SAFARI 2000 BVOC Measurements at Skukuza and Maun Flux Towers, Wet Season 2001

Abstract

Biogenic volatile organic compound (BVOC) emissions were measured in a *Colophospermum mopane* woodland near Maun, Botswana and in a *Combretum-Acacia* savanna in Kruger National Park, 13 km from Skukuza, Republic of South Africa (RSA) during the 2001 wet season campaign of SAFARI 2000. In addition, relaxed eddy accumulation (REA) measurements of BVOC fluxes (30 minute averages) were made on flux towers at these sites, where net CO_2 emissions were also measured simultaneously. The investigators also took advantage of a wide variety of easily accessible plant specimens growing in a nursery in the Kruger National Park to screen an additional 95 species of African plants for their ability to emit isoprene, providing species level isoprene emissions information which can be used to further initial estimates of isoprene emissions from additional ecosystems of southern Africa. A leaf cuvette technique was used to determine the emission capacities of the nursery plants and the temperature and light dependence of the emissions. This research on BVOC emissions contributes to attempts to develop a regional scale BVOC emissions model for southern Africa.

Background Information

Investigators:
Alex Guenther (guenther@ucar.edu)
Peter Harley (harley@ucar.edu)
Jim Greenberg (greenber@ucar.edu)
Luanne Otter (luanne@crg.bpb.wits.ac.za)

Project: SAFARI 2000/SAVE

Data Set Title: SAFARI 2000 BVOC Measurements at Skukuza and Maun Flux Towers, Wet Season 2001

Site: Maun, Botswana

Westernmost Longitude: 23° 33' E
Easternmost Longitude: 23° 33' E
Northernmost Latitude: 19° 54' S
Southernmost Latitude: 19° 54' S

Site: Skukuza, Kruger National Park, South Africa
Westernmost Longitude: 31° 29.813' E
Easternmost Longitude: 31° 29.813'E
Northernmost Latitude: 25° 01.184' S
Southernmost Latitude: 25° 01.184' S

Data Set Citation:

Guenther, A. B., P. Harley, J. P. Greenberg, and L. Otter. 2004. SAFARI 2000 BVOC Measurements at Skukuza and Maun Flux Towers, Wet Season 2001. Data set. Available on-line [http://daac.ornl.gov/] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

Data File Information

Data files contain records of BVOC measurements from the Maun and Skukuza flux tower sites; species level isoprene emissions and physiological data; and site meteorological data. The data files are stored as ASCII text files, in comma-delimited format, with column headers. A description of the data files is provided below:

maun_tower_terpene_flux.csv

Parameter	Units
Day of year	numeric
Time	local time, decimal hour
a-pinene flux	mg m^{-2} h^{-1}

This file contains emissions data for a *mopane* woodland near Maun, Botswana for the period February 2-12, 2001.

skukuza_tower_temp_rad.csv

Parameter	Units
Time of Day	local time, decimal
Air Temperature	degrees Celcius
Std. Error	degrees Celcius
Incoming Shortwave	W m^{-2}
Std. Error	W m^{-2}

This file contains data on average meteorological conditions at theSkukuza tower site for the duration of the tower flux study. Data are hourly means (S.E.) for the period February 1-8, 2001.

skukuza_tower_isoprene.csv

Parameter	Units
Time of Day	local time, decimal
Wind Direction	degrees, clockwise from N
Isoprene Flux	mgC m^{-2} h^{-1}
Isoprene Concentration	ppbv

This file contains a summary of isoprene concentrations (ppbv) and fluxes (mgC/m^2/h) measured at Skukuza tower site for the period February 1-8, 2001. Isoprene concentrations were measured at 19 meters.

skukuza_nrsry_isoprene_leaf.csv

Parameter	Units
Plant Family	family name
Species	genus species
Leaf Area	cm^2

Leaf mass	g dry weight
specific leaf mass	g cm^2
Photosynthesis	µmol m^{-2} s^{-1}
Stomatal Conductance	mmol m^{-2} s^{-1}
Internal CO_2 concentration	µmol/mol
Transpiration	mmol m^{-2} s^{-1}
Air Temperature	deg C
Leaf Temperature	deg C
Enclosure Flow rate	ml min^{-1}
Photosynthetically Active Radiation	µmol m^{-2} s^{-1}
Enclosure outlet isoprene concentration	ppm
Isoprene emission rate	µgC g h^{-1}
Enclosure type	text

This file contains a summary of species level isoprene emissions and physiological data for 95 species of African plants.

Sites

Maun, Botswana

The Harry Oppenheimer Okavango Research Center (HOORC) site is located in a broad-leaved *Colophospermum mopane* savanna woodland 20 km east of Maun, Botswana. Measurements were carried out at the Maun site in February of 2001. The long-term climate of this site is semi-arid with an annual mean rainfall of 46.4 cm. There is a distinct dry season during the winter months, May to September. Peak rainfall normally occurs between December and March. Intermittent dry spells during the rainy season are common. The field measurements described here were conducted near the end of a 2-month dry spell.

