# Biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: The LBA-EUSTACH experiments

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[1] The biogeochemical cycling of carbon, water, energy, aerosols, and trace gases in the Amazon Basin was investigated in the project European Studies on Trace Gases and Atmospheric Chemistry as a Contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA-EUSTACH). We present an overview of the design of the project, the measurement sites and methods, and the meteorological conditions during the experiment. The main results from LBA-EUSTACH are: Eddy correlation studies in three regions of the Amazon Basin consistently show a large net carbon sink in the undisturbed rain forest. Nitrogen emitted by forest soils is subject to chemical cycling within the canopy space, which results in re-uptake of a large fraction of soil-derived $NO_x$ by the vegetation. The forest vegetation is both a sink and a source of volatile organic compounds, with net deposition being particularly important for partially oxidized organics. Concentrations of aerosol and cloud condensation nuclei (CCN) are highly seasonal, with a pronounced maximum in the dry (burning) season. High CCN concentrations from biomass burning have a pronounced impact on cloud microphysics, rainfall production mechanisms, and probably on large-scale climate dynamics. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0330 Atmospheric Composition and Structure: Geochemical cycles; 1655 Global Change: Water cycles (1836); 3322 Meteorology and Atmospheric Dynamics: Land/atmosphere interactions; *KEYWORDS:* carbon cycles, aerosols, rainfall, nitrogen oxides, VOC, CCN

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## 1. Introduction

[2] Human activities are changing the face of Amazonia and the way this region functions as an integral system, in which biota, atmosphere, and human population interact with one another. This change is expected to have far-reaching effects on the global carbon balance, the concentrations of greenhouse gases and aerosol particles, and on the oxidizing power of the global atmosphere. Present scientific knowledge is inadequate to assess these changes and their impacts on global change with the required degree of reliability. Therefore, to address the key questions—(1) how does Amazonia currently function as a regional entity? and (2) how will changes in land use and climate affect the biological, chemical and physical functions of Amazonia, including the sustainability of development in the region and the influence of Amazonia on global climate?—the international multidisciplinary research initiative *Large-Scale Biosphere-Atmosphere Experiment in Amazonia* (LBA) is now taking place in Amazonia. Some of the outstanding scientific issues are outlined in the next paragraphs.

[3] The Amazon Basin plays a key role in the global carbon cycle, in terms of both carbon turnover and storage [*Raich and Potter*, 1995]. Changes in land use and variations in climate and atmospheric chemistry influence the exchange of carbon between the biosphere and the atmosphere. Forest clearing and agricultural development in tropical forests are a source of $CO_2$ to the atmosphere, whereas regrowth on abandoned land and enhanced carbon uptake due to $CO_2$ fertilization and other feedbacks represent a sink [*Houghton et al.*, 1998]. The magnitude, and even the sign, of the net carbon flux between the Amazon Basin and the atmosphere, however, is still under dispute. $CO_2$ flux and tree biomass measurements made in Amazonia over the last decade indicate that undisturbed forests may be a large net $CO_2$ sink [*Grace et al.*, 1995a, 1995b; *Malhi et al.*, 1998; *Phillips et al.*, 1998]. On the other hand, assessments based on geographic analysis of remote sensing data have concluded that the Amazon Basin is at present nearly balanced with respect to carbon [*Houghton et al.*, 2000], with emissions from deforestation being offset by the carbon sink in undisturbed forests.

[4] It has been proposed that the Amazonian tropical forest represents a significant source for nitrous oxide ($N_2O$) [*Potter et al.*, 1998]. Another greenhouse gas, methane ($CH_4$) is emitted at high rates from wetlands [*Bartlett and Harriss*, 1993], and forest-to-pasture conversion may transform the soils from $CH_4$ sinks to sources [*Steudler et al.*, 1996]. However, regional net emissions are not quantified, and the responses of emission rates to climate change or to forest clearing and associated agricultural development, land abandonment and ecological succession are still inadequately understood [*Keller and Matson*, 1994; *Veldkamp et al.*, 1998].

[5] Aerosols have a strong impact on global and regional climate, because of both their direct radiative effects and their ability to modify cloud properties [*Andreae*, 1995]. Amazonia is thought to be one of the major sources of aerosol particles (primarily organic) to the global atmosphere [*Andreae and Crutzen*, 1997]. The size and elemental composition of aerosol particles are important variables that influence their radiative effect and their role as cloud condensation nuclei (CCN). Changes in CCN concentrations have important and far-reaching consequences for rainfall production and climate dynamics [*Rosenfeld*, 1999; *Graf et al.*, 2001]. In spite of their climatic importance, there is little information available on the distribution and properties of CCN in the tropics in general, and in Amazonia in particular.

[6] The tropical troposphere contains the world's highest concentrations of the OH radical, and is therefore responsible for about 70% of the global atmospheric oxidation of long-lived gases, including $CH_4$, carbon monoxide (CO), hydrogenated chlorofluorocarbons and methyl bromide [*Crutzen*, 1995]. However, there is considerable uncertainty in estimates of photochemical turnover rates, because concentrations and sources of nitrogen oxides ($NO_x$), reactive hydrocarbons and CO are poorly characterized. It is well established that the forest soil and canopy are sources of $NO_x$ and volatile organic compounds (VOCs), respectively, and are sinks for ozone ($O_3$), but the processes regulating these fluxes and their magnitudes are still inadequately known [*Guenther et al.*, 1995; *Kesselmeier and Staudt*, 1999; *Ludwig et al.*, 2001].

[7] The importance of the issues presented in the preceding paragraphs prompted the development of the project European Studies on Trace Gases and Atmospheric Chemistry as a Contribution to the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA-EUSTACH). Its aim is to contribute to the LBA initiative by focusing on the following two key questions: (1) What is the contribution of Amazonia to the global atmospheric carbon balance? and (2) What is the contribution of Amazonia to the global atmospheric budgets of radiatively active trace gases ($H_2O$, $CO_2$, $CH_4$, $N_2O$, $O_3$) and aerosol particles, as well as of other trace gases ($NO_x$, VOCs) that are chemically reactive in the global tropospheric ozone cycle?

[8] The central element of the approach followed in LBA-EUSTACH is the integration of measurements and modeling. At three representative sites in the Amazon Basin, micrometeorological and enclosure techniques for long-term and campaign measurements were used to determine the fluxes of water, energy, $CO_2$, $CH_4$, $N_2O$, aerosol particles, $O_3$, $NO_x$, and VOC. Integrative and interpretative modeling of the results uses a hierarchy of models (soil-vegetation-atmosphere transfer, ecology and climate models as well as atmospheric chemistry-transport models) to scale in space (local to global) and time (hours to decade).

[9] In conjunction with LBA-EUSTACH, a major multidisciplinary effort named LBA Atmospheric Mesoscale Campaign (LBA-AMC) was carried out during the wet season of 1999 in Rondônia, wherein an integrated set of measurements of meteorology and atmospheric chemistry was undertaken. The campaign was collocated with a Tropical Rainfall Measuring Mission (TRMM) satellite validation campaign and included aircraft for remote sensing and cloud microphysics, two meteorological radars, four radiosonde sites, and three surface and boundary layer sites, one in forest, two in pasture and one in a mixed landscape. *Silva Dias et al.* [2002] present an overview of the main results regarding the behavior of rainfall during the wet season and its possible feedbacks to the large-scale circulation, and to the atmospheric composition. This paper will provide an overview of the experimental layout of LBA-EUSTACH and present highlights of the results obtained so far. Details will be reported in other papers in this issue.

## 2. Site Descriptions

[10] Field measurements were made at three locations: (1) forest and pasture sites in Rondônia at the southwest periphery of the Amazon Basin, (2) the Cuieiras forest reserve 60 km north of Manaus in central Amazonia, and (3) the Caxiuanã forest reserve about 350 km west of Belém (Figure 1). Continuous measurements of $CO_2$, water, and energy fluxes were made at all three locations (Table 1). At the Rondônia sites, campaign-mode measurements of concentrations and fluxes of aerosol particles, $O_3$, $NO_x$ and VOCs were performed, and VOC concentration and flux measurements were made at the Manaus site. The characteristics of these sites will be outlined in the following sections.

### 2.1. Rondônia

[11] The rain forest in Rondônia has been progressively cleared by organized colonization during the last 25 years. After construction of the Cuiabá-Porto Velho highway (BR

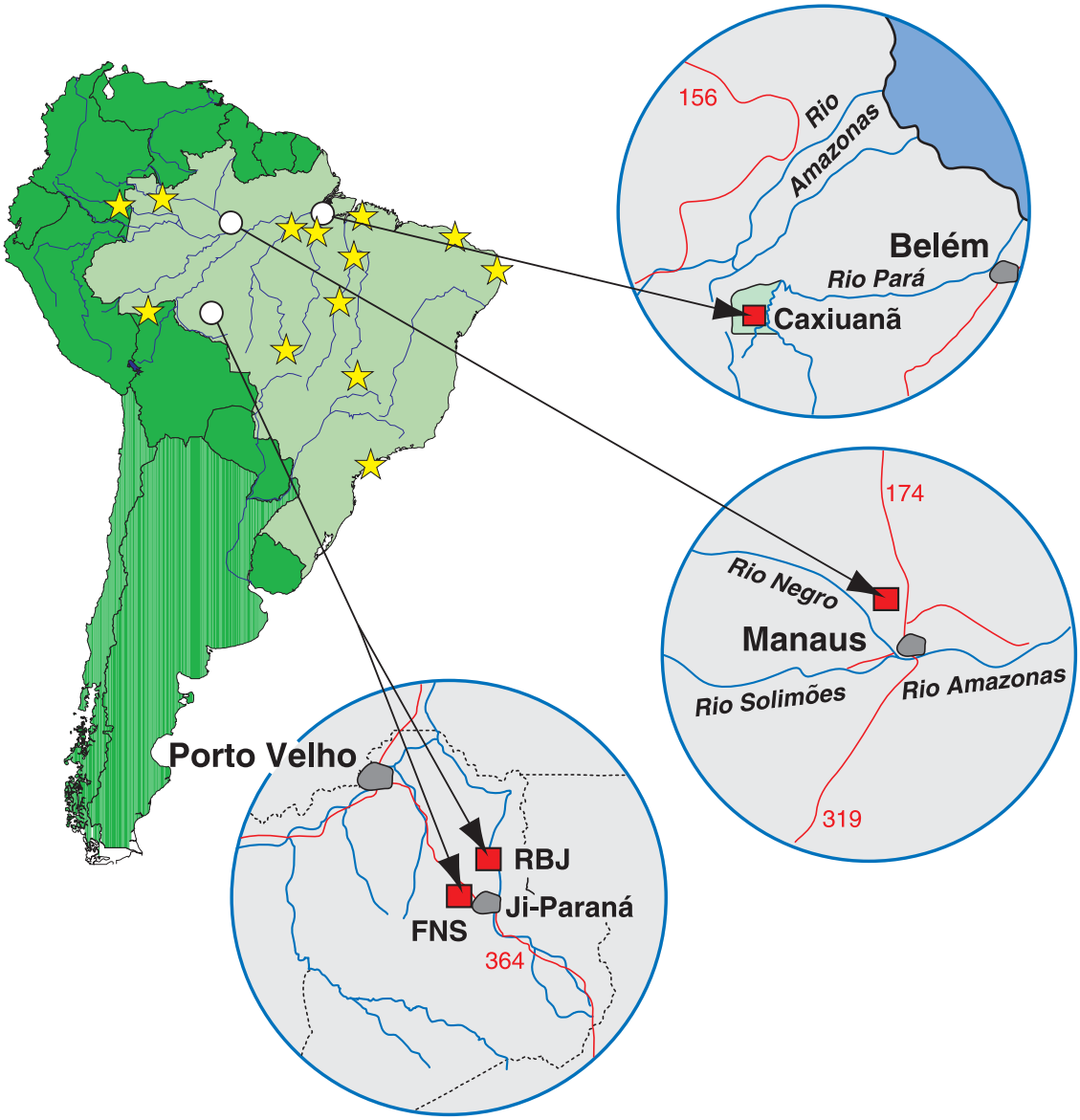


**Figure 1.** Overview map showing the location of the LBA-EUSTACH sites. The stars indicate the location of other LBA sites.

364) in 1968, a network of roads was laid out from this highway and is still enlarging. Originally, plots of 2 × 2 km were allocated to the settlers, who cleared the forest progressively backwards from the roads, creating a "fishbone"-like pattern of plantations, pastures, degraded land and forest patches. This pattern can be seen on satellite images and is characteristic for Rondônia (Figure 2). A representative pair of forest and pasture experimental sites has been set up in 1991 as part of the Anglo-Brazilian Amazonian Climate Observation Study (ABRACOS) [*Gash et al.*, 1996]. The LBA-EUSTACH experimental sites were chosen to be identical with the former ABRACOS forest and pasture sites, Reserva Biológica Jarú (RBJ) and Fazenda Nossa Senhora Aparecida (FNS), respectively (Figure 2). At both sites, long-term measurements of energy and $CO_2$ fluxes, soil moisture and temperature began in February 1999, while measurements of concentrations and fluxes of trace gases and aerosol particles were performed in two campaigns, LBA-EUSTACH-1 (April/May 1999) and LBA-EUSTACH-2 (September/October 1999). The two campaigns coincided with the 1999 "wet-to-dry season transition" and "dry-to-wet season transition" periods, respectively.

[12] An indigenous people's reserve stretches northeast of the city of Ji-Paraná, followed further north by the primary rain forest ecological reserve, RBJ (about 90 km north of Ji-Paraná). The Brazilian Environmental Protection Agency IBAMA (Instituto Brasileiro de Meio Ambiente e Recursos Renováveis) owns the reserve and controls it from a rain forest camp site (IBAMA Camp, 10°08.72′S, 61°54.45′W, 120 m asl). The ABRACOS tower (RBJ-A) was erected in 1991, and a similar tower (RBJ-B) was built 700 m away in late 1998. As reported by *Culf et al.* [1996], there is sufficient fetch over forest for several tens of km in the main wind direction (i.e., from NW over N to SSE), whereas the fetch over forest is only 1 km or less in the remaining sector. The Rio Machado, which partly forms the eastern

