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Biogenic VOC emissions from forested Amazonian landscapes

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Abstract

A tethered balloon-sampling platform was used to study biogenic volatile organic compounds (BVOCs) in the atmospheric boundary layer in three distinct moist tropical forest ecoregions, as well as an extensive pasture area, in Amazonia. Approximately 24–40 soundings, including as many as four VOC samples collected simultaneously at various altitudes, were made at each site. Concentrations in the mixed layer increased during morning hours and were relatively constant midday through afternoon. Since most important meteorological and chemical parameters were very similar among the sites during the measurement periods, a BVOC canopy emission model was used with a model of the chemistry of the boundary layer to reproduce the atmospheric concentrations observed. The simulations indicated significantly different midday landscape isoprene and α-pinene emission rates for the three forest ecoregions (2200, 5300, 9800 $\mu g\, m^{-2}\, h^{-1}$ isoprene and 90, 120, and 180 $\mu g\, m^{-2}\, h^{-1}$ α-pinene for the three moist forest ecoregions studied, respectively). The differences in emissions among the ecoregions may be attributed to the species composition, which were markedly different and in which the percentage of isoprene and terpene emitting species also differed significantly.

Keywords: Amazonia, biogenic emissions, isoprene, terpenes, tethered balloon, tropical forest

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Introduction

Biogenic volatile organic compound (BVOC) emissions from vegetation comprise over 90% of the organic compounds (excluding CH_4) emitted into the global atmosphere annually (Guenther *et al.*, 1995). The largest source regions of BVOC emissions are assumed to be tropical forests, especially the Amazon forest. The Amazon tropical forest is, however, not one uniform landscape. Variations in the vegetation cover of the Amazon rain forest have resulted from differences in climate, history, and geology. BVOC emissions are species specific and, therefore, may vary with landscape species composition; they also should vary with environmental factors and season.

BVOCs are especially important in the chemistry of the atmosphere. They are responsible for photochemical production of O_3 and other atmospheric oxidants (Fehsenfeld *et al.*, 1992) and transport of nitrogen (Singh *et al.*, 1992); they also may be important in the landscape carbon cycle (Greenberg *et al.*, 2003). Consequently, considerable effort has been made to include BVOCs in atmospheric chemistry and transport models (CTMs) to describe present and future atmospheric chemistry and climate (Jacob *et al.*, 1993; Houweling *et al.*, 1998; Kanakidou & Crutzen, 1999; Granier *et al.*, 2000; Collins *et al.*, 2002; Derognat *et al.*, 2003). Significant changes in modeled concentrations and distributions of important atmospheric trace gases, such as O_3, result from changes in emissions of BVOCs used as inputs in atmospheric models (Guenther *et al.*, 1999).

Attempts have been made to define regional and global BVOC emission databases (Lamb *et al.*, 1993; Geron *et al.*, 1994; Guenther *et al.*, 1995; Simpson *et al.*,

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1999). Emissions are best described for temperate areas of North America and Europe, where most experimental studies have taken place and where species diversity is more limited. Few studies have been made in the tropics and subtropics, where the variety of ecoregions, species diversity, inaccessibility, etc., have limited the number of investigations (e.g., Zimmerman *et al.*, 1988; Guenther *et al.*, 1996; Greenberg *et al.*, 1999a; Kesselmeier *et al.*, 2000). In practice, tropical ecoregions are assigned emission factors based on a few studies (Guenther *et al.*, 1995). As a result, BVOCs emissions in the tropical are likely poorly described in CTMs.

The studies presented here are an attempt to describe BVOC emissions (here limited to isoprene and monoterpenes) in several large tropical broad leaf forest ecoregions of Amazonia. While leaf-level emission measurements are useful in describing the dependence of emissions on environmental factors, high species diversity, inaccessibility of overstory leaves for sampling, and the lack of species distribution data have made difficult the extrapolation of leaf-level measurements to emission estimates. Tower-based concentration or eddy flux measurements may integrate over species diversity, but in a measurement footprint of a few hundred meters. The tower-based measurements are, consequently, difficult to extrapolate to larger regions, where the species distribution may differ.

BVOC emissions were studied as part of the large-scale biosphere–atmosphere interactions in Amazonia (LBA) activities. A tethered balloon platform was used to integrate emission phenomena over landscape variations in species composition, temperature, light, moisture, and other environmental and ecological variables. The atmospheric concentrations and emission estimates derived from this study may be used to characterize landscapes at the resolution of regional and global atmospheric CTMs.

Materials and methods

Site descriptions

The forest areas studied belong to three distinct ecoregions (Fig. 1): the Tapajos forest (Para) in the Tapajos/Xingu moist forest, Balbina (Amazonas) in the Uatuma moist forest, and Jaru (Rondônia) in the Purus/Madeira moist forest (Dinerstein *et al.*, 1995). The ecoregions, defined essentially by the adjacent river watersheds, are relatively intact, since they are largely protected (Fearnside, 2001). In addition, a pasture area adjacent to the Jaru forest was also an experimental site.