A 13.5 m micrometeorological tower that has served as a platform for CO_2 flux measurements for approximately 3 years was utilized for this study. The study area is under communal land use and has been used primarily for cattle grazing

and firewood collection. During the period of this study, cattle were not present. The tower is situated in the middle of a homogeneous stand of tall *mopane* trees (maximum canopy height 8 m), with patches of short (shrub) *mopane* (maximum canopy height 2 m) about 300 m to the northeast and west of the tower. *C. mopane* stands are often found associated with *Ximenia americana*, a hemiparasitic shrub. The canopy cover of the *mopane* trees was 30-40%. The marginal understory consists of grasses and some herbs with a ground cover of less than 15%. *C. mopane* is a drought-resistent deciduous tree with an almost total absence of leaves during the dry season. However, during the wet season (including the time of the study), maximum leaf area index for the stand varies from 0.9 to 1.3 (Matlana, 2002).

Skukuza, Kruger National Park, South Africa

The field flux study was carried out in February 2001 at a savanna flux measurement site in Kruger National Park, RSA. Located 13 km WSW of Skukuza camp, the site was one of the intensive study sites of SAFARI 2000. Meteorological parameters as well as exchanges of energy, CO_2, and H_2O measured using eddy covariance, have been monitored at this site continuously since April 2000. The 21-m walk-up flux tower is situated 365 m above sea level 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* family. This *Combretum*-dominated savanna is replaced by a fine-leafed *Acacia* savanna on clay soils at the lower end of this slope. This is a characteristic and repeated catenal pattern throughout the undulating topography of the region (Chappell, 1992), and savannas of this type cover a wide area of the broad coastal plain, or "lowveld", at elevations 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 are found within the tower footprint, totaling only about one eighth of the woody biomass.

The climate at Skukuza is semi-arid subtropical, with hot, wet summers and warm, dry winters. The annual rainfall averages 55 cm. 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 this measurement activity.

VOC Concentration

Maun

Two gas chromatographs (GC), equipped with flame ionization detectors, were used in the HOORC laboratory for the determination of terpene concentrations. The two GCs used the same analytical chromatographic columns [30 m 0.25 mm internal diameter (i.d.), 1.4 mm film thickness] and temperature program (initial temperature 40°C, 2 min hold, then 15°C min-1 to 150°C, then hold 5 min).

The GCs were also instrumented with identical sample inlet systems. These allowed VOCs from ambient air samples to be preconcentrated for analysis and focused on the analytical column at the time of injection. Samples were introduced to a first stage trap (60-80 mesh, 2.2 mm i.d. 100 mm length) and cooled electrically to 10°C; this procedure trapped the VOCs of interest (isoprene, monoterpenes, calibration standards), but not nitrogen, oxygen, most of the water vapor, and other lighterweight VOCs. The concentrated sample was then heated and transferred (with helium flow of 10 cm^3 min^{-1} STP) to the second stage cryofocusing trap (0.53 mm i.d. 500 mm long), and cooled electrically to 30°C. Both the first and second stage traps were wrapped over their entire length with insulated nickel-chromium heating wire (0.25 mm diameter, 0.2 omega cm^{-1}), which allowed them to be heated for desorption of sample aliquots (to 150°C, slowly for first stage trap, but rapidly, in 10 seconds, for the second stage, cryofocusing trap).

The identification of isoprene and terpenes was made from the retention times compared to a mixture of isoprene and terpene analyzed repeatedly during the experiment. Quantification of concentrations was made with respect to a mixture of 2,2-dimethyl butane in nitrogen (0.206 ppm), previously intercompared with other standards. Sample volumes were typically 250-500 ml and were introduced directly from the Teflon bag samples collected from the REA or cuvette. Detection limits, for these sample volumes, were approximately 50 ppt, with the precision of the GC analysis computed from a propagation of errors of

approximately 10% for a-pinene at 1000 ppt.

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

Instrumentation used at the Maun and Skukuza Sites

Instrument	Manufacturer	Model	Site
gas chromatograph	SRI Instruments Inc., Las Vegas, NV	310	Maun
gas chromatograph	Shimadzu Inst., Kyoto, Japan	GC Mini2	Maun
analytical chromatographic columns	Restek Corp., Bellefonte, PA	MTX-624	Maun
solid absorbent cartridges (first or second stage)	Supelco Inc., Bellefonte, PA	Tenax TA, Carbotrap B, Carbosieve	Maun, Skukuza
second stage cryofocusing trap	Restek Corp., Bellefonte, PA	MTX-QPlot	Maun
sonic anemometer	ATI, Boulder, CO	unknown	Skukuza
sonic anemometer	Gill Instruments, Lymington, UK	Solent R3	Maun

control flow pump	AFC Intl., DeMotte, IN	AirPro Surveyor	Skukuza
primary flow calibrator	AFC Intl., DeMotte, IN	BIOS Dry-Cal DC-Lite	Skukuza
gas chromatograph-mass spectroscopy	Hewlett-Packard	HP5890 with HP5972 detector	Skukuza