**Table 1.** Tower Locations and Measurements Performed at the Various Towers During LBA-EUSTACH[a]

| Site | Rondônia | | | | Manaus | | Caxiuanã |
|---|---|---|---|---|---|---|---|
| Vegetation type | Forest | | Pasture | | Forest | Forest | Forest |
| Tower | RBJ-A | RBJ-B | FNS-A | FNS-B | C14 | K34 | |
| Latitude | 10°04.92′S | 10°04.70′S | 10°45.73′S | 10°45.73′S | 2°35.35′S | 2°35.55′S | 1°43.06′S |
| Longitude | 61°55.80′W | 61°56.02′W | 62°21.45′W | 62°21.45′W | 60°06.89′W | 60°12.56′W | 51°27.60′W |
| Elevation at base | 147 | 145 | 267 | 267 | 90 | 93 | 20 |
| Tower height | 53 | 60 | 5 | 8 | 40 | 53 | 52 |
| Meteorological quantities | | | | | | | |
| Wind speed and direction | 53 | n = 4; 61–25 | n = 4; 0.5–4.5 | 9.3 | 42 | n = 4; 52–28 | 53 |
| Air temperature | n = 8; 53–0.3 | 60 | n = 4; 0.5–4.5 | 8.3 | 42 | n = 6; 51–5.2 | n = 3, 53–18 |
| Water vapor | n = 8; 53–0.3 | n = 6; 63–0.05 | n = 2; 0.5, 4.5 | 8.3 | 42 | n = 6; 53–0.5 | n = 6, 56–0.2 |
| Canopy surface temperature | – | 59 | – | 8.1 | | 50.4 | 46 |
| Rainfall | n = 2; 53, 1.0 | 60 | 1.2 | 0.4 | 42 | 52 | 53 |
| Barometric pressure | n = 2; 53, 1.0 | 41 | 1.5 | 4.0 | | 32.5 | |
| Soil moisture | – | n = 10; −0.01 to −1.0 | – | n = 10; −0.01 to −1.0 | – | n = 10; −0.01 to −1.0 | – |
| Soil heat flux | n = 3; −0.05[b] | n = 2; −0.01 to −0.10 | n = 2; −0.10 | n = 8, −0.01 to −0.10 | – | n = 2; 0.03 | – |
| Soil temperature | n = 6; −0.05 | n = 10; −0.01 to −1.0 | n = 6; −0.005 to −0.20 | n = 9; −0.01 to −1.0 | – | n = 9; −0.01 to −1.0 | n = 2, −0.05 |
| Soil water content | n = 3; −0.05 | n = 6; −0.1 to −3.6 | n = 1; 0 to −0.15 | n = 6; −0.1 to −3.6 | – | – | – |
| Groundwater level | – | – | −6.5 | −6.5 | – | – | – |
| Surface wetness | – | – | √ | – | – | – | – |
| Fluxes | | | | | | | |
| $CO_2$ flux (EC) | 53 | 63 | 4.5[c] | 4.0 | 46 | 53 | 56 |
| Momentum, sensible heat (EC) | n = 4–6; 53–1.0[d] | 63 | 4.5[c] | 4.0 | 46 | 53 | 56 |
| PAR | – | 61 | – | 9.0 (in + out) | – | 52 | 53(in), 46(out) |
| Water vapor | 53.0 | 63 | 4.5[c] | 4.0 | 46 | 53 | 56 |
| Long- and short-wave radiation (in/out) | (n = 2, 50–1.0)[b] | 54 | global & net radiation; 4.5 | 8.5 | global & net radiation; 42 | 45 | 46 (in + out) |
| NO | n = 1–3; 53–1[d] | – | – | – | – | – | – |
| $O_3$ | n = 2–4; 53–11[d] | – | – | – | – | – | – |
| VOC (REA) | 53[b] | – | – | – | – | 53 | – |
| Aerosol particles (EC) | 53 | – | – | – | – | – | – |
| $N_2O$, $CH_4$ (EC) | – | – | 4.5[c] | – | – | – | – |
| $NO_2$ photolysis rate | n = 3; 53–20 | – | – | – | – | – | – |
| Exchange of $H_2O$, $CO_2$, NO, $NO_2$, $O_3$, and Rn at soil-atmosphere interface | √ | √ | campaign 2 | – | – | – | – |
| Concentrations | | | | | | | |
| $CO_2$ | n = 8; 53–0.3 | n = 6; 63–0.05 | 4.5[c] | 4.0 | 46 | n = 6; 53–0.5 | n = 6, 56–0.2 |
| $N_2O$, $CH_4$ | – | – | 4.5[c] | – | – | – | – |
| CO | n = 8; 53–0.3[b] | – | – | – | – | – | – |
| Black carbon | n = 8; 53–0.3[d] | – | 3.6 | – | – | – | – |
| VOC | n = 3–4; 50–1[d] | – | – | – | – | – | – |
| Aerosol size distribution | 51 | – | 3.6 | – | – | – | – |
| Aerosol mass and number concentration | number; 51 | – | number, mass; 3.6 | – | – | – | – |
| Size-resolved aerosol composition | 51 | – | 3.6 | – | – | – | – |

**Table 1.** (continued)

| Site | Rondônia | | | | Manaus | | Caxiuanã |
|---|---|---|---|---|---|---|---|
| Vegetation type | Forest | | Pasture | | Forest | Forest | Forest |
| Tower | RBJ-A | RBJ-B | FNS-A | FNS-B | C14 | K34 | |
| CCN | 51 | – | 3.6 | – | – | – | – |
| $O_3$ | n = 8; 52–0.3 | – | n = 2; 4.5, 0.5 | – | – | – | – |
| NO, $NO_2$ | n = 8; 52–0.3 | – | 3.5 ($NO_x$) | – | – | – | – |
| Rain chemistry | – | – | √ | – | – | – | – |
| Light scattering | 51 | – | 3.6 | – | – | – | – |
| Aerosol optical depth | IBAMA camp | – | 1 | – | – | – | – |

[a] For each measurement, the sensor height is indicated (in m), where appropriate. When multiple sensors were used, their number and the height range covered are given.
[b] Campaign 2 only.
[c] Campaign 1 only.
[d] Various levels during campaign 1 and campaign 2. For details, see original papers.

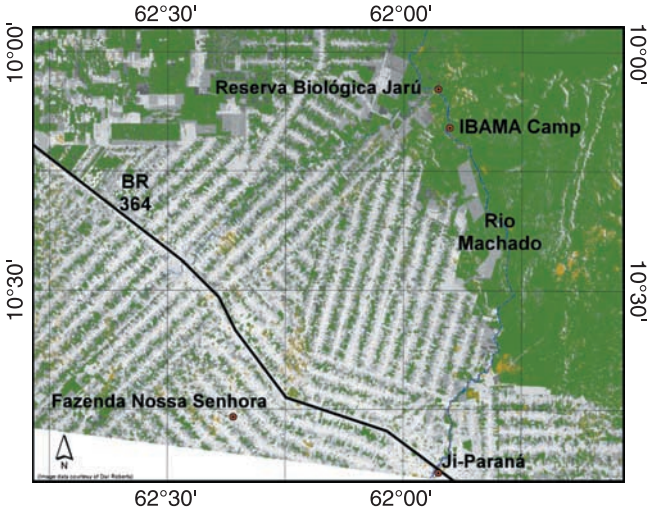


**Figure 2.** Satellite image of southeastern Rondônia showing Ji-Paraná, the Rio Machado, the Cuiabá-Porto Velho highway (BR 364), and the locations of the LBA-EUSTACH experimental sites, Reserva Biológica Jarú (RBJ), IBAMA Camp, and Fazenda Nossa Senhora Aparecida (FNS).

boundary of RBJ, is about 400 m and 800 m west of RBJ towers A and B, respectively. Both towers are accessible by foot only. Since 1998, colonization has sporadically reached the western bank of the Rio Machado, and landless people developed small-scale slash and burn activities N and NE of RBJ-B beginning in mid-1999. The main transport route during the wet season from Ji-Paraná to RBJ is by boat (4 to 6 hours), while a 4-wheel drive vehicle is preferentially used in the dry season (125 km).

[13] The measurements performed at the RBJ towers during the LBA-EUSTACH-1 and -2 campaigns are summarized in Table 1, and the setup of instrumentation at RBJ-A and the IBAMA camp (7 km SSW of RBJ-A) is shown schematically in Figure 3. At the IBAMA Camp, the exchange of VOCs, $CO_2$ and $H_2O$ between tree branches and the atmosphere was measured by cuvette techniques from a 10 m high scaffolding tower [*Kesselmeier et al.*, 2002; *Kuhn et al.*, 2002]. The flux data were accompanied by measurements of VOC, $CO_2$ and $O_3$ concentrations, wind speed and direction, air temperature and relative humidity, and photosynthetic active radiation (PAR). Also at the IBAMA camp, the integral aerosol optical depth was determined by means of a shadow-band sun photometer.

[14] The LBA-EUSTACH pasture site (FNS) belongs to the cattle ranch Fazenda Nossa Senhora Aparecida (Figure 2). It is situated ~8 km SW of the town Ouro Preto do Oeste. FNS is ~4.5 km WNW of "Toga Hill," one of the radar sites of the companion project LBA-AMC [*Silva Dias et al.*, 2002]. The FNS land was first deforested by fire in 1977. Since 1991 it has consisted of a homogenous sward of perennial grass. During the campaigns LBA-EUSTACH-1 and -2, the camp was stocked with a breeding herd of ~150 "Blanco" cattle (Bos indicus hybrid). More details about the history and description of the FNS site are given by *Kirkman et al.* [2002] and (M. J. Waterloo et al., Above-ground biomass and leaf area index of pastures in Rondônia, Brazil, submitted to *Journal of Geophysical Research*, 2001, hereinafter referred to as M. J. Waterloo et al., submitted manuscript, 2001). In 1991, the 5-m tall ABRACOS "pasture" scaffolding tower was set up at FNS (FNS-A). At the end of 1998, another tower (FNS-B, 8 m tall) was built WSW and 70 m apart from FNS-A. The cattle ranch is within a strip of cleared land about 4 km wide and several tens of kilometers long [*Culf et al.*, 1996]. There is sufficient uniform fetch for 1–2 km in each direction; however, some distortions are caused by structures of shelters and instrument housings in the NW and NE sectors of FNS towers A and B, respectively. Measurements performed during the LBA-EUSTACH campaign at FNS are given in Table 1.

[15] A characterization of RBJ soils had already been made within the ABRACOS project [*Hodnett et al.*, 1996]. The soil at RBJ-A is derived from in situ weathering of the bedrock, has a depth of 3 m and was tentatively classified as medium textured red-yellow podzol (Podzólico vermelho amarelo de textura média—Brazil; typic paleudult—Soil Taxonomy; or orthic acrisol—FAO), with a high sand content (88%) at the surface, clay and silt contents increase with depth. Rock outcrops east of the tower indicate that the bedrock in the area is an acid gneiss (composed of mainly quartz and biotite). The soil depth at the new tower B varies from <1 m to ~2 m and the texture is classified as sandy loam. In 1999, surface soils at RBJ-A were classified to have a loamy-sand texture (approximately 10% clay and 80% sand) with a pH (0.01 M $CaCl_2$) of 3.5. Field cores showed a bulk surface soil density of 1.33 Mg $m^{-3}$ (1.36 Mg $m^{-3}$ in 1993; [*Hodnett et al.*, 1996]). The first 0.05 m of the RBJ soil contains a dense mat of fine roots. *Wright et al.* [1996] reported strong evidence for soil water extraction by deep roots penetrating to depths greater than 3.5 m at all ABRACOS forest sites. *Hodnett et al.* [1996] also provide a detailed description for FNS soils. The soil is deep (>6 m) and the surface has a weathered, sand/loamy-sand texture (~10% clay and 80% sand) and has the same classification as the RBJ soil. At the soil surface (0–0.05 m), a pH of 5.2 and a bulk density of 1.56 Mg $m^{-3}$ was observed in 1999 (1.50 Mg $m^{-3}$ in 1993; [*Hodnett et al.*, 1996]). The rather high surface soil density seems to be due to compaction by cattle. The bulk density increases further down in the soil profile to 1.6–1.7 Mg $m^{-3}$ at a depth of around 0.4 m, only to decrease at greater depths (1.0 m) to 1.5 Mg $m^{-3}$ (M. J. Waterloo et al., submitted manuscript, 2001). More details of RBJ and FNS surface soil characterization are given by *van Dijk and Meixner* [2002]. In a pit profile at RBJ, roots have been found to a depth of 1.65 m, and living roots down to 3 m depth have been reported [*Hodnett et al.*, 1996; *Wright et al.*, 1996].

[16] A mean canopy height of 30–35 m was observed at the time of the ABRACOS project [*Culf et al.*, 1996]. For the 1999 experiments, *Rummel et al.* [2002] reported 32 m mean canopy height, single jutting trees up to a height of 45 m, and a palm-rich understory of only a few meters height under a relatively open stem space up to 20 m. *McWilliam et al.* [1996] characterized the plant species around RBJ-A. The following tree species were selected at the IBAMA camp site to measure the leaf/atmosphere exchange of water vapor, $CO_2$, and VOCs by cuvette techniques: *Hymenaea courbaril* L. var. (Jatoba), *Apeiba tibourbou* (Pente de Macaco), and

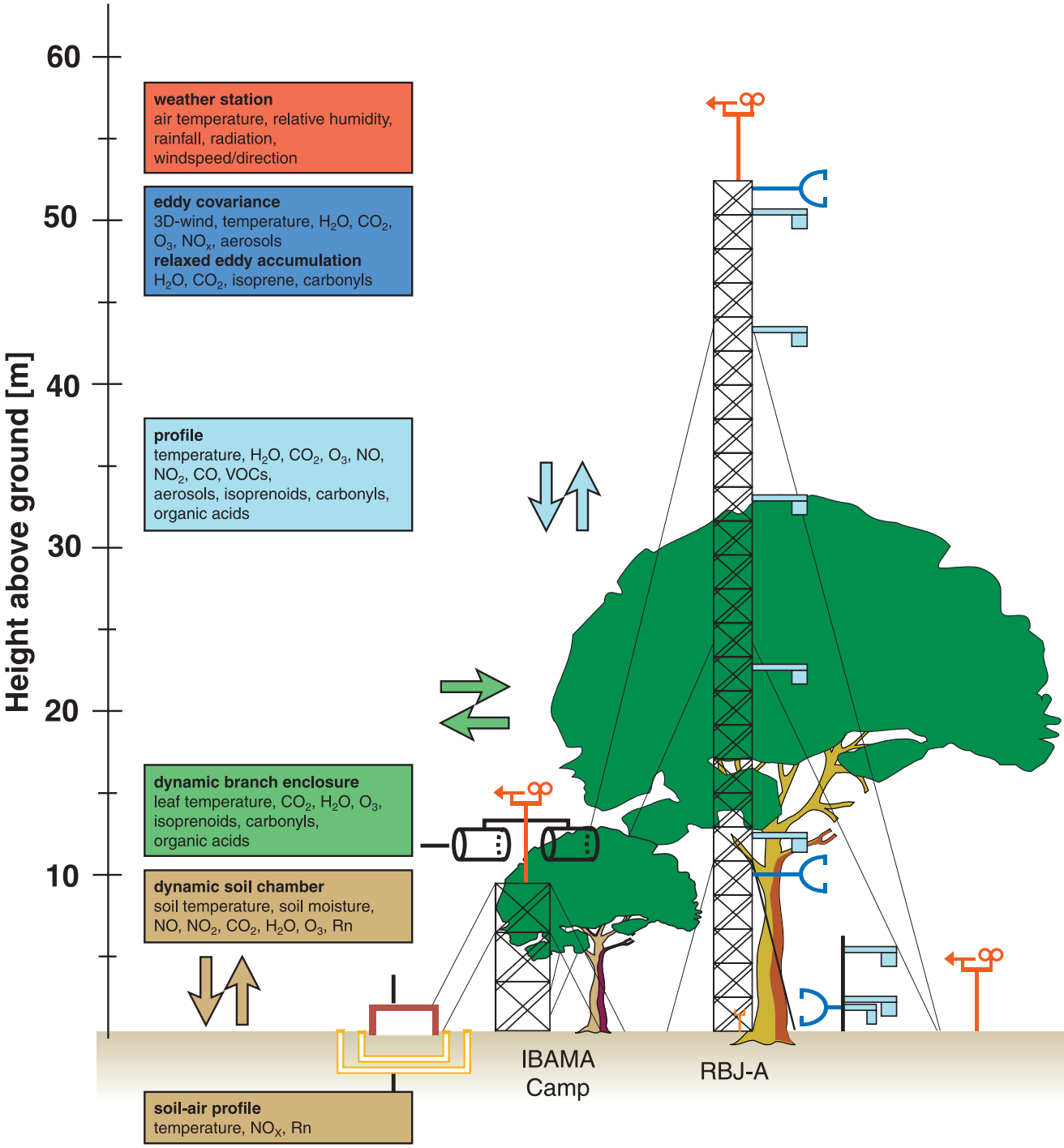


**Figure 3.** Setup of concentration profile, flux, and surface exchange instrumentation at the LBA-EUSTACH experimental sites RBJ-A and IBAMA Camp.