The Tapajos forest site (2°51′S, 54°58′W) is approximately 50 km south of Santarém. The region receives about 2000 mm of annual rain; the monthly rainfall extremes are March (375 mm) and October (50 mm). Tethered balloon measurements were made in Tapajos in late January–mid-February 2000. Balbina (1°59′S, 59°12′W) is located approximately 150 km northeast of Manaus. The area has a mean annual precipitation of 2200 mm and average temperature of 27 °C. The wettest months are March and April (300 mm per month), and July, August, and September are the driest (<100 mm per month). Tethered balloon measurements were made in Balbina in March 1998. Two other sites were located in Rondônia: a forest reserve (Rebio Jaru, 10°8′S, 61°54′W) and a pasture (Fazenda Nossa Senhora Aparecida (FNS), 10°46′S, 62°20′W). The mean annual temperature is about 27 °C and varies by less than 4 °C between warmest and coldest months. Central Rondônia gets 1800 mm of rainfall annually, with a wet season from October to April and a dry season from May to September. The Rondônia tethered balloon measurements were made in February 1999.

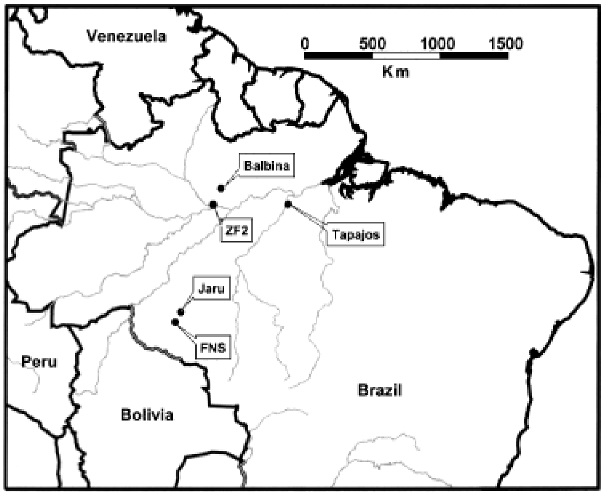

Fig. 1 Locations of the experimental sites of the present study. The numerous Amazonian ecoregions are defined, to a large extent, by the watersheds of major river systems.

Instrumentation

Tethered balloon platform. Details of the tethered balloon platform are given in Greenberg & Guenther (2002). Several balloons, 9–15 m^3 (Blimpworks, Statesville, NC, USA) were used during the different deployments. These were blimp shaped, with rigid steering fins to point balloons into the wind. The static lift of balloons increased with volume and was approximately 3–5 kg. A portable winch (AIR model TS-3AW, Vaisala, Boulder, CO, USA) was run from line AC power or from storage (automobile) battery with a DC/AC power inverter.

Air samplers collected BVOCs onto solid absorbents (Greenberg *et al.*, 1999a, b). The air sampler consisted of a solid absorbent cartridge (preceded by an O_3 trap), a sample pump, flow sensor, and a microcomputer, which monitored flow through the cartridge and maintained the prescribed flow. The samplers also included sensors for pressure, temperature, and relative humidity. The data from all sensors was logged by the microcomputer and downloaded after each sampling period. Packages were designed to attach to the tether line and pivot freely into the wind. Up to four samplers were deployed in individual soundings, usually at 200, 400, 600, and 1000 m above the ground, in order to routinely observe concentrations in and above the mixed layer. Samples were collected at constant flow rate (200 sccm) over a 30 min sampling period, several times longer than the scale of the largest convective eddies in the mixed layer (Lenschow *et al.*, 1980).

Temperature, relative humidity, pressure, wind speed, and wind direction were measured with a commercial meteorological sonde (AIR TS-5A-SP, Vaisala, Boulder, CO, USA) in Tapajos and on the ground in Balbina (Kesselmeier *et al.*, 2000). The meteorological sonde was attached near the base of the balloon. A separate study (Fisch *et al.*, 2002) measured boundary layer meteorology simultaneously with BVOC profiling in Rondônia. Ozone was measured at canopy top by UV absorption (Model 49, UV Photometric Ozone Analyzer, ThermoEnvironmental, Waltham, MA, USA). NO and NO_x were measured at canopy top in Rondônia and Tapajos with a commercial NO/NO_x analyzer (Model 42S, ThermoEnvironmental, Waltham, MA, USA).

After balloon sampling, BVOC cartridges were sealed and stored at −30 °C until analysis (except during transport from Brazil to the NCAR Boulder laboratory, when they were at ambient temperatures for approximately 24 h). All BVOC analyses were made at the NCAR Boulder laboratory. Cartridges were desorbed by a custom thermal desorption system directly into a GC–MS (HP 5890 GC/5972 Mass Selective Detector, Hewlett-Packard, Palo Alto, CA, USA). Details of the analytical procedures have been described previously (Greenberg *et al.*, 1999a, b). Isoprene and terpenes were detected by selected ion monitoring and were quantified with respect to a laboratory prepared standard of isoprene and camphene (approximately 10 ppb each). The mixing ratio of the standard was confirmed by GC–FID analysis.

Quantitative standards were not prepared for individual terpenes, since many, including α-pinene, are unstable and isomerizes in some storage cylinders. However, camphene has excellent storage characteristics. For calibration, we have alternatively established relative response factors of other terpenes to camphene. In our method we quantify terpenes with respect to the abundance of the m/z 93 ion. We compute for individual terpenes the ratio of the abundance m/z 93 to the total ion abundance, using the NIST mass spectrum database (http://webbook,nist.gov/chemistry/#search). We subsequently adjust the concentrations of individual terpenes to account for differences in this ratio with respect to the ratio calculated for camphene. The relative response factors (with respective to camphene) determined for α-pinene (the most abundant terpene observed at all sites), β-pinene, sabinene, and limonene were 1.83, 1.46, 1.80, and 0.56, respectively.

