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Authors
SERÇA, D
GUENTHER, A
KLINGER, L
et al.

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EXPRESSO flux measurements at upland and lowland Congo tropical forest site

By D. SERÇA[1]*, A. GUENTHER[2], L. KLINGER[2], L. VIERLING[2,3], P. HARLEY[2], A. DRUILHET[1], J. GREENBERG[2], B. BAKER[2,3], W. BAUGH[2], C. BOUKA-BIONA[4] and J. LOEMBA-NDEMBI[4], [1]*Laboratoire d'Aérologie, (UMR 5560), 14 Avenue E. Belin, F-31400, Toulouse, France;* [2]*Atmospheric Chemistry Division, National Center for Atmospheric Research, PO Box 3000, Boulder CO 80307-3000, USA;* [3]*CIRES, University of Colorado, Boulder, CO, USA;* [4]*Laboratoire de Physique de l'Atmosphère-CERGEC, B.P. 125, Brazzaville, Congo*

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ABSTRACT

As part of the EXPRESSO program (EXPeriment for the REgional Sources and Sinks of Oxidants), biosphere-atmosphere exchanges of trace gases were investigated in a ground-based forest site of the Republic of Congo. Experiments were carried out in March and November-December 1996. A 60-meter walkup tower was erected in an undisturbed mixed tropical forest typical of upland vegetation in the Nouabalé-Ndoki National Park. Eight belt transects radiating from the tower were used to characterize the species composition and structure of the upland mixed forest. As a comparison, and to investigate horizontal heterogeneity of the trace gases exchanges, additional measurements were made in a nearby monospecific forest stand characteristic of lowland *Gilbertiodendron dewevrei* (Gilbert. *dew.*) forest. Micrometeorological data, trace gas concentrations and flux measurements were made from the tower. We report daily above-canopy variation in temperature and radiation, energy partitioning into latent and sensible heat flux, volatile organic compound (VOC) mixing ratios, isoprene and CO_2 fluxes. Fluxes of isoprene and CO_2 were measured above the canopy using relaxed eddy accumulation and eddy covariance methods, respectively. These fluxes show a seasonal variation between the two experiments, as does energy partitioning. However, difference in isoprene emission between the two seasons are difficult to reconcile with meteorological (T, PAR) data only, and more data such as plant water potential are needed to modeled the seasonal isoprene emission cycle. Isoprene emission at the leaf level was also determined for plant species at both upland and lowland sites using environmentally controlled leaf enclosures. Together with the ecological survey, the leaf level work suggests that lowland *Gilbert. dew.* forests act as hot spots in terms of isoprene emissions. Future climate and land use changes could greatly affect the isoprene regional emission estimate through changes in the respective proportion of the upland and lowland forests, and the extent of dry versus wet season.

1. Introduction

Tropical regions are of great significance in the study of global chemistry. They are of particular importance because of the intense biogenic activity at these latitudes, the increasing pressure of human populations, the frequent occurrence of biomass burning, and the influence of deep tropical convection on global chemistry. It is expected, for example, that intensification of tropical forest conversion to savanna will lead to changes in the fluxes of major trace gases, aerosols, and energy, with consequent changes in the hydrological cycle

* Corresponding author.
e-mail: serd@aero.obs-mip.fr

and climate. A number of papers published in previous special issues of the Journal of Geophysical Research (vol. 93, 1988; vol. 101, 1996) have demonstrated the impact of tropical sources of trace gases on atmospheric composition.

Biomes present in these regions, mainly grassland savanna, woodland savanna, and tropical rainforest, account for more than half of global net primary productivity (Rodin et al, 1975), which is an indicator of the ecological efficiency of carbon, nitrogen and sulfur exchanges through biogeochemical cycles. Emissions of trace gases from the biosphere to the atmosphere are directly or indirectly associated with these cycles. Primary emissions of trace gases are important in the global radiation balance (e.g., methane, CH_4, and nitrous oxide, N_2O, in addition to water vapor and CO_2) and in the regional oxidant balance (e.g., VOCs and nitrogen oxides, NO_x). These trace gases have an indirect influence on the quantity and distribution of other reactive gases in the troposphere (Crutzen, 1973), and on tropospheric ozone production (Fishman et al., 1991).

A number of compounds are directly exchanged with the atmosphere, either from soil (NO, N_2O, CO_2, CH_4) or vegetation (VOCs, CO_2). The former are primarily associated with bacterial processes in the soil (Galbally and Roy, 1978) while VOCs are significantly produced and emitted from foliage of a variety of living organisms. A few measurements of hydrocarbons were made in the Amazon Basin during the GTE/ABLE 2A experiment (Zimmerman et al., 1988; Rasmussen and Khalil, 1988), and the effect of biogenic emissions on photochemistry over the Amazon forest is discussed by Jacob and Wofsy (1988).

The vast majority of existing data on biogenic emissions in tropical ecosystems has been collected in Central and South American ecosystems, while few studies have focused on biogenic emissions in African tropical ecosystems. Some have dealt with CH_4 or NO (Delmas et al., 1992; Serça et al., 1998, respectively) emitted from soil. Prior to EXPRESSO, only one study had examined biogenic VOC emissions from Africa (Guenther et al., 1996), despite estimates that South America and Africa account for two thirds of the global total of VOC emissions (Guenther et al., 1995). To our knowledge, no similar work has been conducted on African tropical forests, although the mixing ratios of some light hydrocarbons in air masses above the Central African forest were measured during the 1988 DECAFE experiment (Bonsang et al., 1991; Rudolph et al., 1992).

This lack of data on the African continent was one of the motivations for the EXPRESSO program (see overview in Delmas et al. (1999)). The work described here deals mainly with the first stated EXPRESSO goal, that is it focuses upon exchanges between the forest canopy and the atmosphere. It should be considered as a preliminary study in an ecosystem never before studied, with much work still needing to be done.

The experimental program was designed to quantify fluxes of a number of carbon species (CO_2, VOCs), water vapor and sensible heat over a range of spatial scales from the individual leaf and branch, up to landscape scales. Several field trips were necessary to characterize the vegetation (e.g., species composition and abundance, leaf area index) in this part of the Central African tropical forest (Klinger et al., 1998). As a result of this preliminary ecological and VOC study, a site characteristic of an upland forest ecosystem was chosen at which to erect a 60-m tall walk-up tower to study diurnal and seasonal variations of above canopy fluxes and concentrations.

We report here the diurnal variations of latent and sensible heat fluxes, and of isoprene and CO_2 emissions measured from the tower above the upland forest canopy. The seasonal effect is presented comparing the flux values for two experiments conducted in March and November–December 1996. Climbing gear was used to gain access to the canopy of an adjacent *Gilbertiodendron dewevrei* (*Gilbert. dew.- Caesalpiniaceae* family) monodominant stand typical of lowland Central African forest. Isoprene emissions at the leaf level from a variety of species and effects of varying light and temperature on isoprene emissions were studied using a temperature- and radiation-controlled leaf cuvette on species present in both lowland and upland forest sites.

Isoprene emission data were incorporated into an isoprene emission model and canopy level fluxes were used to constrain that model in order to estimate hourly emissions on a spatial scale of about 1 km^2 (Guenther et al., 1999).

2. Experimental domain and design

The EXPRESSO domain is described in Delmas et al. (1999), so we only give here a brief site

description with some additional information on the experimental design.

