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Surface exchange of nitric oxide, nitrogen dioxide, and ozone at a cattle pasture in Rondônia, Brazil

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[1] Measurements of NO–NO₂–O₃ trace gas exchange were performed for two transition season periods during the La Niña year 1999 (30 April to 17 May, “wet–dry,” and 24 September to 27 October, “dry–wet”) over a cattle pasture in Rondônia. A dynamic chamber system (applied during the dry–wet season) was used to directly measure emission fluxes of nitric oxide (NO) and surface resistances for nitrogen dioxide (NO₂) and ozone (O₃) deposition. A companion study was simultaneously performed in an old-growth forest. In order to determine ecosystem-representative NO₂ and O₃ deposition fluxes for both measurement periods, an inferential method (multiresistance model) was applied to measure ambient NO₂ and O₃ concentrations using observed quantities of turbulent transport. Supplementary measurements included soil NO diffusivity and soil nutrient analysis. The observed NO soil emission fluxes were nine times lower than old-growth rain forest emissions under similar soil moisture and temperature conditions and were attributed to the combination of a reduced soil N cycle and lower effective soil NO diffusion at the pasture. Canopy resistances (R_c) of both gases controlled the deposition processes during the day for both measurement periods. Day and night NO₂ canopy resistances were significantly similar ($\alpha = 0.05$) during the dry–wet period. Ozone canopy resistances revealed significantly higher daytime resistances of 106 s m⁻¹ versus 65 s m⁻¹ at night because of plant, soil, and wet skin uptake processes, enhanced by stomatal activity at night and aqueous phase chemistry on vegetative and soil surfaces. The surface of the pasture was a net NO_x sink during 1999, removing seven times more NO₂ from the atmosphere than was emitted as NO. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions

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1. Introduction

[2] Over the last 25 years, more than 70 million ha of the native vegetation in Brazil have been replaced by pastures mostly planted to grasses of the African genus *Brachiaria* for cattle grazing. Rondônia has seen a large proportion of this development and stands today as one of the best examples of how rapidly South American tropical ecosystems are undergoing anthropogenic change. Several years after deforestation and establishment of agriculture, there is a marked decline in soil productivity and crop yields, forcing farmers to either abandon their land or establish permanent agriculture [Moran, 1993]. Changes in soil

productivity are accompanied by changes in the air–surface exchanges of trace gases such as nitrogen oxides (NO_x = NO + NO₂) and ozone (O₃).

[3] The measurement of all three species of the NO₂–NO–O₃ triad is necessary for studying and making inferences on the air–surface exchanges at the landscape scale. First, the fast chemical reactions of nitric oxide (NO) with O₃ or peroxy radicals, which form nitrogen dioxide (NO₂) [Crutzen, 1995; Kolar, 1990], and the reverse photodissociation of NO₂ during the day (<400 nm), occur on timescales of minutes, the same timescales for turbulence mixing at the surface [Kramm *et al.*, 1991]. Second, the gases are governed by quite different air–surface exchange regulating processes. For instance, the predominant natural source of NO is the soil where biotic (nitrification and denitrification) and abiotic (chemodenitrification) processes produce this gas. Within the soil environment, the aerobic process of nitrification (predominant at <60% water-filled pore space–WFPS) is maintained primarily by autotrophic bacteria resulting in the conversion of ammonium (NH₄⁺) to nitrate (NO₃⁻) via nitrite (NO₂⁻). There are two groups of

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nitrifiers, namely the ammonium oxidizing nitrifiers, which convert NH_4^+ via hydroxylamine to NO_2^- , and the nitrite oxidizing nitrifiers, which oxidize NO_2^- to NO_3^- . Denitrification on the other hand is an anaerobic process (predominant at >60% WFPS) in which denitrifiers reduce NO_3^- via NO_2^- , NO and nitrous oxide (N_2O) to molecular nitrogen (N_2). The complete denitrification pathway results in the reduction of NO_3^- to N_2 , but significant amounts of NO and N_2O can be emitted before complete reduction to N_2 [Remde and Conrad, 1991; Remde et al., 1989; Cardenas et al., 1993]. Soil pH, metallic ion composition, and soil organic matter (SOM) all control the abiotic process of chemodenitrification, whereby microbially produced NO_2^- is decomposed to NO and NO_2 [van Cleemput and Baert, 1984; Davidson, 1992].

[4] Recent work in Rondônia has shown that NO fluxes from old pastures can be 25 times lower than fluxes from adjacent forest [Garcia-Montiel et al., 2002]. Further, Davidson et al. [2000] found for a variety of tropical sites in Costa Rica, Puerto Rico, and Brazil that old tropical pastures produce consistently lower NO fluxes than old-growth tropical forests. The reasons for these differences between the two ecosystems are changes in the environmental factors controlling NO emissions. These factors include a combination of soil water, temperature, nutrient status, pH, diffusion, plant biomass characteristics, and ambient atmospheric conditions [Davidson et al., 2000; Ludwig et al., 2001].

[5] The air-surface exchanges of O_3 and NO_2 occur via dry deposition onto vegetation (plant stomata/cuticle), onto bare soil surfaces, or into solution with surface water [Meixner, 1994a]. The rate at which plant stomatal uptake occurs is determined by the concentration gradient between the gas phase inside and outside the leaf, leaf temperature, water vapor deficit, and intensity of photosynthetic radiation, although some uncertainty surrounds the magnitudes of these processes, particularly for NO_2 [Lerdau et al., 2000]. Removal rates of O_3 by soils with high levels of organic matter and moderate moisture content have been shown to be significant [Wesely and Hicks, 2000]. Less is known about bare soil as a NO_2 sink. There are, however, reports of NO_2 reactions with humic acids and phenols on dry soils and stone surfaces [Baumgartner et al., 1992] and chemical scavenging ($\text{NO}_2 + \text{NO}_2^- \rightarrow \text{NO}_3^- + \text{NO}$) in low pH, high SOM content soils [van Cleemput and Baert, 1976]. Recent work suggests some ammonia oxidizers are able to consume NO_2 and produce NO and NO_2^- under both oxic and anoxic soil conditions [Zart and Bock, 1998; Schmidt and Bock, 1997]. Equally unclear are the effects of wet surface uptake, for which aqueous phase chemistry has been reported to enhance O_3 deposition to foliage [Fuentes et al., 1992].

[6] As part of the European Studies on Trace Gases and Atmospheric Chemistry within the Large-Scale Biosphere-Atmosphere Experiment in Amazonia project (LBA-EUSTACH), results from measurements over a cattle pasture in Rondônia (cf. section 2.1) are presented. A companion study was simultaneously performed in an old-growth forest (see companion papers by Gut et al. [2002a, 2002b]). Measurements were performed during both the LBA-EUSTACH-1 and LBA-EUSTACH-2 campaigns [Andreae et al., 2002], which represent two transition seasons during 1999 (30 April to 17 May, wet-dry, and 24 September to 27 October, dry-wet), a La Niña year. The objectives of this

study were to (1) quantify the air exchanges of NO, NO_2 , and O_3 for an established cattle pasture during two distinct seasons, (2) propose possible reasons for the expected lower NO emission fluxes from the pasture in light of those from an old-growth primary forest for the same period, and (3) examine and discuss the surface resistances and deposition fluxes of NO_2 and O_3 and their possible environmental controlling factors.

2. Experimental

[7] The primary tool used for gas exchange measurements was a dynamic chamber system (applied during LBA-EUSTACH-2 only), which measured emission and deposition fluxes of NO, NO_2 and O_3 (cf. section 2.3). In order to determine ecosystem-representative NO_2 and O_3 deposition fluxes for both the LBA-EUSTACH-1 and LBA-EUSTACH-2 periods, an inferential method (multiresistance model) was applied to measured ambient NO_2 and O_3 concentrations using observed quantities of turbulent transport (cf. section 2.4). In the case of O_3 , the resulting fluxes could be compared to a limited data set of independent flux measurements by the aerodynamic gradient approach (cf. section 2.5). Supplementary measurements included soil NO diffusivity and soil nutrient analysis (cf. section 2.6).

2.1. Site Description

[8] Rondônia is situated on the fringe of the Amazon basin is comprised of seasonally dry tropical rain forest (*Floresta ombrofila aberta*) and various forms of degraded land (*Floresta de transição*), cultivated land (*plantação*), and pasture (*pastagem*). It is also situated along the "arc of deforestation" of Brazil and is known for its characteristic "fishbone" deforestation pattern and rapid land conversion rates [Andreae et al., 2002]. Human settlement in this area increased considerably after construction in 1968 of the Cuiabá-Porto Velho highway (BR 364), which cut through some of the more fertile parts of the weathered soils in this region [Moran, 1993]. Paving of this highway was completed in 1984. It increased immigration and stimulated markets for agriculture and forest products [Browder and Godfrey, 1997], which led to slash-and-burn agriculture, cropping and established cattle pasture, and abandonment.

[9] The measurement site was located on the commercial cattle ranch *Fazenda Nossa Senhora Aparecida* (FNS) (Figure 1), which lies between the unpaved roads Linha 12 and 16 off the paved RO-470 at $10^\circ 45' 44''\text{S}$, $62^\circ 21' 27''\text{W}$ at an elevation of ca. 315 m. Soils at FNS are highly weathered, sandy (>75%) red-yellow podzols (*Podzólico vermelho amarelo de textura média-Brasil* or *Orthic Acrisol-FAO*) [Hodnett et al., 1996]. The nearest town is Ouro Preto d'Oeste, situated on the paved federal highway BR 364 between the towns Jaru and Ji-Paraná, ca. 8 km NE from the site. A small charcoal kiln off the BR 364 ca. 8 km from the site was in operation during the wet-dry season.

