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tropics**

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# Dry and wet deposition of inorganic nitrogen compounds to a tropical pasture site (Rondônia, Brazil)

I. Trebs<sup>1</sup>, L. L. Lara<sup>2</sup>, L. M. M. Zeri<sup>3</sup>, L. V. Gatti<sup>4</sup>, P. Artaxo<sup>5</sup>, R. Dlugi<sup>6</sup>, J. Slanina<sup>7</sup>, M. O. Andreae<sup>1</sup>, and F. X. Meixner<sup>1</sup>

<sup>1</sup>Max Planck Institute for Chemistry, Biogeochemistry Department, Mainz, Germany

<sup>2</sup>Centro de Energia Nuclear na Agricultura (CENA), Laboratorio de Ecologia Isotópica, Universidade de São Paulo, Piracicaba, São Paulo, SP, Brazil

<sup>3</sup>Max Planck Institute for Biogeochemistry, Jena, Germany

<sup>4</sup>Instituto de Pesquisas Energéticas e Nucleares, CQMA, Atmospheric Chemistry Laboratory, Cidade Universitaria, São Paulo, SP, Brazil

<sup>5</sup>Instituto de Física, Universidade de São Paulo (USP), São Paulo, SP, Brazil

<sup>6</sup>Working Group Atmospheric Processes (WAP), Munich, Germany

<sup>7</sup>University of Wageningen, Department of Environmental Sciences, Wageningen, AP, The Netherlands

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Correspondence to: I. Trebs (ivonne@mpch-mainz.mpg.de)

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## Abstract

The input of nitrogen (N) to ecosystems has increased dramatically over the past decades. While total N deposition (wet + dry) has been extensively determined in temperate regions, only very few data sets exist about wet N deposition in tropical ecosystems, and moreover, experimental information about dry N deposition in tropical environments is lacking. In this study we estimate dry and wet deposition of inorganic N for a remote pasture site in the Amazon Basin based on in-situ measurements. The measurements covered the late dry (biomass burning) season, a transition period and the onset of the wet season (clean conditions) (12 September to 14 November 2002, LBA-SMOCC). Ammonia ( $\text{NH}_3$ ), nitric acid ( $\text{HNO}_3$ ), nitrous acid (HONO), nitrogen dioxide ( $\text{NO}_2$ ), nitric oxide (NO), ozone ( $\text{O}_3$ ), aerosol ammonium ( $\text{NH}_4^+$ ) and aerosol nitrate ( $\text{NO}_3^-$ ) were measured in real-time, accompanied by simultaneous (micro-)meteorological measurements. Dry deposition fluxes of  $\text{NO}_2$  and  $\text{HNO}_3$  are inferred using the “big leaf multiple resistance approach” and particle deposition fluxes are derived using an established empirical parameterization. Bi-directional surface-atmosphere exchange fluxes of  $\text{NH}_3$  and HONO are estimated by applying a “canopy compensation point model”. Dry and wet N deposition is dominated by  $\text{NH}_3$  and  $\text{NH}_4^+$ , which is largely the consequence of biomass burning during the dry season. The grass surface appeared to have a strong potential for daytime  $\text{NH}_3$  (re-)emission, owing to high canopy compensation points, which are related to high surface temperatures and to direct  $\text{NH}_3$  emissions from cattle excreta.  $\text{NO}_2$  also significantly accounted for dry N deposition, whereas  $\text{HNO}_3$ , HONO and N-containing aerosol species were only minor contributors. We estimated a total (dry + wet) N deposition of 7.3–9.8 kgN  $\text{ha}^{-1} \text{yr}^{-1}$  to the tropical pasture site, whereof 2–4.5 kgN  $\text{ha}^{-1} \text{yr}^{-1}$  are attributed to dry N deposition and  $\sim 5.3$  kgN  $\text{ha}^{-1} \text{yr}^{-1}$  to wet N deposition. Our estimate exceeds total (wet + dry) N deposition to tropical ecosystems predicted by global chemistry and transport models by at least factor of two.

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## 1. Introduction

The supply of reactive nitrogen (N) to global terrestrial ecosystems has doubled as a consequence of human activities, such as fertilizer application, cultivation of N fixing legumes and production of nitrogen oxides by fossil-fuel burning (Galloway, 1998). The deposition of atmospheric N species constitutes a major nutrient input to the biosphere. On a long-term scale, the increase of N inputs into terrestrial ecosystems may result in (i.) intensified trace gas exchange (ii.) enhanced leaching of nitrate and soil nutrients (e.g.,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ), (iii.) ecosystem eutrophication and acidification, (iv.) reduction in biodiversity, and (v.) increased carbon storage (Vitousek et al., 1997). Enhanced carbon storage due to N deposition has been shown to increase the terrestrial carbon sink in N-limited temperate ecosystems, which may have substantial impacts on global  $CO_2$  concentrations (e.g., Townsend et al., 1996).

N deposition is considered to be relevant in the tropics due to widespread biomass burning activity and increasing fertilizer application. It was suggested by e.g., Matson et al. (1999) and Asner et al. (2001) that in contrast to temperate ecosystems, nitrogen-rich/phosphorus (P)-limited tropical rainforest soils may have a reduced productivity following excess N deposition, resulting in a decreased C-storage. Moreover, the humid tropical zone is a major source area for biogenic nitrous oxide ( $N_2O$ ) and nitric oxide (NO) emissions from soils (Reiners et al., 2002). Enhanced N inputs to tropical forests are likely to increase nitrification/denitrification rates and, hence, the emission of NO and  $N_2O$  to the atmosphere (Hall and Matson, 1999). The conversion of tropical rainforest into cultivated land and pasture may lead to a sustained disturbance of the natural N cycle. During clearing and burning of tropical rainforest, biomass-associated N is volatilized and a large fraction is emitted in form of gaseous  $NH_3$  (Trebs et al., 2004), which may result in considerable N losses of tropical ecosystems (Kauffman et al., 1998; Kauffman et al., 1995). This is affirmed by that fact that, in contrast to primary rain forests, plant growth in deforested areas is suggested to be limited by N rather than by P (Davidson et al., 2005; Oliveira et al., 2001).

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The deposition of atmospheric N compounds occurs via dry and wet processes. Nitrogen dioxide ( $\text{NO}_2$ ), ammonia ( $\text{NH}_3$ ), nitric acid ( $\text{HNO}_3$ ) and nitrous acid ( $\text{HONO}$ ) are the most important contributors to dry N deposition.  $\text{HNO}_3$  usually features a rapid downward (net deposition) flux to the surface (Huebert and Robert, 1985). By contrast, the exchange of  $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{HONO}$  and also  $\text{NO}_2$  between surface and atmosphere may be bi-directional. The rates of production and consumption in vegetation elements and/or soils mainly determine whether net emission or net deposition of these species takes place. Turbulent diffusion controls the transport of gases and particles from the surface layer to the earth's surface. The uptake of trace gases by surfaces is considered to be dependent on physico-chemical and biological surface properties (Hicks et al., 1987), but also on the solubility and reactivity of the gaseous compound (Wesely, 1989). Hence, soil characteristics, plant stomata activity and trace gas chemical properties largely determine the deposition velocity. The atmospheric dry removal of aerosol particles, which may contain N species such as ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ), is a function of the particle size (Nicholson, 1988) but also depends on the particle density. Dry deposition is enhanced for large particles (especially those larger than a few micrometers) due to the additional influence of gravitational settling.

Wet N deposition is a result of in-cloud scavenging ("rainout") and below-cloud scavenging ("washout") of atmospheric N constituents (Meixner, 1994). The total (wet + dry) N deposition ranges from 1–2 kgN ha<sup>-1</sup> yr<sup>-1</sup> for rural locations (e.g., North Canada) up to 30–70 kgN ha<sup>-1</sup> yr<sup>-1</sup> for urban N receptor regions (e.g., North Sea, European NW coast and NE U.S.) (Howarth et al., 1996). In contrast to moderately fluctuating air pollution levels that prevail in Europe, the United States and Asia throughout the year, tropical environments such as the Amazon Basin experience every year a dramatic change from the "green ocean" clean background atmosphere to extremely polluted conditions during the biomass burning season. Only few studies exist where atmospheric wet N removal was determined experimentally in the tropics (Clark et al., 1998; Galloway et al., 1982; Likens et al., 1987; Srivastava and Ambasht, 1994). The chemical composition of precipitation in the Amazon region was determined in

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previous studies by Andreae et al. (1990), Stallard and Edmond (1981), Lesack and Melack (1991) and Williams et al. (1997). Global chemistry and transport models (CTMs) such as MOGUNTIA have been applied to estimate total N deposition on a global scale (Holland et al., 1999). Model results suggest that net N deposition in the northern temperate latitude exceeds contemporary tropical N deposition by almost a factor of two. However, experimentally derived quantitative information about dry N deposition in tropical environments, required to validate these model predictions, has been lacking.

Kirkman et al. (2002) determined the surface-atmosphere exchange of NO, NO<sub>2</sub> and ozone (O<sub>3</sub>) at a pasture site in the Amazon Basin (Rondônia, Brazil). In this paper, we complement their study by additionally estimating the surface-atmosphere exchange fluxes of NH<sub>3</sub>, HNO<sub>3</sub>, HONO, aerosol NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> at the same pasture site. Our analysis is based on real-time measurements, supported by simultaneous measurements of (micro-) meteorological quantities covering the late dry (biomass burning) season, the transition period, and the onset of the wet season (clean conditions). Fluxes of NO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub> and HONO are estimated by inferential methods. Wet N deposition was determined by collection of rainwater and subsequent analyses. We estimate the total (dry + wet) annual N deposition at this pasture site and the relative contribution of the individual N species.