The EXPRESSO region we investigated is dominated by tropical upland or lowland evergreen forest, and swamp forest, depending on drainage. The measurement site (2°12.394′N, 16°23.514′E, elevation 351 m) is located in the Nouabalé-Ndoki National Park (NNNP), a 400,000 ha preserved area in Northern Congo. Rainfall averages $\sim$1600–1700 mm yr^{-1}, with maximum precipitation in October (240 mm $month^{-1}$) and a secondary maximum between March and May (170 mm $month^{-1}$) (Fontan et al., 1992). The dry season extends from December to February with rainfall averaging 80 mm $month^{-1}$, with a secondary minimum in July (65 mm). The mean annual temperature is 25.6°C with monthly minimum in July (24.8°C), and maximum between March and May (26.6°C). The first field experiment (16–24 March 1996) took place at the beginning of the wet season and the second experiment (21 November–11 December 1996) occurred at the end of the wet season.

Forests in the region are generally characterized as evergreen or semi-evergreen, although some trees are deciduous (Hamilton, 1989). This site is representative of much of the Central African rainforest biome with a mosaic of mixed-species forests (containing $\sim$175–200 species ha^{-1}) and extensive monodominant forests (formed by members of the family *Caesalpiniaceae* such as *Gilbert. dew.*) (Moutsamboté et al., 1994).

The 60-m walkup tower was erected within a mixed forest. A summary of the installed equipment and of the measured parameters is presented in Table 1. Meteorological data were acquired at either 2Hz (CR10 Campbell Scientific datalogger, 57 m AGL), referred to here as slow data, or at 10 Hz, referred to here as fast data (Sonic anemometer, Applied technology, 52m AGL).

Vegetation transects (100 · 10m) were located along the eight cardinal directions from the tower. Another 260-m transect was located in the nearby *Gilbert. dew.* monodominant stand. In each plot, trees were identified as living individuals >4 cm diameter at breast height (DBH) and >1.5 m tall. Tree layer leaf area index (LAI; m^2 leaf m^{-2} ground) and understory layer LAI were also recorded for each plot. Specific leaf density (g m^{-2}) was determined for all dominant tree species from

Table 1. *Detailed list of measurements made and equipment used during the two field campaigns*

Study	Measurements and equipment used
Above canopy chemical constituents	VOCs: Isoprene and other VOCs – mixing ratios: cartridges sampling GC/MS analysis in lab (HP5860/HP5972); in-situ GC measurements (detector: RGD-2, trace analytical) – fluxes: isoprene (relaxed eddy accumulation) CO_2 fluxes (eddy correlation, LICOR 6262) H_2O fluxes (eddy correlation, LICOR 6262)
Above canopy physical environment	Energy fluxes: – net radiation (REBS Q6 sensor) – latent heat (LICOR 6262) – sensible heat (Vaisala HPM35C) – PAR (LICOR 190SA) Winds – 3-D turbulence direction (Applied technology SWS/3K) – mean wind speed and direction (05305-5 R. M. Young) relative humidity (Vaisala HPM35C) precipitation: tipping bucket rain gauge (Texas electronics)
Foliar gas exchange (CO_2, H_2O, isoprene)	Leaf and branch isoprene emission rates (Campbell MPH-1000; LICOR 6400) – influence of PAR and temperature on isoprene – measurements on sun and shade leaves transpiration and photosynthesis measurements in cuvette (LICOR 6400)

leaf area and leaf dry weight measurements. Mean dry weight for all species is 63.9 g m^{-2} (SD = 27.0). Canopy foliar density was estimated from LAI and specific leaf density measurements. Overstory leaf biomass was determined using the methodology reported in Helmig et al. (1999) which is based on LAI, DBH and specific leaf density.

Common species in several important ecosystem types were qualitatively screened for hydrocarbon emissions using a hand-held photoionization detector (PID) which is sensitive to a wide range of VOCs. Species were sampled for isoprene and stored VOCs using the technique described in Klinger et al. (1998). About 20% of the species were sampled more than once in order to test the accuracy of the PID technique. Repeated measurements agreed $90 \pm 5\%$ of the time in categorizing isoprene emission rates for a given species as high (H; >16 μgC m^{-2} h^{-1}), low (L; >0.8 and <16 μgC m^{-2} h^{-1}), or none (N; <0.8 μgC m^{-2} h^{-1}). Comparison of the PID and GC results indicates that the PID technique correctly identified 96% of the isoprene emitters (H and L) and 94% of the non-emitters (N). The PID technique was able to distinguish high from low isoprene emitters 80% of the time, and high from non-emitters species in all the case. In addition, cartridge samples were collected from branch enclosures for 32 species, identified by the PID as VOC emitters, and analyzed later by GC-MS in the NCAR laboratory.

Carbon dioxide and sensible and latent heat (water vapor) fluxes were calculated for 30-min periods using the eddy covariance method (Lenschow, 1995). Isoprene fluxes were measured using the relaxed eddy accumulation (REA) technique (Businger and Oncley, 1990; Pattey et al., 1993, Bowling et al, 1998; Fuentes et al, 2000). This technique involves sampling air into updraft and downdraft reservoirs at constant flow rate, based on the sign of the vertical wind speed w. The flux is then proportional to the vertical wind speed standard deviation and to the difference in concentrations between the two reservoirs. Estimates of the total uncertainty associated with eddy flux systems is typically determined by comparison with other systems. The flux systems used for this study were compared to a CO_2 flux system used for long term measurements at a site near Oak Ridge, TN, USA. The eddy covariance system was within $\pm 5\%$, and the REA within $\pm 13\%$ of the reference system (Guenther et al., 1996). Terrain near the tower is quite flat and fetch conditions can be assumed to be similar for all wind directions.

A system for measuring isoprene fluxes from leaves under controlled environmental conditions was established at the tower base. Incoming air, scrubbed of hydrocarbons by activated charcoal, was pumped through a mass flow controller to a temperature-controlled leaf cuvette (Campbell MPH-1000) maintained at 30°C. Air exiting the cuvette was injected into an isothermal gas chromatograph equipped with a mercuric oxide reduction gas detector with a detection limit of approximately 300 pptv for isoprene (Greenberg et al., 1995). For typical amount of leaf in the cuvette and flow rate, this would represent a detection limit and a accuracy for isoprene emission rate of approximately 0.3 μgC g^{-1} h^{-1}. Measurements were duplicated at least once on each species, and from 3 to 5 times on high isoprene emitters. In addition, 500 sccm of air exiting the cuvette was collected onto solid adsorbent cartridges for subsequent analysis (details in Greenberg et al., 1999). The measurements were calibrated hourly with respect to secondary standards (1.5, 20, and 50 ppb isoprene in nitrogen). Guenther et al. (1999) used an isoprene emission model to compare the enclosure and REA measurements and report very good agreement between these two independent measurement methods.

We collected ambient air samples from the tower (adsorbent cartridges and stainless steel canisters) to characterize the composition of forest air and the abundance of biogenic VOCs and oxidation products. Both canister and cartridge storage techniques had been previously characterized for atmospheric VOCs in general and biogenic VOCs in particular (Greenberg et al., 1999). Precision of repeated measurements on canisters presented here is approximately 2%.

Average above-canopy environmental conditions (temperature, direct and diffuse photosynthetically active radiation (PAR), wind speed and humidity) were also estimated from the NCEP/NCAR reanalysis of NCEP global model data. Note that NCEP data are given four times a day, so that we had to extrapolate to give every 2 h evolution of the parameters.