[10] The land was first deforested in 1977 by the current owner and planted to rice (*Oryza sativa*, *Agulhinha/IAC* (*comum*)), beans (*Phaseolus vulgaris*, *Carioquinha*, *Rosinha*, *Tibagi*) and maize (*Zea mays*, *Asteca e Híbridos*). Fire was used as the primary deforestation tool and all burns typically took place between June and September. Combustion of slashed material was generally considered to be partial

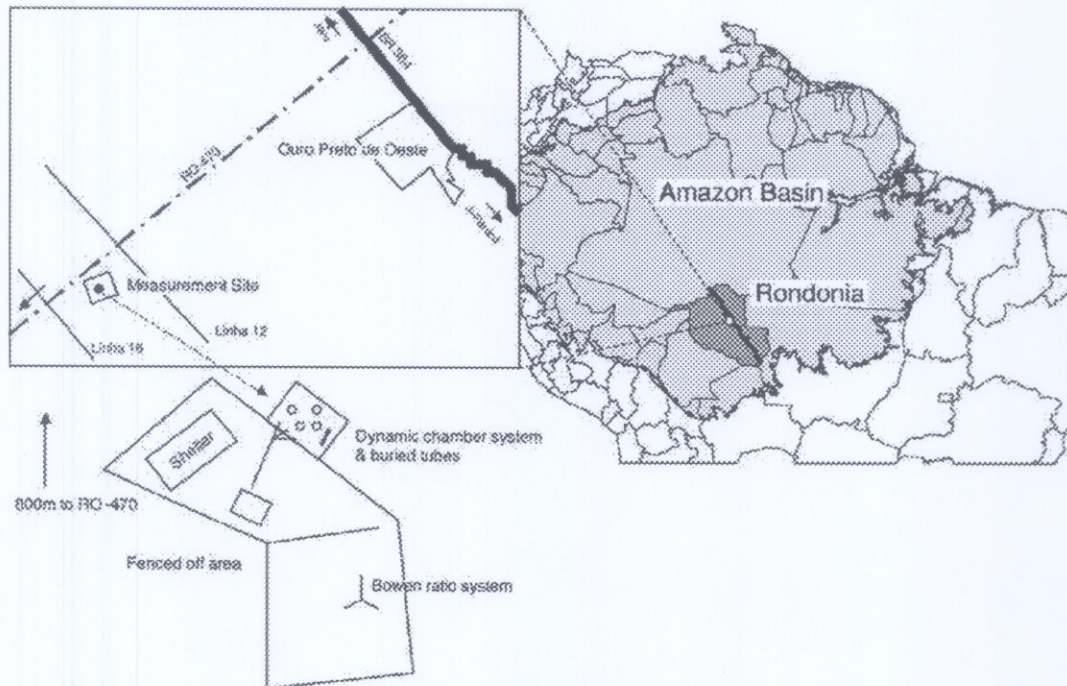


Figure 1. Location of the LBA-EUSTACH measurement site *Fazenda Nossa Senhora Aparecida* (FNS) in Rondônia, Brazil.

or poor. The first two seasons of cropping were the most lucrative with yields surpassing those of later years. Thereafter the land underwent a sequence of burn and *Brachiaria decumbens* pasture grass (*Braquiária australiana*, *Braquiária comum*, *Braquiária de alho*, *Capim*) for 12 seasons, after which a disk harrow (20 cm) was used in 1992 to liberate the old-growth forest soil organic matter below the grass root zone. One season of beans was planted, and yields equaled the first two seasons after deforestation. The camp was then burned for two seasons and planted to a predominately homogenous sward of *Brachiaria brizantha* (A. Rich.) Stapf. (*Brachiarão*, *Brizantão*, *Brizantha*, *Braquiarao*, *Capim braquiária*, *Capim marandu*, *Capim ocinde*) and thereafter was never burned again. The camp has never been fertilized.

[11] *B. brizantha* is a fire-sensitive exotic perennial grass species with stout erect culms and broadly lanceolate leaf blades, which can reach a height of up to 120 cm if left ungrazed. It produces poor seed and propagates vegetatively [Fernando, 1961]. The sward at FNS had a leaf area index of $1.2 \text{ m}^2 \text{ m}^{-2}$ (Kirkman, unpublished data, 1990) during the dry-wet season and $2.1 \text{ m}^2 \text{ m}^{-2}$ during the wet-dry season (Waterloo, personal communication, 2000). Assuming a leaf N content of ca. 0.67%, as found by Davidson (personal communication, 2000) at the *Fazenda Vitoria* in Pará, the total above ground N for FNS was estimated to be 21 kg ha^{-1} .

[12] During the measurement campaign FNS was stocked with a breeding herd of *Blanco* cattle (*Bos indicus hybrid*). The grass sward had a carrying capacity of ca. 2 animal units (1 A.U. = 450 kg) per hectare. Soon after deforestation and for a period after the ploughing in 1992, the carrying capacity was in the order of 3–4 A.U. ha^{-1} . The 4 cattle pastures at FNS were typically rotated every 3 months, resulting in a camp utilization of 3–4 months per year, depending on sward

conditions. Data from *Fazenda Vitoria* has shown that export of N as cattle harvesting is estimated at about $7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, including return from feces and urine (but excluding NH_3 volatilization). At the time of measurement the camp was stocked with a breeding herd comprised of cows, heifers and two bulls.

2.2. Monitoring of Ambient Trace Gas Concentrations

[13] During the LBA-EUSTACH-1 and LBA-EUSTACH-2 campaigns, concentrations of NO , NO_2 , and O_3 were monitored at FNS. A glass tube (2-cm diameter) of a total length of 2.0 m, continuously purged by an auxiliary pump with a flow rate of 28 L min^{-1} , was used as the sample intake system. The rain-protected sampling head was mounted 3.5 m above ground on top of an instrument trailer. From a glass manifold mounted inside the trailer, sample air was fed through 1/4 in. PTFE tubing (2 m) to 47 mm PTFE filters ($0.5 \mu\text{m}$) mounted on the sample intake ports of the NO/NO_x and O_3 analyzers. Commercial gas-phase chemiluminescence and spectrometric analyzers were used to measure NO , NO_2 , and O_3 concentrations, respectively (Table 1). NO and NO_2 calibrations were conducted with the use of a Thermo Environmental Instruments Inc., Model 146C gas phase titration and ozone generator instrument by mixing known concentrations of NO calibration gas with nondried zero air from a Thermo Environmental Instruments Inc., Model 111 zero air supply. To this, a lesser amount of O_3 was added and the amount of NO_2 produced was then determined by the measured loss of NO . Subsequently O_3 was calibrated by assuming that the loss of NO was equivalent to the concentration of O_3 produced such that



Table 1. Trace Gas Detectors, Micrometeorological Instrumentation, and Sensors Used at *Fazenda Nossa Senhora Aparecida* (FNS) during LBA-EUSTACH-2 (24 September to 27 October 1999) and LBA-EUSTACH-1 (30 April to 17 May 1999)

Quantity	Technique or sensor	Model, manufacturer	Detection limit or precision	Integra./exec. or averaging time, s
NO concentration (3.5 m above ground)	Gas-phase chemiluminescence	Model 42C TL (trace level) Thermo Environment Instruments Inc., U.S.A.	0.025 ppb	300
NO ₂ concentration (3.5 m above ground)	Catalytic conversion of NO ₂ to NO by molybdenum converter (at 300°C) and gas phase chemiluminescence	Model 42C TL (trace level) Thermo Environment Instruments Inc., U.S.A.	0.025 ppb	300
O ₃ concentration (3.5 m above ground)	UV absorption, symmetric dual cell design	Model 49C Thermo Environment Instruments Inc., U.S.A.	0.5 ppb	300
NO concentration (dynamic chambers)	Gas-phase chemiluminescence	Model 42C TL (trace level)	0.07 ppb	60/1800
NO ₂ concentration (dynamic chambers)	Catalytic conversion of NO ₂ to NO by molybdenum converter (at 300°C) and gas phase chemiluminescence	Model 42C TL (trace level) Thermo Environment Instruments Inc., U.S.A.	0.14 ppb	60/1800
O ₃ concentration (dynamic chambers)	UV absorption, symmetric dual cell design	Model 49C Thermo Environment Instruments Inc., U.S.A.	0.03 ppb	60/1800
²²⁰ Rn concentration	Alpha particle detection	Alphaguard PQ 2000 Pro, Genitron, Germany	2 Bq m ⁻³ ± 10%	–
O ₃ concentration (aerodynamic gradient)	UV absorption, symmetric dual cell design, switched intakes at 0.53 and 4.5 m above ground	Model 49 Thermo Electron Inc., U.S.A.	0.5 ppb ± 0.56 ppb	2/1800
Soil temperature (dynamic chambers)	Thermistors at 0.05m below ground		–	–
Volumetric soil moisture (dynamic chambers)	Time domain reflectometry (TDL) sensors at 0.05m below ground	TRIME-ES P2M IMKO GmbH, Germany	–	–
Surface wetness (dynamic chambers)	Surface wetness grids at soil surface	237 WSG Campbell Scientific Ltd., U.K.	–	–
Wind speed profile at 0.53, 1.02, 2.02, and 4.50 m above ground	3-cup-anemometers (optical switch)	A100ML Vector Instruments, U.K.	0.25 m/s ± 0.10 m/s	10/1800
Wind direction, 4.50 m above ground	Potentiometric wind vane	W200P Vector Instruments, U.K.	±5°	10/1800
Air temperature profile at 0.53, 1.02, 2.02, and 4.50 m above ground	Fine-wire (0.72µm), nonaspirated thermocouples, chrome-constantan (E-type)	Campbell Scientific Ltd., U.K.	±0.02 K	1/1800
Global radiation flux 2.02 m above ground	Pyranometer sensor	LI200SZ LI-COR Inc., U.S.A.	< ± 3%	10/1800

[14] The NO_x analyzer employed was equipped with a molybdenum (Mo) NO₂ to NO converter, which is non-specific for determination of NO₂ [Winer *et al.*, 1974; Fehsenfeld *et al.*, 1987]. The instrument also converts other reactive nitrogen compounds to NO, in particular, nitric acid (HNO₃), nitrous acid (HONO), the nitrate radical (NO₃), dinitrogen pentoxide (N₂O₅), peroxyacetyl nitrate (PAN), and other organic nitrates. PAN is a thermally unstable compound at temperatures well below those found at FNS. HNO₃ was probably the most important of these interfering nitrogenous compounds at FNS. However, HNO₃ is also known for its high affinity to the inner walls of intake systems, especially if these (1) consist of glass and/or stainless steel and (2) are covered with a molecular layer of water, which was certainly the case for the humid conditions at FNS. It is therefore assumed that HNO₃ (and also HNO₂, if present) was completely destroyed within the glass sample line (described above) and stainless steel fittings inside the instruments. Interference from gaseous ammonia (NH₃) is most unlikely, since the Mo converter was operated at 300°C and conversion of NH₃ is usually not observed for temperatures below 400°C. The other interfering nitro-

genous compounds mentioned above are assumed to be negligible compared to NO₂.

2.3. Dynamic Chamber System

[15] During the LBA-EUSTACH-2 campaign, a second set of identical NO, NO_x, and O₃ analyzers (Table 1) was applied to a dynamic chamber system. This system was similar to that described by Gut *et al.* [2002a, 2002b]. Weekly NO and NO₂ calibrations were conducted with the same gas-phase titration and zero air supply system described above.