Skukuza Flux Measurements and VOC

The 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 liter 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, 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 cm^3 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. If vertical wind speed was below a threshold value (± 0.6 $sigma_w$ computed from the previous half hour period, where $sigma_w$ 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, samples of air from each reservoir were collected onto 2-stage solid absorbent cartridges, consisting of 200 mg Tenax or 200 mg Carbotrap B, followed by 200 mg Carbosieve, by pumping sample air for 5 min directly through the cartridge, using a controlled-flow pump located

downstream from the cartridge. The flow rate of air through the cartridges was nominally 300 cm^3 min^{-1}, but varied slightly since each cartridge offered a different flow resistance. Actual flows were measured using a portable primary flow calibrator, and the total volume collected onto the cartridges varied from 1250 cm^3 to 1680 cm^3. Cartridges were stored under refrigeration at approximately 0° C and subsequently analyzed in the laboratory at the NCAR using gas chromatography-mass spectroscopy (GC-MS) in selected ion mode. The detection limit for the GC-MS analysis was approximately 1 pptv 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.

Fluxes were calculated according to the relationship,

$$F = ß * sigma_w * (C_u - C_d),$$

where

F	is the flux of the trace gas of interest (µg m^{-2} h^{-1}),
ß	is a unitless coefficient estimated by similarity with virtual temperature as measured by the sonic anemometer (Businger and Oncley, 1990; Bowling et al., 1998),
$sigma_w$	is the standard deviation of the vertical wind speed (m h^{-1}) during the 30 min of sampling,
C_u, C_d	represent the concentrations of the VOC of interest (µg m^{-3}), collected from the up and down reservoirs, respectively,

Reliable wind and cartridge concentration data were obtained from a total of 15 half-hour measurement periods, from which isoprene fluxes were estimated.

Additional measurements were made on wide variety of easily accessible plant specimens growing in a nearby nursery in KNP. These specimens were used to screen an additional 95 species of southern African plants for the ability to emit isoprene, thus providing species level isoprene emission information which can be used to further initial estimates of isoprene emissions from additional ecosystems in southern Africa (Otter et al., 2002).

Additional Sources of Information

Related Data Sets

Otter, L. 2004. SAFARI 2000 Estimated BVOC Emissions for Southern Africa Land Cover Types. Data set. Available on-line [http://daac.ornl.gov/] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

James, A. E., S. M. Owen, C. N. Hewitt, J. Greenberg, A. Guenther, L. Otter, E. M. Veenendaal, and K. Mantlana. 2004. SAFARI 2000 Leaf-Level VOC Emissions, Maun, Botswana, Wet Season 2001. Data set. Available on-line [http://daac.ornl.gov/] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

Lloyd, J., O. Kolle, E. Veenendaal, A. Arneth, and P. Wolski. 2004. SAFARI 2000 Meteorological and Flux Tower Measurements in Maun, Botswana, 2000. Data set. Available on-line [http://daac.ornl.gov/] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

References

Bowling, D. R., A. A. Turnipseed, A. C. Delany, et al. 1998. The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and of her biological trace gases. OECOLOGIA, 116 (3): 306-315.

Businger, J. A. and S. P. Oncley. 1990. Flux measurement with conditional sampling. J. Atm. Ocean. Technol., 7: 349-352.

Chappell, C. 1992. The ecology of sodic sites in the Eastern Transvaal Lowveld. M.S. Thesis, Univ. of the Witwatersrand, Johannesburg, South Africa.

Greenberg, J. P., A. Guenther, P. R. Zimmerman, W. Baugh, C. Geron, K. Davis, D. Helmig, and L. F. Klinger. 1999a. Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. Atmos. Environ., 33: 855-867.

Greenberg, J. P., A. B. Guenther, S. Madronich, W. Baugh, P. Ginoux, A.

Druilhet, R. Delmas, and C. Delon. 1999b. Biogenic volatile organic compound emissions in central Africa during the Experiment for the Regional Sources and Sinks of Oxidants (EXPRESSO) biomass burning season. J. Geophys. Res., 104: 30,659-30,671.

Greenberg, J. P., A. Guenther, P. Harley, L. Otter, E. M. Veenendaal, C. N. Hewitt, A. E. James, and S. M. Owen. 2003. Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana, J. Geophys. Res., 108(D13): 8466, doi:10.1029/2002JD002317. Available for download (PDF).

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

Mantlana, B. K. 2002. Physiological characteristics of two forms of Colophospermum mopane growing on Kalahari sand. M.S. Thesis, University of Natal., Durban, South Africa.

Otter, L., A. Guenther, and J. Greenberg. 2002. Seasonal and spatial variations in biogenic hydrocarbon emissions from southern African savannas and woodlands. Atmos. Environ., 36: 4265-4275.

Scholes, R. J., et al. 2001. The environment and vegetation of the flux measurement site near Skukuza, Kruger National Park. Koedoe, 44: 73-83.

Point of Contact:

Alex Guenther
Atmospheric Chemistry Division
National Center for Atmospheric Research
P.O. Box 3000
Boulder, CO USA 80307-3000
E-mail: guenther@ucar.edu
Phone: +01 303 497 1447
Fax: +01 303 497 1477

Revision Date: Tuesday, September 28, 2004