## 2. Experimental

### 2.1. Field site

Measurements were performed during 12–23 September 2002 (dry season, biomass burning), 7–31 October 2002 (transition period) and 1–14 November 2002 (wet season, clean conditions) at a pasture site in the state of Rondônia, Brazil (“Fazenda Nossa Senhora Aparecida”, FNS, 10°45′44″ S, 62°21′27″ W, 315 m a.s.l.). The site is located in the south-western part of the Amazon Basin. The location and a simplified sketch

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of the measurement site are shown in Fig. 1. The primary rain forest at FNS was cleared by slash & burn activities in 1977. The vegetation at FNS is dominated by grass (*Brachiaria brizantha*) with small patches of *Brachiaria humidicola* and very few isolated palms and bushes, and the site is used as a cattle ranch (~200 “Blanco” cattle, *Bos indicus hybrid*). FNS is located within a strip of cleared land about 4 km wide and several tens of kilometers long (Culf et al., 1996). The towns Ouro Preto do Oeste (~40 800 inhabitants) and Ji-Paraná (~110 000 inhabitants) are situated approximately 8 km and 40 km to the ENE and ESE of the site, respectively.

The instrumentation for trace gas/aerosol sampling and online analyses was arranged in an air conditioned wooden house. Rain samples were collected nearby the house (see Fig. 1). An automatic weather station (Met 1) was located in a distance of ~20 m to the S, and a meteorological tower (Met 2) was situated ~200 m to the NE of the inlets for trace gas and aerosol measurements. While the sampling site provides a sufficient uniform fetch expanding for 1–2 km from the sampling location in each direction (Andreae et al., 2002), local flow distortions may be caused by the wooden house and some instrument shelters. A more detailed description of the measurement site is given in Andreae et al. (2002) and Kirkman et al. (2002).

## 2.2. Sampling and analysis

Table 1 summarizes the specifications of the instruments for the measurement of trace gases, aerosol species and (micro)-meteorological quantities. Water-soluble N containing trace gases ( $\text{NH}_3$ ,  $\text{HNO}_3$  and HONO) and related aerosol species ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) were measured on-line. Air was taken from a height of 5.3 m above ground through a sophisticated inlet system, which was designed to reduce wall losses of soluble gases (especially  $\text{HNO}_3$ ) and to minimize aerosol losses due to non-isokinetic sampling (Trebs et al., 2004). Soluble gases were scavenged with a wet-annular denuder (WAD) (Wyers et al., 1993), which was combined with a Steam-Jet-Aerosol Collector (SJAC) (Khlystov et al., 1995) to collect particulate N species. For both gaseous and aerosol compounds, sample collection was followed by subsequent online anal-

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ysis (ion chromatography (IC)) for anions and flow-injection analyses (FIA) for  $\text{NH}_4^+$ . Cycle times were set to 20 min (dry season), 40 min (transition period) and 60 min (wet season) (Trebs et al., 2004). Aerosol samples of either PM 2.5 ( $D_p \leq 2.5 \mu\text{m}$ ) or total suspended particulate matter (TSP) were collected. A detailed description and verification of the measurement method and of the inlet system can be found in Slanina et al. (2001) and Trebs et al. (2004).

The chemiluminescence  $\text{NO}/\text{NO}_x$  analyzer (Thermo Environment Instruments) (see Table 1) was equipped with a molybdenum converter to transform ambient  $\text{NO}_2$  to  $\text{NO}$ . However, the converter basically responds to the sum of  $\text{NO}_2 + \text{HNO}_3 + \text{HONO} + \text{PAN} + \text{aerosol NO}_3^- + \text{organic nitrates}$ . Therefore, it is likely that  $\text{NO}_2$  measurements might be biased by a positive artifact (Fehsenfeld et al., 1990). During our study, the inlet line for  $\text{NO}/\text{NO}_x$  measurements had a length of 25 m (inner diameter = 4.4 mm). Therefore, highly soluble and sticky species such as  $\text{HNO}_3$  and  $\text{HONO}$  are assumed to be at least partly removed within the long inlet tubing. In addition, mixing ratios of  $\text{HNO}_3$  and  $\text{HONO}$  were usually below 0.5 ppb (Trebs et al., 2004), indicating that interferences would be marginal in case any of these gases would reach the chemiluminescence analyzer.  $\text{PAN}$  is a thermally unstable compound at temperatures even well below those observed at FNS (Kirkman et al., 2002) and aerosol  $\text{NO}_3^-$  was eliminated by the application of an inlet filter.

Also listed in Table 1 are those (micro)-meteorological sensors that were used to measure the quantities involved in this study, namely air temperature ( $T$ ), relative humidity ( $RH$ ), surface wetness, global radiation flux, momentum, latent and sensible heat flux and ingoing/outgoing short- and longwave radiation. Eddy covariance measurements were conducted using a Gill 3-D-sonic anemometer. The  $\text{H}_2\text{O}$  mixing ratio was monitored by a fast LI-COR infrared gas analyzer, and its analog output was directly fed to the ultrasonic anemometer A/D converter. Post-processing of the eddy covariance data (EDDYWSC, software by Alterra, Wageningen University Research, Netherlands) resulted in 30 min averages of sensible heat flux, latent heat flux, friction velocity and Monin-Obukov length. More details on the eddy covariance measure-



ments and corresponding data evaluation/calibration procedures are given in Araujo et al. (2002).

Precipitation was sampled from 12 September to 14 November 2002 using a wet-only rainwater collector (Aerochem Metrics). A total of 23 rainstorm events were collected representing ~100% of the precipitation in this period. Rain samples were stored in the dark at 4°C using polyethylene bottles which were previously rinsed with deionized water and preserved with Thymol. In order to trace possible contaminations, the sample pH was measured directly after sampling and before analysis. Analyses of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  were performed for all samples using a Dionex DX600 ion chromatograph at the Laboratório de Ecologia Isotópica, CENA/USP (São Paulo, Brazil). The detection limit was 0.05  $\mu\text{M}$  for all species. More details about sampling and analysis procedures are provided by Lara et al. (2001).

Moreover, a twin Differential Mobility Particle Sizer (DMPS) was employed to measure the dry aerosol particle size distribution in the diameter range from 3 to 850 nm. The size distribution of particles with aerodynamic diameters from 1 to 4  $\mu\text{m}$  was measured with an Aerodynamic Particle Sizer (APS) (Rissler et al., 2004; Vestin et al., 2005<sup>1</sup>).

### 3. Theory: estimation of dry and wet N deposition

#### 3.1. Trace gas fluxes

Dry deposition fluxes of trace gases have been estimated using the inferential method, which is based on the “big leaf multiple resistance approach” (Wesely and Hicks, 1977; Hicks et al., 1987). The deposition flux ( $F$ ) ( $\mu\text{g m}^{-2} \text{s}^{-1}$ ) of a nonreactive trace gas for

<sup>1</sup> Vestin, A., Rissler, J., Swietlicki, E., and Frank, G.: Cloud nucleating properties of the Amazonian dry season biomass burning aerosol – measurements and modeling, in preparation, 2005.

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which the surface is a sink under all ambient conditions is defined by:

$$F = -V_d \cdot X(z_{ref}) = -\frac{X(z_{ref})}{R_a + R_b + R_c} \quad (1)$$

where  $X(z_{ref})$  is the trace gas concentration ( $\mu\text{g m}^{-3}$ ) at the reference height  $z_{ref}$  (m) and  $V_d$  denotes the dry deposition velocity ( $\text{m s}^{-1}$ ), which is the reciprocal of the sum of the turbulent resistance ( $R_a$ ) ( $\text{s m}^{-1}$ ), the quasi-laminar or viscous boundary layer resistance ( $R_b$ ) ( $\text{s m}^{-1}$ ), and the surface resistance ( $R_c$ ) ( $\text{s m}^{-1}$ ). According to Hicks et al. (1987)  $R_a$  between the reference height ( $z_{ref}$ ) and the roughness length  $z_0$  (m) is given by:

$$R_a = \frac{1}{\kappa \times u_*} \left[ \ln \left( \frac{z_{ref}}{z_0} \right) - \Psi_H \left( \frac{z_{ref}}{L} \right) \right] \quad (2)$$

where  $\kappa$  denotes the von Karman constant (0.41) and  $L$  is the Monin-Obukov length (m), a measure of atmospheric stability that is derived from the sensible heat flux and the friction velocity  $u_*$  (Garratt, 1992).  $\Psi_H(z_{ref}/L)$  is the stability correction function for heat and inert tracers in its integral form (see Thom, 1975). The roughness length  $z_0$  of the grass surface at the FNS site was taken as 0.11 m (cf. Kirkman et al., 2002) and  $z_{ref}$  was 5.3 m and 10 m for the WAD/SJAC and for the  $\text{NO}_x$  measurements, respectively (Table 1). To account for conditions when the reliability of micrometeorological techniques was low, data were rejected for  $u_* \leq 0.01 \text{ m s}^{-1}$  and  $z_{ref}/L \leq 5$ , i.e. when extremely low turbulence and/or very high thermal stability was prevailing. Also, data were rejected for  $z_{ref}/L \geq -5$ , which reflects cases of very high thermal turbulence production (when Monin-Obukov similarity is no longer valid; Ammann, 1999).

$R_b$  determines the exchange of gaseous matter by molecular-turbulent diffusion across the viscous laminar sublayer immediately above the vegetation elements and can be described by (Hicks et al., 1987):

$$R_b = \frac{2}{\kappa \times u_*} \left( \frac{Sc}{Pr} \right)^{\frac{2}{3}} \quad (3)$$

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where  $Sc$  and  $Pr$  are the Schmidt and Prandtl number, respectively.  $Pr$  is 0.72 and  $Sc$  is a strong function of the molecular diffusivity of the trace gas. Values for  $Sc$  were taken from Hicks et al. (1987) and Erisman et al. (1994) for the different trace gas species. The surface resistances  $R_c$  could not be directly determined from our field measurements; hence values were adopted from the literature (see Sect. 4.4).