[16] Chamber measurements were used to (1) quantify surface emission fluxes of NO directly and (2) evaluate surface resistances for NO₂ and O₃ by relating chamber fluxes to chamber concentrations (cf. section 2.4). The system comprised three chambers placed over a previously grazed *B. brizantha* sward and sealed to the surface with TEFLON[®] foil weighted by small sandbags (Figure 2), such that no root destructive frames were necessary. Ambient airflow through the chambers was controlled by small air-entry fans (model D243M-012GK-1, Micronel, Switzerland) producing an average flow rate (Q) of ca. 28 L min⁻¹ such that the average air residence time was ca. 25 s. Air inside the

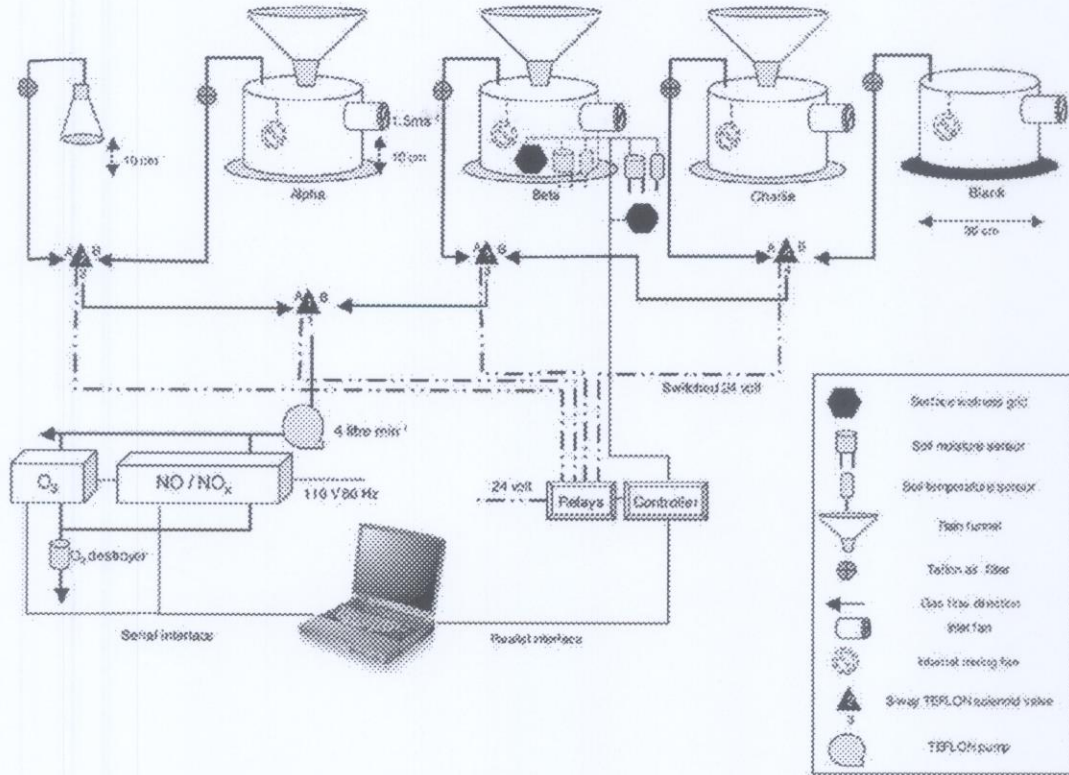


Figure 2. Dynamic chamber system.

chamber was continuously mixed with an additional fan (model F62MM-012GK-0, Micronel, Switzerland) to prevent concentration gradients [Meixner et al., 1997]. A fourth “blank” chamber, closed at the bottom, was employed for in situ quantification of chemical reactions and chamber wall deposition effects (see below). A sample inlet for measurement of ambient NO, NO₂, and O₃ concentrations was positioned close to the inlet of one of the chambers (10 cm above the soil surface). The chambers were constructed from polycarbonate (which is transparent to light of wavelengths above 420 nm) with a cross-section area (*A*) of 0.066 m², a height of 0.18 m, and thus giving a total volume of 11.8 L. Solenoid valves (model Galtek 203-3414-215, Entegris, USA) controlled the flow of sample air (4 L min⁻¹) to the analyzers through blue-colored PTFE tubing. All fittings in contact with the sample air were constructed of TEFLON[®].

[17] The concentrations of all trace gas species *j* inside the chambers (*C*(*j*)_{chamber}) were measured sequentially for 3 min followed by 2 min of ambient air (*C*(*j*)_{ambient}) measurements. Half a minute flush time was discarded prior to each measurement such that fluxes for each of the four chambers could be determined once every 24 min. Chamber fluxes (*F*(*j*)_{chamber}) of each trace gas *j* were determined by mass balance,

$$F(j)_{\text{chamber}} = Q/A [C(j)_{\text{chamber}} - C(j)_{\text{ambient}}] \quad (j = \text{NO}, \text{NO}_2, \text{O}_3) \quad (2)$$

which accounted for the individual losses to the chamber walls, and gains and losses due to NO–NO₂–O₃ reactions

within the air sample while passing through the dynamic chamber. A complete and detailed description of the flux evaluation procedure is given by Meixner et al. [1997].

[18] Uncertainty of the chamber flux measurements was determined by the sum of the errors due to nonstationarity (trend) in the ambient concentrations and to instrument drift/noise such that

$$\sigma(F(j)_{\text{chamber}}) = Q/A [(\sigma(C(j)_{\text{trend}})^2 + 2(\sigma(C(j)_{\text{instrument}})^2)]^{1/2} \quad (3)$$

The trend related error $\sigma(C(j)_{\text{trend}})$ in the data was quantified as half the absolute difference between ambient concentra-

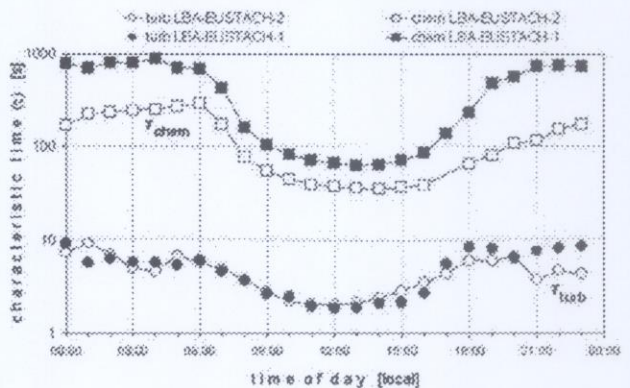


Figure 3. Chemical and turbulent characteristic times scales.

tions $C(j)_{\text{ambient}}$ measured directly before and after the measurement of chamber air. It ranged 0–0.13 ppb for NO, 0–0.25 ppb for NO₂ and 0–2.9 ppb for O₃. The standard deviation of all the zero air measurements, during calibration, was used for the determination of the instrument error $\sigma(C(j)_{\text{instrument}})$ (Table 1). Thereafter flux data whose total error exceeded their magnitude or whose trend error exceeded the instrument error were removed in accordance with

$$(\sigma(F(j)_{\text{chamber}}) > |F(j)_{\text{chamber}}|) \text{ or } (\sigma(C(j)_{\text{trend}}) > \sigma(C(j)_{\text{instrument}})) \quad (4)$$

Due to power failures, instruments failure, and the above data rejection criteria, dynamic chamber flux data were reduced by more than 50% during LBA-EUSTACH-2 (cf. Figures 4, 5, 6, and 7).

[19] Chamber flux measurements were also accompanied by measurements of soil temperature, soil moisture, and soil surface wetness inside and outside the chambers (Table 1). Identical concurrent measurements were conducted at the EUSTACH forest site at *Reserva Biologica Jarú* (RBJ) 80 km NE of FNS [Gut et al., 2002a, 2002b].

2.4. Inferential Method for Determination of NO₂ and O₃ Fluxes

[20] The emission flux of NO ($F(\text{NO})_{\text{chamber}}$) as determined by the dynamic chamber system (above) is considered to be representative of actual field conditions. This holds true as NO consumption and emission processes are predominantly controlled by soil nutrients, diffusivity, moisture, and temperature [Davidson et al., 2000; Ludwig et al., 2001]. In contrast, dry deposition fluxes of NO₂ and O₃ depend on surface uptake characteristics, surface concentrations, and turbulent transfer conditions close to the surface. The design of the chamber and particularly the rapid exchange (2.4 times per minute) of the headspace air ensured that air temperature, relative humidity, and light intensity were close to ambient conditions [Ludwig, 1994; Meixner et al., 1997]. However, turbulent transfer conditions controlling the supply of trace gases to the surface may differ from conditions outside the chamber. Therefore chamber NO₂ and O₃ fluxes were not representative for ambient field conditions. In order to account for this difference, we applied an inferential method based on the “big leaf multiple resistance approach” [Wesely and Hicks, 1977; Hicks et al., 1997], where surface resistances inside and outside the chambers were assumed to be similar. The dry deposition flux $F(j)$ of a nonreactive trace gas compound j , for which the surface represents a general sink at all ambient conditions, may be expressed as,

$$F(j) = C(j)/R_{\text{tot}}(j) \quad (5)$$

where $C(j)$ is the ambient mixing ratio of the trace gas compound j at the reference height and $R_{\text{tot}}(j)$ a gas transfer resistance in analogy to an electrical resistance according to Ohm's law. Correspondingly, $R_{\text{tot}}(j)$ is split into a series of partial resistances,

$$R_{\text{tot}}(j) = R_a + R_b + R_c(j) \quad (6)$$

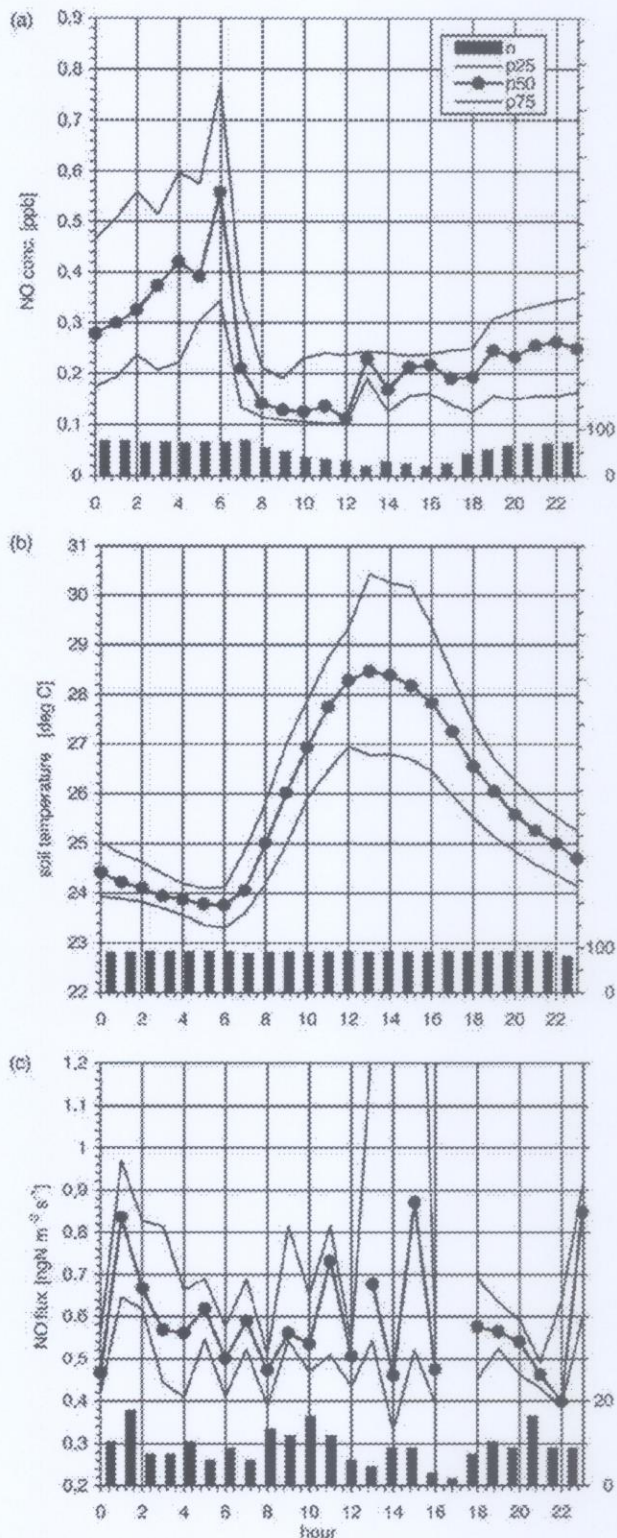


Figure 4. Mean diel variation of (a) NO concentration (ppb), (b) soil temperature (°C), and (c) soil NO emission flux ($\text{ng N m}^{-2} \text{s}^{-1}$) at FNS for the dry-wet transition season during LBA-EUSTACH-2 (24 September to 27 October 1999). Bars indicate actual data counts used to derive the hour averages (solid points).

such that R_a is the resistance against turbulent exchange in the air; and R_b the molecular-turbulent boundary layer resistance close to the surface elements. $R_c(j)$ is the canopy resistance of the trace gas compound j and comprises stomata, cuticle, soil, water, and other surface-related resistances. Due to the artificial ventilation of the chamber, the transport-related resistances (aerodynamic), R_a and R_b , differ from natural (outside) conditions, whereas the surface related resistance, $R_c(j)$, is the same inside and outside the chamber. Thus, for a transfer of chamber deposition measurements to representative natural conditions, R_a and R_b inside and outside the chamber must be quantified.