3. Results

3.1. Ecological data

In the process of investigating potential ground research sites in 1994 and 1995, a considerable amount of preliminary ecological information was collected (Klinger et al., 1998). At the tower site, the mature mixed forest was approximately 40–45 m tall, with 50-m emergent trees. Figs. 1a, b show the approximate tree height and DBH distributions of the 1300 trees sampled in the eight radial belt transects. Almost 78% of the trees are present in the sub-canopy (tree height below 15 m, DBH between 4 and 12 cm). A total of 173 species (48 in the canopy, and 125 in the sub-canopy) were characterized. The LAI of this mixed forest stand in March 1996 was about 6.25 with a tree cover of 100% (Klinger et al., 1998). Approximately 800 m east of the tower, near the Ndoki River, is an extensive monodominant forest of *Gilbert. dew.*, an isoprene emitter. The LAI of the entire monodominant forest is approximately 7.0, with 85% of the leaf area index comprised of *Gilbert. dew.* assuming that stem basal area roughly equates to LAI contribution.

3.2. Meteorological data

Mean diurnal variations were calculated for all the meteorological data acquired during both experiments. Due to instrument failure, we obtained a very limited amount of PAR data during the November experiment and so we present here PAR estimates from the NCEP model. Figs. 2a–c show variations for temperature (T), and for total and diffuse PAR. The maximum temperature was higher during the March campaign (33°C) than in November (30.5°C). The

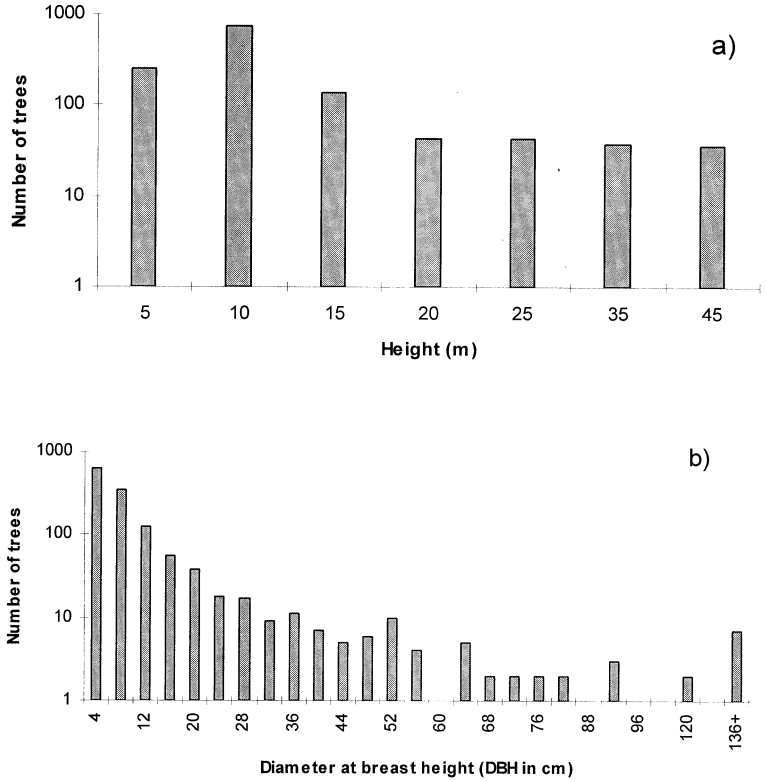

Fig. 1. (a) Height class distribution of mixed-forest trees in the eight 10 × 100 m transects radiating from the tower; note the logarithmic *Y* axis. (b) Diameter at breast height distribution of mixed-forest trees in the eight 10 × 100 m transects radiating from the tower; note the logarithmic *Y* axis.

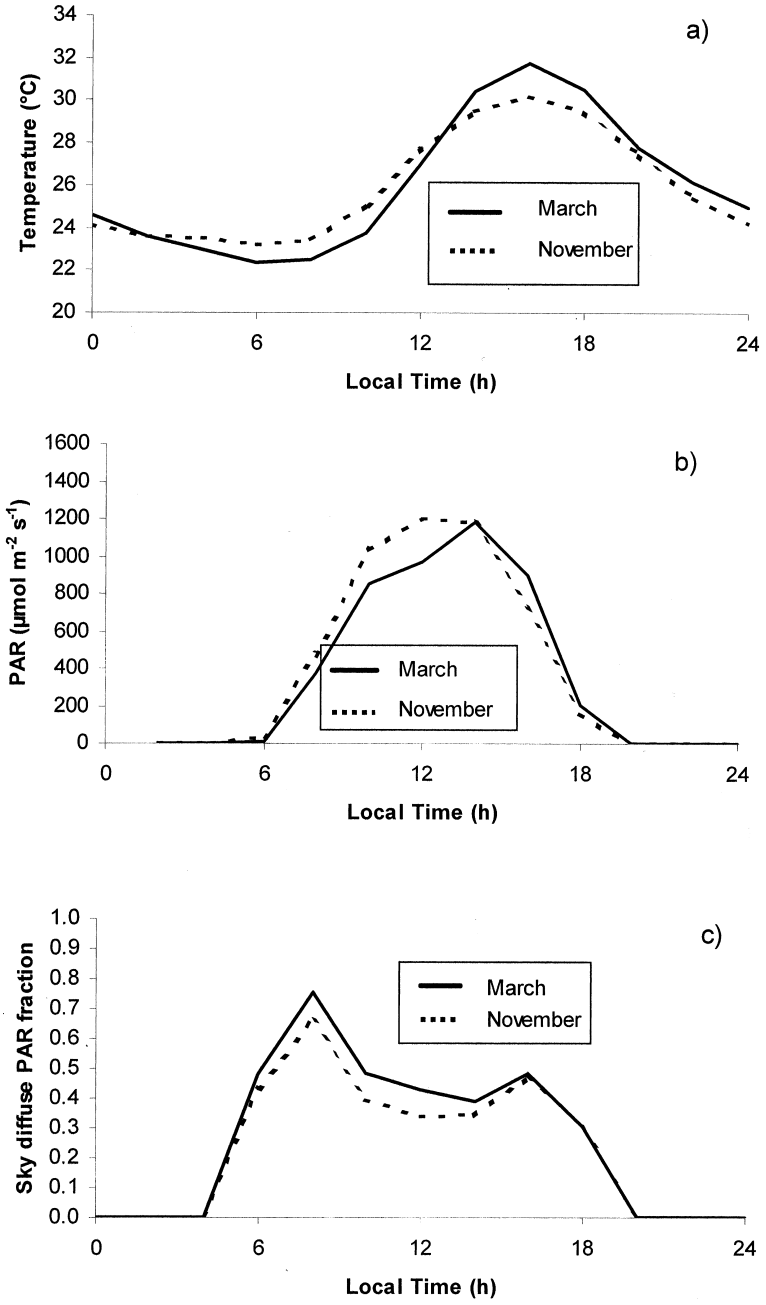

Fig. 2. (a) Measured ambient temperature mean diurnal variation. (b) Direct photosynthetically active radiation (PAR) mean diurnal variation (estimated by NCEP model). (c) Sky diffuse photosynthetically active radiation (PAR) mean diurnal variation (estimated by NCEP model).

March temperatures, however, are lower before noon, and the mean temperature calculated over the entire day for the two measurement periods is almost identical (26.2 versus 26.1°C). Mean values of total and diffuse PAR fluxes at solar noon were 994 μmol $m^{-2} s^{-1}$ and 695 μmol $m^{-2} s^{-1}$ during the March experiment, and 1240 and 600 μmol $m^{-2} s^{-1}$ during the November trip. Data analysis of NOAA-AVHRR satellite images (Ceccato, personal communication) shows greater cloud coverage during March than during November, which corroborates the PAR data. Relative humidity (not shown here) varied between about 60 and 95%, with minimum values (between 1 p.m. and 5 p.m.) 4% lower in March (58%) than in November (62%).