The inferential method is valid for trace gases whose mixing ratio at the soil and/or vegetation elements is zero. The observation of a net  $\text{NO}_2$  deposition flux to the FNS pasture by Kirkman et al. (2002) justifies the application of the inferential model for  $\text{NO}_2$  in our study. This is also valid for  $\text{HNO}_3$ , which typically features a rapid downward flux with negligible  $R_c$  and corresponding high  $V_d$  (Hanson and Lindberg, 1991).

By contrast,  $\text{NO}$ ,  $\text{HONO}$  and  $\text{NH}_3$  may be both deposited to and emitted from surfaces. Formally, this can be accounted for by a so-called canopy compensation point concentration  $X_c$  ( $\mu\text{g m}^{-3}$ ) (Hesterberg et al., 1996) that generally refers to the concentration of the compound just above the soil and/or vegetation elements (Nemitz et al., 2004a):

$$F = \frac{X_c - X(z_{ref})}{Ra + R_b + R_c} \quad (4)$$

The net  $\text{NO}$  emission from the FNS pasture site determined by Kirkman et al. (2002) was very low ( $0.65 \text{ ngN m}^{-2} \text{ s}^{-1}$  or  $0.17 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ ), thus we neglected any contribution of  $\text{NO}$  to the surface-atmosphere exchange of N species in our study.  $\text{HONO}$  is generally assumed to be formed by heterogeneous reaction of  $\text{NO}_2$  with surface water (Harrison et al., 1996) and it may subsequently be emitted from plant foliar cuticles or soil surfaces. Since there is no indication for any direct  $\text{HONO}$  emissions by plants (Schiemang et al., 2004), the  $\text{HONO}$  compensation point concentration  $X_c$  ( $\text{HONO}$ ) is expected to be a function of the  $\text{NO}_2$  mixing ratio (see Sect. 4.4).

To predict the bi-directional surface-atmosphere exchange of  $\text{NH}_3$  at the FNS site, we applied a dynamic resistance model proposed by Sutton et al. (1998). Besides uptake and emission of  $\text{NH}_3$  via plant stomata, the dynamic model accounts for absorption

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of  $\text{NH}_3$  by epicuticular water films under very humid conditions, and subsequent re-evaporation (capacitive leaf surface exchange). Since the FNS site is used as a cattle ranch and the  $\text{NH}_3$  flux directly from the soil is assumed to be negligible compared to that originating from cattle excreta, we considered a direct  $\text{NH}_3$  flux from cattle manure and urine  $F(\text{NH}_3)_{\text{excreta}}$ . The net  $\text{NH}_3$  flux  $F(\text{NH}_3)$  can be related directly to the  $\text{NH}_3$  canopy compensation point concentration  $X_c(\text{NH}_3)$  (Sutton et al., 1998) and is composed of its component fluxes through plant stomata,  $F_s(\text{NH}_3)$ , the flux in or out of the epicuticular water film (adsorption capacitor),  $F_d(\text{NH}_3)$ , and  $F(\text{NH}_3)_{\text{excreta}}$ :

$$F(\text{NH}_3)_t = \underbrace{\frac{X_s(\text{NH}_3) - X_c(\text{NH}_3)}{R_s(\text{NH}_3)}}_{F_s(\text{NH}_3)} + \underbrace{\frac{X_d(\text{NH}_3)_t - X_c(\text{NH}_3)}{R_d(\text{NH}_3)}}_{F_d(\text{NH}_3)} + F(\text{NH}_3)_{\text{excreta}}$$

$$= \frac{X_c(\text{NH}_3) - X(\text{NH}_3, Z_{\text{ref}})}{R_a + R_b} \quad (5)$$

where  $X_s(\text{NH}_3)$  denotes the  $\text{NH}_3$  stomata compensation point concentration ( $\mu\text{g m}^{-3}$ ) and  $R_s(\text{NH}_3)$  denotes the  $\text{NH}_3$  stomata resistance ( $\text{s m}^{-1}$ ).  $X_d(\text{NH}_3)_t$  is the  $\text{NH}_3$  adsorption concentration ( $\mu\text{g m}^{-3}$ ) associated with the “leaf surface capacitor” at time step  $t$  and  $R_d(\text{NH}_3)$  is the charging resistance of the capacitor ( $\text{s m}^{-1}$ ) (see Sutton et al., 1998).  $X_c(\text{NH}_3)$  is then determined by (Sutton et al., 1998):

$$X_c(\text{NH}_3)_t = \frac{X(\text{NH}_3, Z_{\text{ref}})/(R_a + R_b) + X_s(\text{NH}_3)/R_s(\text{NH}_3) + X_d(\text{NH}_3)_t/R_d(\text{NH}_3) + F(\text{NH}_3)_{\text{excreta}}}{(R_a + R_b)^{-1} + R_s(\text{NH}_3)^{-1} + R_d(\text{NH}_3)^{-1}} \quad (6)$$

$X_s(\text{NH}_3)$  can be parameterized according to (Farquhar et al., 1980; Sutton et al., 1994):

$$X_s(\text{NH}_3) = \frac{161\,512}{T_S} \cdot 10^{(-4507.11/T(z_0))} \cdot \Gamma \cdot 17\,000 \quad (7)$$

where  $T_S$  is the surface temperature (K) which was derived from the outgoing longwave radiation by applying the Stefan-Boltzmann law.  $\Gamma$  is the ratio of apoplastic  $[\text{NH}_4^+]/[\text{H}^+]$

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and was adopted from the literature (Sect. 4.4).  $R_s(\text{NH}_3)$  can be calculated from the measured latent heat flux  $LE$  ( $\text{W m}^{-2}$ ) for relatively dry daytime conditions and in the absence of precipitation using the algorithm of Nemitz et al. (2004a). Furthermore,  $X_d(\text{NH}_3)$  at time step  $t$  is a function of the adsorption charge and of the capacitance of the epicuticular water film (for details see Sutton et al., 1998). The values for the adsorption charge were adopted from Sutton et al. (1998) and the capacitance is a function of the epicuticular pH (see Sect. 4.4)

### 3.2. Aerosol fluxes

Up to date, no well established bulk resistance models exist for particle deposition. Significant discrepancies have been observed between experimental results and model predictions (Ruijgrok et al., 1995). The theoretical framework proposed by Slinn (1982) is widely used in modeling studies to predict particle deposition velocities. However, Wesely et al. (1985) derived an empirical parameterization for the dry deposition velocity  $V_p$  ( $\text{m s}^{-1}$ ) of submicron sulfate aerosols ( $D_p = 0.1\text{--}1.0 \mu\text{m}$ ) to grass surfaces:

$$V_p = u_* \cdot 0.002, \quad \text{for } L \geq 0 \quad (8a)$$

$$V_p = u_* \cdot 0.002 \cdot \left[ 1 + \left( \frac{-300}{L} \right)^{\frac{2}{3}} \right], \quad \text{for } L < 0 \quad (8b)$$

This approach generally results in much higher  $V_p$  values for submicron particles than predicted by the Slinn model. Several other studies (Garland, 2001; Nemitz et al., 2004b; Vong et al., 2004) also showed that  $V_p$  to surfaces of low aerodynamic roughness may be much larger than predicted by the Slinn model, even for particles of different chemical composition than studied by Wesely et al. (1985). In this study, however, either PM 2.5 or TSP was sampled.  $\text{NH}_4^+$  it is known to be largely attributed to fine mode aerosols with  $D_p \leq 1.0 \mu\text{m}$  (Seinfeld and Pandis, 1998), which was also observed dur-

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ing the SMOCC measurement campaign (Decesari et al., 2005<sup>2</sup>). By contrast, aerosol  $\text{NO}_3^-$  exhibited a bimodal size distribution (Falkovich et al., 2005). Since we did not find an empirical relationship in the literature to estimate  $V_p$  for aerosols with  $D_p \geq 1.0 \mu\text{m}$  and the contribution of coarse mode aerosol  $\text{NO}_3^-$  relative to that of fine mode aerosol  $\text{NH}_4^+$  is presumably small (cf. Sect. 4.2, Table 2), the parameterization by Wesely et al. (1985) is considered as a reasonable approximation for both PM 2.5 and TSP samples.

### 3.3. Determination of characteristic time scales

The resistance-based approaches presented above to calculate surface-atmosphere exchange fluxes rely on the “constant flux layer assumption”, which implies that the trace compounds considered are chemically-non-reactive tracers, such that their flux within the atmospheric surface layer is constant. However, sufficiently accurate fluxes of compounds that undergo rapid chemical transformation can be estimated as long as characteristic chemical time scales are one order of magnitude larger than turbulent transport times (Damköhler ratio  $D_r < 0.1$ ) (De Arellano and Duynkerke, 1992). Following De Arellano and Duynkerke (1992) the characteristic time of turbulent transport  $\tau_{turb}$  (s) can be calculated as:

$$\tau_{turb} = \kappa \cdot (z_{ref} + z_0) \cdot \left( \frac{\sigma_w^2}{U_*} \right)^{-1} \quad (9)$$

where  $\sigma_w$  denotes the standard deviation of the vertical wind component ( $\text{m s}^{-1}$ ). Atmospheric stability strongly determines the time scale of turbulent transport, which

<sup>2</sup>Decesari, S., Fuzzi, S., Facchini, M. C., Maenhaut, W., Claeys, M., Rudich, Y., Artaxo, P., Guyon, P., Andreae, M. O., Mayol-Bracero, O. L., and Fisch, G.: Overview of the inorganic and organic composition of size-segregated aerosol in Rondonia, Brazil, from the biomass burning period to the onset of the wet season, in preparation, 2005.

typically ranges from a couple of seconds under unstable conditions up to 2.5 h under stable conditions (Dlugi, 1993).