*Soraceaguilleminiana* (Jaca-branca, Jaca-brava). All three deciduous tree species are commonly distributed in both the primary, as well as the secondary forest. *Hymenaea* and *Apeiba* are deciduous trees with a leafless period within the dry season whereas *Soracea* is an evergreen species [*Kesselmeier et al.*, 2002; *Kuhn et al.*, 2002]. A leaf area index (LAI) of 4.63 (leaf litter fall method) was reported for the RBJ rain forest in 1993 [*Roberts et al.*, 1996], whereas in 1999, the total LAI at RBJ-A was found to be about 5.5 (optical method, LI-COR, LI-2000) and 5–6 at RBJ-B. At RBJ-A, vertical profiles of LAI have been determined in 1992 and 1993 [*Kruijt et al.*, 1996], the corresponding 1999 data are given by C. Ammann et al. (Canopy reduction effect on nitric oxide emission from Amazonian rain forest, submitted to *Journal of Geophysical Research*, hereinafter referred to as C. Ammann et al., submitted manuscript). The forest floor at RBJ-A was covered with leaf litter of about 0.24 kg $m^{-2}$ dry weight in May and 0.28 kg $m^{-2}$ in September/October 1999. Since the time of ABRACOS, the dominant grass species at FNS is *Brachiaria brizantha* (A.

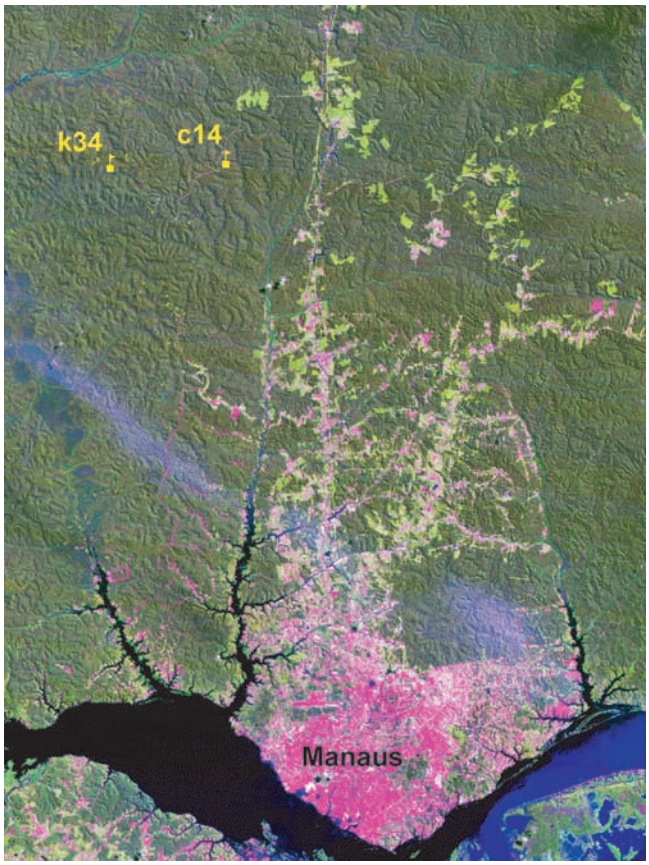


**Figure 4.** Satellite image showing Manaus, the Reserva Biológica do Cuieiras, and the location of the measurement towers (Landsat TM image courtesy of S. Bergen).

Rich.) Stapf. [*McWilliam et al.*, 1996]. This is a fire sensitive, fairly drought-tolerant, perennial African grass species. Throughout 1999, grazing at FNS resulted in an average grass height of 0.16 ± 0.02 m, ranging from 0.22 m (wet season) to 0.15 m (dry season), and 0.10 m shortly after grazing (M. J. Waterloo et al., submitted manuscript, 2001). The average total aboveground biomass of the *Brachiaria* sward was 0.28 ± 0.06 kg $m^{-2}$, the litter mass 0.20 ± 0.09 kg $m^{-2}$ and the bare soil exposure varies between about 50% (dry season) to <10% (wet season) (M. J. Waterloo et al., submitted manuscript, 2001). For FNS, *Roberts et al.* [1996] reported a leaf area index of 3.9 ± 1.0 (April 1993), 2.6 ± 0.8 (June 1993), and 1.7 ± 0.6 (September 1992). In 1999, corresponding data were 2.1 ± 1.1, 1.5 ± 0.3, and 1.3 ± 0.4, respectively (M. J. Waterloo et al., submitted manuscript, 2001).

### 2.2. Manaus

[17] The Reserva Biológica do Cuieiras (2°35.37′S, 60°06.92′W) is located ~60 km NNW of Manaus, Amazonas (Figure 4). The site has belonged to the Instituto Nacional de Pesquisas da Amazônia (INPA) since the early seventies, when a small access road (ZF2) was opened. Due to the distance to rivers and difficulty of access, the area is thought to be completely undisturbed. Manaus is located more than 1000 km inland from the Atlantic Ocean. The prevailing trade winds blow over vast expanses of undisturbed rain forest before reaching the two towers in the Cuieiras Reserve. Average yearly rainfall is 2200 mm with two marked seasons (November–May wet; June–October dry). Although highly variable, rainfall is present throughout the year. During El Niño years, the wet season gets drier, whereas during La Niña years the dry season becomes wetter than normal.

[18] The loose sediments of the tertiary Barreiras formation are covered mostly by clayey yellow oxisols (latosol in the Brazilian classification) on the plateaus and sandy spodosols (podzol) on the lowland. Kaolinite, quartz, and oxides and sesquioxides of Fe and Al are the predominant minerals. Soils are very poor and acidic (pH 4.3), mostly saturated by $Al^{3+}$, with a very efficient biotic nutrient cycling for base cations and P [*Chauvel*, 1982]. Carbon in soil microbial biomass from 0 to 20 cm varies from 266 to 1460 μg $g^{-1}$, or 1.8 to 4.8% of total soil C, and has a turnover time of 0.13 to 0.17 years. Even though tree demography is extremely complex due to the high diversity, the Lecythidaceae, Sapotaceae, Euphorbiaceae and Caesalpinaceae families are found most frequently [*Jardim and Hosokawa*, 1987]. One estimate of basal area, volume and fresh aboveground phytomass for this forest was 29 $m^2$ $ha^{-1}$, 438 $m^3$ $ha^{-1}$ and 561 Mg $ha^{-1}$ respectively [*Higuchi et al.*, 1998]. Aboveground dry phytomass has also been measured as 344–393 Mg $ha^{-1}$ [*Klinge et al.*, 1975] in the general area. Canopy height is 30 m and leaf area index is 5–6. Measured litterfall was 8.3 Mg $ha^{-1}$ $a^{-1}$, with increased deposition during dry season, and faster decomposition in the wet season [*Luizão*, 1989]. The decomposition rate constant for the litter layer is 0.09–0.13 $a^{-1}$.

[19] The old tower (c14), located at km 14 of the ZF2 access road, has the longest eddy flux $CO_2$ exchange data set in Amazonia (operation started October 1995). It also has shown the largest carbon sink values both in daily peak averages and in long-term means [*Malhi et al.*, 1998; *Araujo et al.*, 2002]. The new tower (k34) is located at km 34 of ZF2, 11 km in a straight line from c14 (operational since July 1999).

### 2.3. Caxiuanã

[20] The Floresta Nacional de Caxiuanã is situated approximately 350 km to the west of the city of Belém, Pará (Figure 5). The site is administered by the Estação Cientifica Ferreira Penna, which belongs to the Museu Paraense Emílio Goeldi (MPEG). The forest is extensive (33,000 ha) and largely undisturbed, having been a reserve since the mid-1970s, and consists of dense lowland terra firme forest. Mean annual rainfall at the site is 2000 mm [*Lisboa and Ferraz*, 1999] and canopy height is 35 m, with an aboveground dry biomass of 200 $m^3$ $ha^{-1}$ [*Lisboa and Ferraz*, 1999], a basal area of 30–35 $m^2$ $ha^{-1}$ (S. S. de Almeida, unpublished data, 1999), and a leaf area index of 5–6. More than 2450 tree species have been identified within the reserve, almost a quarter of which are considered rare [*Lisboa et al.*, 1997]. There are, on average, 190 tree species and 555 individuals (with a diameter at breast height greater than 10 cm) per hectare. Families with the greatest number of species present are the Sapotaceae, Chrysobalanaceae and Lauraceae families. Both vines and palms are well represented, at highly variable proportions. The tower used for flux measurements is situated on a large plateau,

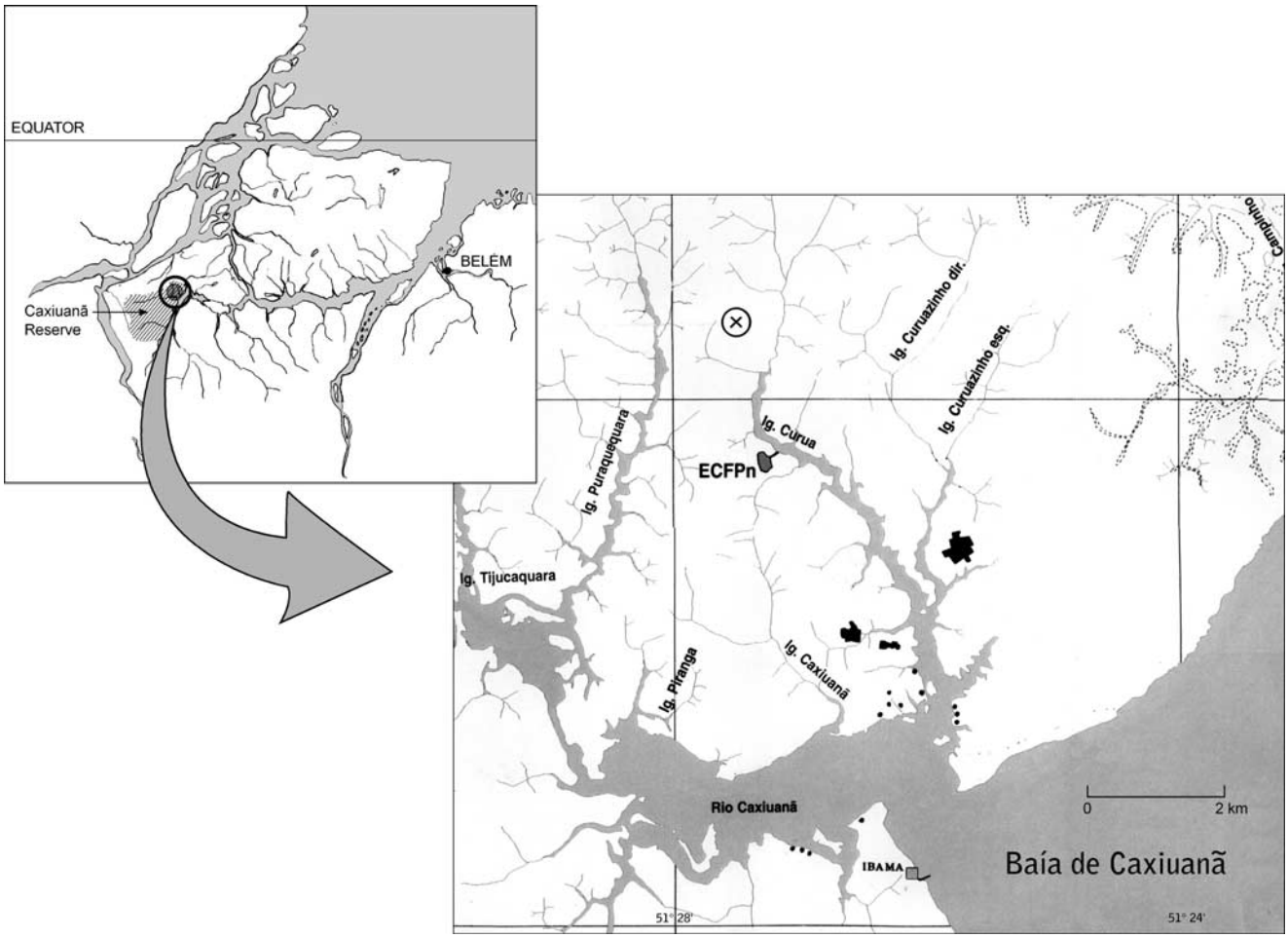


**Figure 5.** Map showing the relative position of the Caxiuanã Reserve to Belém (inset) and the position of the field station (ECFPn) with respect to both the Baía de Caxiuanã and the tower from where eddy flux measurements were made (marked as **X**).

approximately 2 km to the north of the field station. Access is by river, then foot only.

[21] Because its proximity (6 km) to the Baía de Caxiuanã, the study area likely experiences a more riverine climate than the Manaus [*Malhi et al.*, 1998] and Jarú sites [*Grace et al.*, 1995a, 1995b]. There is little annual variation in temperature, with a year-round minimum temperature of approximately 23°C [*Lisboa and Ferraz*, 1999]. The maximum temperature is slightly lower during the peak of the wet season (32°C) of January–March, compared with the "dry" season (34°C) of October–December. Most of the rainfall occurs between the end of January and the middle of July, although there is rain throughout the year. The maximum rainfall is in March (mean is 370 mm), and the minimum in October (mean is 75 mm). The rainfall pattern can vary greatly between years.

[22] The Caxiuanã soil is largely a yellow oxisol formed from plantation surfaces, as is characteristic of much of the Amazon Basin. Planosols, gleys and charcoal are also present [*Kern*, 1996]. The base is kaolinite intercalated with laterite and there are areas of iron sand approximately 3–5 m below the surface. The yellow latosol present in the A, B and C horizons is mostly well drained, although the texture varies from sand to clay. Large variations exist in soil porosity, as well as in the acidity and quality of the organic matter of the soil, but the soil is largely nutrient-poor, as found commonly in Amazonia. The pH ranges from 4.6 to 4.9, biological activity increasing with pH. The organic carbon content is extremely variable (from 4 g $kg^{-1}$ to 130 g $kg^{-1}$), containing a higher proportion of fulvic than humic acids.

## 3. Meteorological Overview for the LBA-EUSTACH 1999 Campaigns

[23] Rondônia is located in the southwestern Amazon Region and has typically a wet season from October through April and a dry season from May through September. During 1999, the rains lasted until about 16 May and started again by 15 September with a yearly total of about 1500 mm, which is below the normal total of 2100 mm. The maximum half-hourly rainfall in 1999 was 29.5 mm. Figure 6 shows the monthly precipitation at the FNS station. During the dry season, which is more pronounced in Rondônia than at the Manaus and Caxiuanã sites, only a few rain episodes were observed. The meteorological evolution during 1999 may be seen through the temperature observed in the Fazenda Nossa Senhora Aparecida

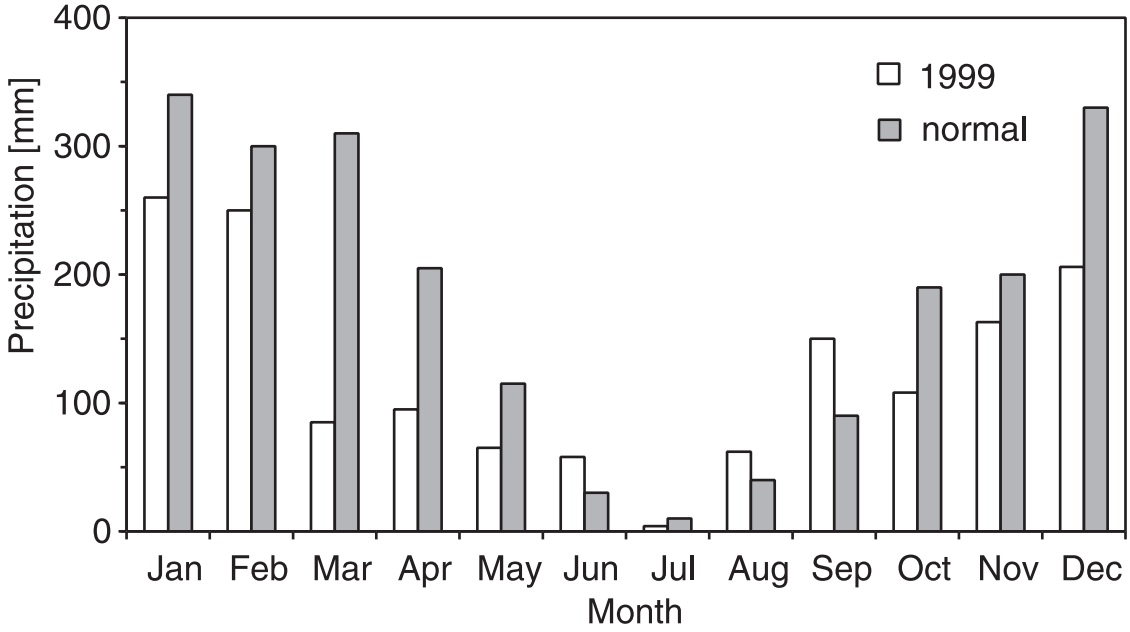


**Figure 6.** Monthly precipitation (in mm) at Fazenda Nossa Senhora Aparecida during 1999 and the normal value from 1961 to 1990 at Porto Velho (from the Brazilian weather service station INMET).