[21] The aerodynamic resistance inside the chamber ($R_{aero, chamber}$), which is the sum of the turbulent resistance and molecular-turbulent boundary layer resistance inside the well-mixed chamber

$$R_{aero, chamber} = R_{a, chamber} + R_{b, chamber} \quad (7)$$

was determined experimentally [Galbally and Roy, 1980]. The soil surface enclosed by a dynamic chamber was replaced by a saturated potassium iodide (KI) solution, which represents a virtually ideal sink for ozone (i.e., its surface resistance to O_3 uptake is virtually zero) [Ludwig, 1994]. Dividing the chamber O_3 concentration by the flux (given by the flow rate through the chamber, the surface area of the KI solution, and the difference between ambient and chamber O_3 concentrations according to equation (2)) yielded an $R_{aero, chamber}$ of 60 s m^{-1} . Consequently the surface resistance for NO_2 and O_3 deposition in the chamber ($R_c(NO_2)$ and $R_c(O_3)$) was derived from the concentrations $C(NO_2)_{chamber}$ and $C(O_3)_{chamber}$, the chamber fluxes $F(NO_2)_{chamber}$ and $F(O_3)_{chamber}$ such that

$$R_c(NO_2) = C(NO_2)_{chamber} / F(NO_2)_{chamber} - R_{aero, chamber} \quad (8a)$$

$$R_c(O_3) = C(O_3)_{chamber} / F(O_3)_{chamber} - R_{aero, chamber} \quad (8b)$$

[22] According to equation (6), the R_c has to be added to R_a and R_b , determined for ambient conditions outside the chamber, to yield representative values for $R_{tot}(NO_2)$ and $R_{tot}(O_3)$. From FNS wind speed and air temperature profile data (cf. section 2.5), representative turbulent resistances (R_a) and molecular-turbulent boundary layer resistances (R_b) were estimated according to Hicks *et al.* [1987]. R_a was determined using friction velocities (u^*) and Monin-Obukhov lengths (L) calculated using a generalized algorithm [Ammann, 1999] from wind speed and air temperature profiles such that

$$R_a = (k u^*)^{-1} [\ln(z_{ref}/z_0) - \Psi_c(z_{ref}/L)] \quad (9)$$

where the von Karmán constant (k) was 0.4, z_0 was the roughness length (LBA-EUSTACH-1: 0.15 m; LBA-EUSTACH-2: 0.11 m), z_{ref} was the reference height of 3.5 m, and $\Psi_c(z_{ref}/L)$ is a function, which corrects for atmospheric nonneutral stability conditions [Ammann, 1999]. The molecular-turbulent boundary layer resistance (R_b) is described by

$$R_b = (2/k u^*)(Sc/Pr)^p \quad (10)$$

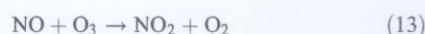
where the Schmidt number (Sc) was 1.07 for the trace gases of interest, the Prandtl number (Pr) was 0.72 and p was 2/3.

[23] Substitution of equations (8a), (8b), (9), and (10) into equation (6) gives $R_{tot}(NO_2)$ and $R_{tot}(O_3)$. According to equation (5), ecosystem-wide dry deposition fluxes of $F(NO_2)$ and $F(O_3)$ were then calculated using the NO_2 and O_3 concentrations, which were measured at a reference height of 3.5 m above the surface of FNS (cf. section 2.2).

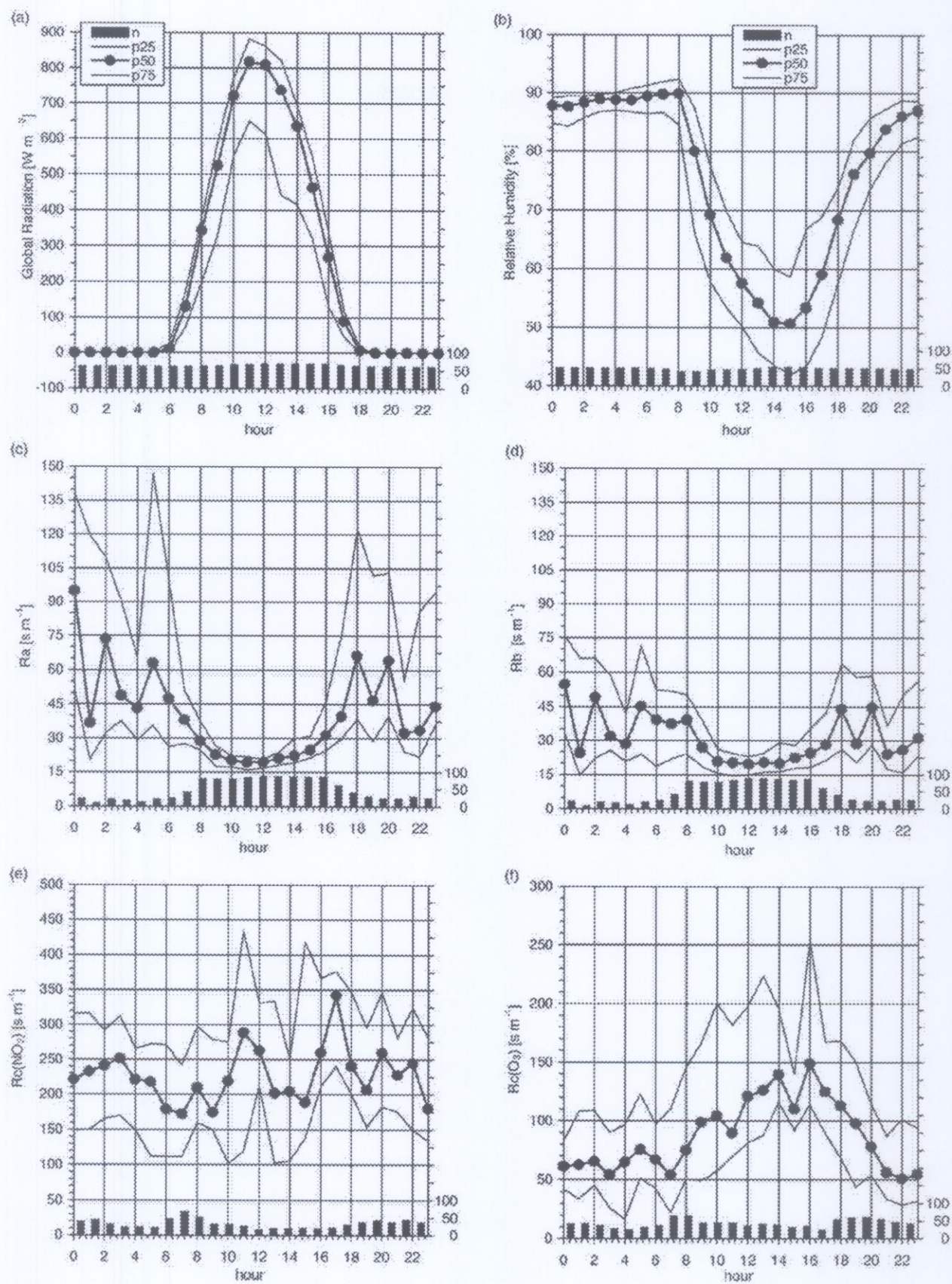
[24] As previously mentioned, the application of the inferential method is strictly valid for nonreactive trace gases only. An inferential method for reactive trace gases has to consider chemical reactions/transformations of these trace gases during the turbulent transport between the reference height and the surface [Kramm *et al.*, 1996]. However, the "nonreactive" flux-resistance relationship expressed by equation (5) can also be applied as a sufficient proxy in the case of reactive trace gases if "slow chemistry" is prevalent [Villá-Guerrau de Arellano and Duynkerke, 1992] (i.e., if characteristic chemical reaction times are much larger than corresponding turbulent transport times). Following Villá-Guerrau de Arellano and Duynkerke [1992], the characteristic time of turbulent transport (τ_{turb}) was calculated by

$$\tau_{turb} = k(z_{ref} + z_0)(\sigma_w^2/u^*)^{-1} \quad (11)$$

approximating σ_w/u^* by $1.25(1 - 3z_{ref}/L)^{1/3}$ and $1.25(1 + 0.2z_{ref}/L)$ for unstable and stable atmospheric conditions, respectively [Ammann, 1999]. The overall characteristic timescales for the $NO-NO_2-O_3$ triad (τ_{chem}) are given by the combination [Lenschow, 1982] of $\tau_{NO} = (k_{13}[O_3])^{-1}$, $\tau_{NO_2} = k_{12}^{-1} = j(NO_2)^{-1}$, and $\tau_{O_3} = (k_{13}[NO])^{-1}$, with the reaction constants $k_{12} = j(NO_2)$ (s^{-1}) and $k_{13} = 2 \times 10^{-12} \exp(-1400/T)$ ($cm^3 \text{ molecules}^{-1} s^{-1}$) for the reactions,



The NO_2 photolysis rate $j(NO_2)$ was calculated from global radiation data (Table 1) using a relationship derived from simultaneous measurements of global radiation and the NO_2 photolysis rate at RBJ during LBA-EUSTACH-1 and LBA-EUSTACH-2 (Ammann, C., U. Rummel, A. Gut, M. Scheibe, F. X. Meixner, and M. O. Andreae, Canopy reduction effect on nitric oxide emission from Amazonian rain forests, submitted to *J. Geophys. Res.*). Monitored NO , NO_2 , and O_3 concentrations and micro-meteorological data (cf. sections 2.2 and 2.5) were used to calculate mean diel variations of τ_{turb} and τ_{chem} for the LBA-EUSTACH-1 and LBA-EUSTACH-2 periods. Turbulent transport times were generally found to be at least one order of magnitude faster than chemical reaction times (Figure 3). "Slow chemistry" between $z_{ref} = 3.5$ m and the surface could therefore be assumed, justifying the application of equation (5) to infer NO_2 and O_3 dry deposition fluxes for conditions at FNS during LBA-EUSTACH-1 and LBA-EUSTACH-2.



2.5. Micrometeorological Gradient System

[25] Profiles of wind speed and air temperature were obtained from corresponding continuous measurements at four levels on a 5-m tall tripod mast, which was set up 15 m south of the dynamic chamber system and 25 m southeast of the NO, NO₂, and O₃ monitoring intake system (Figure 1). Wind direction was measured at 4.5 m and global radiation at 2.02 m aboveground. Data acquisition and averaging (30 min) was performed by a micrologger (21X, Campbell Sci. Ltd., U.K.). Micrometeorological sensors and their precision are listed in Table 1. Profile data have been rejected for wind sectors 217–265° and 301–322°, for which substantial flow distortions for the profile measurements were observed due to instrument shelters and other nearby structures. A generalized algorithm by Ammann [1999] was used to infer surface roughness (z_0), friction velocities (u^*), Monin–Obukhov lengths (L), and stability correction functions $\Psi_c(z/L)$ necessary for the calculation of the resistances R_a and R_b (equations (9) and (10); cf. section 2.4). To account for conditions of very low wind speeds and/or high thermal stability (where atmospheric turbulence seldom exists and micrometeorological techniques fail), data were rejected for $u^* < 0.025 \text{ m s}^{-1}$ and $z_{\text{ref}}/L > 10$. Stringent application of data rejection criteria reduced daytime (nighttime) data availability to 76% (17%) and 74% (21%) during the LBA-EUSTACH-1 and LBA-EUSTACH-2 periods, respectively.