For the characteristic chemical time scale of the NO-NO<sub>2</sub>-O<sub>3</sub> triad, its photo-stationary equilibrium has to be considered. NO<sub>2</sub> is rapidly photolyzed to NO in the troposphere and it is formed back by reaction of NO with O<sub>3</sub>. The overall chemical time scale of the NO-NO<sub>2</sub>-O<sub>3</sub> triad  $\tau(\text{NO-NO}_2\text{-O}_3)$  is given by the combination of  $\tau(\text{NO})=(k_2 \times [\text{O}_3])^{-1}$ ,  $\tau(\text{NO}_2) = k_1^{-1} = j(\text{NO}_2)^{-1}$  and  $\tau(\text{O}_3) = (k_2 \times [\text{NO}])^{-1}$  (Lenschow, 1982) (where  $k$  is the reaction rate constant) and was calculated in accordance to Kirkman et al. (2002). Thereby,  $j(\text{NO}_2)$  was estimated from global radiation data using a relation derived from simultaneous measurements of global radiation and  $j(\text{NO}_2)$  in Amazonia during LBA-EUSTACH (cf. Kirkman et al., 2002).

HONO is rapidly photolyzed during daylight hours. The chemical time scale for daytime HONO photolysis is given by  $\tau(\text{HONO})_{\text{photol.}} = j(\text{HONO})^{-1}$ , whereby the parameterization provided by Kraus and Hofzumahaus (1998) was used to relate  $j(\text{HONO})$  to  $j(\text{NO}_2)$ . The chemical time scale of heterogeneous HONO formation at nighttime  $\tau(\text{HONO})_{\text{het.}}$  was derived by considering the HONO production rate  $P_{\text{HONO}}$  (ppb h<sup>-1</sup>) determined directly from our measurements (see Sect. 4.3). Homogeneous daytime HONO formation may proceed via reaction of NO with OH radicals; however, this process is very slow and can be neglected compared to daytime HONO photolysis (Lammel and Cape, 1996).

Photochemical reactions involving NH<sub>3</sub> and HNO<sub>3</sub> are not considered to contribute to any flux divergence since their chemical time scale is much larger than the time scale of turbulent transport (Pandis et al., 1995). By contrast, time scales to achieve gas/aerosol equilibrium between gaseous NH<sub>3</sub>, HNO<sub>3</sub> and particulate NH<sub>4</sub>NO<sub>3</sub> may occur within the time frame of turbulent transport (few seconds for submicron particles) and have to be explicitly considered here (Dlugi, 1993; Meng and Seinfeld, 1996). As reported by Trebs et al. (2005), the measured concentration product of NH<sub>3</sub> × HNO<sub>3</sub> was persistently below the theoretical equilibrium dissociation constant of the pure NH<sub>3</sub>/HNO<sub>3</sub>/NH<sub>4</sub>NO<sub>3</sub> system during daytime ( $RH < 90\%$ ), but approached the theoreti-

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cal equilibrium value during nighttime ( $RH > 90\%$ ). The desired equilibration time scale  $\tau(\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3)$  can be estimated according to (Wexler and Seinfeld, 1992):

$$\tau(\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3)^{-1} = 3\bar{D} \times \int_0^{\infty} \frac{m(R_p)dR_p}{\left(1 + \frac{\lambda}{\alpha + R_p}\right) \times R_p^2 \times \rho_p} \quad (10)$$

whereby the measured aerosol number size distribution was related to the aerosol mass size distribution  $m(R_p)dR_p$ .  $R_p$  is the particle radius (m),  $\bar{D}$  is the geometric mean of the diffusivity of semi-volatile gaseous species ( $\text{m}^2 \text{s}^{-1}$ ),  $m$  is the water-soluble particle mass ( $\text{kg m}^{-3}$ ),  $\lambda$  is the mean free path of air ( $6.51 \times 10^{-8} \text{ m}$  at 293.15 K),  $\alpha$  denotes the accommodation coefficient ( $0.001 < \alpha < 1$ ) (Wexler and Seinfeld, 1990), and  $\rho_p$  is the particle density. A value of  $\rho_p = 1.35 \pm 0.15 \text{ g cm}^{-3}$  was used as determined by Reid and Hobbs (1998) for Amazonian biomass burning aerosols.

The comparison of  $\tau_{\text{turb}}$  with  $\tau(\text{NO-NO}_2\text{-O}_3)$ ,  $\tau(\text{HONO})_{\text{photol.}}$ ,  $\tau(\text{HONO})_{\text{het.}}$  and  $\tau(\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3)$  allows to test whether reactive species can be treated as a passive tracer during their vertical transport within the surface layer ( $D_r < 0.1$ ) and, consequently, if the application of the “big leaf multiple resistance approach” and the “canopy compensation point model” are justifiable.

### 3.4. Wet N deposition

Storm size influences the chemical composition of the rainwater, in the sense that larger storms tend to be more dilute. This dependence demands the use of volume weighted means (VWM) for the calculation of monthly and annual concentration averages. For each rainwater solute, the concentrations measured in the sample were combined to create a VWM concentration for each collection date:

$$\text{VWM}_a = \frac{\sum_{i=1}^n C_{ai} \times V_i}{\sum V_i} \quad (11)$$

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where  $c_{ai}$  is the concentration of species  $a$  in sample  $i$ ,  $n$  is the number of samples and  $v_i$  is the volume of precipitation solution for sample  $i$ . The corresponding wet deposition rates for September, October and November were derived by summation of the VWM concentration determined for each precipitation event throughout the month, and subsequent multiplication by the mean of rainfall in the respective month obtained from historical time series (see <http://www.aneel.gov.br>). The annual wet N deposition was derived in a similar way; for instance, the VWM concentration obtained during September was considered as representative of the entire dry season and then multiplied by the historical mean rainfall for the dry season. The same procedure was performed for October and November representing transition period and wet season, respectively.

## 4. Results and discussion

In the following, the general patterns of our results will be shown as diel courses of the medians of measured and inferred quantities. Diel courses will be presented either for part of the dry season (biomass burning, 12–23 September) or, where the investigated quantities are relatively independent of season, for the entire measurement campaign (12 September–14 November 2002). To derive surface-atmosphere exchange fluxes of N-containing compounds, (micro)-meteorological data and  $\text{NO}_x/\text{O}_3$  data were synchronized to the time resolution of the WAD/SJAC system. The convention of negative downward fluxes (net deposition) and positive upward fluxes (net emission) has been adopted.

### 4.1. Meteorological conditions

In the Amazon Basin, nighttime radiative cooling usually results in the formation of a shallow, decoupled nocturnal boundary layer of high thermodynamic stability characterized by very low wind speeds; while the development of a deepening, convectively mixed layer starts with the heating of the surface in the morning (Nobre et al., 1996;

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Fisch et al., 2004). Median nighttime wind speeds at FNS were low ( $\leq 1 \text{ m s}^{-1}$ ). By contrast, wind speeds were substantially higher during daytime, ranging from 2 to  $3 \text{ m s}^{-1}$ . The 24-h average friction velocity ( $u^*$ ) was  $\sim 0.16 \text{ m s}^{-1}$  and reached maxima of  $\sim 0.4 \text{ m s}^{-1}$  around noon. Differences of  $u^*$  between the dry season, the transition period, and the wet season were marginal. As a consequence of high global radiation fluxes ( $500\text{--}900 \text{ W m}^{-2}$ , median) during daytime, ambient temperatures at the FNS site ranged between  $30$  and  $36^\circ\text{C}$  during sunlight hours, while nighttime temperatures were much lower ( $20\text{--}25^\circ\text{C}$ ). High relative humidities ( $RHs$ ) were observed during nighttime ( $90\text{--}100\%$ ), while daytime  $RH$  values usually dropped to  $40\text{--}50\%$  during afternoon hours. Local meteorology changed only marginally from the dry season to the wet season. Strong rain events ( $\geq 30 \text{ mm h}^{-1}$ ) occurred in the afternoon hours during the transition period and the wet season. A more detailed description of diel meteorological conditions can be found in Trebs et al. (2005).

#### 4.2. Concentrations

Median diel variations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$ , HONO and the inorganic aerosol species  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are shown in Fig. 2a–h for 12 to 23 September (dry season, biomass burning). Table 2 summarizes ambient mixing ratios measured during the dry season (12–23 September), the transition period (7–31 October) and the wet season (1–14 November). A detailed discussion of seasonal and diel cycles observed for  $\text{NH}_3$ ,  $\text{HNO}_3$ , HONO and aerosol  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is given in Trebs et al. (2004, 2005).

Despite intensive biomass burning activity during the dry season,  $\text{NO}$  mixing ratios were very low (Fig. 2d). The sharp peak between 06:00 and 09:00 LT was most likely due to rapid photolysis of accumulated nighttime  $\text{NO}_2$  shortly after sunrise, when  $\text{O}_3$  mixing ratios were still too low to re-oxidize significant amounts of  $\text{NO}$  (see Fig. 2e, f).  $\text{NO}_2$  was the most abundant N-containing trace gas during all three seasons and reached an average mixing ratio of  $\sim 5 \text{ ppb}$  during the dry season.  $\text{NO}_2$  featured a pronounced diel cycle with nighttime mixing ratios two times higher than during daytime

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(Fig. 2e). Apparently,  $\text{NO}_2$  was accumulated in a shallow nocturnal boundary layer of high thermodynamic stability due to: (i.) the low water-solubility of  $\text{NO}_2$  and consequently its low affinity to be taken up by epicuticular water films and (ii.) chemical production through reaction of  $\text{NO}$  with  $\text{O}_3$  in the absence of  $\text{NO}_2$  photolysis. Through the transition period until the wet season,  $\text{NO}_2$  mixing ratios declined by a factor of four.  $\text{O}_3$  mixing ratios exhibited a typical diel variation, which mirrors that of  $\text{NO}_2$  (high values during daytime and lower values during the night (Fig. 2f)). This was mainly caused by (i.) photochemical daytime production, (ii.) convective mixing within the boundary layer and from the free troposphere during daytime and (iii.) dry deposition and reaction with  $\text{NO}$  in a thermally stable stratified nocturnal boundary layer.