(Figure 7) and the winds from the global analysis of Centro de Previsão de Tempo e Estudos Climáticos/Instituto Nacional de Pesquisas Espaciais (CPTEC/INPE): Figure 8 shows the meridional wind component at a grid point in central Rondônia (11°S, 62°W) at 925 hPa and Figure 9 the zonal wind component at 850 hPa at the same grid point.

[24] According to *Rickenbach et al.* [2002], the wet season of 1999 was characterized by a succession of periods with low-level winds alternating between an easterly and a westerly component. According to their analysis, convective systems were more isolated and vigorous during the easterly phase and more widespread and stratiform during the westerly phase. Westerlies can be observed in Rondônia at low levels (from 950 to 700 hPa) when a midlatitude frontal boundary approaches the southern Amazon from the south. The frontal boundary only rarely moves to the north of Rondônia in the wet season, therefore the air-mass-typical parameters of temperature and moisture are not changed [cf. *Rickenbach et al.*, 2002]. Figure 9 shows that

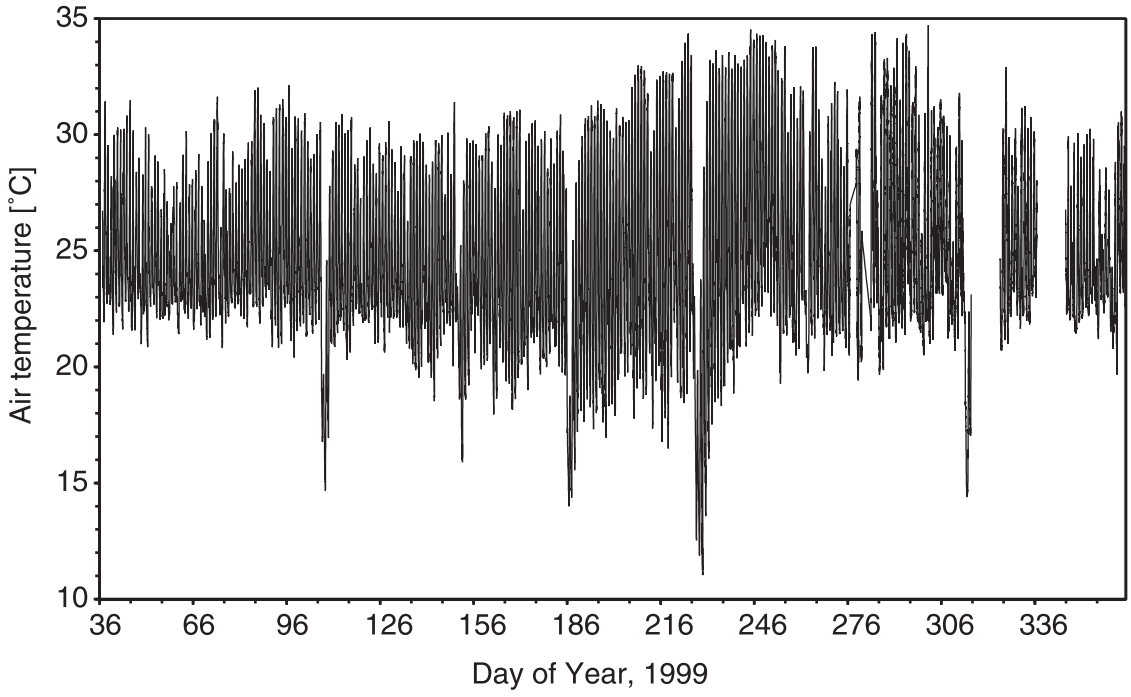


**Figure 7.** Temperature at the Fazenda Nossa Senhora Aparecida site.

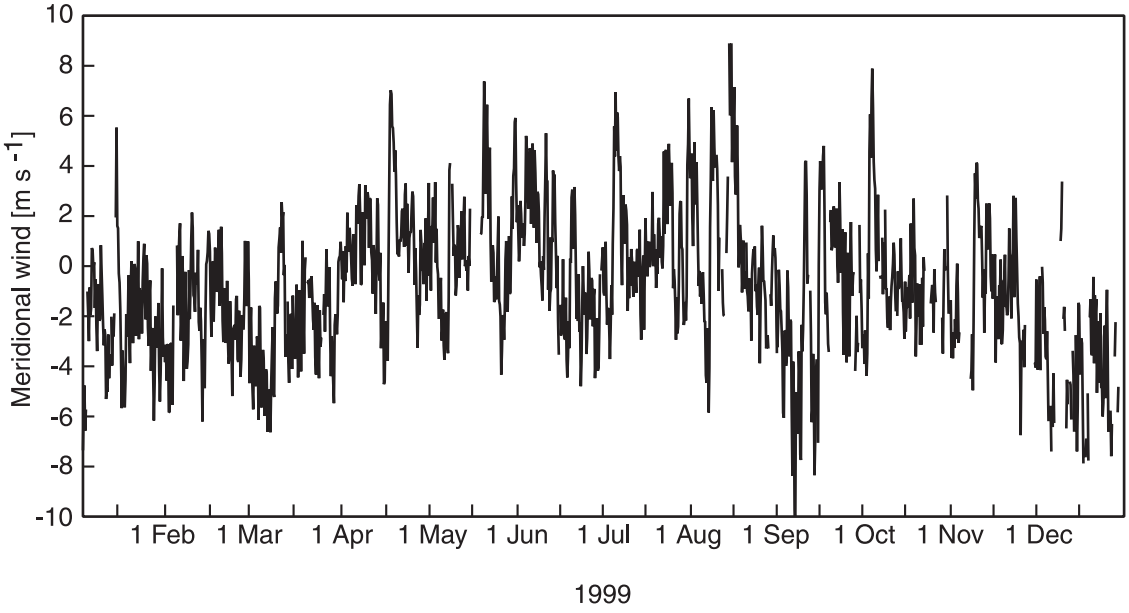


**Figure 8.** Meridional wind component from the CPTEC global analysis at 11°S, 62°W, at 925 hPa.

successive periods of easterlies and westerlies occurred from the beginning of the year until the end of March. From April to the first half of September, an easterly regime dominates. With the beginning of the wet season, the succession of alternating easterlies and westerlies resumes.

[25] Figure 7 shows that the surface temperature at the FNS site has an annual variation with warmer temperatures and larger daily amplitude during the dry season. A few episodes of colder temperatures occur, which last in general just a couple of days and are associated with southerly winds (Figure 8). As described by *Marengo et al.* [1997], frontal boundaries often penetrate well into the Amazon region, causing a temperature drop and a shift of surface winds to a southerly direction. The main episodes of well-defined cooling are on 18 April, 1 June, 6 July, 16 August and 10 November. The minimum temperature reached was 11.1°C on 17 August. These cold air intrusions, the so-called ''friagem,'' often penetrate up to the region of Manaus and represent the substitution of the tropical air mass by one from midlatitudes with different meteorological and chemical characteristics.

[26] The easterlies/westerlies regimes during the wet season and the incursion of colder air masses during the dry season, may be seen as intraseasonal oscillations [*Madden and Julian*, 1994]. On a day to day basis, the modulation of the Chaco Low in northern Argentina and the

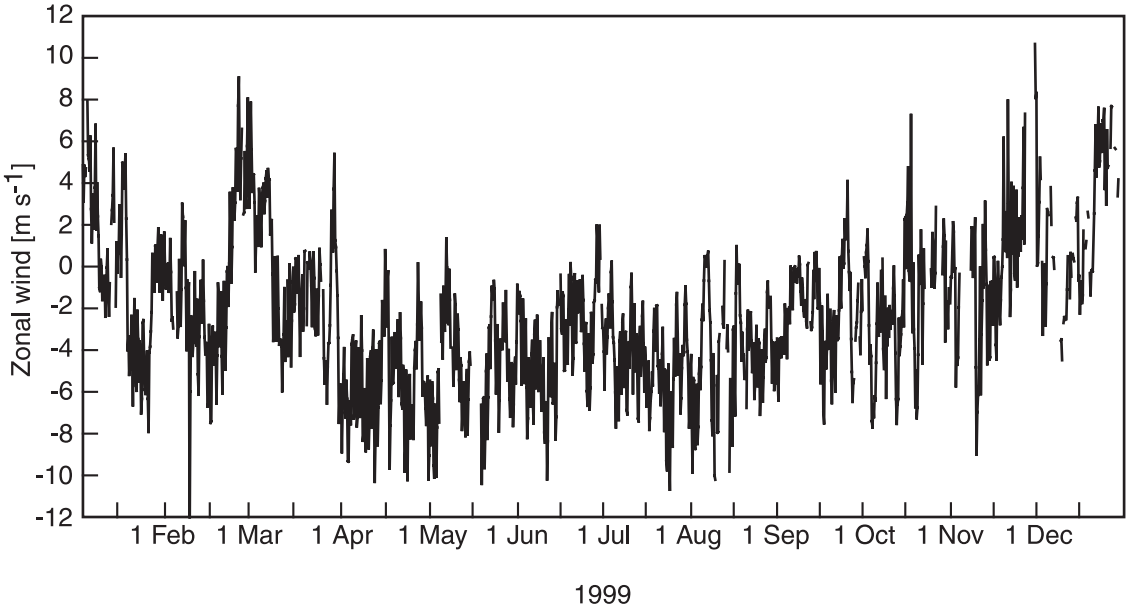


**Figure 9.** Zonal wind component from the CPTEC global analysis at 11°S, 62°W, at 850 hPa.

progression of baroclinic waves from midlatitudes are seen as the local response to these intraseasonal oscillations.

## 4. Carbon, Water, and Energy Fluxes

[27] One of the major goals of LBA-EUSTACH was to attempt to extend our knowledge of the energy, water and carbon budgets of Amazonia to larger spatial and temporal domains than has been possible in the past. In particular, we wanted to investigate whether the high rates of $CO_2$ uptake previously seen over a shorter period at the Manaus and Jarú sites [*Grace et al.*, 1995a, 1995b; *Malhi et al.*, 1998] were a general and persistent phenomenon in Amazonia. This objective has been addressed by using the currently accepted approach of establishing a network of flux stations that operate continuously for several years; an approach that is a considerable challenge in remote areas of Amazonia.

[28] Within LBA-EUSTACH, flux-measuring sites have been established in Rondônia, Manaus and Caxiuanã. Sites run by other projects within the LBA framework have since begun operation in Santarem and Brasilia. The EUSTACH sites were instrumented with variations of the EUROFLUX (Long term carbon dioxide and water vapor fluxes of European forests and interactions with the Climate System) system described in detail by *Aubinet et al.* [2000] and began operation in 1999. Data recovery from the sites has been good and comparable with that achieved over European forests. There have been significant problems, however. The system at RBJ-B was destroyed by a direct lightning strike in late 1999 (it was subsequently replaced) and high temperatures adversely affected the calibration of infrared gas analyzers at several sites. Eighteen months of near-continuous automatic weather station data now exist for each site (A. Manzi et al., Measurements of energy, water and carbon dioxide fluxes over tropical forest in south-west Amazonia, submitted to *Journal of Geophysical Research*, 2001) [*Araujo et al.*, 2002; *Carswell et al.*, 2002; *Malhi et al.*, 2002] and, for the first time in Amazonia, include individually measured components of the radiation balance, canopy surface temperature and PAR.

[29] The climate of the region during 1999 to 2000 was strongly influenced by "La Niña" which typically leads to high rainfall in Amazonia. For example, in September 1999 Manaus had more than double the long-term average rainfall. There has not yet been the opportunity to observe the effect of substantial drying of the soil on forest evaporation rates. We are awaiting a strong "El Niño" year to make these observations.

[30] Preliminary flux calculations using the procedures developed for the EUROFLUX program resulted in poor closure of the energy budget [*Araujo et al.*, 2002]. A large amount of effort has, therefore, been directed at trying to determine the reasons for this poor closure over what should be a relatively simple, extensive and homogeneous surface for flux measurements. This process has revealed a number of problems that have relevance to $CO_2$ flux measurement programs in other regions. In particular, it is becoming clear that the standard methods of detrending, rotating coordinates and applying frequency loss corrections must be carried out with great care when working over these aerodynamically rough surfaces where low frequency transport is likely to be important (B. Kruijt et al., Aspect of the robustness in eddy correlation fluxes for Amazon rainforest conditions, submitted to *Journal of Geophysical Research*, 2001, hereinafter referred to as B. Kruijt et al., submitted manuscript, 2001) [*Malhi et al.*, 2002]. Part of the problems with energy closure may also be related to an underestimation of the $H_2O$ flux when using the Licor 6262 sensor.

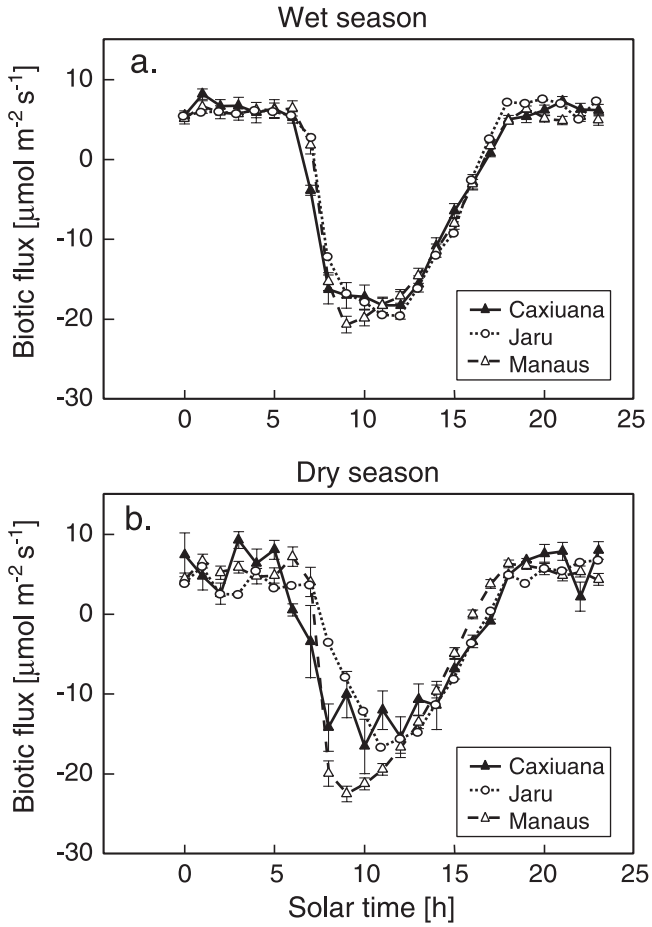


**Figure 10.** Ensembles of data representing $CO_2$ exchange, expressed as biotic fluxes, of three Amazonian rain forests in the wet and dry seasons, covering over 100 days in each case. The error bars represent standard errors.