3.3. *VOC ambient concentrations*

We present here the results from 13 pairs of canisters filled from the REA bags in March, and from 16 pairs of isoprene concentrations in bags in November. Samples were analyzed for those light hydrocarbons (up to benzene) with mixing ratios greater than 20 pptv. As seen in most forested ecosystems, isoprene was by far the dominant biogenic constituent of ambient air. This was particularly true in March with a mean isoprene concentration between 10 a.m. and 2 p.m. of 1820 pptv (SD = 870 pptv, 10 pairs). This is lower than published data for Amazon forests (Zimmerman et al., 1988; Rasmussen and Khalil, 1988) showing maximum concentrations up to 7 ppbv at noon, but the diurnal pattern with maximum mixing ratios at midday is consistent. Concentrations in November were even lower, with mean isoprene concentration (10 a.m.–2 p.m.) of 730 pptv (SD = 480 pptv, 13 pairs). Monoterpenes were present in extremely low concentrations, mostly below 20 pptv, much lower than those (30–130 pptv) reported in the Amazon basin (Zimmerman et al., 1988).

Benzene, propene and propane, three combustion products, were present in the March samples in concentrations ranging from 100 pptv to about 1 ppbv, with no diurnal pattern as for isoprene. In the Amazon, Zimmerman et al. (1988) report similar propane concentrations, lower benzene concentrations (80 pptv), and no propene detected. The presence of biomass combustion products is consistent with the presence of fires detected north of the site (Gregoire and Pinnock, 1999) and air mass trajectories (Roberts, personal communication). The other compounds detected (iso-butane, iso-pentane, and n-pentane) were in the range of 20 to 260 pptv, with mean values of about 90, 50, and 60 pptv, respectively. This is of the same order of magnitude (50–100 pptv) as mean data reported by Zimmerman et al. (1988). These concentrations can be compared to aircraft observations (Greenberg et al., 1999) of lower values of alpha-pinene around 90 pptv and 25 pptv over forest and savanna environments, respectively. Concentrations of beta-pinene measured from the tower represented about 30% of all the monoterpenes, or less than 10 pptv.

3.4. *Emission data*

A number of plant species in the tower footprint and in the lowland monodominant stand were screened for VOC emissions (Table 2) in the normalized condition of temperature (30°C) and PAR (1000 μmol $m^{-2} s^{-1}$). Note that the tower footprint for a trace gas represents the area from which 90% of its flux comes from. As estimated from a model based on the work of Horst and Weil (1994), the tower footprint was within 600 m of the tower. 28 species from the eight transects in the mixed forest, and 4 other species occurring in the monodominant stand were sampled. Note that *Gilbert. dew.* occur in both forest types. Of the 28 species from the mixed forest, only 3 (*Anthonotha macrophylla*, *Gilbert. dew.* and *Klainedoxa gabonensis*) were found to be high isoprene emitters (emission rate >16 μgC $g^{-1} h^{-1}$). In the monodominant stand 2 species (*Gilbert. dew.* and *Berlinia grandifolia*) had high emission rates (45 and 62 μgC $g^{-1} h^{-1}$, respectively) for the same conditions of temperature and PAR. Thus, of the species measured, there are only 4 species with significant isoprene. The mean emission rate for these 4 species is 57 μgC $g^{-1} h^{-1}$ a value somewhat lower than previously sampled species in Africa (Guenther et al., 1996), and lower than the average emission rate (mean of about 70 μgC $g^{-1} h^{-1}$) determined on North American genera (Guenther et al., 1994). One should note that because branches were generally growing in deep shade and were cut for analysis, emission rates presented here probably represent substan-

Table 2. *Isoprene emission rates for the 32 species sampled with environmentally controlled cuvettes in the mixed forest and the monodominant stand; plants with emissions rates between the detection limit (0.3 pgC g^{-1} h^{-1}) and 0.8 pgC g^{-1} h^{-1} are considered non-emitters*

Species	Mixed forest	Isoprene system (μgC g^{-1} h^{-1})		Non, low or high emitters (N, L or H)
Aframomum latifolia		not detected	Campbell	N
Afrostyrax lepidophyllus	X	not detected	Campbell	N
Albizzia ferruginea	X	not detected	Campbell	N
Alchornea cordifolia		0.4	Campbell	N
Allophyllus africanus	X	not detected	Campbell	N
Amphimas pterocarpoides	X	not detected	Campbell	N
Anthonotha macrophylla	X	60	Campbell	H
Berlinia grandifolia		62	Campbell	H
Caloncoba welwitschii	X	not detected	LICOR	N
Celtis mildbraedii	X	not detected	Campbell	N
Chytranthus spp.	X	1.0	Campbell	L
Coelocaryon prenssii	X	not detected	Campbell	N
Dialium pachyphyllum	X	not detected	Campbell	N
Drypetes chevalieri	X	9	Campbell	L
Entadrophragma candollei	X	not detected	Campbell	N
Erythrophleum ivorense	X	not detected	Campbell	N
Fagara macrophylla	X	not detected	Campbell	N
Gilbertiodendron dewevrei	X	45	LICOR	H
Irvingia gabonensis	X	7	Campbell	L
Klainedoxa gabonensis	X	60	Campbell	H
Manniophyton fulvum	X			N
Musanga cecropiodes		not detected	Campbell	N
Palisota ambigua	X	not detected	Campbell	N
Pancovia laurentii	X	0.9	Campbell	L
Pauridiantha dewevrei	X	not detected	Campbell	N
Polyalthia suaveolens	X	not detected	Campbell	N
Rinorea cerasifolia	X	0.5	LICOR	N
Tabernaemontana crassa	X	not detected	LICOR	N
Terminalia superba	X	not detected	Campbell	N
Thomandersia laurifolia	X	not detected	Campbell	N
Trichilia gilgiana	X	not detected	Campbell	N
Xylopia hypolampra	X	not detected	Campbell	N

tial underestimates of the emission capacities of sun-lit upper canopy foliage for these species. This possible underestimation of emission rates is considered in the regional emission model estimates described by Guenther et al. (1999). Although we sampled less than 20% of the tree species (28 species sampled versus 173 identified) found in the footprint of the tower, it appears that significant isoprene emission is confined to a small percentage of species, consistent with qualitative data collected with the PID (see Subsection 3.4.3). This is also consistent with the isoprene flux measurements from the tower (Subsection 3.5.3), which suggest that a relatively small proportion of leaf biomass within the tower footprint emitted isoprene in significant amounts.

From the cartridges obtained from leaf enclosures, and based on the sub-sample of the flora investigated, it appears that significant monoterpene emissions are uncommon among trees of the Congo Basin, only appearing in a single species, *Musanga cecropioides*. It is interesting to mention that this tree appears after disturbance in clearings, along logging roads and in secondary forest. The very low percentage of monoterpene emitting species is consistent with the very low monoterpene concentrations measured in ambient air samples.