### 4.3. Characteristic timescales

Characteristic turbulent time scales ( $\tau_{turb}$ ) have been calculated according to Eq. (9) for  $z_{ref}=10$  m ( $\text{NO}_x/\text{O}_3$  measurements) and for  $z_{ref}=5.3$  m (WAD/SJAC measurements) (cf. Table 1). To calculate the characteristic time scale for heterogeneous nighttime HONO buildup ( $\tau(\text{HONO})_{het.}$ ) (Fig. 3a), only dry season nighttime HONO production rates ( $P_{\text{HONO}}$ ) were considered. For the transition period and the wet season  $P_{\text{HONO}}$  could not be determined since the HONO diel variation was substantially reduced (cf. Trebs et al., 2004). In contrast to other studies (e.g., Alicke et al., 2003; Harrison and Kitto, 1994; Lammel and Cape, 1996), our measurements revealed a relatively small average value of  $P_{\text{HONO}}=0.04$  ppb  $\text{h}^{-1}$ . Figure 3a shows that  $\tau_{turb}$  was at least two orders of magnitude smaller than  $\tau(\text{HONO})_{photol.}$  and  $\tau(\text{HONO})_{het.}$ , resulting in  $D_r \ll 0.1$ . Considering the chemical time scale of the  $\text{NO}-\text{NO}_2-\text{O}_3$  triad  $\tau(\text{NO}-\text{NO}_2-\text{O}_3)$  (Fig. 3a), largest  $D_r$  values are found between 17:00 LT and 20:00 LT, exceeding a value of 0.2 ( $z_{ref}=10$  m). However, during all other periods  $D_r$  for the  $\text{NO}-\text{NO}_2-\text{O}_3$  triad ranged between 0.05 and 0.1. Therefore, we conclude that the application of Eqs. (1) and (4) to calculate surface-atmosphere exchange fluxes of  $\text{NO}_2$  and HONO are justified, since chemical transformations are too slow to affect the vertical constancy of turbulent fluxes.

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The estimation of the equilibration time scale  $\tau(\text{NH}_3\text{-NO}_3\text{-NH}_4\text{NO}_3)$  was performed by integrating over the measured particle size distribution according to Eq. (10), whereby two different cases were considered. Case 1 is an upper estimate (Fig. 3b), using an accommodation coefficient  $\alpha=0.1$  (Wexler and Seinfeld, 1992) and taking into account only the inorganic water-soluble aerosol fraction ( $\leq 20\%$  of  $\text{PM}_{tot}$ ) (cf. Trebs et al., 2005). Case 2, the lower estimate (Fig. 3c), was calculated using  $\alpha=1$  and considering also water-soluble organic carbon (WSOC). The total water-soluble fraction (organic and inorganic) accounted on average for  $\sim 60\%$  of the total aerosol mass (Decesari et al., 2005<sup>2</sup>). As shown in Fig. 3b, c  $\tau(\text{NH}_3\text{-NO}_3\text{-NH}_4\text{NO}_3)$  increased substantially from the dry season through the transition period to the wet season. This is obviously caused by much higher particle number concentrations measured during the dry season when biomass burning took place (Vestin et al., 2005<sup>1</sup>). For case 1 (upper estimate) (Fig. 3b),  $D_r$  for the  $\text{NH}_3\text{-NO}_3\text{-NH}_4\text{NO}_3$  triad during the dry season ranges from 0.1 to 0.17 at nighttime and is smaller than 0.1 during the day. During the transition period and wet season,  $D_r$  for the  $\text{NH}_3\text{-NO}_3\text{-NH}_4\text{NO}_3$  triad is always significantly smaller than 0.1 (Fig. 3b). However, for case 2 (lower estimate) (Fig. 3c) nighttime  $D_r$  substantially exceeds a critical value of 0.1 during the dry season and the transition period.

To verify the theoretically derived values, results from a laboratory study will be discussed briefly. Condensation and evaporation of  $\text{NH}_3$  and  $\text{HNO}_3$  to/from particles have been investigated under controlled laboratory conditions. Particles were collected during field campaigns in 1991 (Brunnemann et al., 1996; Seidl et al., 1996) and 1993/1994 in the eastern part of Germany (Melpitz). The chemical aerosol composition was dominated by  $(\text{NH}_4)_2\text{SO}_4$ , NaCl and soot and is comparable to that described in Brunnemann et al. (1996) and Seidl et al. (1996). More than 90% of the  $\text{NH}_4\text{NO}_3$  mass was found in the accumulation mode ( $D_p \leq 1 \mu\text{m}$ ). Timescales  $\tau(\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3)$  were calculated using the algorithm proposed by (i.) Kramm and Dlugi (1994) and (ii.) Meng and Seinfeld (1996), resulting in  $\tau(\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3)=100\text{--}500$  s for fine mode particles and  $\geq 880$  s for coarse mode particles. These values are comparable to

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characteristic times reported by Harrison et al. (1990) and Meng and Seinfeld (1996) and are in strong favor of our case 1 (upper estimate, Fig. 3b), which implies that the equilibration time scale was always much larger than that of turbulent transport. Nevertheless, it should be noted that the influence of the large soluble organic aerosol fraction typical for the Amazon Basin (cf. Trebs et al., 2005) on gas/aerosol partitioning processes is not exactly known. Taking into account the potential role of WSOC in enhancing aerosol water uptake and subsequently the uptake of gaseous species, equilibration time scales may be equal or even faster than turbulent transport (cf. Fig. 3c).

#### 4.4. The inferential approach: discussion of input parameters

Some surface parameters required for the inferential method to estimate of surface-atmosphere exchange fluxes for trace gases (Eq. 1–7) could not be directly derived from the results of our field measurements. Thus, lower and upper scenarios were estimated, comprising a certain range of surface-atmosphere exchange fluxes. These scenarios were obtained by varying surface parameters over a selected range based on results obtained from studies in temperate latitudes. Note that for all parameters and quantities presented, values indicated as “low” and values indicated as “high” correspond to the resulting lower and upper flux estimates, respectively.

##### 4.4.1. Surface resistances $R_c(\text{HNO}_3)$ , $R_c(\text{HONO})$ and $R_c(\text{NO}_2)$ :

$R_c(\text{HNO}_3)$  was found to be zero in many studies (Dollard et al., 1987; Huebert and Robert, 1985). Very recently, Nemitz et al. (2004a) showed that non-zero, however, relatively small  $R_c(\text{HNO}_3)$  may exist ( $R_c=15\text{--}95\text{ s m}^{-1}$ ).  $R_c(\text{HONO})$  is considered to be only slightly higher than that of  $\text{HNO}_3$  (Wesely and Hicks, 2000). The ranges of  $R_c(\text{HNO}_3)$  and  $R_c(\text{HONO})$  used to estimate lower and upper surface-atmosphere exchange fluxes are given in Table 3. The surface uptake of  $\text{HNO}_3$  and  $\text{HONO}$  is considered to be enhanced by the presence of epicuticular water films under the humid conditions at the site (lower  $R_c$  values were chosen for nighttime).  $R_c(\text{NO}_2)$  has al-

ready been determined previously at the FNS site by Kirkman et al. (2002), hence no flux scenario is calculated for  $\text{NO}_2$  and median diel  $R_c(\text{NO}_2)$  values are taken directly from Kirkman et al. (2002) ( $R_c(\text{NO}_2)=200\text{--}300\text{ s m}^{-1}$ ).

#### 4.4.2. Bulk surface resistance $R_c(\text{NH}_3)$ :

$R_c(\text{NH}_3)$  is derived from the sum of the parallel resistances  $R_s(\text{NH}_3)$  and  $R_d(\text{NH}_3)$ .  $R_d(\text{NH}_3)$  is calculated in accordance to Sutton et al. (1998) which resulted in  $R_d(\text{NH}_3) > 1000\text{ s m}^{-1}$  (daytime) and  $R_d(\text{NH}_3) \leq 100\text{ s m}^{-1}$  (nighttime). Since  $R_s(\text{NH}_3)$  is not known for *Brachiaria brizantha* grass species, we limited the range of  $R_s(\text{NH}_3)$  by considering the diffusion of  $\text{H}_2\text{O}$  and  $\text{O}_3$  through plant stomata. For the upper  $\text{NH}_3$  flux estimate,  $R_s(\text{NH}_3)$  is derived from the measured latent heat flux ( $LE$ ) during daytime (10:00–18:00 LT) (see Sect. 3.1). The transfer of  $\text{H}_2\text{O}$  through plant stomata is considered as a very efficient process, representing an upper boundary for trace gas stomata exchange. By contrast, the transfer of  $\text{O}_3$  through plant stomata is considered to be limited by the low solubility of  $\text{O}_3$ . Therefore,  $R_c(\text{O}_3)$  determined by Kirkman et al. (2002) is assumed to be equal to the bulk surface resistance  $R_c(\text{NH}_3)$  during daytime, and  $R_s(\text{NH}_3)$  is calculated as  $R_s(\text{NH}_3)^{-1} = R_c(\text{O}_3)^{-1} - R_d(\text{NH}_3)^{-1}$ , whereby the different diffusivities of  $\text{O}_3$  and  $\text{NH}_3$  are taken into account. From 07:00 to 10:00 LT, when evaporation of epicuticular water films contributed to  $LE$ ,  $R_s(\text{NH}_3)$  derived from  $R_c(\text{O}_3)$  is used for both the lower and the upper flux estimate. Since stomata are thought to be closed during nighttime,  $R_s(\text{NH}_3)$  is set to  $1000\text{ s m}^{-1}$  for nighttime periods.