[26] To determine the dry deposition O₃ flux from its vertical gradient, another O₃ analyzer (cf. Table 1) was used for the gradient system during LBA-EUSTACH-1 and LBA-EUSTACH-2 campaigns. This O₃ analyzer was cross-compared with the “monitoring” O₃ analyzer (cf. section 2.2) for a total of 96 hours on four different occasions and showed good agreement (within ± 1 ppb). For the determination of the vertical O₃ gradient, two 1/4 in. (6.35 mm) PTFE tubes of identical length (6.25 m) were installed with inlets at $z_4 = 4.5$ m and $z_1 = 0.52$ m aboveground. The two intake lines were switched, alternating every 3 min, by a stainless steel 3-way valve, which fed into the sample port of the analyzer equipped with a 47-mm PTFE filter ($>2 \mu\text{m}$). One-minute flush time was discarded prior to each measurement. Every 30 min, means and standard deviations of O₃ concentrations from both levels were calculated by the micrologger routine. Thereafter, data where the observed standard deviation of the O₃ concentrations exceeded the magnitude of the gradient were removed. This procedure reduced daytime (nighttime) vertical O₃ gradient data to 38% (35%) and 41% (38%) during LBA-EUSTACH-1 and LBA-EUSTACH-2, respectively. The O₃ dry deposition flux was calculated by the aerodynamic flux–gradient relationship given by Müller *et al.* [1993] and Meixner [1994b].

[27] Subsequently, the total dry deposition resistance $R_{\text{tot}}(\text{O}_3)$ was calculated according to equation (5) and the canopy resistance ($R_c(\text{O}_3)$) was finally obtained (according to equation (6)) by subtracting R_a and R_b .

The latter were quantified by equations (9) and (10). Nighttime $R_{\text{tot}}(\text{O}_3)$ data obtained by the micrometeorological technique were not considered for this study since the data rejection procedures on both micrometeorological and O₃ gradient data reduced these to less than 10% their original size.

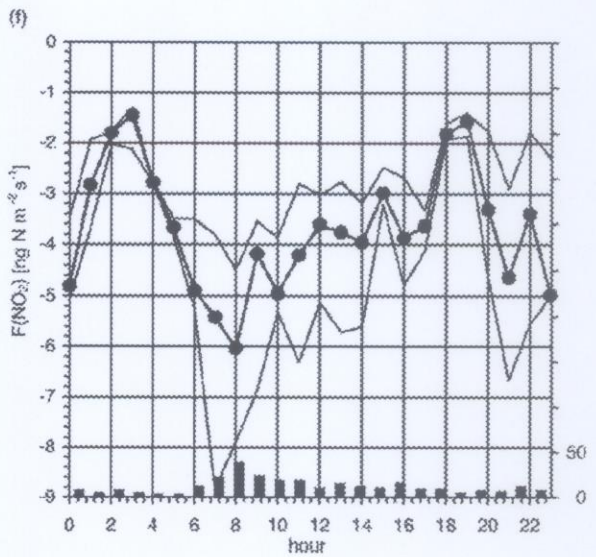
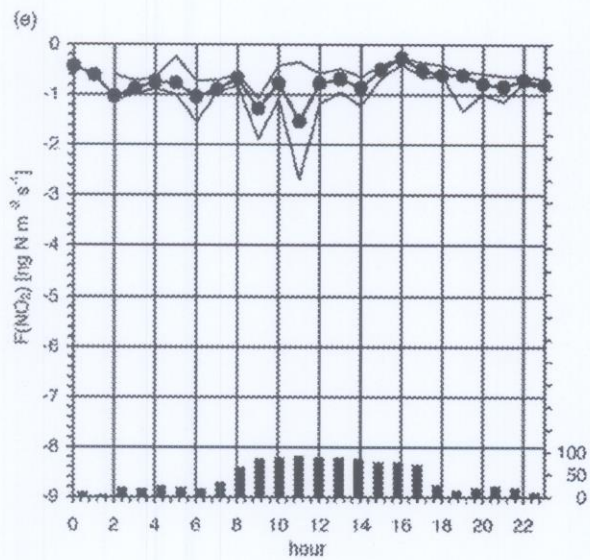
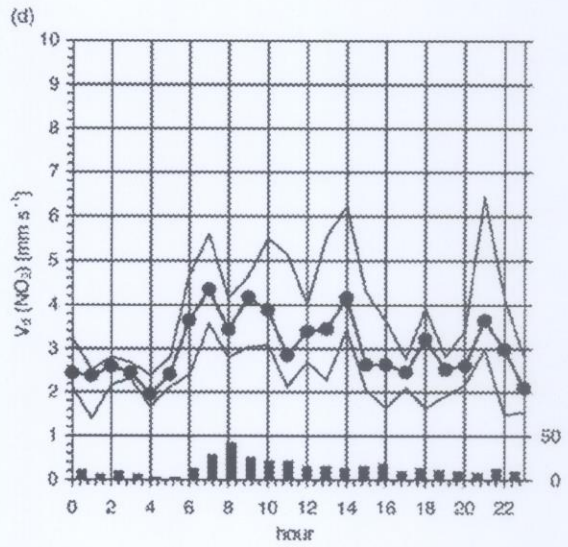
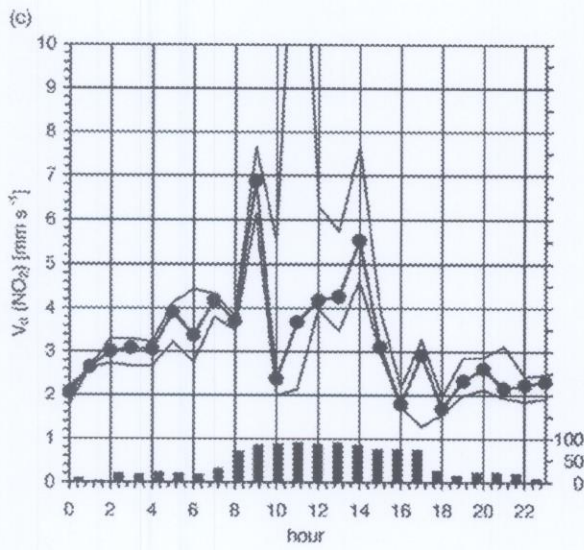
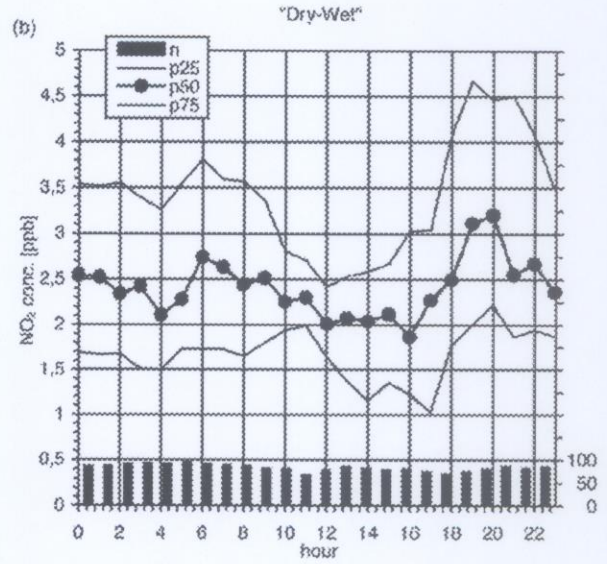
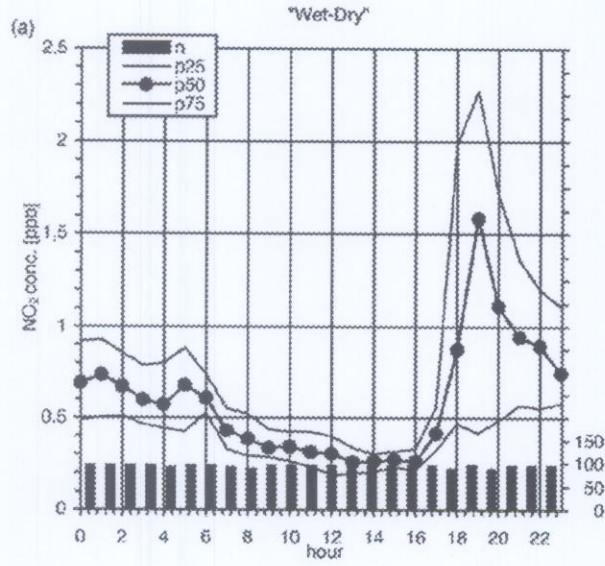
2.6. Determination of Soil Properties

[28] For the interpretation of the gas-exchange measurements, physical and chemical soil properties were determined for the measurement site. Soil diffusivity was determined by measurement of the naturally occurring transport tracer ²²²Rn with a system identical to that used at *Reserva Biológica Jarú* [Gut *et al.*, 1999, 2002a]. It comprised a closed system of two 1-m gas permeable membrane tubes (Acurrel[®]) buried at 3 cm, a ²²²Rn gas detector (Table 1), and a ventilated soil chamber. Determination of the soil bulk diffusion coefficient was estimated according to Fick’s first law using measurements of ²²²Rn soil–atmosphere gradient and the ²²²Rn surface flux [Gut *et al.*, 1998] at 10-min intervals for 3 days. The top 5 cm of soil from the chamber measurement site at FNS was analyzed for organic carbon, total phosphorous, total nitrogen, total sulfur, plant available phosphorous, potassium, pH (CaCl₂), bulk density, texture, and cation exchange capacity in accordance with methods described by Emde and Szöcs [2000]. Determination of ammonium, nitrate, net mineralization, net nitrification, and potential nitrification rates were performed in accordance with methods described by Hart *et al.* [1994].

3. Results and Discussion

[29] In this section, time series data are presented as mean diel courses for reasons of compactness and simplicity. Furthermore, data were grouped into 1-hour intervals centered at the local time hour. Medians together with first and third quartiles were used to graphically present results for both measurements campaigns LBA-EUSTACH-1 (18 days) and LBA-EUSTACH-2 (34 days). For all trace gas fluxes, the micrometeorological convention of negative downward fluxes and positive upward direction has been adopted. As previously mentioned stringent data rejection criteria (detection limits, nonstationarities, and “low turbulence”) were applied to ensure data quality thereby reducing data counts by more than 50%. This is especially the case at night where 1-hour averages are derived from fewer than 10 data points. In this case “low turbulence” events result in these data being discarded (not possible to derive R_a and R_b). Data counts are presented as bars in the Figures 4, 5, 6, and 7. Nevertheless, we felt it appropriate to supplement the presentation of the first measurements of the NO–NO₂–O₃ exchange over a tropical pasture during two separate seasons by adding an annual mean estimate. This is justifiable given the paucity of similar measurements in this environment.