Detection limits for the BVOCs were approximately 1 parts per trillion by volume (ppt). However, ambient concentrations of isoprene were on the order of 1000 ppt; α-pinene concentrations were typically 100–500 ppt. Measurement precision for isoprene at 1000 ppt was approximately 50 ppt; for α-pinene, the precision at 200 ppt was approximately 20 ppt.

Atmospheric chemistry modeling. A zero-dimensional (box) photochemical model, which included a diurnally varying boundary layer, was used to describe biogenic isoprene concentrations in the boundary layer over the forest landscapes (Greenberg *et al.*, 1999a). A chemical mechanism was adapted from the mechanism of Madronich & Calvert (1990). Photolysis rates were calculated for the appropriate time periods of the experiments (Madronich & Flocke, 1998). Time integration of the chemical rate equations was started at midnight and was carried out for 5 days, with results reported (below) from the fifth day.

During the growth of the boundary layer, the rate of entrainment of air was represented as a first order source or sink for chemical species in the boundary layer. Surface emissions and surface deposition velocities were transformed into effective zero-order and first-order rate constants, respectively. O_3, NO and NO_x, temperature, and water vapor, measured either at canopy top or on the balloon platform, were used as chemical input; CH_4, CO and other reactive chemicals were assigned concentrations from a previous and similar model calculation (Jacob & Wofsy, 1988, 1990); while the literature concentrations may differ somewhat from actual concentrations, the influence on the result is not significant, when compared to the influence of isoprene. Convection was incorporated into the model as a convective turbulence velocity and treated similar to entrainment. The percentage of cloud cover was also included for afternoon hours, to allow for cloud effects on photolysis and isoprene emission rates.

Results

All experiments were conducted during the wet season. Mornings were mostly clear to partly cloudy, with clouds increasing in the afternoon. Strong convective storms occurred after mid-afternoon on some days. Balloon soundings were not made during storms or near the time of strong convective activity. Diurnal variations of boundary layer height were measured during the experiments in Rondônia (Fisch *et al.*, 2004) and Tapajos (from tethersonde observation made during balloon air sampling; also D. Fitzjarrald, personal communication). The boundary layer was shown to be approximately 100 m at night, and to grow monotonically between 07:30 and 14:00 hours, and remained about the maximum height until about 17:00 hours, after which a nocturnal boundary layer began to reform (Table 1). The boundary layer growth was not characterized for Balbina, but was assumed to behave similar to that in Tapajos and Rondônia. Minimum and maximum temperature (24–32 °C) and humidity

Table 1 Boundary layer (BL) average minima and maxima (m) observed during the balloon experiments

Site	BL_{min}*	BL_{max}*
Rondônia-Jaru†	124 ± 50	1002 ± 195
Rondônia-FNS†	94 ± 29	927 ± 166
Tapajos	75 ± 25‡	800 ± 100
Balbina	75 ± 25‡	800 ± 100‡

*Boundary layer height, minimum (m) at 08:00 LT; maximum (m) at 17:00 LT.

†Fisch *et al.* (2002).

‡Estimated.

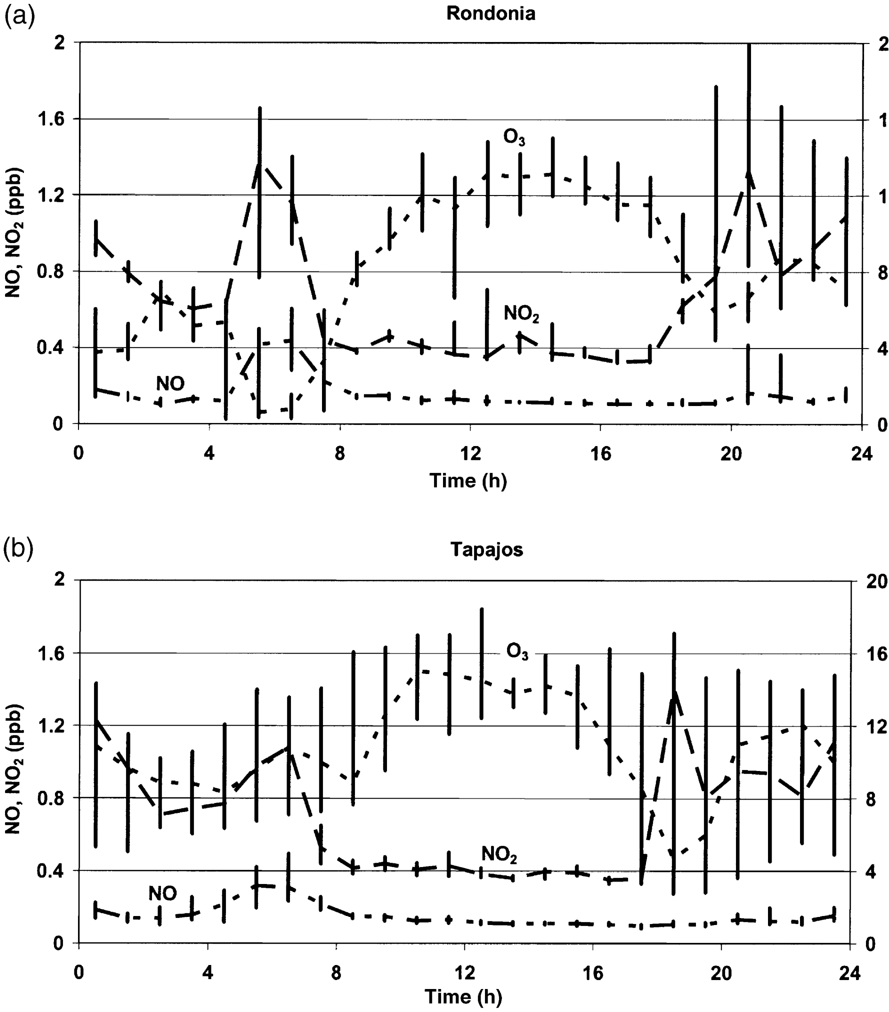

Fig. 2 O_3, NO, and NO_2 concentrations measured at the surface during the Jaru (a) and Tapajos (b) balloon experiments. Dashed trend lines indicate median hourly measurements. Vertical hourly bars indicate the interquartile range (middle 50%) of observations for the experimental periods.