#### 4.4.3. Compensation point concentration $X_c(\text{HONO})$ :

Up to date, only two studies provide an estimate for  $X_c(\text{HONO})$  (Harrison and Kitto, 1994; Stutz et al., 2002). Here, the relationship  $X_c(\text{HONO})=0.03 \cdot X(\text{NO}_2, Z_{ref})$  was used, which was found for grassland in the recent study by (Stutz et al., 2002). This corresponds on average to  $X_c(\text{HONO})=85\text{ ppt}$  at the FNS site.

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### 4.4.4. Apoplastic $[\text{NH}_4^+]/[\text{H}^+]$ ratio $\Gamma$ and epicuticular pH:

For  $\Gamma$ , we have chosen values of 100 (lower estimate) and 200 (higher estimate), which range at the lower end of data reported for grass in the literature (Loubet et al., 2002; Spindler et al., 2001; van Hove et al., 2002). This may be justified by the poor soil N status at FNS (Kirkman et al., 2002), because N absorbed by the root medium strongly affects the leaf tissue  $\text{NH}_4^+$  concentration (Schjoerring et al., 1998a). The capacitance of the epicuticular water film is a function of the pH (see Sect. 3.1, Sutton et al., 1998), that is predominantly acidic (Flechard et al., 1999) and is taken as 4.5 (lower estimate) and as 4.0 (higher estimate) (cf. Sutton et al., 1998).

### 4.4.5. $\text{NH}_3$ flux from cattle excreta $F(\text{NH}_3)_{\text{excreta}}$ :

In order to estimate the contribution of cattle excreta to the net  $\text{NH}_3$  flux, we considered results of Boddey et al. (2004), who investigated the cycling of N in *Brachiaria* pastures in the south of the Brazilian province Bahia. According to their results, *Bos indicus* cattle excreted  $37 \text{ kgN animal}^{-1} \text{ yr}^{-1}$  in manure and  $49 \text{ kgN animal}^{-1} \text{ yr}^{-1}$  in urine when the pastures were stocked with two animals per hectare. The stocking rate at FNS was about one animal per hectare. About 8% of the excreted N may be released as  $\text{NH}_3$  (L. Bouwman, personal communication, 2004). Hence, the average  $F(\text{NH}_3)_{\text{excreta}}$  is estimated to be  $\sim 10 \text{ ngN m}^{-2} \text{ s}^{-1}$ , which is applied for the entire measurement period (Eq. 5, 6).

### 4.5. Resistances, $\text{NH}_3$ canopy compensation point, transfer- and deposition velocities

4.5.1. The turbulent resistance  $R_a$  and the quasi-laminar boundary layer resistance  $R_b$  (Fig. 4a, b):

These resistances feature a typical diel variation with lowest values during daytime ( $R_a=20 \text{ s m}^{-1}$ ,  $R_b=30 \text{ s m}^{-1}$ ), because of strong turbulent mixing within the surface

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layer, and higher values during nighttime ( $R_a=70\text{ s m}^{-1}$  and  $R_b=50\text{ s m}^{-1}$ ).

### 4.5.2. The bulk surface resistance $R_c(\text{NH}_3)$ (Fig. 5):

The median diel cycle of the bulk surface resistance  $R_c(\text{NH}_3)$ , that is the sum of the parallel resistances  $R_s(\text{NH}_3)$  and  $R_d(\text{NH}_3)$  (see Sect. 4.4) shows a pronounced diel fluctuation with higher values during sunlight hours and lower values at night. The upper estimate  $R_c(\text{NH}_3)_{\text{high}}$  (estimated from  $R_s(\text{NH}_3)_{\text{LE}}$  and  $R_d(\text{NH}_3)$ ) varies between 20 and  $60\text{ s m}^{-1}$  during daytime and is estimated to be  $<10\text{ s m}^{-1}$  during the night. The lower estimate  $R_c(\text{NH}_3)_{\text{low}}$  (estimated from  $R_c(\text{O}_3)$  and  $R_d(\text{NH}_3)$ ) ranges from 100 to  $200\text{ s m}^{-1}$  during the day and from 20 to  $50\text{ s m}^{-1}$  during nighttime. Presumably, this diel pattern reflects the strong influence of nighttime epicuticular water layers on the surface uptake of  $\text{NH}_3$ .

### 4.5.3. The $\text{NH}_3$ canopy compensation point concentration $X_c(\text{NH}_3)$ (Fig. 6):

The  $X_c(\text{NH}_3)$  scenario for the dry season calculated according to Eq. (6) lies well within the range of values determined for grassland in other studies (Hesterberg et al., 1996; Meixner et al., 1996; Spindler et al., 2001; Sutton et al., 2001) and is a strong function of surface temperature (cf. Eqs. 6, 7).  $X_c(\text{NH}_3)$  is predicted to be particularly high at daytime, although low values of  $\Gamma$  were used to run the model. This is caused by prevailing high surface temperatures at the FNS pasture site ( $35\text{--}40^\circ\text{C}$  at daytime and  $20\text{--}25^\circ\text{C}$  at night during the dry season).  $\text{NH}_3$  deposits “and dissolves in” epicuticular water films at high  $RHs$  during nighttime. After sunrise when the surface temperature increases the  $\text{NH}_3$  partial pressure above the epicuticular solution increases in accordance to Henry’s law. This is visible in Fig. 6 as a distinctive peak of  $X_c(\text{NH}_3)$  after sunrise between 08:00 and 09:00 LT. Once most of the epicuticular  $\text{NH}_4^+$  has evaporated,  $X_c(\text{NH}_3)$  subsequently decreases (after 09:00 LT). Lower surface temperatures during the transition period and the wet season have caused lower estimates of



$X_c(\text{NH}_3)$  ( $0.3\text{--}1\ \mu\text{g m}^{-3}$  during nighttime and  $1\text{--}4\ \mu\text{g m}^{-3}$  during daytime).

4.5.4. Transfer- and deposition velocities  $V_{tr.}(\text{NH}_3)$ ,  $V_{tr.}(\text{HONO})$ ,  $V_d(\text{HNO}_3)$ ,  $V_d(\text{NO}_2)$  (Fig. 7a–d) and  $V_p(\text{aerosol})$  (Fig. 8):

For compounds featuring a bi-directional surface exchange the concept of a dry deposition velocity  $V_d$  is no longer useful (e.g., Kramm and Dlugi, 1994). Thus, for bi-directional  $\text{NH}_3$  and HONO surface-atmosphere exchange the term transfer velocity ( $V_{tr.}$ ) will be used henceforth.

The estimated upper median diel variation of  $V_{tr.}(\text{NH}_3)$  (Fig. 7a) indicates net deposition (= downward flux) at nighttime ( $V_{tr.}(\text{NH}_3) > 0$ ) and net emission = upward flux ( $V_{tr.}(\text{NH}_3) < 0$ ) during the day, whereas the lower estimate of  $V_{tr.}(\text{NH}_3)$  shows only net emission. Typically,  $V_{tr.}(\text{NH}_3)$  is predicted to range between  $-1.5\ \text{cm s}^{-1}$  during the day and  $1.0\ \text{cm s}^{-1}$  at night for the upper estimate, and  $V_{tr.}(\text{NH}_3)$  is estimated to vary between  $-0.25\ \text{cm s}^{-1}$  during the day and  $-1.0\ \text{cm s}^{-1}$  at night for the lower estimate. For cases of  $\text{NH}_3$  net deposition,  $V_{tr.}(\text{NH}_3)$  is in good agreement with values of  $0.1\text{--}2\ \text{cm s}^{-1}$  observed by Erisman and Wyers (1993), Hesterberg et al. (1996), Nemitz et al. (2004a), Phillips et al. (2004) and Rattray and Sievering (2001). For cases of  $\text{NH}_3$  net emission,  $V_{tr.}(\text{NH}_3)$  agrees well with values reported by e.g., Nemitz et al. (2004a).

The estimated median diel variation of  $V_{tr.}(\text{HONO})$  (Fig. 7b, dry season only) similarly shows net deposition at night and net emission during the day, with  $V_{tr.}(\text{HONO})$  ranging from  $-1\ \text{cm s}^{-1}$  to  $1.3\ \text{cm s}^{-1}$  (upper flux estimate) and between  $-0.5\ \text{cm s}^{-1}$  and  $0.5\ \text{cm s}^{-1}$  (lower flux estimate). For cases of HONO deposition, these values are comparable to  $V_{tr.}(\text{HONO})$  of  $0\text{--}1.7\ \text{cm s}^{-1}$  reported by Harrison and Kitto (1994) and Stutz et al. (2002).