Figure 5. (opposite) Diel (a) global radiation (W m^{-2}), (b) relative humidity (%), (c) R_a (s m^{-1}), (d) R_b (s m^{-1}), (e) $R_c(\text{NO}_2)$ (s m^{-1}), and (f) $R_c(\text{O}_3)$ (s m^{-1}) first, second, and third quartiles for the dry–wet transition season during LBA-EUSTACH-2 (24 September to 27 October 1999). Bars indicate actual data counts used to derive the hour averages (solid points).



3.1. Soil Emission of NO and Its Relation to Soil Properties

3.1.1. NO Emission Fluxes

[30] As mentioned previously, NO soil fluxes were determined directly from dynamic chamber measurements during the LBA-EUSTACH-2 campaign (September–October 1999). A statistical summary of the observed results is given in Table 4 and average diel cycles are displayed in Figure 4. The minimum detectable NO emission flux was $0.28 \text{ ng N m}^{-2} \text{ s}^{-1}$. Soil moisture ranged from 19.5 to 70.7% WFPS with a mean of 35.7% WFPS. Soil temperature averaged 25.5°C and ranged between 19 and 38°C (Figure 4). The observed NO soil emissions were some of the lowest fluxes measured on an established pasture in the Amazon basin with a mean of $0.65 \text{ ng N m}^{-2} \text{ s}^{-1}$ ($\pm 0.37 \text{ ng N m}^{-2} \text{ s}^{-1}$). NO emission fluxes also showed no diel dependence on soil temperature and/or soil moisture WFPS ($r^2 = 0.03$, $\alpha = 0.05$; cf. Figure 4c). The pronounced early morning peak in ambient NO concentration measured at 10 cm aboveground (Figure 4a) was most likely due to photolysis of accumulated nighttime NO_2 shortly after sunrise and is not a microbial response to increased surface wetness.

[31] Median NO emission fluxes at FNS were nine times lower than at the RBJ primary rain forest site under similar soil moisture and temperature conditions (see companion papers by Gut *et al.* [2002a, 2002b] and van Dijk *et al.* [2002]). We discuss below the possible physical and chemical soil factors (soil gas diffusion and nitrogen status) that explain the difference between the FNS and the RBJ sites.

3.1.2. Soil Diffusivity

[32] Bulk density tends to increase with pasture age [Feigl *et al.*, 1995], which directly affects soil gas diffusion. Compaction through mechanized forest clearing, ploughing, seed drilling, and cattle hoof action results in an increase in soil bulk density, soil tortuosity, and thereby the length of time a NO gas molecule takes to diffuse through the soil profile. Thereby increasing the chance of utilization (consumption) of the gas by denitrifiers (M. G6dde and R. Conrad, Influence of soil properties on the turnover of nitric oxide and nitrous oxide by nitrification and denitrification at constant temperature and moisture, submitted to *Biology and Fertility of Soils*, 2000). Flux measurements and vertical profiles in soils have shown the half-life of NO to be in the order of minutes [Rudolph and Conrad, 1996]. The resultant emission flux is therefore a combination of NO production and consumption in the soil, which is largely soil diffusion dependant [Remde *et al.*, 1993]. Bulk density, for the top 5 cm of soil at FNS was 1.56 Mg m^{-3} , which was considerably higher (41%) than for the RBJ soil [Gut *et al.*, 2002a] and somewhat higher (16%) than for other pasture soils older than 20 years in Rond6nia [Neill *et al.*, 1995, 1996, 1997, 1999; Feigl *et al.*, 1995; Kirkman, unpublished data, 1999]. This is similarly reflected in the NO effective diffusion coefficients measured at FNS, $6.4 \pm 3.0 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, and at RBJ, $7.9 \pm 4.0 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, for a range of soil–water conditions (10–20%) where

maximum NO production is expected (S. van Dijk and F. X. Meixner, Production and consumption of NO in forest and pasture soils from the Amazon basin: A laboratory study, submitted to *Water, Air, and Soil Pollution*, 2000, hereinafter referred to as van Dijk and Meixner, submitted manuscript, 2000). This represents a 23% difference in soil diffusion between the two sites and can be attributed to the higher bulk density and the relative absence of soil macro pores and soil fauna (termite and earthworm passages) at FNS (personal observation). However, this difference is too small to explain the observed difference in the NO emission flux between pasture and forest.

3.1.3. Soil Nitrogen Status

[33] The repeated effects of slash-and-burn agriculture on tropical ecosystems are postulated to result in reduced overall soil N cycling and have been shown (cf. section 2.1) to result in lower productivity with time [Palm *et al.*, 1996]. Reduced bulk litter inputs result in poor N availability and a suppression of nitrification and mineralization [Piccolo *et al.*, 1994, 1996; Neill *et al.*, 1999]. This is partly manifested in the high soil C/N ratios (21:1) that were found at FNS.

[34] Inorganic ammonium pools ($16.2 \mu\text{g NH}_4^+ \text{ g}^{-1}$ soil or $12.6 \mu\text{g N-NH}_4^+ \text{ g}^{-1}$ soil) were a factor 10 larger than the inorganic nitrate pools ($5.3 \mu\text{g NO}_3^- \text{ g}^{-1}$ soil or $1.2 \mu\text{g N-NO}_3^- \text{ g}^{-1}$ soil). N pool sizes are considered to be reasonable indicators of soil nitrogen cycle dynamics, which suggests that FNS had a conservative rather than fast nitrogen soil turnover rate [Davidson *et al.*, 2000]. Nitrogen cycling of the soils at FNS showed similar characteristics to older pastures in Rond6nia (Tables 2 and 3). Negative net mineralization ($-0.89 \mu\text{g NH}_4^+ \text{ g}^{-1} \text{ soil d}^{-1}$) and the weak positive net nitrification rates ($0.40 \mu\text{g NO}_3^- \text{ g}^{-1} \text{ soil d}^{-1}$) also suggest a large portion of the N turnover was immobilized by microbes [Hart *et al.*, 1994]. Potential nitrification rates indicate the maximum rate of NH_4^+ oxidation by ammonium oxidizers [Besler, 1979] (Table 3), and rates at FNS ($1.69 \mu\text{g NO}_3^- \text{ g}^{-1} \text{ d}^{-1}$) were found to be within the upper ranges measured by Verchot *et al.* [1999] in Par6 ($0.18\text{--}1.70 \mu\text{g NO}_3^- \text{ g}^{-1} \text{ d}^{-1}$) for active and degraded old pastures. They are, however, a factor three lower than those of forest and secondary forest soils (Kirkman, unpublished data, 1999), indicating that ammonia oxidizers are possibly restrained by conversion from forest to pasture [Verchot *et al.*, 1999]. The low NO emissions measured at FNS during September–October 1999 are assumed to be a combination of lower NO effective soil diffusion and a reduced N cycle. This is supported by field measurements of diffusion, a dominant inorganic ammonium nitrogen pool, and lower potential nitrification rates, corroborated by a site history of declining agricultural productivity. Established pastures in Rond6nia may possess similar soil NO emission conditions.

3.2. Surface Resistances of NO_2 and O_3

[35] The measurement of daytime and nocturnal resistances has important implications for multiresistance modeling. Results presented here are among the first observations from

Figure 6. (opposite) Diel (a and b) NO_2 concentrations (ppb), (c and d) deposition velocities (mm s^{-1}), and (e and f) parameterized NO_2 fluxes ($\text{ng N m}^{-2} \text{ s}^{-1}$) first, second, and third quartiles for LBA-EUSTACH-1 and LBA-EUSTACH-2. Bars indicate actual data counts used to derive the hour averages (solid points).

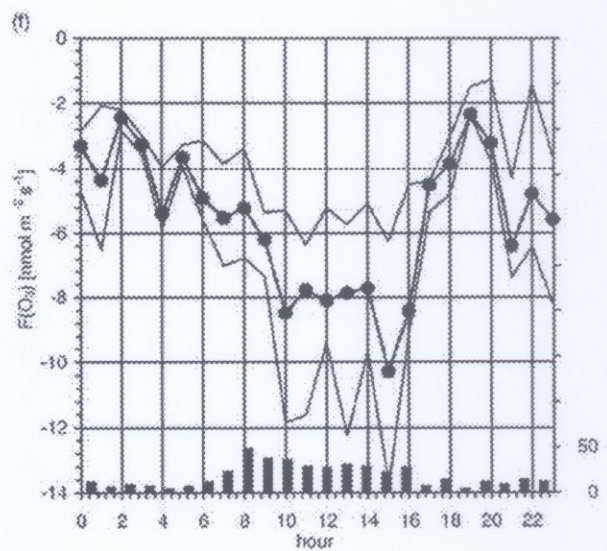
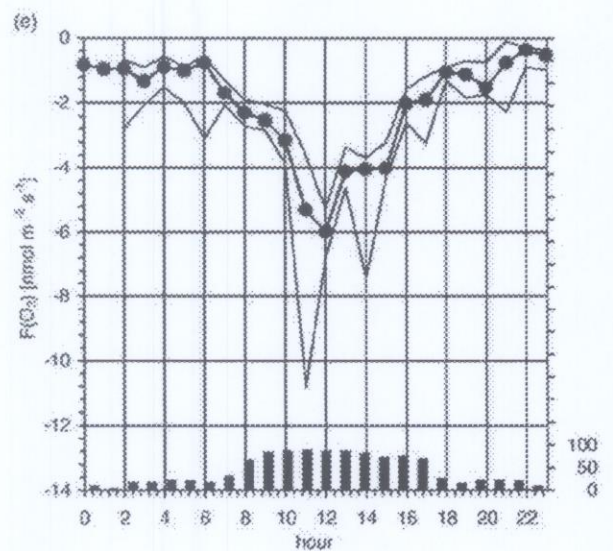
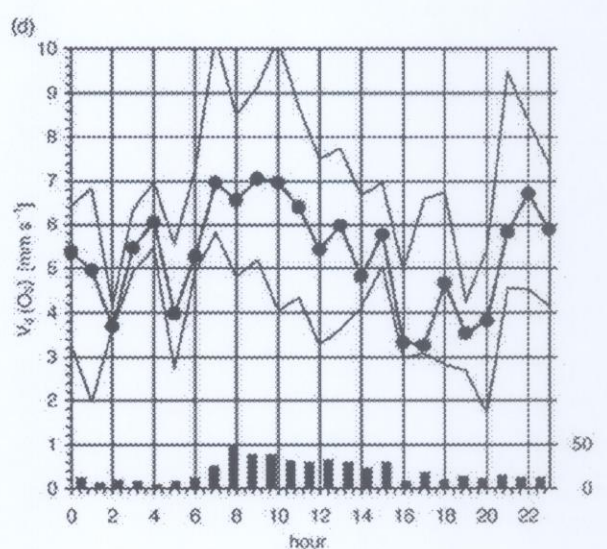
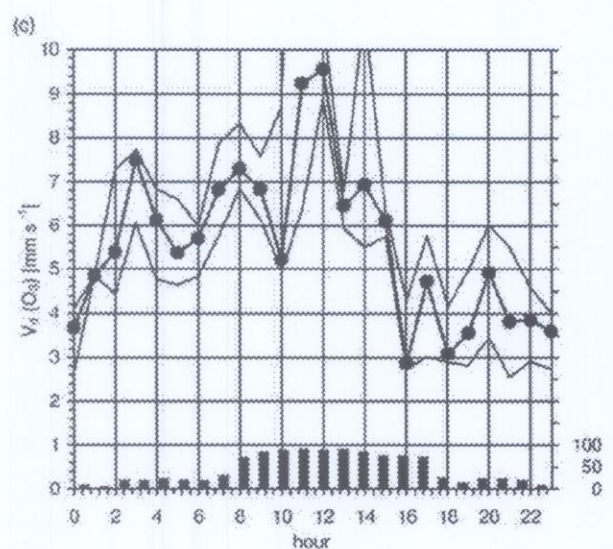
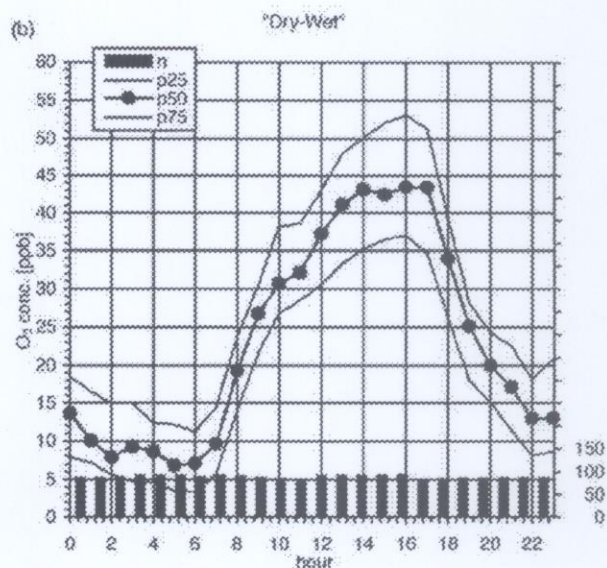
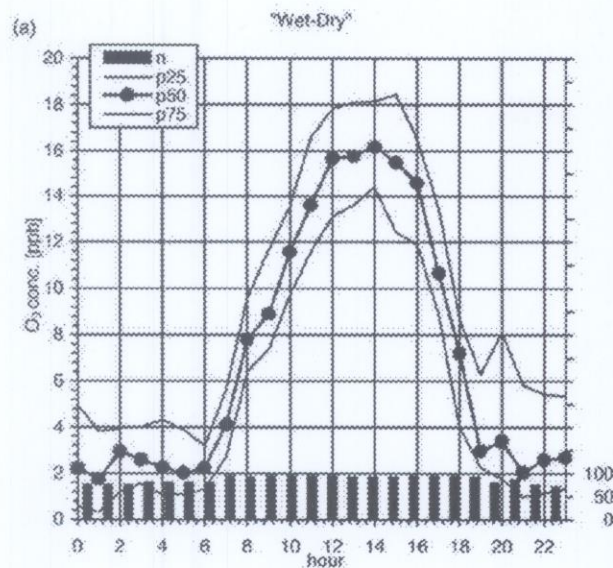