($>$70%) were similar at all sites, for the purpose of the subsequent discussion.

O_3, NO, and NO_x were measured at 10 m Rondônia (FNS) and above canopy at Tapajos. O_3 has been reported for the Balbina campaign (Kesselmeier *et al*., 2000). At all sites, O_3 mixing ratios were highest in the early afternoon (approximately 15 ppb) and decreased to near zero during the night (Fig. 2). The diurnal concentrations of NO and NO_x were similar in Tapajos and Rondônia: NO was approximately 100 ppt day and increased up to 200 ppt at night; NO_x was lowest near midday at 370 ppt and increased to approximately 750 ppt at night. NO and NO_x were not measured during the 1998 Balbina campaign. However, Bakwin *et al*. (1990) reported NO concentrations, during the wet season for a site approximately 100 km from Balbina, very similar to data from Tapajos and Rondônia.

Concentrations of isoprene and α-pinene, the most abundant terpene observed, for several altitude ranges within the mixed layer (Table 2) indicate that the mixed layer was indeed well mixed, except near the top, where BVOC-depleted air was entrained into the mixed layer. Mixed-layer median mixing ratios for isoprene and α-pinene, as well as total terpenes, are given in Table 3 for the time periods of 09:00–12:00, 12:00–15:00, and 15:00–18:00 hours. Up to four samples were averaged from those collected along the tether-line, depending on time of day (height of the mixed layer). Average mixed-layer concentrations from several wind direction sectors were compared for Tapajos (Table 4a); Balbina average mixed-layer concentrations at three spatially separated sites (up to 50 km distant) were compared (Table 4b).

Table 2 Normalized concentrations of isoprene and α-pinene in the lower atmosphere at Tapajos

Altitude (z/z_i)	$([I]_z/[I])_{200\,\mathrm{m}}$	$[\alpha\text{-pinene}]_z/$ $[\alpha\text{-pinene}]_{200\,\mathrm{m}}$
<0.4	1.0*	1.0*
0.4–0.7	1.0 (0.9–1.0)	1.0 (07–1.0)
0.7–1.2	0.9 (0.5–1.0)	0.8 (0.6–1.0)

Isoprene and α-pinene concentrations, measured at various altitudes during each sounding, were normalized to the concentration at the lowest sampling altitude (usually 200 m). The results for all soundings were tabulated for several altitude ranges in and at the top of the mixed layer (normalized to the boundary layer height, z_i, at the measurement time). Interquartile ranges of these normalized concentrations are given in parentheses. The normalized concentrations indicate that the mixed layer, defined by the tethered balloon meteorological soundings, was indeed well mixed and that the average concentrations used in the model represented average concentrations in the mixed layer.

*By definition.

Discussion

BVOC source distribution in Amazonian ecoregions

The BVOC concentrations measured in the mixed layer were assumed to average emissions from the diverse species distribution of the three moist forests studied (Fig. 1) over the footprint of the measurements ($\sim$20 km radius, from an average wind speed of 5 m s^{-1} and isoprene lifetime of 1 h). The forest landscapes comprise almost exclusively one ecoregion within the measurement footprint for the Balbina (Uatuma moist forest) and Jaru (Purus/Madeira moist forest) sites. The Tapajos (Tapajos/Xingu moist forest) footprint may have included cleared areas ($<$20%). The species distributions in the footprints are not known, except for a few small study plots (Harley *et al*., 2004).

The daytime variation of BVOCs within ecoregions was examined for the Balbina and Tapajos regions. Average mixed-layer concentrations from several wind direction and areas separated up to 50 km (Tables 4a and 4b) were separately subjected to 'Bonferroni' corrected multiple *t*-tests (at a $P<0.05$ confidence level). The test indicated that the isoprene, α-pinene and total terpene concentrations were not significantly different among the three wind sectors at Tapajos (total terpenes may have been significantly different in the S–SW sector compared with the NE and E–SE sectors) or the three sites surveyed near Balbina. Consequently, we used the average mixed-layer concentrations to represent landscape or ecoregion averages. Night-time variations with direction of BVOCs were not studied, since isoprene emissions (and, possibly, some terpene emissions) occur only during sunlit periods.

In Rondônia, the Jaru and FNS, lie on opposite sides of Rio Machado, which separates the protected forest (Jaru) to the east from the pasture-dominated landscapes (e.g., FNS) to the west. The footprints of the observed concentrations at Jaru and FNS were dominated by the forest and pasture, respectively. The pasture landscape contains small, isolated areas of woody plant vegetation (primary and secondary forest remnants), and pioneer palms (isoprene emitters).

