h^{-1}$ for isoprene and 0.04–0.06 mg $C m^{-2} h^{-1}$ for monoterpenes; whereas if the dominant species are monoterpene emitters then emission capacities vary between 0.6 and 0.7 mg $C m^{-2} h^{-1}$ for isoprene and 2.3–3 mg $C m^{-2} h^{-1}$ for monoterpenes (Table 3). Kalahari woodlands produce between 3.6 and 8.2 mg $C m^{-2} h^{-1}$ as isoprene and 0.1–0.2 mg $C m^{-2} h^{-1}$ as monoterpenes. These emission capacities are all in the same range and the actual area covered by each vegetation type will determine the composition of the regional emissions.

4.3. Seasonal variations

Predicted isoprene and monoterpene emissions from Nylsvley show a seasonal variation, which is much more

Table 3
Estimated area average isoprene and monoterpene emission capacity of important southern African savanna types

Landscape	Location	Woody foliage (g m^{-2})	Isoprene EC (mg C m^{-2} h^{-1})	Monoterpene EC (mg C m^{-2} h^{-1})	Reference
Savannas—with dominant isoprene emitters					
Combretum apiculatum savanna	Ntoma, SA	76	1.0	0.04	Guenther et al. (1996)
Acacia nigrescens savanna	Ntoma, SA	66	8.7	0.06	Guenther et al. (1996)
Burkea africana savanna	Nylsvley, SA	80	5.5	0.05	This study
Savannas—with dominant monoterpene emitters					
Colophospermum mopane savanna	Ntoma, SA	80	0.6	3	Guenther et al. (1996)
Acacia tortilis savanna	Nylsvley, SA	80	0.7	3.0	This study
Woodlands—with dominant isoprene emitters					
Brachystegia—Erythrophleum woodland (Kalahari woodland)	Senanga, Zambia	240	3.6	0.2	This study
Brachystegia—Guibortia woodland (Kalahari woodland)	Mongu, Zambia	237	8.2	0.1	This study
Woodlands—with dominant monoterpene emitters					
Colophospermum mopane woodland	Maun, Botswana	90	0.7	2.4	This study
Shrublands					
Acacia mellifera—Terminalia sericea shrubland (open Kalahari shrubland)	Okwa River Crossing, Botswana	24	0.7	0.2	This study

pronounced for isoprene (Fig. 2). Isoprene emissions are dependent on foliar density, temperature and PAR which all show a seasonal variation, while terpene emissions (with some exceptions) are not dependent on PAR, but are mainly influenced by foliar density and temperature making the seasonal variation less pronounced.

During the winter months (June–September) estimated emissions are low (<10 mg C m^{-2} d^{-1}). This is because foliar density declines rapidly in winter as the deciduous trees drop their leaves in winter. Emissions increase with foliar density after the first spring rains, which is in October in this case. BVOC emissions are shown to be highest during the months of December and March when foliar densities are at their peak.

Leaf temperature contributes slightly to seasonal variation in isoprene and terpene emissions, but is shown to have a much stronger influence on the daily variation in emissions (Fig. 2). Isoprene emissions are light dependent, whereas only some plant species' monoterpene emissions are light dependent. In the case of Nylsvley, the light-dependant monoterpene emitters are very few so this does not have such an impact on the savanna terpene emission pattern. However, in the case of Mopane or Kalahari wood-lands, where the light-dependant monoterpene emitters (*C. mopane* and *A. erioloba*) are present in large numbers, the seasonal pattern of monoterpenes may differ from that shown at the Nylsvley savanna. Although light dependency of monoterpenes were not studied here, they could be modeled using algorithms similar to that for isoprene emissions as the isoprene algorithms developed by Guenther et al. (1991) have been shown to describe these emissions quite well (Bertin et al., 1997; Ciccioli et al., 1997). The variation between summer and winter is therefore likely to become more pronounced, with the seasonal terpene emission pattern in these landscapes becoming similar to that of isoprene.