3.4.1. Influence of leaf temperature and PAR. The effects on isoprene emission of varying leaf temperature and PAR were determined for a single species, *Anthonotha macrophylla* (Figs. 3a, b). The responses were similar to the light and temperature dependencies established for several temperate species. With PAR held constant at 1000 μmol $m^{-2} s^{-1}$, temperature was varied between 20 and 40°C, which is roughly the range of temperature experienced by leaves during the day. Each individual measurement was made after a period of 25–30 min (between 20°C and 37.5°C) and 10–20 min (40°C measurements) for temperature equilibrium in the cuvette. Isoprene emissions generally increase exponentially with temperature up to approximately 35°C, reach an optimum near 40°C, and then decline at higher temperatures. This is shown in Fig. 3a by the dashed line, which depicts the temperature algorithm of Guenther et al. (1993). Isoprene emissions of *Anthonotha* increased by a factor of 3.5 between 20 and 30°C, but only by a factor of 2.5 between 30 and 40°C. This evolution conformed closely to the Guenther et al. (1993) model up to 35°C. Then the modeled evolution of the isoprene emission declines and tends to slightly underestimate the experimental data. This can be partially due to the difference of equilibration time between experimental (10–20 min) and modeled emissions (30 min). It has been observed that isoprene emission at high temperature (>35°C) declined over time in the cuvette with emission measured after 20 min 10% lower than emission measured after 10 min. Note that some temperate plants such as *sweetgum* (*Liquidambar styraciflua*) (Harley et al., 1996) exhibit temperature optimum above 40°C like observed here with *Anthonotha.*

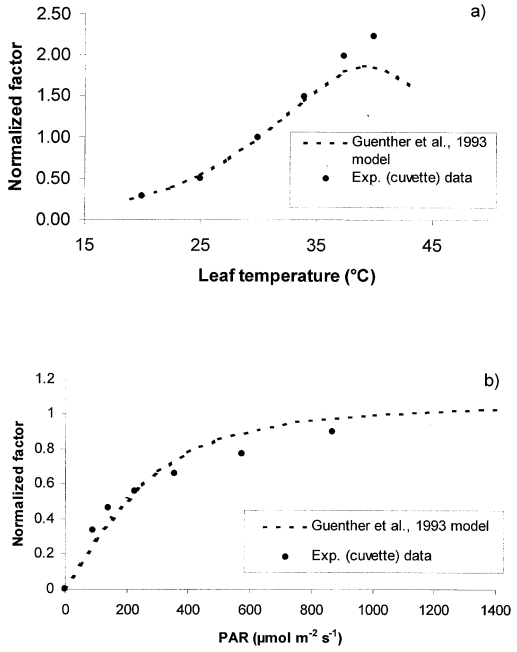

Fig. 3. (a) Influence of leaf temperature on isoprene emission from *Anthonotha macrophylla.* Normalized isoprene emission is the ratio of the factor for a given temperature and PAR to the factor at $T = 30°C$ and PAR = 1000 μmol $m^{-2} s^{-1}$. Dash line is obtained from the model developed in Guenther et al. (1993) and cuvette experimental data are represented by circles. (b) Influence of PAR on isoprene emission from Anthonotha macrophylla. Normalized factor is the ratio of the factor for a given temperature and PAR to the factor at $T = 30°C$ and PAR = 1000 μmol $m^{-2} s^{-1}$. Dash line is obtained from the model developed in Guenther et al. (1993). Solid line is obtained from the model developed in Guenther et al. (1993) and cuvette experimental data are represented by circles.

With temperature held constant at 30°C, we increased PAR from 0 to 1500 μmol $m^{-2} s^{-1}$, the maximum value reached during the March experiment. The emission rate increases almost linearly between 0–250 μmol $m^{-2} s^{-1}$. Then, the rate of increase slows and emission levels off at PAR values above about 900 μmol $m^{-2} s^{-1}$. In general, the light dependency for Anthonotha conforms to the light algorithm of the Guenther et al. (1993) model (dashed line in Fig. 3b).

3.4.2. Comparison of mixed forest and monodominant stand. Based on the PID work, isoprene emission capacity values (high, low, or no emission; see definition Subsection 2.1) were assigned to the canopy and sub-canopy species (Table 3). Although we determined the emission capacity for only about 61% of the forest tree species, this represents 82% of the total leaf area index. We therefore conclude that the mixed forest is well characterized in terms of biomass. The breakdown in terms of percentage of total LAI is 75% of non-emitting species and 7% of low or high emission capacity. In the monodominant stand, about 85% of the leaf area index is comprised of *Gilbert. dew.*, which is a high isoprene emitter with a normalized sun-leaf emission rate of 45 μgC $g^{-1} h^{-1}$. As for comparison, results from the Duke temperate

Table 3. *Qualitative isoprene emission capacities and corresponding Leaf Area Index (LAI) for the species characterized in the sub-canopy and canopy of mixed forest (PID work)*

	No. of species characterized	Leaf area index (LAI) $cm^2\ m^{-2}$	% of the total number of species characterized	% of the total LAI
		sub-canopy (0–15m)		
isoprene emitters (H, L)	13	34	10	8
non-emitters (N)	56	312	45	77
total determined (H, L, N)	69	346	55	85
undetermined (U)	56	60	45	15
total (H, L, N, U)	125	406	100	100
		canopy (>15m)		
isoprene emitters (H, L)	4	15	8	4
non-emitters (N)	33	253	69	72
total determined (H, L, N)	37	268	77	76
undetermined (U)	11	84	23	24
total (H, L, N, U)	48	352	100	100
		canopy + sub-canopy		
isoprene emitters (H, L)	17	49	10	7
non-emitters (N)	89	565	51	75
total measured (H, L, N)	106	614	61	82
undetermined (U)	67	144	39	18
total (H, L, N, U)	173	758	100	100

forest are given. With a tree cover of 100%, a slightly smaller LAI (5.2 versus 7.0), and a normalized sun-leaf emission rate of about 37 μgC $g^{-1}\ h^{-1}$ for the whole canopy (Geron et al., 1996), Duke Forest presents great similarity with the Ndoki *Gilbert. dew.* forest. With temperature and PAR conditions close to the ones experienced during the March and the November experiments, Geron et al. (1996) found canopy level emissions in the order of 10 mgC $m^{-2}\ h^{-1}$ at midday (10 a.m.–2 p.m.). As a result, one can expect the monodominant stand to show much higher emission at the canopy scale than the mixed forest. Isoprene emission across the landscape, then, is likely to be quite heterogeneous, with hot spots over the monodominant forest stands.

3.5. *Flux data — seasonal effect*

3.5.1. Latent and sensible heat fluxes. The surface energy budget is given by:

$$R_n = H + L_E + S$$

where R_n is net radiation, H the sensible heat flux, L_E the latent heat (evaporation) flux, and S the storage flux in vegetation and ground (soil heat flux, canopy heat storage, and photosynthetic energy flux), all expressed in W m^{-2}. The storage flux was not measured, and is calculated as a residual term ($R_n - H - L_E$); as such, it includes errors made measuring the parameters to calculate the terms H and L_E.