Estimation of landscape emissions from mixed-layer concentrations

Average mixed-layer concentrations differed significantly among the three moist forest ecoregions. The mixed-layer concentrations, however, are related

Table 3 Median mixed-layer concentrations and interquartile ranges (ppt) during morning, midday, and late afternoon time periods

Site	09:00–12:00	12:00–15:00	15:00–18:00
Tapajos			
Isoprene	400 (240–550)	740 (600–1050)	480 (270–810)
α-Pinene	45 (25–55)	40 (30–65)	50 (25–60)
Terpenes	75 (75–120)	80 (50–145)	90 (50–140)
n Samples	16	31	29
Balbina			
Isoprene	1680 (1160–2530)	2860 (2250–3640)	3080 (2170–3810)
α-Pinene	100 (70–110)	115 (85–160)	145 (120–190)
Terpenes	185 (145–230)	210 (175–310)	255 (215–350)
n Samples	19	53	26
Rondônia–Jaru			
Isoprene	6590 (3640–7410)	6890 (2780–7730)	6550 (4050–7230)
α-Pinene	175 (105–220)	245 (155–300)	250 (135–300)
Terpenes	550 (440–720)	830 (560–2650)	700 (400–2110)
n Samples	11	22	13
Rondônia–FNS			
Isoprene	2000 (1710–2630)	1320 (1170–2070)	1150 (750–1520)
α-Pinene	40 (35–45)	35 (20–40)	25 (15–30)
Terpenes	100 (90–110)	85 (50–105)	60 (30–65)
n Samples	22	17	18

Table 4a Tapajos mixed-layer mixing ratios and interquartile ranges (ppt) separated into several wind direction footprints

	NE	S–SW	E–SE
Isoprene	560 (290–690)	x	530 (250–840)
α-Pinene	40 (25–60)	65 (40–65)	45 (30–55)
Terpenes	125 (80–170)	200 (140–225)	125 (90–190)

x, no measurements. ppt, parts per trillion by volume.

Table 4b Average mixed-layer concentrations and interquartile ranges (ppt) at three areas in the Balbina ecoregion

Location	Main (E. Balbina)	5 km west	50 km west
Isoprene	2340 (2030–3420)	2100 (1900–3750)	2860 (2640–3170)
α-Pinene	110 (80–150)	160 (140–180)	115 (110–130)
Terpenes	220 (160–280)	250 (230–340)	210 (200–240)
n Samples	67	7	11

ppt, parts per trillion by volume.

directly to landscape BVOC emissions. A zero-dimensional (box) model was used to simulate the chemistry and dynamics of the mixed layer, in order to relate BVOC emissions to the chemical concentrations observed in the atmosphere.

Campaigns at all forest sites were made well within the normal wet season; the Balbina experiment was in March; the Jaru and Tapajos experiments were mostly in February. Diurnal temperatures, humidity, sunlight, cloudiness, O_3, NO, NO_x were observed to be similar at the three moist forest sites. The source area influencing atmospheric concentrations was assumed to be homogeneous (horizontal advection was ignored); this is probably a reasonable assumption for the forested sites.

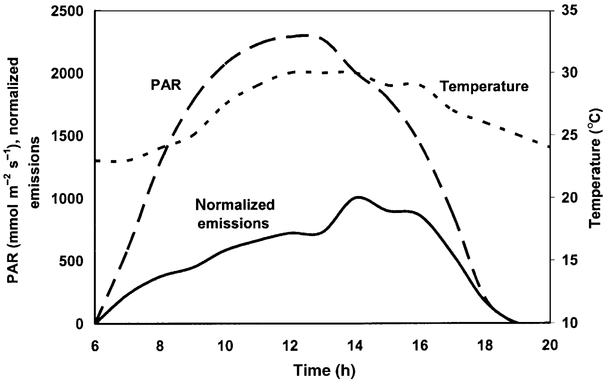

Fig. 3 Model scenario for isoprene emissions (shown here for Jaru). Temperature pattern was the same for all sites. PAR was dependent on day of year of campaign and the latitude of the site, as well as clouds (cloudiness was input the same for each site). Isoprene emissions were calculated from a canopy model (Guenther *et al.*, 1995); the normalized pattern is indicated (scaled to 1000 μg m^{-2} h^{-1} at maximum emissions); the emission profile was scaled linearly in the box model to reproduce mixed-layer concentrations.

Identical parameterization was used in the simulations for each site, except isoprene emission, which are described below.

The height of the boundary layer was varied with time of day according to observations. Dilution due to the growth of the boundary layer was set to observed average boundary layer growth rates at each site (Table 3). The concentration of isoprene in entrained air was estimated at 35% of the afternoon mixed-layer median value; this represents the concentration of isoprene in the residual layer from the previous day, after overnight chemical losses; actual values were not observed, since the highest balloon sampling levels were often made in the entrainments zone. However, the estimation approximates concentrations used in previous, more detailed simulations (Jacob & Wofsy, 1988, 1990). The concentration of O_3, NO, and NO entrained into the mixed layer was set from surface observations to the midday level (approximately 15 ppb and 100 and 400 ppt, respectively).

Deposition velocities for chemical species, including isoprene and O_3, were set to values used in earlier simulations (Jacob & Wofsy, 1988). Afternoon convective activity (significant on most afternoons, but not measured quantitatively) was represented by a convective velocity of 25 cm s^{-1} for all locations for the hours 15:00–17:00, compared with 10 cm s^{-1} estimated, but not measured, in a previous dry season box model simulation (Jacob & Wofsy, 1988). The higher velocity improved agreement with afternoon concentrations.