[31] During LBA-EUSTACH, $CO_2$ exchange at the three tropical rain forest sites was measured from four towers, using eddy covariance methodology [*Moncrieff et al.*, 1997; *Aubinet et al.*, 2000]. Here, we present a comparison of three undisturbed forests: Manaus, Jarú and Caxiuanã, in the period 1999–2000. Further information about these data sets is presented elsewhere in this issue [*Carswell et al.*, 2002; B. Kruijt et al., submitted manuscript, 2001] (B. Kruijt et al., The bulk ecosystem physiology relating to NEP of three Amazon rain forests, *Geophysical Research Letters*, in preparation, 2001, hereinafter referred to as Kruijt et al., in preparation, 2001).

[32] Following the demonstration that forests even in central Amazonia have sufficient seasonality in their water balance to cause detectable variation in $CO_2$ fluxes [*Malhi et al.*, 1998], we compared fluxes measured in the wet and dry seasons. We measured in-canopy concentrations of $CO_2$ to enable hour-by-hour storage fluxes to be calculated. In

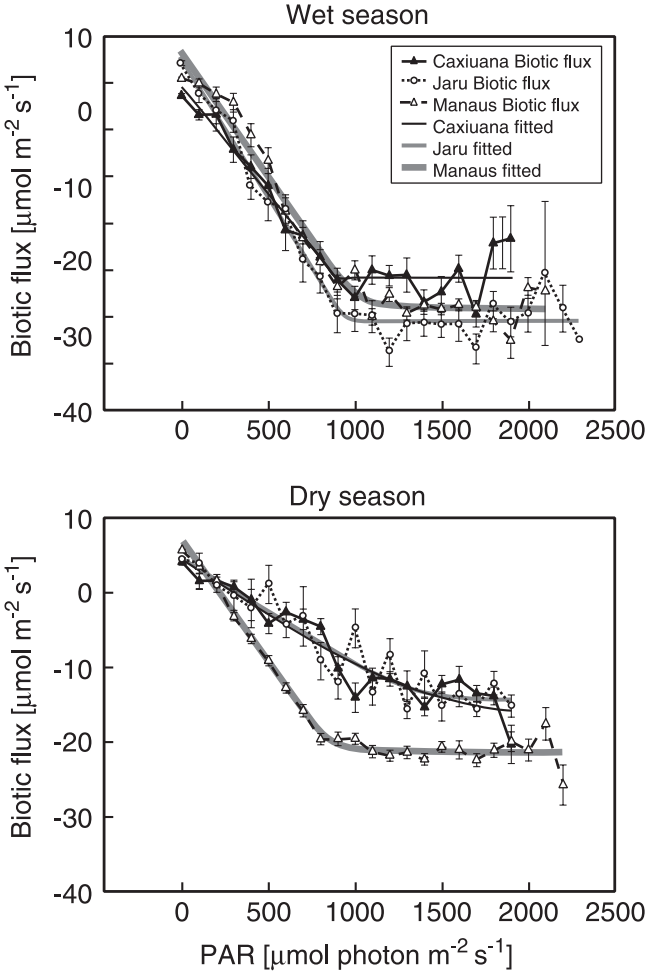


**Figure 11.** Light response curves of three Amazonian rain forests in the wet and dry seasons. The error bars represent standard errors. The curves are fitted nonrectangular hyperbolas (parameters are given in Table 2).

this report, we have added these storage fluxes to the above-canopy fluxes to obtain the biotic fluxes [*Grace et al.*, 1995a]. This has the effect of "cleaning" the hourly data, which would otherwise appear as a smeared pattern, in which physiological responses are obscured by exchanges between the canopy air space and the atmosphere.

[33] The graphs in Figure 10 represent net $CO_2$ exchanges of the whole ecosystem, integrated over a flux footprint of 0.1–3 $km^2$. We have plotted ensemble diurnal trends in the biotic fluxes for those days where both the eddy covariance system and the profile-measuring system were operating. In the wet season the nocturnal (respiratory) $CO_2$ net effluxes varied from 5 to 10 $\mu mol\ m^{-2}\ s^{-1}$ (Figure 10a). The net influxes during the period of maximal net photosynthesis in the day were as high as 20 $\mu mol\ m^{-2}\ s^{-1}$. The patterns for the three sites were remarkably similar. In common with previous measurements in Amazonia, the problem of the apparent loss from the system of carbon dioxide at night is relatively small in comparison with measurements made during the Boreal Ecosystem-Atmosphere Study (BOREAS) or in Harvard Forest [*Goulden et al.*, 1996].

[34] In Manaus, the new tower site (k34) is some 11 km from the site used by *Malhi et al.* [1998] to measure carbon dioxide fluxes over the forest (c14). A flux measurement system has been kept running at this old site in the interest of making comparisons on relatively small spatial scales. The results of the comparison between these two sites are intriguing, with the new site apparently acting as a greater sink for $CO_2$ than the old [*Araujo et al.*, 2002]. Analysis of the percentage of plateaus and valleys within the fetches of the two towers shows that the fetch of the old tower contains a much higher proportion of lower terrain, which may explain the difference between the two sites. There remains, however, the possibility of some experimental artifacts, which is still being investigated.

[35] In the dry season the $CO_2$ fluxes observed at Jarú were somewhat diminished. Nocturnal effluxes varied from 3 to 9 $\mu mol\ m^{-2}\ s^{-1}$ and maximal influxes by day were only 18 $\mu mol\ CO_2\ m^{-2}\ s^{-1}$ (Figure 10b). At Caxiuanã the effect of the dry season is also apparent from the diurnal plots. Net photosynthesis and respiration at Caxiuanã is relatively unaffected by the dry season, and there is evidence of an unusually high rate of net photosynthesis in the early hours of the morning. At Manaus the $CO_2$ fluxes in the dry season are not markedly different from the wet season.

[36] Direct, branch level exchange measurements (enclosures) of different tree species at the Jarú camp site showed daytime $CO_2$ net photosynthesis rates of sunlit leaves between 6 and 10 $\mu mol\ m^{-2}\ s^{-1}$ on the leaf area basis and agree well with means found for tree species in other

**Table 2.** Parameters of the Nonrectangular Hyperbola Fitted to the Data Shown in Figure 11[a]

| Parameters | Manaus | | Caxiuanã | | Jarú | |
|---|---|---|---|---|---|---|
| | Wet | Dry | Wet | Dry | Wet | Dry |
| $R_{day}$, respiration by day ($\mu mol\ CO_2\ m^{-2}\ s^{-1}$) | 8.2 ± 1.14 | 6.7 ± 1.00 | 4.5 ± 1.29 | 4.55 ± 1.5 | 7.5 ± 1.1 | 4.6 ± 1.5 |
| $\alpha$, quantum efficiency ($mol\ CO_2\ mol\ photon^{-1}$) | 0.027 ± 0.003 | 0.033 ± 0.003 | 0.023 ± 0.003 | 0.016 ± 0.004 | 0.029 ± 0.002 | 0.014 ± 0.003 |
| $A_{max}$, maximal photosynthesis ($\mu mol\ CO_2\ m^{-2}\ s^{-1}$) | 27.5 ± 1.4 | 28.2 ± 1.2 | 20.4 ± 1.4 | 23.5 ± 9.8 | 28.0 ± 1.2 | 19 ± 4 |
| $\theta$, convexity, (dimensionless) | 0.99 | 1.00 | 1.00 | 0.93 | 1.00 | 0.99 |
| $Q_{comp}$, PAR at light-compensation point ($\mu mol\ photon\ m^{-2}\ s^{-1}$) | 388 | 205 | 199 | 298 | 254 | 322 |
| $Q_{sat}$, PAR required to saturate photosynthesis ($\mu mol\ photon\ m^{-2}\ s^{-1}$) | 1341 | 1066 | 1096 | 1814 | 1677 | 1200 |

[a] Nocturnal data are omitted from this analysis. The values stated are fitted values ± asymptotic standard deviation.

tropical regions of the world [*Kuhn et al.*, 2002]. The direct gas exchange was only moderately affected by the seasonal changes of the environmental conditions. $CO_2$ assimilation rates seem to correspond more to the ecological environment rather than to the particular tree species. Species that occupy a particular ecological niche might behave in a similar fashion, like a functional group [*Körner*, 1993].

[37] A revealing comparison of the functionality of gas exchange is made by plotting biotic fluxes as a function of the incident PAR (Figure 11). This plot enables comparison between sites to be made at equal irradiance, and a nonrectangular hyperbola may then be fitted to the data to construct a simple ''big-leaf'' model of photosynthesis [*Lloyd et al.*, 1995]. The comparison shows that Jarú and Caxiuanã experience a substantial reduction in their apparent quantum efficiency during the dry season (Figure 11 and Table 2). At Jarú this reduction is as much as 50%. Moreover, the shape of the light-response curve varies with season: in the wet season a definite light-saturation occurs, but not in the dry season. Further work is needed to see whether this change in the shape of the light response curve is physiological, such as the effect of stomatal closure, or simply the result of a change in the structural organization of the canopy, such as a change in the leaf area index (B. Kruijt et al., in preparation, 2001). Preliminary inspection of the data suggests that both sorts of change may be involved. However, at Manaus the photosynthetic response to light in the dry season is not very different from that in the wet season. There is a tendency for higher quantum efficiency in the dry season. This is in contrast to results obtained in Manaus during a one-year measurement period in 1995/6, when there was indeed a reduction of photosynthesis in the dry season [*Malhi et al.*, 1998].

[38] Integration of flux data over a year provides an estimate of the annual source/sink strength. All three forests appear to be strong sinks for carbon, in the range previously reported for Jarú in 1992/3 and for Manaus in 1995/6 [*Grace et al.*, 1995b; *Malhi et al.*, 1998]. The size of the calculated sink is highly sensitive to the assumptions made in the calculations, especially when dealing with stable conditions at night when there may be ''flux loss.'' It is becoming clear that when data collected under stable nocturnal conditions are replaced by modeled values (or values obtained only in high wind speed conditions), lower estimates of sink strength are obtained. As yet, however, there is no scientific consensus on whether such ''corrections'' are valid, and until this is resolved, the annual flux remains uncertain.

[39] Extrapolating these fluxes to the whole land area of Amazonia is not yet possible as there are major uncertainties caused by carbon fluxes arising from (1) disturbances, (2) lateral drainage of air at night, (3) lateral transfers to the river, and (4) the efflux of volatile organic materials (see below).

## 5. VOC Emission From Terrestrial Vegetation and Ambient Concentrations of Primary and Secondary Products

[40] According to the International Global Atmospheric Chemistry/Global Emissions Inventory Activity (IGAC/GEIA) inventory [*Guenther et al.*, 1995], the Amazon Basin accounts for a large fraction of global VOC emissions (mainly isoprene), and any change in the atmospheric chemical processes in this area can have a profound impact on global climate [*Andreae and Crutzen*, 1997]. Accurate predictions of these changes are made difficult, however, by the uncertainties associated with present estimates. Figures on VOC emissions are mostly based on extrapolations from temperate regions, on the early measurements performed by *Zimmerman et al.* [1988] and *Rasmussen and Khalil* [1988], and on the recent work carried out by *Helmig et al.* [1998] in the Peruvian Amazon. Although the information collected in other regions of the world, e.g., Africa [*Guenther et al.*, 1999], has helped to better understand the mechanisms of isoprene production from tropical vegetation, experimental work was urgently needed to check if the algorithms developed elsewhere were also valid for the tropical vegetation of the Amazon Basin, and could be used to assess the carbon budget of the different ecosystems there. Systematic research was also required to understand and parameterize the processes responsible for the emission and transformation of other biogenic compounds (such as terpenes, aldehydes and acids), which can contribute to ozone production, secondary organic aerosol formation and acid deposition.

[41] To meet all these requirements, an integrated approach was followed in LBA-EUSTACH. VOC measurements carried out at branch level were complemented with observations made at canopy level using micrometeorological techniques, such as relaxed eddy accumulation (REA) and time-resolved eddy correlation. Investigations were not limited to isoprenoid compounds, but were extended to those oxygenated VOCs known or suspected to be emitted by terrestrial plants, formed in the atmosphere, or associated with biomass burning.

[42] Results obtained in Rondônia showed a clear seasonality in the ambient VOC concentrations. The levels of isoprene, formic and acetic acid, formaldehyde and acetaldehyde measured in the dry season were all 4–5 times higher than those measured in the wet season [*Kesselmeier et al.*, 2002]. In particular, isoprene levels well above 10 ppb were recorded at 10–20 m above the canopy. The total content of monoterpenes in the air also increased from the wet to the dry season, but to a lesser extent than that of isoprene. A change in relative composition, probably reflecting changes in the phenological state of plants, was observed for monoterpenes. All major constituents were characterized by clear diurnal patterns showing maximum values in the middle of the afternoon. The concurrent increase of isoprene and its degradation products (methacrolein, MAC, and methylvinylketone, MVK) indicates that both emission and photochemical processes reached their maximum value during the dry season due to more intense solar radiation and, consequently, higher temperatures. The substantial increase of ozone (from 12 to 60 ppb) indicates that photochemical processes were highly active during the dry season. In addition to reflecting the phenological state of the plants, the smaller seasonal variations of the monoterpenes relative to those of isoprene may be indicative of more efficient conversion of these compounds into gaseous secondary products or aerosols. Enhanced photochemical processing of biogenic hydrocarbons was probably also responsible for some of the increase of volatile aldehydes

**Table 3.** Percent Composition and Total Content of VOC Excluding Very Volatile Hydrocarbons, Carbonyls (Formaldehyde, Acetaldehyde) and Acids (Formic, Acetic) Measured Above the Canopy in Rondônia and Manaus During Various Seasons[a]

| Compound | End of the wet season Rebio Jarú 16–17 May 1999 (%) | End of the dry season Manaus 29 November 1999 (%) | End of the dry season Rebio Jarú 8–10 November 1999 (%) | Beginning of the wet season Manaus 10 December 1999–20 January 2000 (%) |
|---|---|---|---|---|
| $CCl_4$ | 1.74 | 1.33 | 1.74 | 1.86 |
| Acetone | 16.1 | 16.0 | 5.36 | 1.22 |
| Methacrolein | 5.75 | 6.90 | 8.84 | 6.70 |
| Methylvinyl ketone | 22.7 | 17.5 | 28.2 | 17.4 |
| 2-Methyl furan | 0.83 | 0.17 | 2.99 | 0.13 |
| 3-Methyl furan | 0.06 | 0.96 | – | 1.04 |
| Butanal | 4.83 | 2.01 | – | 1.18 |
| Pentanal | 2.5 | 1.04 | – | 0.57 |
| Hexanal | 1.48 | 0.27 | 1.10 | 0.09 |
| Heptanal | 0.87 | 0.51 | 0.49 | 0.33 |
| Octanal | 0.49 | 2.61 | 0.76 | 1.26 |
| Nonanal | 0.69 | 1.09 | 0.45 | 1.88 |
| Decanal | 0.3 | 1.31 | – | 2.50 |
| Benzaldehyde | 0.72 | 1.99 | 1.13 | 0.44 |
| Benzene | 2.07 | 3.26 | 1.51 | 1.05 |
| Toluene | 0.44 | 0.57 | 0.47 | 0.11 |
| 2-Butanone | – | 8.47 | 5.85 | 5.80 |
| 6-MHO[b] | 0.31 | 3.69 | 0.34 | 1.17 |
| Isoprene | 29.72 | 21.84 | 22.11 | 47.64 |
| a-Pinene | 1.52 | 2.09 | 1.55 | 3.68 |
| Sabinene | – | 0.32 | 0.30 | 0.68 |
| b-Pinene | 0.08 | 1.11 | 0.53 | 1.66 |
| Limonene | 0.19 | 0.26 | 0.07 | 0.45 |
| others | 6.71 | 4.69 | 16.21 | 1.15 |
| Total (%) | 100 | 100.00 | 100.00 | 100.00 |
| Total (ppb) Formic acid (ppb) | 5.05 | 6.94, 7.55 | 6.50 | 4.22, 1.9 |

[a] For the sake of comparison, the average levels of formic acid are reported. For the average concentrations and diurnal cycles of organic acids, aldehydes and isoprenoids in Rondônia, see *Kesselmeier et al.* [2002].
[b] 6-methyl-5-heptene-2-one.

and acids, but a large fraction of these compounds was due to pyrogenic emissions [*Kesselmeier et al.*, 2002].