Mean diurnal variations of L_E and H were calculated for the two experimental periods (Figs. 4a, b). Fluxes show a diurnal cycle with maximum values around noon. This is expected because both heat and evaporation increase with increasing available net radiation. The mean net radiation (between 10 a.m. and 2 p.m.) is 25% higher in March than in November. The distribution of sensible and latent heat flux is quite different for the two campaigns. Sensible heat flux reaches about 200 W m^{-2} in March and about 150 W m^{-2} in November. In contrast, midday (10 a.m.–2 p.m.) latent heat maximum flux is lower in March (about 200 W m^{-2}) than in November (about 300 W m^{-2}). This indicates that evaporation is stronger in November, while surface heating is enhanced in March. Note that the residual term relative to net radiation (S/Rn) is only 9% of the total in November, whereas it reaches 32% in March. The storage part of the residual term is unlikely to change very much between the two seasons relative to net radiation. Previous studies (Barr et al., 1997, and references therein) in forest

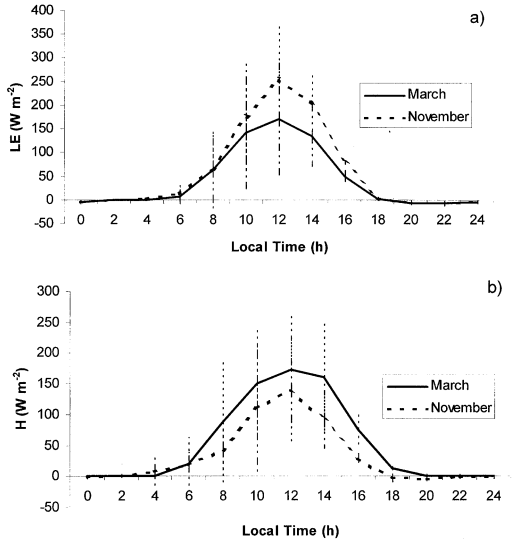

Fig. 4. (a) Comparison of observed latent heat flux mean diurnal variation for March and November. Vertical bars represent ±standard deviation. (b) Comparison of observed sensible heat flux mean diurnal variation for March and November. Vertical bars represent ±standard deviation.

sites estimate the term S/Rn to be between 6 and 17%. Residual terms of 30% were found in a boreal forest study (Oncley et al., 1997) and of 28% from aircraft measurement above the EXPRESSO forest site (Delon et al., 2000). Residual terms obtained in this study are of the same order of magnitude as values reported in the literature, with between one third and one half of the residual term due to H and L_E measurement errors.

Bowen ratio is calculated from the ratio of H over L_E. As expected from variation in H and L_E, this ratio is very different between the two experiments. The midday (10 a.m.–2 p.m.) calculated mean value is close to one (1.04) in March, and drops to half of this value (0.5) in November. Oncley et al. (1997) and Barr et al. (1997) report Bowen ratios between 0.6 and 1.28 in boreal forest. In other words, in March the energy is evenly divided between latent and sensible heat flux. In November, the latent heat flux is twice as large as the sensible heat flux. In this latter case, the surface energy available is first used for evaporation, implying that the forest ecosystem is sufficiently supplied in water.

3.5.2. CO_2 fluxes. Standard diurnal variations (midnight to midnight) of carbon dioxide above-canopy fluxes are given in Fig. 5. Fluxes are close to zero during the night. During the day, fluxes are negative, corresponding to CO_2 uptake by plants. Mean midday flux (10 a.m.–2 p.m.) is equal to -0.28 mgC m^{-2} s^{-1} (SD = 0.20 mgC m^{-2} s^{-1}) in March, and -0.72 mgC m^{-2} s^{-1} (SD = 0.38 mgC m^{-2} s^{-1}) in November, showing a stronger midday uptake during that season. Previous work (Fan et al., 1990; Wofsy et al., 1993; Yamamoto et al., 1996; Malhi et al., 1998) at tropical forested sites show fluxes similar in shape and in intensity to those found in March (-0.12, -0.05 to -0.22, and -0.15 to -0.31 mgC

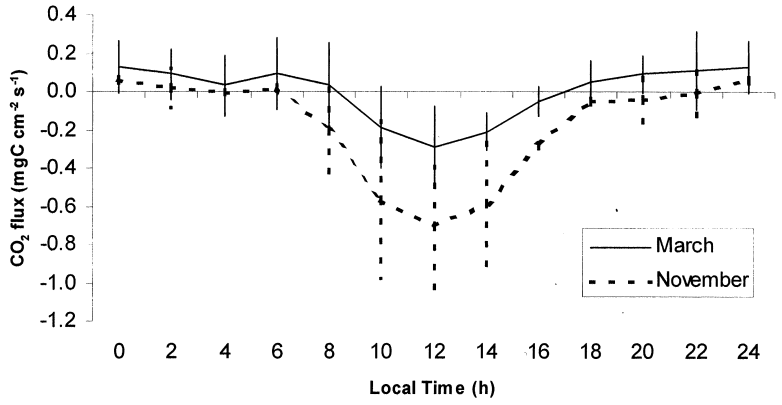

Fig. 5. Comparison of observed CO_2 flux mean diurnal variation for March and November. Vertical bars represent ±standard deviation.

$m^{-2}\,s^{-1}$, respectively) and in November (-0.66 to -0.79 mgC $m^{-2}\,s^{-1}$) for the latter study. Note that we did not measured the nocturnal respired CO_2, nor the within-canopy flux, so that our data are uncorrected for storage. According to Malhi et al. (1998), on average, the nocturnal respired CO_2 is equally partitioned between above-canopy flux and within-canopy storage, though the situation of any particular night ranges from complete storage to complete emission, depending on meteorological conditions. Grace et al. (1996) found large spikes of CO_2 leaving the canopy in the early morning associated with the onset of turbulent conditions following calm nights. Based on Malhi et al. (1998) work, we can reasonably assume a mean storage flux of about -0.21 mgC $m^{-2}\,s^{-1}$ in March and of about -0.54 mgC $m^{-2}\,s^{-1}$ in November. Storage flux is observed between 6 and 10 a.m., with a peak at 8 a.m..

A major part of the CO_2 flux variability is linked to PAR, with lesser roles played by temperature and water availability. Mean temperature was about the same for the 2 experiments, and direct PAR was higher during November. Afternoon relative humidity measurements were slightly higher in November (62%) than in March (58%). The heat fluxes and Bowen ratios suggest that water was likely not a limiting parameter in November, but may have limited photosynthesis to some degree in March. Seasonal changes in diffuse sky conditions may have also been a key parameter in explaining the seasonal CO_2 flux variability. However, the response of canopy carbon uptake to variations in the diffuse character of the sky can be non-linear and thus its direction is specific to the range of diffuse sky conditions observed.

3.5.3. Isoprene fluxes. REA isoprene fluxes were measured a few meters above the canopy. Note that March fluxes were calculated both directly from air sampled in the REA bags, and in the laboratory, from canisters filled from the same REA bags. This latter sampling was made to measure potential emission of all detectable biogenic VOCs. Emissions of biogenic VOCs other than isoprene were detected from the canister analysis, but concentrations were only a few percent of isoprene concentrations; consequently, emission fluxes for other biogenic VOCs were not computed. For both experiments, isoprene fluxes show the diurnal variation observed in the temperate ecosystems, with maximum values measured around noon. Maximum fluxes are about 2.50 mgC $m^{-2}\,h^{-1}$ in March, and around 1.0 mgC $m^{-2}\,h^{-1}$ in November, with mean midday fluxes (10 a.m.–2 p.m.) of 1.40 mgC $m^{-2}\,h^{-1}$ (SD = 1.05; $N = 20$) in March, and 0.46 mgC $m^{-2}\,h^{-1}$ (SD = 0.47; $N = 13$) in November. Since ambient concentrations were also lower in November than in March, it appears that lower isoprene fluxes may be a regional trend and not just associated with the vegetation within the flux footprint. Neither PAR nor temperature could explain seasonal differences, as temperatures were similar and total PAR was higher during November (Subsection 3.2), when isoprene fluxes were less. Note that diurnal variations in isoprene emission predicted by Guenther et al. (1999) are within a factor of 2 or better of the tower-based REA flux measurements presented here.

4. Discussion and conclusion

The lack of data for the African continent has already been emphasized, and as a result, the ecophysiology and biogeochemistry of African tropical forests remain little known. This work has been conducted in order to describe the ecology of the site and, more generally, of the forests of the Congo basin, and to describe trace gases exchanges of these forests with the atmosphere.