Table 5 Maximum midday emission fluxes (μg m^{-2} h^{-1}) from the three ecoregions, estimated from box model

Site	Ecoregion*	Isoprene	α-Pinene	Terpenes
Tapajos	Tapajos/Xingu moist forest	2200	90	180
Balbina	Uatuma moist forest	5300	120	230
Jaru Moist forest	Purus/Madeira	9800	180	610

*Dinerstein *et al.* (1995).

A normalized isoprene emission pattern, using average daytime light (derived from latitude and time of year), clouds, and temperature, was calculated for each site from a canopy model (Guenther *et al.*, 1999); the emission scenario was then scaled linearly so as to produce the mixed-layer concentrations observed (e.g., Fig. 3). Midday emissions of α-pinene were assumed to balance atmospheric chemical losses. The chemical loss of α-pinene was calculated from the isoprene box model simulations, since isoprene chemistry, at the concentrations observed, dominated the VOC contribution to the chemistry simulation. The total terpene flux was, for simplicity, estimated from the percentage of α-pinene to total terpenes in samples, since the relative abundance of other terpenes was generally much lower. Estimated midday emissions of isoprene, α-pinene and terpenes are listed in Table 5.

The box model adequately reproduces the average daytime concentrations of isoprene in the mixed layer for the moist forest sites (Fig. 4). Midday concentrations remain fairly constant, a balance of strong emissions, atmospheric chemistry losses of isoprene, and convective exchange with the atmosphere above.

The low morning concentrations of isoprene in Balbina were a result of the smaller footprint of balloon measurements (the maximum altitude of sampling was 500 m), which increased the influence of the cleared area (town of Balbina) in the footprint. The much higher BVOC concentrations measured over the Jaru forest are directly related to the higher isoprene emission rates. The chemistry in the mixed layer was very much slowed by the large amount of isoprene release into the atmosphere; isoprene destroyed much of the OH radical and O_3, which serve as the primary oxidant; their absence allowed the concentration of isoprene and terpenes to increase to the high levels observed. The full diurnal pattern of concentrations was not studied in these experiments, since most measurements were confined to the period from 10:00 to 17:00 to hours.

The FNS pasture measurements show decreasing concentrations of isoprene and terpenes during day-

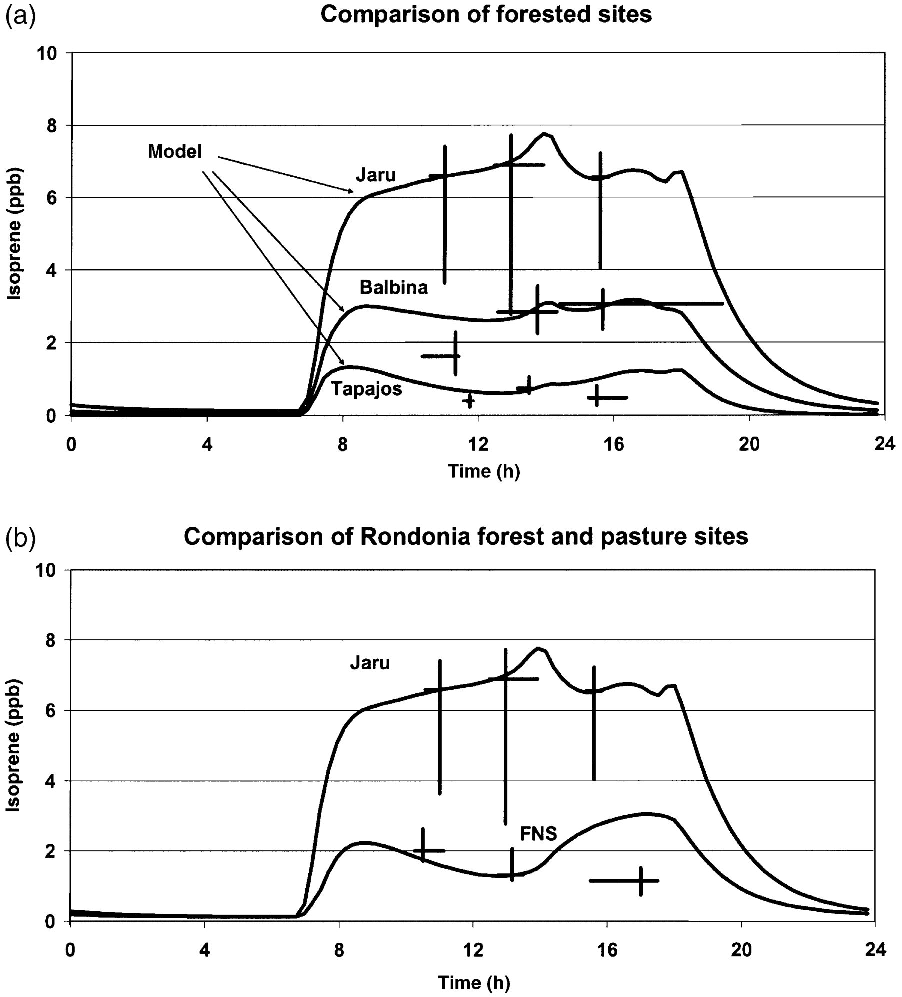

Fig. 4 Diurnal concentrations of isoprene in the mixed layer. The solid line represents the model predicted diurnal isoprene concentrations. Tethered balloon concentration is represented during the midday periods by crosses indicating central 50% of measurements in the mixed layer (vertical line indicates concentration range, horizontal line indicates time range). (a) Compares the three forested sites. (b) Compares the forest and pastures sites in Rondônia.

time. Since grasses are not known to be a major source of isoprene and terpenes, the area is probably a small source of these emissions. The concentration of isoprene measured at FNS in the afternoon period is lower than model predictions because it was not feasible to describe the source of isoprene in the pasture/forest mosaic of the balloon footprint. It was assumed that a large part of the isoprene and terpenes measured was entrained into the mixed layer during its morning growth and through afternoon convective activity; these BVOCs were likely advected from nearby forested areas.