The data indicate that although BVOC are produced at the beginning of the rainy season due to the increased foliar density, it is not the peak period for vegetation BVOC emissions. Even if woody plants expand their leaves just before the first rains as suggested by Scholes and Scholes (1997) indications are that emissions would increase slowly and still only peak in December or January. A springtime (September) ozone maximum has been noted off the coast of southern Africa (Fishman et al., 1990). It has been suggested that BVOCs (from vegetation) and NO$_x$ (from soils) could
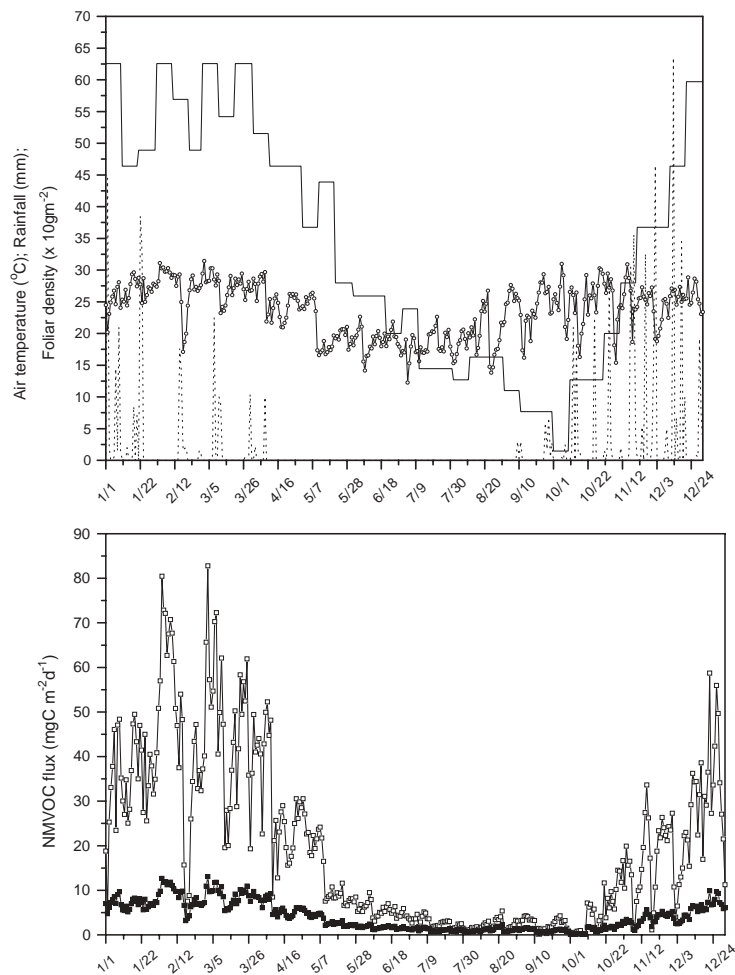
Fig. 2. Seasonal variations in temperature (°C, open circles), rainfall (mm, dotted line) and foliar density (g m^{-2}, solid line) at Nylsvley Nature Reserve during 1998. These values, as well as PAR data, were used to estimate isoprene (open squares) and monoterpene (solid squares) emission rates (mg C m^{-2} d^{-1}) during the year.

contribute to this ozone maximum (Scholes and Scholes, 1997).

September is the southern hemisphere springtime when rainfall begins and vegetation produces new leaves. At this time NO emissions increase due to increased soil moisture availability and temperatures, and there is a large pulse of NO after the first rains (Davidson et al., 1991; Johansson and Sanhueza, 1988; Levine et al., 1996; Otter et al., 1999; Scholes et al., 1997; Zepp et al., 1996). Biogenic NO emission could therefore contribute towards the ozone production during spring. The peak BVOC emissions, however, occur in February and March and are thus unlikely to contribute to this springtime ozone high. This data suggests that at any one site there would not be a correlation between the NO pulse and peak BVOC emissions because of the dependence on different controlling factors. This does not, however, exclude biogenic

emissions from contributing to the September ozone high on a regional scale.

It should also be considered that it is the ratio of NO$_x$ to VOCs, rather than the individual concentrations, which is the most important factor for determining whether O$_3$ is produced or destroyed. Therefore, the variation in this ratio during springtime needs investigation. Furthermore, if the ozone peak is a result of NO$_x$ limited chemistry, then an increase in NO$_x$ alone will increase the ozone levels. Ozone chemistry is very complex and more detailed studies together with modeling efforts, such as those of Diem (2000) and Thunis and Cuvelier (2000), need to be conducted to determine the contribution of BVOCs to ozone formation in the southern African region.

Annual isoprene and monoterpene emission rates from savannas were calculated to be 6.9 and 1.5 g C m^{-2} yr^{-1}, respectively. The range in annual emissions

was calculated by investigating the possible variation in emission rates and environmental conditions. Changes in light and temperature will affect the emission rates and rainfall influences foliar density and peak NPP. Harrison (1984) and Scholes and Walker (1993) report on the average climatic conditions and the variation shown at Nylsvley over a 30-yr period. Ambient temperatures vary between $0.4°C$ and $2.2°C$ annually, radiation can change by 5% and rainfall shows a 134 mm deviation over the 30-yr period. These extreme conditions were used to estimate the possible range in BVOC emissions from the Nylsvley savanna. Isoprene emission rates from savannas were estimated to range from 1.9 to $9.3 \, g \, C \, m^{-2} \, yr^{-1}$ and for monoterpenes from 0.7 to $1.7 \, g \, C \, m^{-2} \, yr^{-1}$. Southern African (area south of the Equator) savannas cover an area of $6.7 \times 10^{12} \, m^2$, thus are estimated to emit 37.5 ± 24.79 and $8.3 \pm 3.35 \, Tg \, C \, yr^{-1}$ of isoprene and monoterpenes, respectively. The total BVOC emission for southern African savannas falls within the range of 17.6 and $73.9 \, Tg \, C \, yr^{-1}$, which is within the broad range $(8.7–164 \, Tg \, C \, yr^{-1})$ calculated by Scholes and Scholes (1997).

5. Conclusions

Although the range of regional BVOC fluxes reported here is still large, this study has reduced the level of uncertainty and will contribute to the improvement of global BVOC and carbon budgets. Regional budgets will continue to improve as more site specific data is incorporated. Seasonal patterns of monoterpenes are suggested to differ between the various landscape types. Landscapes dominated by light-dependent terpene emitters are predicted to show seasonal patterns similar to that of isoprene dominated landscapes. It is, therefore, important that these light-dependant emissions are well understood and that these terpene emitters be identified. While it is possible that soil NO_x emissions could contribute to a springtime ozone maximum, it is unlikely that the BVOC flux estimates from the locations and at the scales reported in this study would contribute to springtime high ozone episodes.

Acknowledgements

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