Table 2. Net Mineralization and Nitrification Rates for Established Pastures in Rondônia

Pasture (older than 20 yrs.)	$\mu\text{g NH}_4^+ \text{g}^{-1} \text{d}^{-1}$	$\mu\text{g NO}_3^- \text{g}^{-1} \text{d}^{-1}$
Neill et al. [1997] (Nova Vida)	-0.023	-0.02
Neill et al. [1999] (Nova Vida)	0.03	0.16
Neill et al. [1997] (Ouro Preto)	-0.22	0.22

a soil and grassland (*B. brizantha*) environment in the tropics where uptake resistances were measured on a 24-hour basis. Studies of NO_2 and O_3 uptake resistances over temperate grasslands are often limited to measurements during the day (e.g., for NO_2 on lawn: 333–769 s m^{-1} [Delany and Davies, 1983] and pasture: 38–67 s m^{-1} [Duyzer et al., 1983]). Rates of removal of O_3 by grasslands have been reported by Pio et al. [2000] to be 500 s m^{-1} at night to 200 s m^{-1} during the day, and Massman et al. [1993] reported 100 s m^{-1} over a semiarid grassland.

[36] Canopy resistance values ($R_c(\text{NO}_2)$ and $R_c(\text{O}_3)$) were measured by the dynamic chamber system during the LBA-EUSTACH-2 (dry–wet) campaign as described in section 2.3. In addition, R_a and R_b and a limited (daytime) data set of R_c values for O_3 were determined from the aerodynamic gradient measurement system during both campaigns (cf. section 2.5). The corresponding median and IQR (interquartile range) for daytime and nighttime R_a , R_b , R_c , and v_d (deposition velocity in mm s^{-1}) for NO_2 and O_3 are listed in Table 4. Diel resistance courses are presented together with global radiation and relative humidity for the dry–wet period in Figure 5.

[37] During LBA-EUSTACH-2 (dry–wet) median turbulent resistances (R_a) were 23 s m^{-1} during the day (0600–1800 LT) and 51 s m^{-1} at night, whereas the day and night molecular-turbulent boundary layer resistances (R_b) were 23 s m^{-1} and 33 s m^{-1} , respectively (Table 4). These near surface boundary layer resistance components (R_a and R_b) followed a typical diel trend in accordance with increased turbulent mixing during daytime due to higher wind speeds and thermal convection (Table 4). However, these data only reflect the nights with relatively high wind speeds that passed the rejection criteria described in section 2.5. For the majority of the nighttime cases which did not pass the rejection procedure, much higher resistances have to be assumed, indicating a very weak or intermittent turbulence. Canopy resistances of both gases controlled the deposition processes during the day for both measurement periods and contributed more than 65% of the total resistance ($R_a + R_b + R_c$). Day and night NO_2 canopy resistance means, during LBA-EUSTACH-2, were significantly similar ($\alpha = 0.05$) at 235 s m^{-1} and 238 s m^{-1} for day and night, respectively. Medians were 209 s m^{-1} and 229 s m^{-1} (Table 4). Ozone canopy resistances were significantly higher during daytime (106 s m^{-1}) than night 65 s m^{-1} (Table 4). The highest O_3 resistances (145 s m^{-1}) were observed at 1600 and at 1700 LT for NO_2 (343 s m^{-1}) each day, which coincided with low relative humidity (Figure 5b), suggesting stomatal closure

due to high water vapor pressure deficit. The gradient and dynamic chamber derived $R_c(\text{O}_3)$ values during the dry–wet period showed reasonable agreement, with daytime medians of 141 s m^{-1} and 106 s m^{-1} , respectively (Table 4). During LBA-EUSTACH-1 (wet–dry), nighttime conditions were even more stable and/or less turbulent, resulting in four times larger R_a and two times larger R_b nighttime values. Slightly lower R_a and R_b during the day were observed (Table 4), because of higher wind speeds [Andreae et al., 2002]. Daytime total resistances, determined by the gradient method ($R_a + R_b + R_c(\text{O}_3)$) for both the wet–dry and dry–wet periods also showed little seasonal difference, such that corresponding O_3 deposition velocities ($v_d(\text{O}_3) = R_{\text{tot}}(\text{O}_3)^{-1} = [R_a + R_b + R_c(\text{O}_3)]^{-1}$) were within 10% of each other during 1999 (Table 4).

[38] The diel patterns in NO_2 and O_3 resistances observed at FNS are considered to be the result of a combination of three processes: (1) stomatal, cuticular and mesophyll uptake, (2) soil uptake, and (3) uptake into solution of wet surfaces. The lower nighttime $R_c(\text{O}_3)$, when plant stomata are expected to be closed, is possibly due to a nighttime uptake of O_3 via stomata and/or foliar cuticle [Kisser et al., 1990] by the *B. brizantha* grass species. The similar daytime and nighttime $R_c(\text{NO}_2)$ values indicates that the same holds true for $R_c(\text{NO}_2)$. However, during the day this stomatal activity gradually decreases with declining leaf water potential. At around 1600 LT when relative humidity was lowest, vapor pressure deficits were highest, causing partial stomatal closure and hence larger resistances [Pathre et al., 1998]. This is in conflict with previous understanding that stomatal activity is typically higher during the day for C_4 plants. However, a closer look at the dry and transition season (August–September 1992 and June 1993) data of McWilliam et al. [1996] suggests not much difference between the early and late part of the day. Unfortunately, night values were not measured (Roberts, personal communication, 2000). In addition, Jacob and Wofsy [1990] had to introduce an efficient nighttime mechanism in their model for NO_2 plant uptake in order to balance their NO_y forest budget during ABLE-2B [Lerdau et al., 2000]. A similar mechanism could be assumed for FNS. Soil uptake, on the other hand, is presumed to be diel invariant and a significant contributor to NO_2 and O_3 uptake at FNS. Soil has been shown to contribute as much as 75% to the total O_3 depositional flux on Colorado semiarid grasslands [Massman, 1993], and ammonia oxidizers are thought to be significant consumers of NO_2 [Zart and Bock, 1998; Schmidt and Bock, 1997].

[39] Surface wetness might also significantly alter the surface resistances of less soluble trace gases like NO_2 and O_3 [Baldocchi, 1993; Chameides, 1987; Fuentes et al., 1992; Schwartz, 1992; Wesely, 1989]. Surface moisture or condensation on soil and grass elements occurred mostly at night (>70% of all measurements of surface wetness) and was detectable by the wetness grids during 45% of all nights during LBA-EUSTACH-2 at FNS. NO_2 and O_3 resistances were 60 and 72% higher, respectively, during

Figure 7. (opposite) Diel (a and b) O_3 concentrations (ppb), (c and d) deposition velocities (mm s^{-1}), and (e and f) O_3 fluxes ($\text{nmol m}^{-2} \text{s}^{-1}$) first, second, and third quartiles for LBA-EUSTACH-1 and LBA-EUSTACH-2. Bars indicate actual data counts used to derive the hour averages (solid points).

Table 3. Soil Properties for FNS, Determined During LBA-EUSTACH-2

Soil parameter	Value
Organic Carbon	1.87%
Total Phosphorus	0.021%
Total Nitrogen	0.122%
Total Carbon	2.58%
Total Sulfur	0.008%
Plant available Phosphorus	2.62 mg PO ₄ 100 g ⁻¹
Plant available Potassium	13.04 mg K 100 g ⁻¹
pH [CaCl ₂]	5.2
Bulk soil density	1.56 Mg m ⁻³
Clay content	11.47%
Silt content	11.73%
Sand content	76.80%
Wilting Point ^a	6.69 cm ³ cm ⁻³
Field Capacity ^a	19.56 cm ³ cm ⁻³
CEC (cation exchange capacity)	16.77 mmol z ⁻¹ 100g ⁻¹
Ammonium pool (NH ₄ ⁺)	16.81 µg NH ₄ ⁺ g ⁻¹
Nitrate pool (NO ₃ ⁻)	5.25 µg NO ₃ ⁻ g ⁻¹
Nitrite pool (NO ₂ ⁻)	0.27 µg NO ₂ ⁻ g ⁻¹
Net mineralization rate	-0.89 µg NH ₄ ⁺ g ⁻¹ d ⁻¹
Net nitrification rate	0.40 µg NO ₃ ⁻ g ⁻¹ d ⁻¹
Potential nitrification rate	1.69 µg NO ₃ ⁻ g ⁻¹ d ⁻¹
C/N ratio	21.6

^aBased on *Tomasella and Hodnett's* [1998] pedotransfer functions.

these wet nights as opposed to nights when no condensation occurred. Reports of enhanced O₃ deposition due to surface wetness have been noted above deciduous forests by *Fuentes et al.* [1992]. Their observations indicated that mechanisms other than stomatal uptake contributed to the O₃ deposition when the foliage was wet. Recent chemical models now make a distinction between foliage wetness caused by rain and dew to account for their different aqueous-phase chemical compositions [*Wesely*, 1989]. Therefore, nighttime $R_c(\text{NO}_2)$ and $R_c(\text{O}_3)$ values measured at FNS during the dry-wet period could be the competing result of plant, soil, and wet skin uptake (plant and soil) processes, accentuated by possible stomatal activity at

night and aqueous-phase chemistry on vegetative and soil surfaces. Moreover, the 24-h average canopy resistances for the pasture ($R_c(\text{NO}_2) = 236$ and $R_c(\text{O}_3) = 107 \text{ s m}^{-1}$), which comprised grass vegetation and soil, were 26 and 43% lower, respectively, than the forest floor ($R_c(\text{NO}_2) = 319$ and $R_c(\text{O}_3) = 188 \text{ s m}^{-1}$), comprising soil, root mat, and dead plant material at RBJ during the dry-wet season [*Gut et al.*, 2002b].