First steps were taken towards determination of important parameters for trace gas emission modeling, such as species characterization, VOC emission characteristics and leaf area index. This work allowed us to distinguish two different ecosystem types within the rain forest: the upland mixed forest, and the lowland monodominant *Gilbert. dew.* forest. These forests are very different in terms of species diversity and in terms of isoprene emissions. PID work conducted in parallel with the ecological survey allowed us to characterize the emission capacities of 82% of the biomass in the mixed forest, and of 85% of the biomass in the *Gilbert. dew.* forest (all percentages given in term of LAI). With the controlled-environment cuvettes, we determined that isoprene emitters represent 1% of the species in the mixed forest (mean emission rate of 54 μgC $g^{-1}\,h^{-1}$) and 85% in the monodominant stand (comprised

entirely by *Gilbert. dew.;* emission rate of 45 μgC $g^{-1} h^{-1}$). The cuvette work confirms the PID results, that is that significant isoprene emissions are confined to a small percentage of species in the mixed forest. Three species out of four high isoprene emitters (*Anthonotha macrophylla*, *Berlinia grandiflora*, and *Gilbert. dew.*) are members of the same plant family, *Ceasalpiniaceae*. This family is probably the most important family in the forests of the northern Congo basin, both in terms of number of species and total biomass. *Gilbert. dew.* is of particular interest because as already mentioned it constitutes dense, nearly monospecific stands in lowland sites. As a matter of consequence, the spatial heterogeneity of isoprene emitters will have an influence when integrating the isoprene emission at the regional scale, with the *Gilbert. dew.* forests acting as significant point sources.

Anthropogenic VOC concentrations were comparable to those collected in the Amazon. These compounds are likely related to biomass burning occurring upwind in the Central African Republic savannas at the time of the experiment. Isoprene and monoterpenes concentrations were lower than those previously observed in the Amazon. This is consistent with the observation of lower isoprene emissions at the NNNP upland site than what has been measured in the Amazonian forest, and with the fact that significant monoterpene emissions are uncommon among trees of the Congo Basin, only observed for the *Musanga cecropioides* species, a tree not characteristic of primary forest. Surface layer concentrations are expected to have a larger footprint than the tower flux measurement. Isoprene concentrations in the surface layer above forest canopies with high emission rates are often around 10 ppbv (Zimmerman et al., 1988; Guenther et al., 1996). The much lower surface layer concentrations at this site (daytime means of 0.7 and 1.8 ppbv for November and March, respectively) indicates that lower emissions are probably more widespread than the tower flux measurement footprint.

As we have seen from the tower measurements, CO_2, isoprene and heat fluxes at the landscape scale change with the season. This can be linked to changes in PAR, temperature, leaf biomass and/or phenology, to plant water availability (through stomatal conductance), and to other ecological and physiological parameters. Differences in isoprene emissions between the two seasons are difficult to reconcile with the temperature and PAR data. Isoprene emission depends primarily on these two parameters at the leaf level (Subsection 3.4.1), but it appears that they were not sufficiently different during the two experiments to explain the emission differences at the landscape scale. The fraction of isoprene emitting leaves is only known for the March experiment, so we cannot draw conclusions about the seasonal influence on the emissions, although changes in isoprene emitting biomass are probably insufficient to explain the greater than 3-fold difference in midday isoprene fluxes measured from the tower. Plant water availability can also be a determining parameter. However, strong water stress was not likely to occur during the two experiments since the latent heat flux was always at least equal to the sensible heat flux. Furthermore, the relative greenness index (Ceccato, personal communication), show a slightly moist to moist vegetation for the two seasons.

More data are needed to document and develop a numerical algorithm to describe the seasonal cycle of isoprene emission in tropical landscapes and to assess the potential atmospheric impact of changes in land use. For example, plant water potential measurements during both wet and dry seasons would be necessary to assess definitely the seasonal effect of water availability to plants on the isoprene fluxes. Conversion of primary forest to savanna/secondary forest and subsequent changes (increase in biomass burning, change in the latent/sensible energy partition, change in the precipitation regime) would affect surface fluxes of trace gases (CO_2, VOCs) in the long term at the regional and, possibly, the global scale. For example, intensification of the precipitation or extension of the wet season length could have a positive effect on isoprene emission through the increasing proportion of high isoprene emitting lowland forest versus low isoprene emitting upland forest. Future estimates could be greatly changed if taking into account lowland forest emissions, and the effect played by the seasonal variations and climate changes over these emissions.

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REFERENCES

Barr, A. G., A. K. Betts, R. L. Desjardins and J. I. MacPherson, 1997. Comparison of regional surface fluxes from boundary-layer budgets and aircraft measurements above boreal forest. *J. Geophys. Res.* **102**, 29213–29218.

Bonsang, B., G. Lambert and C. Boissard, 1991. Light hydrocarbon emissions from African savanna burnings. In: *Global biomass burning*, ch. 3 (ed by J. S. Levine). The MIT Press, Cambridge, 155–161.

Bowling, D. R., A. A. Turnipseed, A. C. Delany, D. D. Baldocchi, J. P. Greenberg and R. K. Monson, 1998. The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and other biological trace gases. *Oecologia* **116**, 306–315.

Businger, J. A. and S. P. Oncley, 1990. Flux measurement with conditional sampling. *J. Atmospheric and Oceanic Technology* **7**, 349–352.

Crutzen, P. J. 1973. A discussion of the chemistry of some minor constituents in the stratosphere and the troposphere. *Pure Appl. Geophys.* **106–108**, 1385.

Delmas, R., J. P. Tathy, M. Labat, J. Servant and B. Cros, 1992. Sources and sinks of methane and carbon dioxide exchanges in mountain forest in equatorial Africa. *J. Geophys. Res* **97**, 6169–6179.

Delmas, R., A. Druilhet, B. Cros, P. Durand, C. Delon, J. P. Lacaux, J. M. Brustet, D. Serça, C. Affre, A. Guenther, J. Greenberg, W. Baugh, P. Harley, L. Klinger, P. Ginoux, G. Brasseur, P. Zimmerman, J. M. Gregoire, E. Janodet, A. Tournier, P. Perros, Th. Marrion, A. Gaudichet, H. Cachier, S. Ruellan, P. Masclet, S. Cautenet, D. Poulet, C. Bouka Biona, D. Nganga, J.-P. Tathy, A. Minga, P. Ceccato and C. Chatham, 1999. Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO): An overview. *J. Geophys. Res.* **104**, 30609–30624.

Delon, C., A. Druilhet, R. Delmas and P. Durand, 2000. Dynamic and thermodynamic structure of the lower troposphere above rain forest and wet savanna during the EXPRESSO campaign, *J. Geophys. Res.* **105**, 14823–14840.

Fan, S.-M., S. C. Wofsy, P. S. Bakwin, D. J. Jacob and D. R. Fitzjarrald, 1990. Atmospheric-biosphere exchange of CO_2 and O_3 in the Central Amazon forest. *J. Geophys. Res.* **95**, 16851–16864.

Fishman, J., K. Fakhruzzaman, B. Cros and D. Nganga, 1991. Identification of widespread pollution in the southern hemisphere deduced from satellite analyses. *Science* **252**, 1693–1696.

Fontan, J., A. Druilhet, B. Benech, R. Lyra and B. Cros, 1992. The DECAFE experiments: overview and meteorology. *J. Geophys. Res.* **97**, 6123–6136.