Uncertainties of the emission estimates

The chemical and meteorological conditions observed at the three moist forest sites allowed for a comparison of the emission rates of isoprene and terpenes. However, absolute uncertainties in key modeled parameters should be considered. The daytime growth of the boundary layer directly affects the BVOC emission calculation through dilution of these emissions with BVOC-depleted air entrained as the boundary layer grows. This growth was observed directly during the Tapajos and Rondônia experiments (Table 1). The concentration of isoprene (and terpenes) in entrained air was more difficult to estimate, since most balloon measurements were made between 11:00 and 16:00 LT, when boundary layer heights were at or above the maximum sampling altitudes. As a consequence, we estimated the concentrations of BVOCs entrained from the box model simulations of chemical loss in the night-time residual layer, resulting in a concentration on the order of that included in previous simulations. In the simulations, the average growth parameters were included with average BVOC concentrations (ranges given in Table 3); simulations were not attempted for individual days. The low NO_x and O_3 conditions during the experiments at the three moist forest sites suggest similar atmospheric chemistry: net O_3 production is near zero (or slightly negative) and the O_3 concentrations are dominated by downward transport from the free troposphere during daytime boundary layer growth and deposition to the forest canopy. Propagation of the uncertainties for midday boundary layer growth, entrainment, and average BVOC concentrations used suggests an overall uncertainty of the flux measurement on the order of 40%, similar to that estimated previously for a comparable scenario (Guenther *et al.*, 1996).

Previous BVOC measurements and emission estimates for Amazonian ecoregions

There have been several reported measurements from different campaigns in Amazonia of ground level, canopy-top, and mixed-layer atmospheric concentrations of isoprene and terpenes (Surinam: Williams *et al.*, 2001; Brazil: Zimmerman *et al.*, 1988; Kesselmeier *et al.*, 2000; Peru: Helmig *et al.*, 1998; Venezuela: Sanhueza *et al.*, 2001). All studies show concentrations of isoprene on the order of a few parts per billion and terpenes as high as a few hundred parts per trillion. While these data indicate that isoprene and monoterpene emissions are widespread over Amazonia, they do not describe, in most cases, the magnitude or variations of landscape emissions. There have been two direct tower flux measurements of isoprene and terpenes. In Tapajos, at the end of the wet season (July), Rinne *et al.* (2002) reported isoprene fluxes of up to $2000\,\mu g\,m^{-2}\,h^{-1}$ and α-pinene flux (the majority of terpene emissions observed) of up to $200\,\mu g\,m^{-2}\,h^{-1}$ for midday, using a disjunct eddy accumulation technique. At the Reserva Biologica do Cuieiras (2°35.4′S 60°7′W, ~60 km from Manaus and 100 km from Balbina, noted as ZF2 in Fig. 1) isoprene and monoterpenes (α-pinene was approximately 50% of the terpene total) fluxes of as high as 5000 and $800\,\mu g\,m^{-2}\,h^{-1}$, respectively, were measured in the afternoon during the wet season (December 1999–January 2000) by a relaxed eddy accumulation technique (Stefani *et al.*, 2000).

Disjunct and relaxed eddy accumulation techniques may not account accurately for horizontal advection. The daytime tower-based fluxes cited have measurement footprints on the order of several hundreds of meters. Large clearings or rivers were not in this footprint and would not influence the flux result. The footprint, however, may not have included or integrated the total diversity of the ecoregions. Nevertheless, the estimated fluxes from the balloon experiments presented here (Table 5) agree in magnitude to these tower flux measurements.

Leaf-level emission capacity

A complementary and independent approach to estimating landscape emission capacities has been developed by Harley *et al.* (2004). Available biomass surveys for ecoregions, including major woody species, were compiled; isoprene emission capacities were assigned to the species or genera. A landscape emission capacity was derived by averaging the emission capacities of individual genera, weighted by the percentage of leaf biomass density of each genus in the landscape. Estimates were compiled for approximately 40 landscapes.

For a comparison with these extrapolations, landscape average emissions from the box model calculations, using balloon data, along with latitude, day of the year, leaf area index (LAI), specific leaf mass (SLM), temperature, cloudiness, were used as input in a canopy model (Guenther *et al.*, 1999) to calculate an average canopy leaf emission capacity from the canopies. LAI was set at $5.7\,m^2\,m^{-2}$ (McWilliam *et al.*, 1993). An SLM of $85\,g\,cm^{-2}$ was also used, which represents an average of SLM data reported for a number of neotropical forest landscapes (Harley *et al.*, 2004).

A comparison of the results of balloon soundings reported here with those derived from the inventory method is shown in Table 6. The inventory approach results in average leaf emission capacities 20–100% higher than that derived from the box and canopy model treatment of the balloon observations. However, the two techniques indicate significant differences in emissions from different ecoregions.

Several factors may contribute to the differences between the emissions estimation methods. SLM used

Table 6 Comparison of isoprene emission capacities ($\mu g\,g^{-1}\,h^{-1}$) at the top of canopy for the three ecoregions derived from balloon soundings and biomass survey methods

Site	Balloon*	Survey†
Tapajos	8	16
Balbina	19	24
Jaru	37	Not reported

*This study.