3.3. NO₂ and O₃ Deposition Fluxes and the NO_x Budget at FNS Site

[40] In order to make a seasonal comparison of NO₂ and O₃ dry deposition fluxes at FNS, fluxes were calculated for both periods using the inferential method described in section 2. For LBA-EUSTACH-2, all day and night values of $R_c(\text{NO}_2)$ and $R_c(\text{O}_3)$ from the dynamic chambers were used, while for LBA-EUSTACH-1 only the daytime $R_c(\text{O}_3)$ from the aerodynamic method were available directly. Unfortunately, number counts rendered nighttime $R_c(\text{O}_3)$ calculated with the aerodynamic method nonsignificant (cf. section 2.5), and these data were substituted with $R_c(\text{O}_3)$ measured by the dynamic chamber system during the dry-wet period. Correspondingly, $R_c(\text{NO}_2)$ were estimated by

$$R_c(\text{NO}_2)_{\text{wet-dry}} = R_c(\text{O}_3)_{\text{wet-dry}} \left[R_c(\text{NO}_2)_{\text{dry-wet}} / R_c(\text{O}_3)_{\text{dry-wet}} \right] \quad (14)$$

as an empirically adjusted first-order estimate of dry deposition flux for the wet-dry transition period. Diel NO₂ and O₃ concentrations and inferred diel NO₂ and O₃ dry deposition fluxes for both periods are presented in Figures 6 and 7. In addition, mean, standard deviation, count, and quartile statistics of NO₂ and O₃ dry deposition fluxes are given in Table 5.

[41] During LBA-EUSTACH-2, NO₂ and O₃ concentrations were considerably elevated above those measured

Table 4. Median and Interquartile Range (IQR) (s m⁻¹) of Canopy Resistances $R_c(\text{NO}_2)$ and $R_c(\text{O}_3)$, Turbulent Resistances R_a , Molecular-Turbulent Boundary Layer Resistances R_b , $v_d(\text{NO}_2) = R_{\text{tot}}(\text{NO}_2)^{-1}$ and $v_d(\text{O}_3) = R_{\text{tot}}(\text{O}_3)^{-1}$ Deposition Velocities (mm s⁻¹) for (a) LBA-EUSTACH-1 and (b) EUSTACH-2 Campaigns^a

(a) LBA-EUSTACH-1, 30 April to 17 May 1999 wet-dry transition period									
	R_a		R_b		$R_c(\text{O}_3)^b$		$v_d(\text{O}_3)^b$		
	day	night	day	night	day	night	day	night	
median	20	79	22	54	100	(65) ^c	6	(5) ^c	
IQR	11	93	17	38	61	17	14	8	

(b) LBA-EUSTACH-2, 24 September to 27 October 1999 dry-wet transition period									
gas	R_a		R_b		R_c		v_d		
	day	night	day	night	day	night	day	night	
NO ₂ (median)	23	51	23	33	209	229	4	3	
NO ₂ (IQR)	13	76	16	41	182	149	6	6	
O ₃ (median)	23	51	23	33	106	65	6	5	
O ₃ (IQR)	13	76	17	41	101	50	8	7	
O ₃ ^a (median)	23	51	23	33	141	–	5	–	
O ₃ ^a (IQR)	13	76	17	41	130	–	6	–	

^aDaily values fall between 0600 and 1800 LT. Values derived from substitution with values from the dry-wet period are in brackets.

^bAerodynamic gradient method for values between 0600 and 1800 LT.

^cValues derived from substitution with dry-wet nighttime data.

Table 5. NO Emission Fluxes ($\text{ng N m}^{-2} \text{s}^{-1}$), Dry Deposition Fluxes of NO_2 ($\text{ng N m}^{-2} \text{s}^{-1}$) and O_3 ($\text{nmol m}^{-2} \text{s}^{-1}$) Derived by the Inferential Method (cf. section 2.4) for LBA-EUSTACH-1 and LBA-EUSTACH-2 Campaigns: Means, Standard Deviations, Counts, Medians and Quartiles

(a) LBA-EUSTACH-1, 30 April to 17 May 1999 wet-dry transition period						
Gas	mean	std dev.	count %	Q25	median	Q75
NO_2^a	-0.91	0.89	46%	-1.05	-0.70	-0.46
O_3^b	-3.39	2.78	46%	-4.34	-2.75	-1.67
(b) LBA-EUSTACH-2, 24 September to 27 October 1999 dry-wet transition period						
Gas	mean	std dev.	count %	Q25	median	Q75
NO	0.65	0.39	9%	0.43	0.55	0.75
NO_2	-4.60	2.91	12%	-5.75	-3.93	-2.80
O_3	-6.76	4.07	19%	-8.74	-6.11	-3.71

^a Values derived from a proxy $R_c(\text{NO}_2)$ (cf. section 3.3).

^b Values derived from substitution with dry-wet nighttime data.

during LBA-EUSTACH-1 at FNS. This can be attributed to biomass burning from forest clearing activities, which typically occur in the later part of the dry season [Andreae *et al.*, 2002]. Nitrogen dioxide concentrations were a factor three higher during the dry-wet transition season (Figure 6) resulting in deposition fluxes six times larger than those of the wet-dry period (-3.93 versus $-0.7 \text{ ng N m}^{-2} \text{ s}^{-1}$) (Table 5). An early evening peak in the NO_2 concentration (more pronounced during the wet-dry period) was observed at ca. 1900 LT during both measurement periods. This peak was due to local advection of moderately aged pollution plumes (from nearby vehicular traffic along the RO-47) dispersing in a very shallow, stable, and young nocturnal boundary layer [Meixner *et al.*, 2000]. Ozone concentrations were equally elevated during the dry-wet period with deposition $F(\text{O}_3)$ fluxes twice as large ($-6.11 \text{ nmol m}^{-2} \text{ s}^{-1}$ or $0.13 \text{ } \mu\text{g m}^{-2} \text{ s}^{-1}$) during the dry-wet in contrast to the fluxes ($-2.75 \text{ nmol m}^{-2} \text{ s}^{-1}$ or $0.29 \text{ } \mu\text{g m}^{-2} \text{ s}^{-1}$) during the wet-dry season. Since resistance conditions are similar through the year (cf. section 3.2), consideration of seasonal ambient O_3 trace gas conditions is vital for quantifying the deposition of O_3 at expanded spatial and temporal scales in the Amazon basin. Assuming that measurements during LBA-EUSTACH-1 and LBA-EUSTACH-2 were representative for both wet and dry seasons and that these seasons were equal in length, the mean O_3 dry deposition was $0.24 \pm 0.013 \text{ } \mu\text{g m}^{-2} \text{ s}^{-1}$. This is slightly higher than the $0.19 \text{ } \mu\text{g m}^{-2} \text{ s}^{-1}$ first suggested as a mean for Amazonian pastures by Sigler *et al.* (J. M. Sigler, J. D. Fuentes, R. C. Heitz, and M. Garstang, Ozone dynamics and deposition processes at a deforested site in the Amazon basin, submitted to *Ambio*, 2000) on the basis of measurements for the 1999 wet season (January and February 1999 only) at FNS.

[42] NO soil emission fluxes were shown above to be extremely low (cf. section 3.1; Table 4) during the dry-wet period ($0.65 \text{ ng N m}^{-2} \text{ s}^{-1}$). Due to higher soil moisture in the wet season, which limits NO production and inhibits soil diffusion (van Dijk and Meixner, submitted manuscript, 2000), it is reasonable to assume that NO fluxes were similar or perhaps slightly lower during the dry-wet period. In this case, emission of NO and dry deposition of NO_2 would be approximately equal during the wet-dry season (Table 5). However, during the dry-wet season, the surface of FNS removed up to seven times more NO_2 from the atmosphere than was emitted as NO. Assuming, despite the low data

counts, that measurements during LBA-EUSTACH-1 and LBA-EUSTACH-2 were representative for the wet and dry seasons and that these seasons are about equal in length, this constitutes a net NO_2 sink of $0.73 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, which is a factor four larger than the NO emitted from the soil ($0.17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) at FNS. Therefore FNS could be considered as a net NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) sink during 1999.

4. Conclusion

[43] Rondônia, Brazil has in recent times undergone rapid replacement of natural forest by cleared land for commercial and small-scale agriculture. These agricultural areas typically decline in productivity within a relatively short period (2–6 yrs) after deforestation and are then either abandoned or planted to grass. Measurements of (1) NO fluxes, (2) NO_2 and O_3 canopy resistances, (3) and NO_2 and O_3 fluxes were conducted for two seasons (wet-dry and dry-wet) on the 22-year-old cattle pasture *Fazenda Nossa Senhora Aparecida* in the state of Rondônia, Brazil. The pattern of declining productivity found on old pastures was corroborated by the low NO flux emissions measured during the 1999 dry-wet season. During this season the pasture was shown to be a significant net NO_x sink, with elevated NO_2 mixing ratios during the dry-wet season when biomass burning was most prevalent. There was little seasonal variation in the NO_2 and O_3 deposition velocities determined in the wet-dry and dry-wet seasons at FNS. However, deposition fluxes were a factor six larger during the dry-wet season. These observations indicate that ambient concentrations largely control dry deposition of NO_2 and O_3 over established pastures.

[44] The measurements of canopy resistances over FNS, which comprised of soil and vegetation (live and dead grass), revealed that these resistances controlled the larger nighttime uptake of NO_2 and O_3 during the two transition seasons in 1999. The combined plant, soil, and wet surface uptake of trace gases, accentuated by stomatal activity and aqueous phase chemistry on vegetative and soil surfaces at night, are believed to result in a trace gas deposition diel pattern only previously observed by Kaplan *et al.* [1988] near Manaus and by Andreae *et al.* [1992] in the Congo Basin. Their results (presented as deposition velocities) could not be explained by changes in stomatal activity alone and were put down to differences in the aerodynamic resistance (R_a) component between the dry and wet seasons.

Further work on forest canopy and pasture soil and plant surface NO₂ and O₃ uptake processes is required to understand the diel pattern of canopy resistances observed in this study.

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