[43] Leaf and branch enclosure experiments have shown that plants can act as a net source or sink of short-chain volatile organic acids. *Kuhn et al.* [2002] found a bidirectional exchange behavior for formic acid and acetic acid, with compensation point concentrations as low as 0.16–0.30 ppb on a leaf area basis, for different tree species in Rondônia. At the concentrations present over the site, a net uptake was mostly observed during both the wet and dry season. Deposition velocities on a leaf area basis were 0.17–0.23 cm $s^{-1}$. Vertical profile measurements in and above the forest canopy support the view that the tropical vegetation acts as a net sink for formic and acetic acid [*Kuhn et al.*, 2002]. These findings suggest that biomass burning and photochemical processes are the major sources for these components in tropical regions.

[44] Ambient concentrations and flux measurements carried out in Manaus at the end of the wet season and at the beginning of the dry season agreed with the observations made in Rondônia, in spite of the differences of latitude and vegetation type. They were performed at a 50-m tower where a relaxed-eddy-accumulation (REA) system, similar to the one described by *Valentini et al.* [1997], was installed. VOC samples were collected on traps filled with carbon adsorbents that were analyzed by GC-MS. In addition to all hydrocarbons with carbon number higher than 4, it was possible to quantify with this method some chlorofluorocarbons and some volatile acids. Table 3 compares the percent composition of VOC, excluding the very volatile hydrocarbons ($C_2$ to $C_4$), carbonyls (formaldehyde and acetaldehyde) and free acids (formic, acetic and propionic) that were measured in Manaus and in Rondônia. Data refer to samples collected above the canopy at midday. They show that isoprene was in all cases the major VOC component, and that monoterpenes accounted for only a small portion of this organic fraction (ca. 10%). Among the oxygenated compounds, acetone, MVK, and MAC were the dominating compounds, although 2-butanone, butanal and benzaldehyde were not negligible. If we compare the total levels of these oxygenated compounds to that of formic acid, we can see, however, that, similarly to what was

**Table 4.** Average Net Fluxes (N = 18) of VOC Showing Consistent Trends of Net Emission (Positive) or Net Deposition (Negative) in the Tropical Forest[a]

| Compound | Net flux ng $m^{-2}$ $s^{-1}$ |
|---|---|
| Acetone | −232 |
| Methacrolein | −28 |
| Methylvinyl ketone | −90 |
| 2-Methyl furan | −2 |
| Butanal | −70 |
| Pentanal | −39 |
| Benzaldehyde | −31 |
| Benzene | −65 |
| Toluene | −15 |
| 2-Butanone | −64 |
| Isoprene | 800 |
| Monoterpenes | 100 |

[a] Data were collected in Manaus at the end of the dry season–beginning of the wet season. For the other compounds, see the text.

**Table 5.** Variability in the Reactivity Indicators of Isoprene Reaction and of the Aging of the Air Masses

| Ratios | Wet season Balbina 2–15 April 1998 | End of the wet season Rebio Jarú 16–17 May 1999 | End of the dry season Manaus 29 November 1999 | End of the dry season Rebio Jarú 8–10 November 1999 | Beginning of the wet season Manaus 10 December 1999–20 January 2000 |
|---|---|---|---|---|---|
| MVK/MAC | 3.1 | 3.9 | 2.5 | 3.2 | 2.6 |
| (MVK + MAC)/Isoprene | 0.1 | 1.0 | 1.1 | 1.7 | 0.5 |
| Toluene/Benzene | 2.5 | 0.2 | 0.2 | 0.3 | 0.1 |

observed in Rondônia, this acid was one of the dominating VOC components. The values of acetic and propionic acids measured in Manaus were also high, but data on these components were affected by large error due to the high background levels present in the traps used at Manaus. The dramatic drop in the concentrations of acetone and formic acid that was observed in Manaus during the transition from the dry to the wet season is consistent with the observations made in Rondônia.

[45] The data reported in Table 4 help to understand how emission and deposition processes might affect tropical ecosystems. In this table, we have reported only the fluxes of VOC for which consistent trends were observed during the measuring period (end of the dry season–beginning of the wet season). Our data show that deposition was taking place for the arenes of anthropogenic origin and for many of the oxygenated compounds listed in Table 3, whereas a net emission was always recorded for isoprene and monoterpenes. Isoprene emission was found to be light and temperature dependent and canopy fluxes were 1500 ng $m^{-2}$ $s^{-1}$ when the top of the canopy reached 30°C under light saturation conditions [*Stefani et al.*, 2000]. In all cases, monoterpenes contributed no more than 10–15% to the total isoprenoid flux.

[46] For some oxygenated compounds, such as MVK, MAC, 2-methyl furan and benzaldehyde, which can only be formed photochemically, only deposition fluxes were to be expected. On the other hand, the deposition of acetone, 2-butanone, butanal and pentanal was not obvious a priori, because these compounds can also be produced by terrestrial plants and emitted through stomata (acetone) or wounds (butanal and pentanal), as well as being released from biomass burning or photochemical processes. Deposition of these components was indicative of input from the boundary layer, where they were enriched because of photochemical processes or transport from anthropogenic sources, particularly biomass burning. The behavior of formic acid was different from that of the compounds reported in Table 4 as both net emission and net deposition was observed. Deposition episodes were more frequently observed at the end of the dry season when concentrations in air exceeded 5 ppb, whereas emission occurred mostly when ambient concentrations were equal to or lower than 2 ppb. The REA measurements thus confirmed the existence of a compensation point, which had been suggested by the cuvette experiments of *Kuhn et al.* [2002].

[47] In Table 5 we have summarized the range of variation of some index ratios that provide information on the atmospheric reactivity in the boundary layer and on the impact that anthropogenic sources, especially of $NO_x$, might have on it. The data show that MVK/MAC values can range from almost 3.1 to 1.5, whereas (MVK + MAC)/isoprene ratios vary from 0.1 to 1.1. These indicators confirm the wide range of production of hydroxyl (OH) radicals that can occur in the Amazon Basin, and the crucial role that $NO_x$ concentrations can play in promoting an efficient removal of isoprene and monoterpenes from the atmospheric boundary layer (ABL) [*Yokouchi*, 1994; *Biesenthal et al.*, 1998]. The toluene/benzene ratios in air provide information on the aging of air masses impacting the site. Fresh emissions from biomass burning, probably the main source of these species in the dry season, have typical toluene/benzene ratios of 0.6 ± 0.2 [*Andreae and Merlet*, 2001]. The observed ratios of 0.1–0.3 are indicative of moderately aged air masses that have been subjected to significant photochemical removal of VOC and $NO_x$. The highest values were observed at the end of the dry season in Rondônia, where fresh smoke was abundant, the lowest values are from the wet season at Manaus, when there are essentially no pyrogenic emissions in the Amazon Basin. The very high value of the toluene/benzene ratio found at Balbina in 1998 remains unexplained.

[48] Since not all the data collected at the different sites and seasons have yet been fully processed and evaluated, the overview of the results presented here is necessarily limited. More detailed conclusions on the emission, fluxes and reactivity of VOC in the Amazon Basin and on the carbon budget will be presented when the analysis of all data has been completed.

## 6. Concentrations and Fluxes of Nitrogen Oxides and Ozone

[49] As pointed out in the previous section, hydrocarbons and carbon monoxide affect the oxidizing power of the atmosphere by providing both sources and sinks of OH and $O_3$, and their net influence on the oxidant cycle depends strongly on the amount of $NO_x$ present [*Crutzen and Zimmermann*, 1991; *Crutzen*, 1995]. Current land clearing processes, industrialization, the growth of traffic, and other social and economic changes in Amazonia already affect the budgets of ozone and its precursors (VOC, $NO_x$). Because of Amazonia's vast size, these regional changes are expected to cause significant change in the oxidizing power of the global atmosphere. To investigate this topic, concentrations and fluxes of $NO_x$ and $O_3$ were measured at a primary rain forest (RBJ) and a pasture (FNS) site in the vicinity of Ji-Paraná, Rondônia, a region where rain forests have been progressively cleared during the last 25 years. Measurements were organized in two campaigns (LBA-EUSTACH-1 and -2) in order to address seasonal influences. The surface exchange of NO, $NO_2$, and $O_3$ was studied by an integrated experimental approach, using soil enclosures, (in-canopy) concentration profile measurements, (above canopy) micrometeorological techniques, and laboratory methods [Ammann et al., submitted manuscript; *Gut et al.*, 2002a, 2002b; *Kirkman et al.*, 2002; *Rummel et al.*, 2002; *van Dijk and Meixner*, 2002] (L. V. Gatti et al.,

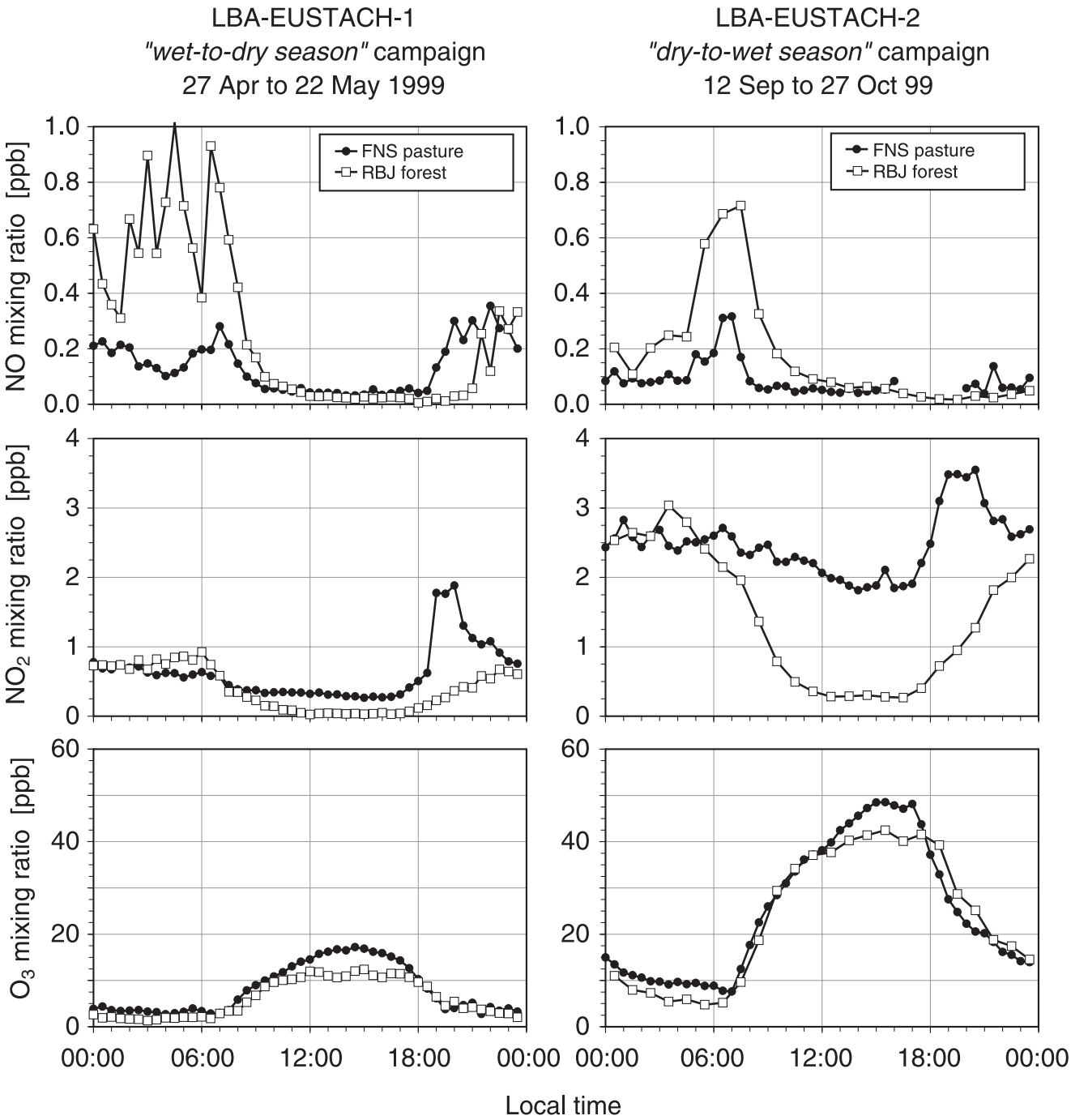


**Figure 12.** Mean daily variation of NO, $NO_2$, and $O_3$ concentrations at the LBA-EUSTACH primary forest site, Reserva Biológica Jarú (RBJ), and at the LBA-EUSTACH pasture site, Fazenda Nossa Senhora Aparecida (FNS). Measurements were taken 3.5 m above ground at the pasture site and at 20 m above the rainforest canopy. Data are presented as 1-hour medians over 27 days of the LBA-EUSTACH-1 campaign (left) and 46 days of the LBA-EUSTACH-2 campaign (right).

Associations between trace gas and aerosol concentrations during dry and wet seasons in Rondonia, Amazonia, *Ecological Applications*, in preparation, 2001, hereinafter referred to as Gatti et al., in preparation, 2001).