Fuentes, J. D., M. Lerdau, R. Atkinson, D. Baldocchi; J. W. Bottenheim, P. Ciccioli, B. Lamb, C. Geron, L. Gu, A. Guenther, T. D. Sharkey and W. Stockwell, 2000, Biogenic hydrocarbons in the atmospheric boundary layer: a review. *Bull. Am. Met. Soc.* **81**, 1537–1575.

Galbally, I. E. and C. R. Roy, 1978. Loss of fixed nitrogen from soils by nitric oxide exhalation. *Nature* **275**, 734–735.

Geron, C. D., D. Nie, R. R. Arnts, T. D. Sharkey, E. L. Singsaas, P. J. Vanderveer, A. Guenther, J. E. Sickles II and T. E. Kleindienst, 1997. Biogenic isoprene emission: model evaluation in a southeastern United State bottomland deciduous forest. *J. Geophys. Res.* **102**, 18,889–18,901.

Grace, J., J. Lloyd, J. McIntyre, A. C. Miranda, P. Meir, H. S. Miranda, C. Nobre, J. Moncrieff, J. Massheder, Y. Malhi, I. Wright and J. Gash, 1995. Carbon dioxide uptake by an undisturbed tropical rain forest in Southwest Amazonia, 1992 to 1993. *Science* **270**, 778–780.

Greenberg, J. P., B. Lee, D. Helmig and P. Zimmerman, 1995. Fully automated gas chromatograph-flame ionization detector system for the in situ determination of atmospheric non-methane hydrocarbons at low parts per trillion concentration. *J. Chrom. A* **676**, 389–398.

Greenberg, J. P., A. B. Guenther, S. Madronich, W. Baugh, P. Ginoux, A. Druilhet, R. Delmas and C. Delon, 1999. Biogenic volatile organic compound emissions in Central Africa during the Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO) biomass burning season. *J. Geophys. Res* **104**, 30,659–30,672.

Gregoire, J.-M. and S. Pinnock, 1999. Satellite monitoring of vegetation fires for the EXPRESSO: Outline of the activity and relative importance of the study area in the global picture of biomass burning. *J. Geophys. Res.* **104**, 30,691–30,700.

Guenther, A., P. Zimmerman, P. Harley, R. Monson and R. Fall, 1993. Isoprene and monoterpene emission rate variability: model evaluation and sensitivity analysis. *J. Geophys. Res.* **98**, 12609–12617.

Guenther, A., P. Zimmerman and M. Wildermuth, 1994. Natural volatile organic compound emission rate estimate for U. S. woodland landscapes. *Atmos. Environ.* **28**, 1197–1210.

Guenther, A., C. Hewitt, D. Erickson, R. Fall, C. Geron,

T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor and P. Zimmerman, 1995. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* **100**, 8873–8892.

Guenther, A., L. Otter, P. Zimmerman, J. Greenberg, R. Scholes and M. Scholes, 1996. Biogenic hydrocarbon emission from southern African savannas. *J. Geophys. Res.* **101**, 25859–25865.

Guenther, A., J. Greenberg, L. Klinger, D. Serça, G. Brasseur, P. Harley and L. Vierling, 1999. Isoprene emission estimates and uncertainties for the Central African EXPRESSO study domain. *J. Geophys. Res* **104**, 30,625–30,640.

Hamilton, A. C. African forest. In: *Ecosystems of the World*, vol. 14B, *Tropical rain forest ecosystems*, edited by H. Leith and M. J. A. Werger, pp.155–182. Elsevier, New York, 1989.

Harley, P., A. Guenther and P. Zimmerman, 1996. Effects of light, temperature and canopy position on net photosynthesis and isoprene emission from *sweetgum* (*Liquidambar styraciflua*) leaves. *Tree Physiology* **16**, 25–32.

Helmig, D., L. F. Klinger, A. Guenther, L. Vierling, C. Geron and P. Zimmerman, 1999. Biogenic volatile organic compound emissions (BVOCs) II. Landscape flux potentials from three continental sites in the US. *Chemosphere* **38**, 2189–2204.

Horst, T. W. and J. C. Weil, 1994. How far is far enough?: The fetch requirements for micrometeorological measurement of surface fluxes. *J. Atmos. Oceanic Technol.* **11**, 1018–1025.

Jacob, D. J. and S. C. Wofsy, 1988. Photochemistry of biogenic emissions over the Amazon forest. *J. Geophys. Res.* **93**, 1477–1486.

Klinger, L. F., J. Greenberg, A. Guenther, G. Tyndall, P. Zimmerman, M. M'Bangui, J.-M. Moutsamboté and D. Kenfack, 1998. Patterns in volatile organic compound emissions along a savanna-rainforest gradient in central Africa. *J. Geophys. Res.* **103**, 1443–1454.

Lenschow, D. H. 1995. Micrometeorological techniques for measuring biosphere-atmosphere trace gas exchange. In: *Biogenic trace gases: measuring emissions from soil and water* (ed. by P. A. Matson and R. C. Harriss). Blackwell Science, Oxford, pp. 126–163.

Malhi, Y., A. D. Nobre, J. Grace, B. Kruijt, M. G. P. Pereira, A. Culf and S. Scott, 1998. Carbon dioxide transfer over a Central Amazonian rain forest. *J. Geophys. Res.* **103**, 31,593–31,612.

Moutsamboté, J.-M., Yumoto, T., Mitani, M., Nishihara, T, Suzuki, S. and Kuroda, S. 1994. Vegetation and list of plant species identified in the Nouabalé-Ndoki forest, Congo. *Tropics* **3**, 277–293.

Oncley, S. P., D. H. Lenschow and T. L. Campos, 1997. Regional scale surface flux observations across the boreal forest during BOREAS. *J. Geophys. Res.* **102**, 29,147–29,154.

Pattey, E., R. L. Desjardins and P. Rochette, 1993. Accuracy of the relaxed eddy-accumulation technique, evaluated using CO_2 flux measurements. *Bound. Layer Met.* **66**, 341–355.

Rasmussen, R. A. and M. A. K. Khalil, 1988. Isoprene over the Amazon Basin. *J. Geophys. Res.* **93**, 1417–1421.

Rodin, L. Y., N. I. Basilevitch and N. N. Rozov, 1975. Production of the World's main ecosystems. In: *Productivity of the world ecosystems.* National Academy of science, Washington, DC.

Rudolph, J., A. Khedim and B. Bonsang, 1992. Light hydrocarbons in the tropospheric boundary layer over tropical Africa/. *J. Geophys. Res.* **97**, 6181–6186.

Serça, D., R. Delmas, X. Le Roux, D. A.B. Parsons, M. C. Scholes, L. Abbadie, R. Lensi, O. Ronce and L. Labroue, 1998. Comparison of nitrogen monoxide emissions from several African tropical ecosystems and influence of season and fire. *Global Biogeochemical Cycles* **12**, 637–651.

Wofsy, S. C., M. L. Goulden, J. W. Munger, S.-M. Fan, P. S. Bakwin, B. C. Daube, S. L. Bassow and F. A. Bazzaz, 1993. Net exchange of CO_2 in a mid-latitude forest. *Science* **260**, 1314–1317.

Yamamoto, S., H. Kondo, M. Gamo, S. Murayama, N. Kaneyasu and M. Hayashi, 1996. Airplane measurements of carbon dioxide distribution on Iriomote Island in Japan. *Atmos. Environ.* **30**, 1091–1097.

Zimmerman, P. R., J. P. Greenberg and C. E. Westberg, 1988. Measurements of atmospheric hydrocarbons and biogenic emissions fluxes in the Amazon boundary layer. *J. Geophys. Res.* **93**, 1407–1416.