†Harley *et al.* (2004) (terpene emission capacities were not estimated).

in both approaches ($85\,\mathrm{g\,cm^{-2}}$) was the average for a number of neotropical forests. However, SLM has been measured at 61.5 and 110 for the Tapajos/Xingu (Tapajos) and Uatuma (Balbina) moist forest ecoregions, respectively, in separate studies (McWilliam *et al.*, 1993; Nepstad *et al.*, 2002). Lower (higher) SLM would result in lower (higher) leaf emission capacities in either approach. Variation in SLM was not determined or practical for the footprint of any balloon site (approximately $1000\,\mathrm{km^2}$). Also, the inventory method uses a leaf-level isoprene emission capacity ($75\,\mu\mathrm{g\,g^{-1}\,h^{-1}}$) for isoprene emitting species in the extrapolation of landscape emissions. The actual variations of leaf emission capacity among these tropical species are unknown. Alternatively, the box model estimation of emissions also contains several large sources of uncertainty (discussed earlier).

Global emission modeling and landscape diversity

In the global biogenic emission model (GLOBEIS) described by Guenther *et al.* (1995), the Amazonian forests were divided into two forest types, tropical rainforest and tropical seasonal forests. The tropical rainforest emission capacity was assigned a value of $24\,\mu\mathrm{g\,g^{-1}\,h^{-1}}$, derived from the Jacob & Wofsy (1988) isoprene emission estimate ($6\,\mathrm{mg\,m^{-2}\,h^{-1}}$) for the Ducke forest reserve near Manaus; tropical seasonal forests were assigned a default landscape average leaf-level emission capacity of $16\,\mu\mathrm{g\,g^{-1}\,h^{-1}}$, based on the average of all woody vegetation measurements at that time. The landscape average emission capacities derived in this study for Tapajos (seasonal tropical forest in the GLOBEIS classification scheme), Balbina, and Jaru (tropical rainforests in the GLOBEIS classification scheme) are 8, 19, and $41\,\mu\mathrm{g\,g^{-1}\,h^{-1}}$, respectively.

The midday landscape emissions of isoprene and terpenes found at the sites (Table 5) differ by a factor of 4. The model of Guenther *et al.* (1995), on the other hand, would predict, for the same climatological conditions, a factor of 2 increase from the tropical seasonal forest to the tropical rainforest, based on only two different landscape emission capacities assigned to Amazonia.

Biomass surveys from various neotropical forests (including Amazonian forests) indicate a different percentage of isoprene emitting genera among woody plant species, likely resulting in different landscape emission capacities. The Ducke forest reserve (in the same ecoregion as Balbina) consist of approximately 40% isoprene emitters, while the Tapajos ecoregion has been reported to be comprised of approximately 25% isoprene emitters (on biomass basis); the standing biomass in these studies was estimated to be nearly the same (Harley *et al.*, 2004). No comparable information on percentage isoprene emitters or standing biomass was available for the Jaru forest ecoregion.

Isoprene emission may increase to a point with increased net primary productivity; eventually, however, self-shading of leaves in more dense forest stands would attenuate light more quickly within the canopy and, consequently, reduce potential isoprene emissions. Significant differences among species in isoprene emission capacity might account for variations in landscape emission rates. Isoprene emission capacity has only been studied for a few species in North America and Europe and no significant differences may presently be assigned (Harley *et al.*, 2004).

Balloon measurements were made at the three moist forest sites in the wet season during January–March; the seasonality of emissions at any of the sites has not been reported. Similar arguments, relating leaf level and landscape level of terpenes are not made, since few tropical terpene emitting species have been reported.

Conclusions

A tethered balloon platform was used to measure concentrations of BVOCs in and above the atmospheric boundary layer in three moist forest ecoregions. A canopy model of BVOC emissions was used with a simple chemical box model, constrained by the observations of isoprene and other chemicals and meteorological variables made simultaneously, to reproduce atmospheric concentrations of isoprene and terpenes.

Landscape isoprene and terpene emissions appear to differ significantly for the three moist forest ecoregions studied in Amazonia. Emission capacities of the major woody plant species and percentage of isoprene or terpene emitters are major influences on landscape emissions in the moist forest ecoregions. Seasonal cycles of emissions were not studied, but would likely reveal other differences in annual emissions. While the present study indicates significant differences in emissions from the three ecoregions studied, Amazonia may include over 50 ecoregions (Dinerstein *et al.*, 1995), each with a landscape emission capacity for various BVOCs dependent on distinct species distribution.

Most global CTMs take isoprene emissions from the GEIA model-database (Guenther *et al.*, 1995), which has a monthly temporal resolution. The emission rates are assumed to be homogeneous within each model grid cell and they are adjusted for diurnal variation using a simple correction factor based on climatological monthly temperature, light intensity, or shortwave radiative flux (Brasseur *et al.*, 1998; Roelofs & Lelieveld, 2000). Recently there have been attempts made to couple atmospheric models with land surface models, which would allow the emissions to be adjusted at every model time step for the local meteorological conditions: cloud cover, temperature, and ambient light (Wang & Shallcross, 2000; Collins *et al*., 2002; Levis *et al*., 2002). Progress has been made in describing biogenic emissions from the remote sensing of the land cover parameters (e.g., Roujean & Lacaze, 2002; Roberts *et al*., 2002). Emission capacities for specific ecoregions, as well as the dependence of emissions on light, temperature, LAI, and seasonality, may now be included in CTMs.

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