[50] Figure 12 presents the mean diel variations of ambient NO, $NO_2$, and $O_3$ concentrations at RBJ and FNS towers A, based on 27 and 46 days of the 1999 ''wet-to-dry season transition'' and ''dry-to-wet season transition'' campaigns, respectively. Measurements were performed at heights of 3.5 m above ground at the pasture site (Gatti et al., in preparation, 2001) and at 20 m above the rain forest canopy (Ammann et al., submitted manuscript). The most striking features are (1) marked diel variations independent of season, revealing low/high NO and $NO_2$ concentrations during day/night, respectively, (vice versa for $O_3$), (2) generally elevated levels of $O_3$ and $NO_2$ during

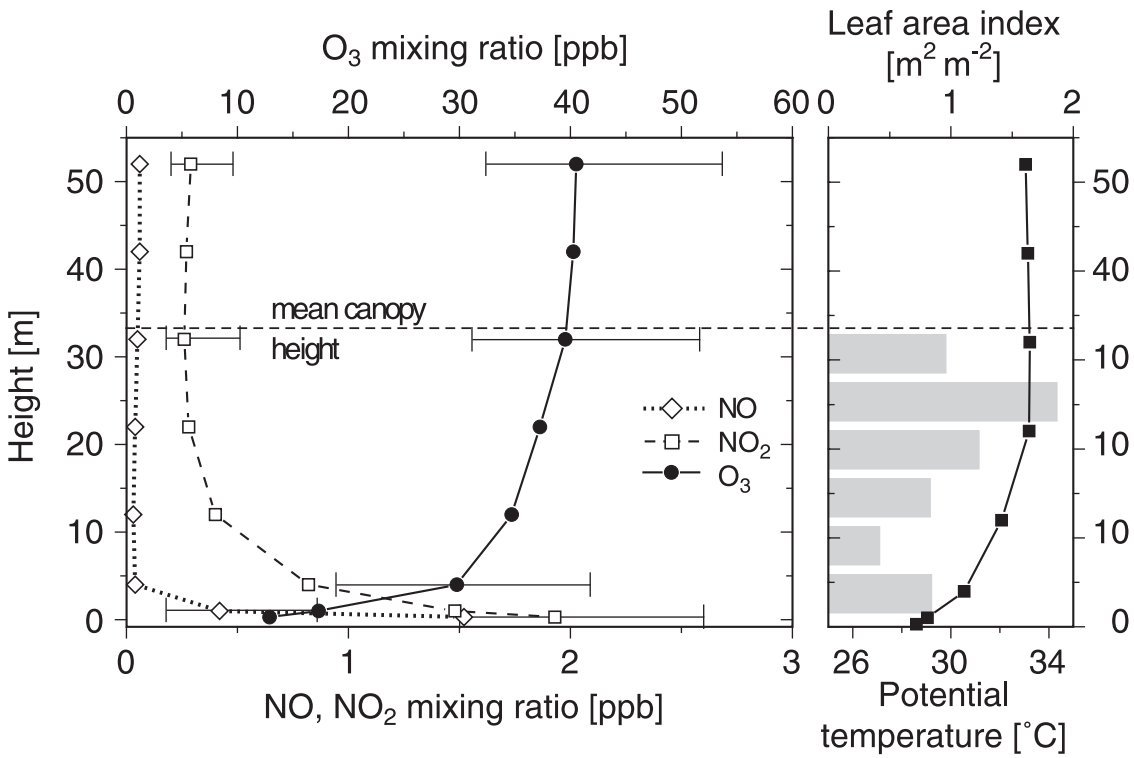


**Figure 13.** (a) Mean vertical profiles at 1400 local time of NO (open squares), $NO_2$ (open diamonds), and $O_3$ (solid circles) at RBJ-A, averaged over 43 days of the LBA-EUSTACH-2 campaign. (b) Vertical distribution of the one-sided leaf area index (gray-shaded area) and a typical profile of potential temperature (solid squares) at 1400 local time. Data points of concentrations are medians (0.5-quantile), while corresponding variations are indicated by horizontal bars (left end: 0.25-quantile, right end: 0.75-quantile). Variation of NO concentration above 5 m is smaller than symbol size.

the September/October experiment, (3) a distinct maximum of $NO_2$ between 1800 and 2100 (local time) at the pasture site during both seasons, and (4) high NO concentrations during the second half of the night. Contrasting with this ''mean'' diel cycle, high $O_3$ concentrations caused by convective downdrafts are sometimes observed at night [*Betts et al.*, 2002].

[51] During the ABLE-2A/B and TRACE-A experiments, similar diel variations of surface $O_3$ and NO concentrations have been observed for several Amazonian sites [*Kaplan et al.*, 1988; *Kirchhoff*, 1988; *Torres and Buchan*, 1988; *Bakwin et al.*, 1990; *Kirchhoff et al.*, 1990, 1996]. Corresponding modeling studies by *Jacob and Wofsy* [1988, 1990] have demonstrated that the observed characteristic diel variations of NO and $O_3$ concentrations are due to the combined action of biogenic emission of NO from the soil, dry deposition of $O_3$ and $NO_2$ to vegetation elements, (photo-)chemistry within and above the canopy, and a different day/night pattern of turbulent transport within and above the forest canopy.

[52] With the onset of large-scale biomass burning in September/October (see Aerosol and CCN section below) concentrations of $NO_2$ and photochemically produced $O_3$ were substantially enhanced compared to the results of the April/May experiment. Analogous measurements of $O_3$ concentrations have been reported by *Kirchhoff et al.* [1996] for the 1990–1992 wet and dry seasons at Cuiabá (860 km SW of Ji-Paraná). During LBA-EUSTACH-2, our results show a moderate increase of $NO_2$ concentration at RBJ-A, whereas a sevenfold increase (as compared to LBA-EUSTACH-1) is observed at the pasture site during the late afternoon hours. This is certainly due to the fact that the dominant upwind sectors of RBJ are comprised of hundreds of kilometers of pristine rain forest, whereas FNS is situated in the center of burning activities. Furthermore, odd nitrogen compounds other than $NO_2$ may have contributed to the $NO_2$ signal at FNS-A, since a nonselective $NO_2$ analyzer (molybdenum converter, 300°C) was used there (whereas a selective, photolytic $NO_2$ converter was applied at the RBJ-A site).

[53] The distinct $NO_2$ maximum that was observed at the pasture site during both experimental periods in the early evening hours could be attributed to local advection of moderately aged pollution plumes (from nearby traffic) dispersing in a very shallow, stable, and just developing nocturnal boundary layer. Later in the night, when $O_3$ concentrations had dropped to very low levels at both experimental sites, the still stable and shallow nocturnal boundary layer favored the accumulation of soil-emitted NO, notably during LBA-EUSTACH-1. Much higher nocturnal NO concentrations over the forest suggest higher biogenic NO emissions from forest than from pasture soils. This hypothesis was fully proven by a combination of field measurements of NO, $NO_2$, and $O_3$ exchange at the soil-atmosphere interface using a variety of techniques [Ammann et al., submitted manuscript; *Gut et al.*, 2002a, 2002b;

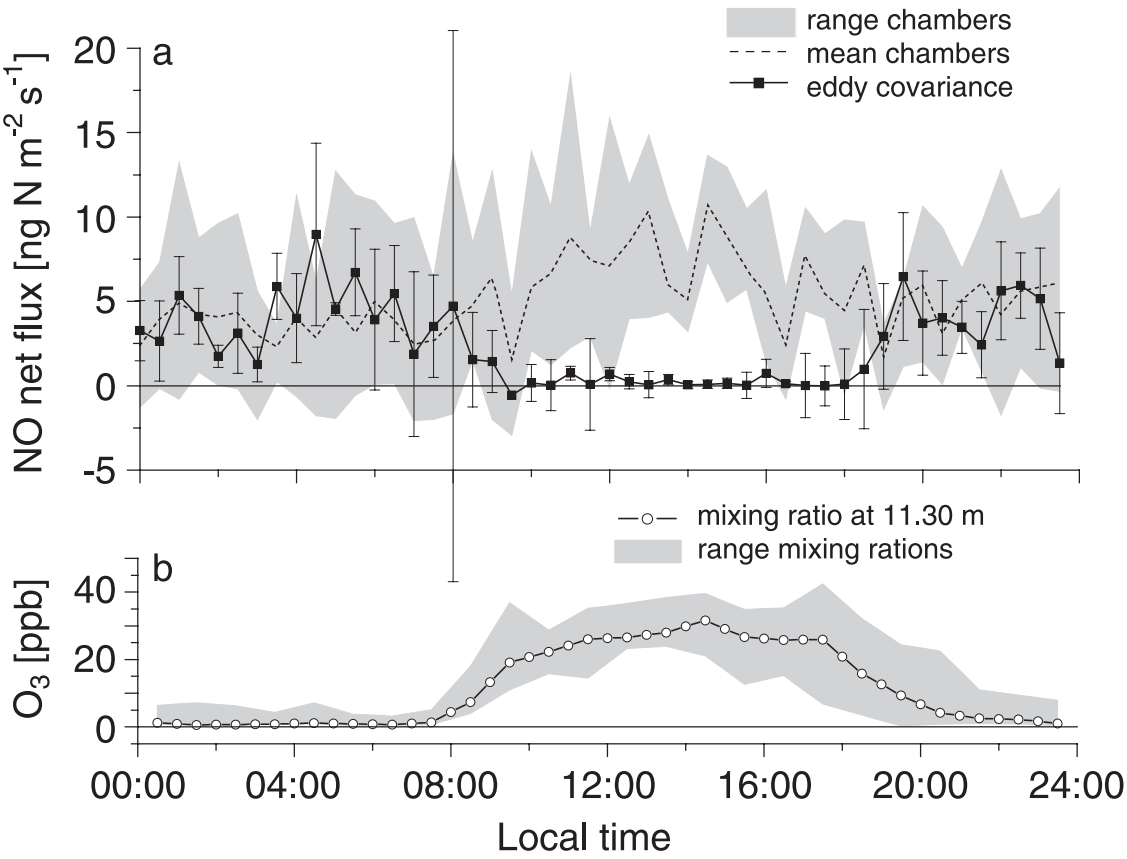


**Figure 14.** Mean (median) diurnal course at RBJ-A, 23 September to 1 October 1999, of (a) the NO flux measured by eddy covariance 11 m height (full squares), NO soil emissions measured by dynamic chambers (median: dashed line, range: gray-shaded area), and (b) $O_3$ mixing ratio at 11.3 m height (median: open circles, range: gray-shaded area). The vertical bars indicate the variability of the eddy covariance data over the averaging period [figure after *Rummel et al.* [2002], modified].

*Kirkman et al.*, 2002; *Rummel et al.*, 2002]. It was recently pointed out that rain forest-pasture conversion is accompanied with losses of nutrients and microbial activity and consequently with decreasing NO production in the soil [*Keller et al.*, 1997; *Neill et al.*, 1999; *Davidson et al.*, 2000]. Indeed, during LBA-EUSTACH-2, the NO emission flux from the 20-yr old FNS pasture was ten times lower that that observed from the RBJ forest floor.

[54] NO fluxes derived from laboratory measurements on FNS and RBJ soil samples provide exactly the same result as the field observations [*van Dijk et al.*, 2002; *van Dijk and Meixner*, 2002]. These laboratory studies also investigated NO production/consumption processes and their controls (soil pH, moisture, temperature, and nutrients) in a total of 35 Rondônian and other Amazonian soil samples taken from a variety of primary and secondary forest as well as pasture sites. NO production in terms of ng of N evolving per kg of soil was found to be $5.46 \pm 4.85$, $0.51 \pm 0.34$, and $0.48 \pm 0.30$ $s^{-1}$ for primary forest, secondary forest, and pasture soils, respectively.

[55] Since the pioneering work by *Kaplan et al.* [1988] and *Bakwin et al.* [1990], we know that only a limited fraction of the NO emitted from the rain forest soil eventually escapes to the boundary layer above the canopy. Modeling by *Jacob and Wofsy* [1990] confirmed that during daytime most NO emitted from the soil reacts with $O_3$ (mixed into the canopy from aloft) to form $NO_2$, which was assumed to be deposited on vegetation elements. Since no selective $NO_2$ measurements were performed during ABLE, the amount of $NO_2$ deposited and the fraction of soil-emitted NO remaining in the rain forest canopy could only be estimated in that study.

[56] Therefore, during LBA-EUSTACH we investigated the exchange of all relevant trace gases (NO, $NO_2$, $O_3$, $CO_2$, and $^{220}Rn$) at the soil/atmosphere interface by soil chamber, soil profile and concentration gradient techniques [*Gut et al.*, 2002a, 2002b]. Additionally, NO, $NO_2$, and $O_3$ concentrations were measured at heights of 0.3, 1, 5, 11, 21, 31, 42, and 52 m above the forest floor at RBJ-A during both LBA-EUSTACH campaigns (Ammann et al., submitted manuscript). Fluxes of momentum, sensible heat, $O_3$ and NO were measured at 52, 11 and 1 m by an eddy covariance technique [*Rummel et al.*, 2002]. The eddy covariance flux measurements of NO within the forest canopy are to our knowledge the first ever reported. The flux studies at the forest floor revealed that uptake of $NO_2$ by the forest soil was 74% of the soil NO emission flux during night and 34% during daytime [*Gut et al.*, 2002a]. In Figure 13, vertical profiles of NO, $NO_2$, and $O_3$ (averaging 43 days of the LBA-EUSTACH-2 campaign) and a typical profile of

potential temperature are shown for midday conditions. As expected for the rather stable stratification within the canopy, most of the soil-emitted NO vanished within a few meters above the forest floor (as a result of reaction with $O_3$). The mean diurnal course of NO fluxes at 11 m (measured by eddy covariance from 23 September to 1 October 1999), $O_3$ concentrations at 11.3 m, and surface NO fluxes (from 3 dynamic chambers) are presented in Figure 14 [*Rummel et al.*, 2002]. During nighttime and early morning (1900–0800), when the $O_3$ concentration is at very low levels (<2 ppb), the agreement between chamber and eddy covariance data for NO fluxes is excellent. This indicates that there is little or no chemical reaction of soil-emitted NO. In contrast, the NO net flux at 11 m was generally close to zero between 0830 and 1830. This shows that all the NO emitted from the soil has reacted with $O_3$ within the lowest few meters to form $NO_2$. A detailed discussion of the canopy reduction effect on soil NO emission is given by C. Ammann et al., (submitted manuscript).

## 7. Aerosols, Cloud Condensation Nuclei, and Climate

[57] The composition and concentration of the atmospheric aerosol over Amazonia undergo pronounced seasonal change [*Artaxo et al.*, 2002]. During the dry season, vast fires release huge amounts of smoke [*Potter et al.*, 2002], and consequently pyrogenic aerosol particles dominate the atmospheric aerosol over most of the Amazon Basin [*Andreae et al.*, 1988; *Talbot et al.*, 1988; *Browell et al.*, 1996; *Artaxo et al.*, 1998]. In the wet season, when biomass burning is limited to small amounts of domestic biofuel use, the aerosol over the Amazon Basin is a complex, and yet poorly understood mixture resulting from a variety of sources. There are highly variable contributions from long-range inputs of dust and marine particles, superimposed on regional production of primary biogenic particles, and the oxidation of biogenic sulfur compounds and hydrocarbons (BVOC) to low-volatility species [*Artaxo et al.*, 1990; *Talbot et al.*, 1990; *Andreae and Crutzen*, 1997; *Artaxo et al.*, 1997]. As part of LBA-EUSTACH, we have investigated the chemical and physical properties of the Amazonian aerosol, with the goal of better understanding its sources and its effect on climate.

[58] The first measurements of CCN in the humid tropics, made during the wet season at the Balbina site north of Manaus, showed surprisingly low concentrations for a continental environment, with a mean $N_{CCN}$ at 1% supersaturation of 270 ± 130 $cm^{-3}$ [*Roberts et al.*, 2001b]. The CCN levels and supersaturation spectra resembled conditions more typical of marine locations than of other continental sites. Subsequent measurements in Rondônia and during an aircraft campaign spanning most of the Amazon Basin showed these observations to be typical of wet-season Amazonia [*Roberts et al.*, 2002] (G. Roberts et al., Airborne measurements of cloud condensation nuclei in the Amazon Basin, in preparation, 2001). A very large fraction of the total particle number were CCN, i.e., contained enough soluble substance to be able to grow into cloud droplets. At 1% supersaturation, for example, about 50–70% of the particles present can be activated to cloud droplets.