The estimates of  $V_d(\text{HNO}_3)$  shown in Fig. 7c, reveal maximal median values of  $2.3\ \text{cm s}^{-1}$  at around 13:00 LT when  $R_c(\text{HNO}_3) = 1\ \text{s m}^{-1}$  is applied (see Table 3, upper flux estimate), coinciding with the period of highest turbulence. The lower estimate, when  $R_c(\text{HNO}_3)$  is taken as  $50\ \text{s m}^{-1}$  during daytime and as  $15\ \text{s m}^{-1}$  during nighttime

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(see Table 3), results in median  $V_d(\text{HNO}_3)$  values nearly equal during day and night ( $\leq 1.1 \text{ cm s}^{-1}$ ), which is attributed to the compensating effect of lower surface uptake and low turbulent exchange during nighttime. Although  $V_d(\text{HNO}_3)$  was found to be higher ( $3\text{--}4 \text{ cm s}^{-1}$ ) in other studies (e.g., Erisman et al., 1988), our values are still in reasonable agreement with deposition velocities determined by Dollard et al. (1987), Müller et al. (1993), Nemitz et al. (2004a) and Rattray and Sievering (2001) for vegetative canopies similar to that at FNS.

The median diel course of  $V_d(\text{NO}_2)$  shown in Fig. 7d exhibits a less distinct pattern with maxima of  $\sim 0.4 \text{ cm s}^{-1}$  during daytime. Values compare relatively well with  $V_d(\text{NO}_2)$  reported by Kirkman et al. (2002); however, the dry deposition of  $\text{NO}_2$  is thought to be mainly featured by uptake through plant stomata, which would imply that much higher dry deposition velocities (and hence much lower  $R_c$ ) occur during daytime. As stated in Kirkman et al. (2002), measured day- and nighttime  $R_c$  values for  $\text{NO}_2$  at FNS were similar, which was assumed to be mainly a result of stomatal closure due to high water vapor pressure deficit at lower  $RH$ 's during daytime.

Deposition velocities  $V_p$  predicted for particles (Fig. 8) are estimated to be highest during daytime ( $\leq 0.8 \text{ cm s}^{-1}$ ) in accordance with higher values of  $u^*$ . During nighttime,  $V_p$  generally remains below  $0.1 \text{ cm s}^{-1}$ . As previously indicated, these values are much larger than  $V_p$  predicted by Slinn (1982) and are therefore considered as an upper estimate. It should be pointed out that aerosol water uptake at high  $RH$ s and the resulting particle growth during the deposition process may enhance deposition velocities (Khlystov, 1998; Gallagher et al., 1997). In our study, this would be particularly relevant for nighttime periods when  $RH$  usually exceeded 90%. However, a quantification of this effect would go beyond the scope of this work.

#### 4.6. Surface-atmosphere exchange fluxes

In this section, the measured mixing ratios (Sect. 4.2), the input parameters for the inferential approach (discussed in Sect. 4.4) and the results presented in Sect. 4.5 will

be used to estimate and discuss surface-atmosphere exchange fluxes of N-containing trace gases and aerosol particles.

#### 4.6.1. Bi-directional fluxes of gaseous $\text{NH}_3$ $F(\text{NH}_3)$ (Fig. 9a):

The application of the dynamic resistance model from (Sutton et al., 1998), which uses non-zero  $X_c(\text{NH}_3)$  values and takes into account that deposited  $\text{NH}_3$  may (re-)evaporate from surfaces, represents a rather conservative N deposition estimate (lower boundary). Since  $X_c(\text{NH}_3)$  was assumed to be zero in several studies (Goulding et al., 1998; Russell et al., 2003; Singh et al., 2001; Tarnay et al., 2001), which implies that  $\text{NH}_3$  is persistently net deposited to the surface (see Eq. 1), we have complemented the upper and lower bi-directional flux scenarios by additionally calculating a net deposition scenario for  $\text{NH}_3$  (see Fig. 9a), assuming  $X_c(\text{NH}_3)=0$  (Eq. 1) and using  $R_c(\text{NH}_3)$ \_high (Fig. 5). Fluxes found at locations in temperate regions with vegetative surfaces similar to the grass surface at FNS are comparable to our upper bi-directional estimate of  $F(\text{NH}_3)$  for the dry season (biomass burning) (Fig. 9a) (Erisman and Wyers, 1993; Flechard et al., 1999; Meixner et al., 1996; Spindler et al., 2001). The net emission peak between 08:00 and 09:30 LT in the upper estimate, corresponds to the peak of the predicted  $\text{NH}_3$  canopy compensation point (cf. Fig. 6) and the highest observed  $\text{NH}_3$  mixing ratios (see Fig. 2a). Relatively high median  $\text{NH}_3$  net emission fluxes ( $5\text{--}70 \text{ ngN m}^{-2} \text{ s}^{-1}$ , upper estimate) during daytime (08:00–17:30 LT) are the result of (i.) relatively high  $\text{NH}_3$  mixing ratios (Fig. 2a), (ii.) direct  $\text{NH}_3$  emission from cattle excreta, (iii.) high surface temperatures and (iv.) corresponding high values of simulated  $X_c(\text{NH}_3)$  (see Fig. 6). The simulated nighttime  $\text{NH}_3$  net deposition (upper estimate) (19:00–06:30 LT) is on average  $-2\text{--}-13 \text{ ngN m}^{-2} \text{ s}^{-1}$ . The lower  $\text{NH}_3$  flux estimate shown in Fig. 9a suggests that surface-atmosphere exchange of  $\text{NH}_3$  may be significantly smaller when a higher epicuticular pH (4.5) (Sect. 4.4), a lower apoplastic  $[\text{NH}_4^+]/[\text{H}^+]$  ratio  $\Gamma$  (Sect. 4.4) and lower  $R_c(\text{NH}_3)$  (Fig. 5) are applied. The estimated  $\text{NH}_3$  net deposition for this case during nighttime is negligible

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and the predicted daytime  $\text{NH}_3$  net emission varies between 1 and  $20 \text{ ngN m}^{-2} \text{ s}^{-1}$ . During the transition period and the wet season, however, the lower  $\text{NH}_3$  flux estimate (not shown) features emission during day and night. The  $\text{NH}_3$  net deposition estimate (Fig. 9a) ( $X_c(\text{NH}_3)=0$ ) exhibits highest fluxes during daytime (08:00–15:00 LT), with values ranging between  $-20$  and  $-40 \text{ ngN m}^{-2} \text{ s}^{-1}$ . At nighttime, net deposition fluxes between  $-5$  and  $-20 \text{ ngN m}^{-2} \text{ s}^{-1}$  were estimated. Median  $V_{tr}(\text{NH}_3)$  values for this case range from  $0.5$  to  $1.5 \text{ cm s}^{-1}$  (not shown).

The predicted bi-directional  $\text{NH}_3$  flux scenarios are most sensitive to the pH of the epicuticular water film and the  $\text{H}^+$  and  $\text{NH}_4^+$  concentrations in the apoplastic fluid ( $\Gamma$ ). If the pH of the epicuticular water film would be  $>4.5$  and  $\Gamma$  is constant (100–200), the upper  $\text{NH}_3$  flux estimate would show net emission also during nighttime. On the other hand, increasing  $\Gamma$  beyond a value of 200 would result in daytime  $\text{NH}_3$  net emissions significantly higher than observed in urban regions in Europe or North America.

#### 4.6.2. Bi-directional fluxes of gaseous HONO $F(\text{HONO})$ (Fig. 9b):

The estimated median diel HONO flux scenario during the dry season (12 to 23 September), shows a small net emission during the afternoon but net deposition of up to  $-1.3 \text{ ngN m}^{-2} \text{ s}^{-1}$  (upper estimate) from 17:00–08:40 LT. The net deposition for the lower flux estimate is smaller ( $\geq -0.75 \text{ ngN m}^{-2} \text{ s}^{-1}$ ) in accordance to higher values of  $R_c(\text{HONO})$  applied. We like to note, that the HONO flux scenario presented here probably reflects the largest uncertainty of all flux estimates since presently neither  $R_c(\text{HONO})$  and  $X_c(\text{HONO})$ , nor the exact HONO formation mechanism is well known.

#### 4.6.3. Fluxes of gaseous $\text{HNO}_3$ $F(\text{HNO}_3)$ (Fig. 9c):

The estimated median diel  $\text{HNO}_3$  flux scenario during the dry season is characterized by highest net deposition values from 09:00–16:30 LT ( $\sim -0.5$ – $-4 \text{ ngN m}^{-2} \text{ s}^{-1}$ , upper estimate), coinciding with highest estimated deposition velocities (cf. Fig. 7c) and the maximal observed  $\text{HNO}_3$  mixing ratios (cf. Fig. 2b). Predicted nighttime  $\text{HNO}_3$  depo-

sition fluxes are lower in accordance with lower turbulence (lower  $V_d$ ) and lower  $\text{HNO}_3$  mixing ratios. The higher values of  $R_c(\text{HNO}_3)$  applied for the lower flux estimate (Table 3) result in daytime net deposition fluxes that are a factor of two lower than for the upper flux estimate.

#### 5 4.6.4. Fluxes of gaseous $\text{NO}_2$ $F(\text{NO}_2)$ (Fig. 9d):

The diel course of the estimated  $\text{NO}_2$  flux (dry season) is always characterized by downward fluxes (net deposition). Median nighttime fluxes (18:00–08:00 LT) are at least two times higher than during the day ( $\geq -12 \text{ ngN m}^{-2} \text{ s}^{-1}$ ). This is mainly due to generally higher  $\text{NO}_2$  mixing ratios measured during nighttime (Fig. 2e) and a small  
10 diel variation of  $V_d(\text{NO}_2)$  (see Fig. 7d), caused by similar day- and nighttime  $R_c(\text{NO}_2)$  determined by (Kirkman et al., 2002).