**Table 6.** Aerosol and CCN Concentrations and Atmospheric Optical Characteristics Observed During the Wet and Dry Seasons in the Rainforest of Rondônia at the Jarú Tower Site During the 1999 LBA-EUSTACH Campaigns

| | Wet season | Dry season |
|---|---|---|
| CCN concentrations ($cm^{-3}$) | | |
| $S_c$ = 0.22% | 50 | 1440 |
| $S_c$ = 0.37% | 105 | 1910 |
| $S_c$ = 0.58% | 175 | 2560 |
| $S_c$ = 0.93% | 244 | 3040 |
| $S_c$ = 1.17% | 272 | 3200 |
| Aerosol number concentration ($cm^{-3}$) | 450 ± 320 | 6200 ± 4800 |
| Aerosol mass concentration ($\mu g\ m^{-3}$) | | |
| $PM_{10}$ (diameter < 10 μm) | 8.6 ± 3.8 | 83 ± 64 |
| coarse (2.5 < diameter < 10 μm) | 5.7 ± 3.1 | 17 + 12 |
| fine (2.5 μm < diameter) | 2.9 ± 1.7 | 65 ± 55 |
| Black carbon concentration ($\mu g\ m^{-3}$) | 0.48 ± 0.24 | 7.4 ± 6.1 |
| Aerosol optical thickness (AOT) | | |
| λ = 416 nm | 0.071 ± 0.061 | 0.85 ± 0.52 |
| λ = 868 nm | 0.030 ± 0.027 | 0.39 ± 0.30 |
| Light-scattering coefficient at 545 nm; noon values ($Mm^{-1}$) | 3.9 | 77 |

[59] The mean aerosol mass concentration in the wet season is 5.7 $\mu g\ m^{-3}$ in the coarse mode, and 3.0 $\mu g\ m^{-3}$ in the fine mode (Table 6 and Figure 15). The coarse aerosol consists mostly of phosphorus-rich, biogenic organic particles. Soil-dust particles containing Fe, Ti, Mn, Al and Si are the second most important aerosol component, accounting for about 10–20% of the aerosol mass. The fine-mode aerosol also consists mostly of organic matter, of about 70% of which is water-soluble [*Graham et al.*, 2002]. The dominant inorganic component is $NH_4HSO_4$, which accounts for less than 10% of the mass of the fine mode aerosol. In addition, soluble inorganic compounds of biological origin (containing mostly K, P, and Ca) are present. Together, the soluble organic and inorganic components can readily account for the CCN activity of the aerosol [*Roberts et al.*, 2002]. The sulfate probably originates from the oxidation of biogenic sulfur gases emitted by the rain forest ecosystem, while the organic fraction of the aerosol is likely to be a combination of primary biogenic material (e.g., spores, bacteria, pollen, and plant detritus) and secondary organic aerosol from the oxidation of VOC. At the low natural levels of ozone and $NO_x$ typical of the unpolluted tropical atmosphere, the oxidation of BVOC proceeds mostly through reaction with OH and has a low aerosol yield. The oxidation products deposit on preexisting particles, e.g., sulfates and primary biogenic particles, and little production of new particles takes place [*Zhou et al.*, 2002]. The resulting aerosol does not absorb water readily at humidities below saturation, but acts as effective CCN once the saturation point is exceeded. Under these low-CCN conditions, cloud droplets grow rapidly to the size where precipitation occurs, and rain production by warm clouds is an important process [*Silva Dias et al.*, 2002].

[60] A very different situation exists in the dry season: Aerosol mass concentrations can reach as high as 400 $\mu g\ m^{-3}$, reflecting the presence of large amounts of smoke aerosol (Figure 15). On average, the CCN and aerosol number and mass concentrations, aerosol optical thickness, scattering coefficient, and black carbon concentrations are all higher by factors of 10–20 (Table 6) [*Artaxo et al.*, 2002; *Roberts*

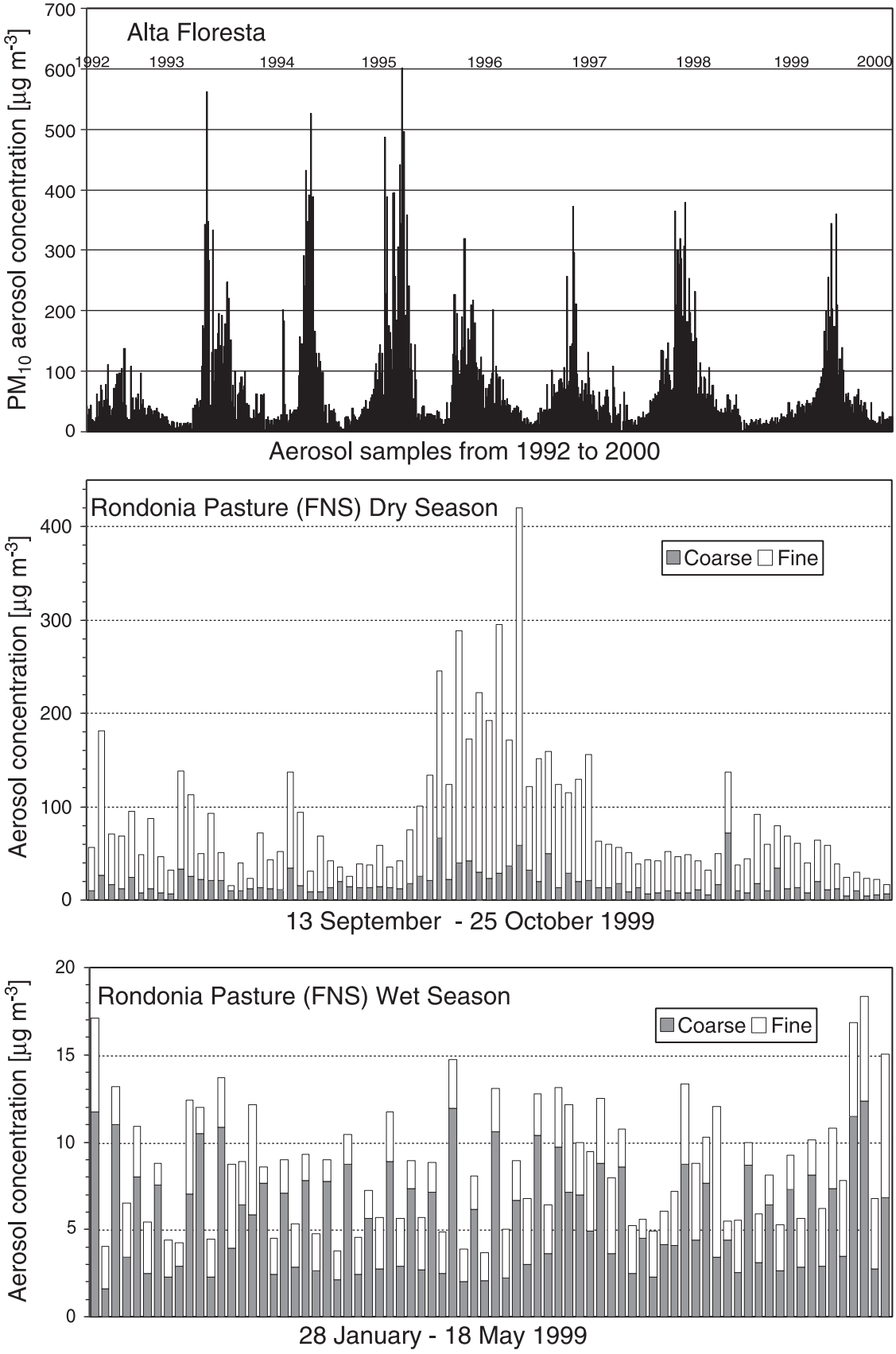


**Figure 15.** Seasonal variations of aerosol concentrations in Rondônia. The upper panel shows the long-term time series of $PM_{10}$ (particle diameter < 10 μm) at Alta Floresta (9°S, 56°W), while the lower panels show the results from the LBA-EUSTACH FNS site obtained during 1999.

*et al.*, 2001a]. This increased aerosol burden results in significant changes in solar irradiance (T. Tarasova et al., Analysis of the air temperature and solar irradiance data sets acquired at the Amazonian observational sites in smoke aerosol conditions, *Journal of Geophysical Research*, in preparation, 2001). Like the biogenic aerosol, the smoke aerosol consists mostly of organic compounds, but analysis by NMR, GC/MS, and Evolved Gas Analysis shows a change in composition, with a higher fraction of black carbon and pyrolysis compounds, particularly levoglucosan [*Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002]. Still, at least half of the organic component is water-soluble and can contribute to CCN activity.

[61] The result of the increased CCN concentrations is a major shift toward clouds with high droplet number concentration (D. Rosenfeld, personal communication, 2000), which require ice formation before rain can be generated. The result is an increase in lightning production, and a shift of the release of latent heat to higher levels in the troposphere [*Williams et al.*, 2002]. This has substantial effects for the redistribution of energy and chemical species in the tropical atmosphere, effects that reach far beyond the tropics [*Graf et al.*, 2001]. It must be expected that the future growth of human activity in the Amazon Basin and the surrounding regions will lead to a further increase of aerosol and CCN number concentrations, because of several effects: (1) the direct release of smoke particles from vegetation fires, (2) the emission and production of aerosols due to fossil fuel use in the region, and (3) the increased conversion efficiency of BVOC to aerosol due to reaction with anthropogenically produced $O_3$ and $NO_3$ [*Kanakidou et al.*, 2000]. The climatic consequences of such changes cannot yet be predicted, but are likely to be substantial.

## 8. Biosphere-Atmosphere Exchange Modeling

[62] The detailed analysis of the LBA-EUSTACH measurement data requires support from numerical modeling, aimed at simulation of atmosphere-biosphere exchange fluxes of reactive trace gases, in particular of isoprene, nitrogen oxides and ozone. The philosophy has been to first develop a detailed multilayer canopy layer representation in a column version of a chemistry-general circulation model [*Roelofs and Lelieveld*, 2000]. The model describes the canopy structure, emissions from soils and vegetation, deposition processes based on the multiresistance concept, turbulent exchanges, radiation processes and comprehensive chemistry [*Ganzeveld et al.*, 2002]. The single-column model has been initialized with vertical profiles of meteorological data that represent the conditions under which measurements have been performed in the Amazon. The model results show that the micrometeorology and boundary layer structure are extremely sensitive to the moisture regime, notably through evapotranspiration and latent heat transfer. Moreover, the wet skin fraction (from precipitation and dew formation) strongly affects the dry deposition of gases that are relatively insoluble but reactive, such as $NO_2$ and $O_3$. The multilayer biosphere model has been tested against available measurement data, i.e., of $NO_x$ and $O_3$ [*Ganzeveld et al.*, 2002]. Subsequently, a number of reduced-layer model versions have been compared to the detailed canopy model to derive an optimum between

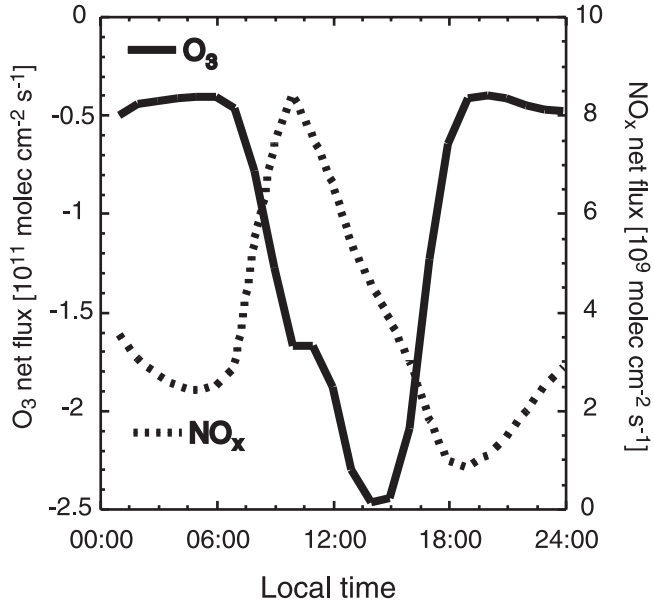


**Figure 16.** Five-day average diurnal cycles of $O_3$ and $NO_x$ canopy top exchange fluxes, simulated with the two-layer canopy model, implemented into a single column version of a chemistry-general circulation model. The chemical and meteorological conditions represent the Brazilian rain forest near Manaus.

numerical costs and accuracy. It appears that, for most applications, realistic results are obtained with a two-layer canopy model, accounting for a soil-to-canopy and a crown layer. Still, the isoprene emission scheme requires subdivision into four layers to account for the vertical distribution of biomass and the associated extinction of solar radiation. A previous study by *Jacob and Wofsy* [1990] inferred the need for an additional thin layer close to the soil surface. We have neglected this layer, because the detailed biogeophysical information needed for its representation in three-dimensional models is lacking.

[63] The model simulations show the great sensitivity of biosphere-atmosphere exchange fluxes to turbulent transport, which determines the residence time of reactive gases within the canopy. The two-layer model generally reproduces the observed canopy-top fluxes of ozone and nitrogen oxides. The $O_3$ flux is negative during the day, owing to dry deposition, and quite small at night as a result of decoupling of the canopy layer from the atmosphere aloft (Figure 16). The $NO_x$ flux is also quite small during the night. During the early morning, however, turbulent mixing causes a peak release of the NO that has accumulated during the night. Although soil exhalation of NO may occur continuously, the turbulent regime and mixing with $O_3$, entrained from the boundary layer, determines the extent to which $NO_2$ is formed and removed by dry deposition. This can even result in a bidirectional $NO_x$ flux from/to the rain forest, depending on the time of day and the $NO_x$ concentrations aloft, similar to what was seen in the field [*Gut et al.*, 2002a; *Rummel et al.*, 2002]. Furthermore, we have applied the model to test the commonly applied approach of calculating the emissions and deposition separately using the so-called "big leaf" approach, in which the biosphere is considered

as one entity. It appears that in extratropical regions, characterized by important anthropogenic emissions, this approach yields similar $NO_x$ fluxes to those calculated by the biosphere model. For more pristine regions, notably in the Amazon, the biosphere model calculates much smaller emissions, in better agreement with observations.

[64] The next application of the biosphere model involves its implementation into the full three-dimensional chemistry-general circulation model (GCM), extending the algorithm by *Yienger and Levy* [1995]. This aims at evaluation of the Amazon rain forest in the context of tropical tropospheric chemistry. Preliminary results with the chemistry-GCM suggest that by representing the biosphere more realistically, $NO_x$ fluxes to the atmosphere in the Amazon are substantially reduced. The corresponding canopy reduction factor for soil NO emissions in the Amazon is approximately 0.4–0.5. This significantly affects the boundary layer photochemistry of ozone and hydroxyl radicals in the $NO_x$ limited regime over the South American rain forest (L. N. Ganzeveld et al., The influence of soil biogenic $NO_x$ emissions on the global distribution of reactive trace gases: The role of canopy processes, submitted to *Journal of Geophysical Research*, 2001).

## 9. Summary and Conclusions

[65] The results from LBA-EUSTACH have shed new light on the way soils, biota, and atmosphere interact in the Amazon system. Linkages and interactions between the different parts of the system have been found at all scales, ranging from processes in the interior of soils and plants through the canopy scale to the effects of Amazonia on the global atmosphere and climate. While the evaluation of the data is still ongoing, and further insights can be expected from integrative analysis of the results between groups and disciplines, some major conclusions are already apparent.

1. Carbon flux studies by eddy correlation at four sites, located in three ecologically and climatically different parts of the Amazon Basin all show a consistent, large $CO_2$ uptake flux. While the absolute value of this flux is still sensitive to details of the algorithms used, the existence of a large deposition flux is a highly robust result. The magnitude of the carbon sink represented by the Amazon Basin is estimated to be of the order of 1 Pg carbon per year.

2. The exchange of VOC between the Amazon forest and the atmosphere is a complex phenomenon, which involves both uptake and deposition, and considerable seasonal variability. Net deposition was observed in particular for many oxygenated VOC species. During the dry season, very large concentrations of biogenic and pyrogenic hydrocarbons were observed, suggesting an extremely active photochemical environment at that time of year.

3. Nitrogen oxides emitted from the soil are undergoing (photo)chemical reactions in the canopy space, which may lead to the trapping of a large fraction of the soil-derived NO by the vegetation. Detailed studies of fluxes at several levels with a variety of methods, and chemistry-transport modeling of the chemical and physical processes within the canopy have made it possible to derive a quantitative and process-based picture of this complex phenomenon.

4. Aerosol and CCN number concentrations during the wet season are very low, resulting in rainfall production predominantly in warm cloud, i.e., below the freezing level. During the dry season, biomass burning is widespread, and aerosol and CCN concentrations increase by an order of magnitude, leading to smaller effective cloud droplet radii and thus rainfall generation involving ice processes. This is likely to have considerable impact on the large-scale dynamics of the atmosphere.

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