#### 4.6.5. Fluxes of aerosol $\text{NH}_4^+$ and $\text{NO}_3^-$ $F(\text{aerosol})$ (Fig. 10):

The estimated median diel flux of aerosol  $\text{NH}_4^+$  for the dry season exhibits a net deposition pattern characterized by highest values just after 09:00 LT ( $\sim -7 \text{ ngN m}^{-2} \text{ s}^{-1}$ ),  
15 which is consistent with maximal aerosol  $\text{NH}_4^+$  mixing ratios observed during this time (see Fig. 2g) and increased turbulent mixing (increasing  $u^*$ ) after sunrise. Although aerosol  $\text{NH}_4^+$  mixing ratios were generally lower during daytime, the dry deposition of aerosol  $\text{NH}_4^+$  is estimated to be highest because of high  $V_p$  predicted during sunlight hours (see Fig. 8). The median diel course of the aerosol  $\text{NO}_3^-$  flux shown in Fig. 10  
20 for the dry season resembles that estimated for aerosol  $\text{NH}_4^+$ , although the net deposition flux was at least three times lower than for aerosol  $\text{NH}_4^+$ , which is a consequence of lower aerosol  $\text{NO}_3^-$  mixing ratios (see Fig. 2g, h). The highest aerosol  $\text{NO}_3^-$  net deposition is predicted at around 09:00 LT ( $\sim -2 \text{ ngN m}^{-2} \text{ s}^{-1}$ ).

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#### 4.7. Seasonal cycles of dry and wet N deposition

Figure 11a, b illustrates the absolute amounts of the estimated monthly N deposition, whereby for dry N deposition (Fig. 11a) only cases of net deposition were considered. The dry deposition of  $\text{NO}_2$  and total ammonium ( $\text{NH}_3$  + aerosol  $\text{NH}_4^+$ ) are estimated to be highest and decline by about 70% from September (late dry season, biomass burning) to November (onset of the wet season, clean conditions) (Fig. 11a). This indicates the influence of biomass burning during the dry season, which significantly enhances the dry deposition of  $\text{NO}_2$  and  $\text{NH}_3$ . The dry deposition of total nitrate ( $\text{HNO}_3$  + aerosol  $\text{NO}_3^-$ ) also decreases by about 70% from September to November (Fig. 11a), but was on average 4 times lower than that of  $\text{NO}_2$  and total ammonium. This is in accordance with lower mixing ratios observed for nitrate in gas and aerosol phase (Table 2) (cf. Trebs et al., 2004). The contribution of nitrite (HONO) to the dry deposition in September is smallest, and is negligible in October and November.

Obviously, wet N deposition (Fig. 11b) is substantially higher than dry N deposition at the FNS site. Wet N removal is dominated by ammonium and nitrate, and wet deposition of nitrite is at least 3 times smaller. Interestingly, the decrease of wet deposition of ammonium and nitrate from September to November is only ~20%, hence, much less pronounced than that for dry N deposition.

During the late dry season (biomass burning) in September, on average 44% of the total N deposition can be attributed to dry deposition and ~56% to wet deposition (Fig. 12a). With increasing rainfall amounts, the contribution of dry deposition drops to only 29% and 21% to the total N deposition during October (transition period) and November (onset of the wet season, clean conditions), respectively (Fig. 12b, c).

Dry N deposition at FNS was always dominated by  $\text{NO}_2$  and  $\text{NH}_3$ . During September (dry season, Fig. 12a) the contribution of  $\text{NO}_2$  and  $\text{NH}_3$  to the total N deposition is estimated to be 18% and 16%, respectively. By contrast, the dry N deposition of  $\text{HNO}_3$  and HONO is estimated to be small, contributing only 2.8% and 1.1% to the total N deposition during the dry season, respectively (Fig. 12a). Aerosol  $\text{NH}_4^+$  and aerosol  $\text{NO}_3^-$

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show comparably small contributions to the total N deposition during the dry season (4.7% and 1.2%, respectively).

Through the transition period (October) until the wet season (November), the contribution of  $\text{NO}_2$  dry deposition to the total deposition declines to about 10% (Fig. 12b, c).

5 The relative contribution of  $\text{NH}_3$  to the total estimated N deposition decreases to 11% during the transition period and to 7.4% during the wet season. The dry N removal associated with  $\text{HNO}_3$ , HONO and aerosol  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is estimated to be negligibly small during the transition period and the wet season ( $\leq 5\%$  in total).

#### 4.8. Annual budget of surface-atmosphere exchange

10 The annual budget of surface-atmosphere exchange of inorganic N species at the FNS pasture site has been determined assuming that: (i.) September is representative for the entire dry season (May to September) ( $\text{PM}_{10} = 100\text{--}200 \mu\text{g m}^{-3}$ ), (ii.) October is representative for the two transition periods (April and October) ( $\text{PM}_{10} = 50\text{--}100 \mu\text{g m}^{-3}$ ), and (iii.) November is representative for the entire wet season (November to March) ( $\text{PM}_{10} \leq 25 \mu\text{g m}^{-3}$ ) (Artaxo et al., 2002). The annual deposition of inorganic N species at the FNS pasture site is estimated to  $7.3\text{--}9.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ , whereof  $2\text{--}4.5 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  can be attributed to dry N deposition and  $\sim 5.3 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  to wet N deposition. Thus, dry deposition may contribute on average 30% to the total annual N deposition. It is expected that  $2.7\text{--}6.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  are net (re-)emitted in form of gaseous  $\text{NH}_3$ , HONO and NO from the pasture site (the annual estimate for net NO emission was taken from Kirkman et al., 2002), whereof at least 90% are expected to be in the form of  $\text{NH}_3$ . Regarding soil emission of nitrous oxide ( $\text{N}_2\text{O}$ ), not included in this study, Garcia-Montiel et al. (2003) reported that the emission of  $\text{N}_2\text{O}$  from Amazonian pastures is even smaller than that of NO. Our study suggests that  $\text{NH}_3$  is net emitted on an annual time scale, owing to high surface temperatures (efficient  $\text{NH}_3$  emission through plant stomata) and direct  $\text{NH}_3$  emission from cattle excreta. The total N budget at FNS is most sensitive to the modeled  $\text{NH}_3$  flux. The FNS site may constitute an effective net sink of total inorganic N, if a zero-canopy compensation point

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$X_c(\text{NH}_3)$  is assumed, or if  $X_c(\text{NH}_3)$  is calculated using an epicuticular  $\text{pH} \leq 4.5$  and a ratio of  $\text{NH}_4^+/\text{H}^+$  in the apoplastic fluid  $\Gamma \leq 200$ .

Kirkman et al. (2002) reported that the FNS site constitutes a net  $\text{NO}_2$  sink of  $0.73 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ . However, based on our measurements and considering  $R_c(\text{NO}_2)$  determined by Kirkman et al. (2002), we calculated an annual  $\text{NO}_2$  deposition of  $1.24 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ , which is nearly two times higher than the value derived by Kirkman et al. (2002). This discrepancy is most likely due to higher  $\text{NO}_2$  mixing ratios observed during the dry (biomass burning) season in our study.

Moreover, it should be noted that water-soluble organic nitrogen (WSO<sub>N</sub>) constitutes a significant part of the total N fraction of Amazonian aerosols. It was found by Mace et al. (2003), that organic N may represent 45% and 43% of the total N in wet and dry season aerosol samples, respectively. Obviously, the total deposition of atmospheric N would be significantly higher if these organic species were also taken into account.

Wet deposition of nitrate and ammonium in Central Amazonia was previously estimated to  $1.7 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ ,  $2.1 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  and  $2.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  by Stallard and Edmond (1981), Andreae et al. (1990) and Williams et al. (1997), respectively. Since the measurement sites were situated in remote areas with less fire density, these estimates are about a factor of two lower than a value of  $4.7 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  (ammonium and nitrate only; nitrite excluded) obtained in this study.

Finally, Fig. 13 shows a comparison of our estimated N deposition with predictions by global chemistry and transport models (CTMs) (Bouwman et al., 2002; Dentener and Crutzen, 1994; Hauglustaine et al., 2004; Holland et al., 1997; Holland et al., 1999). The values from Dentener and Crutzen (1994) and Holland et al. (1997) are averages of N deposition predicted for the Amazon region (MOGUNTIA). The estimates from (Dentener and Crutzen, 1994) exclude dry deposition of  $\text{NO}_x$  and nitrate deposition. The value from Holland et al. (1999) (MOGUNTIA) represents predictions for tropical grasslands. Bouwman et al. (2002) (STOCHEM model) and Hauglustaine et al. (2004) (LMDz-INCA model) provide the total average N deposition for South America, which explains that their estimates are somewhat higher. Hauglustaine et al. (2004) do not

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take into account surface (re-)emission of  $\text{NH}_3$  ( $X_c(\text{NH}_3)=0$ ). Not surprisingly, our N deposition estimate for the Amazonian pasture site is a factor of two to eight higher than model predictions for the Amazon region (Fig. 13).

## 5. Summary and conclusions

5 We have estimated dry and wet deposition of inorganic N at a tropical pasture site (Rondonia, Brazil) based on real-time measurements of inorganic N containing gases and aerosol species during the late dry (biomass burning) season, the transition period and the onset of the wet season (clean conditions) (LBA-SMOCC 2002).  $\text{HNO}_3$ ,  $\text{NO}_2$ , aerosol  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were considered to be net deposited to the pasture site under  
10 all ambient conditions, while surface-atmosphere exchanges of HONO and  $\text{NH}_3$  were considered to be of bi-directional nature. All fluxes have been determined by inferential techniques, making use of aerodynamic and surface related resistances that have been deduced from measurements or were taken from recent literature. For the least-well defined quantities, lower and upper cases have been considered. Bi-directional  
15  $\text{NH}_3$  fluxes were predicted using a dynamic resistance model from Sutton et al. (1998).  $\text{NO}_2$  and  $\text{NH}_3$  are the most important contributors to dry N deposition and their fluxes largely control the total dry N deposition pattern at the pasture site. Mixing ratios of  $\text{NO}_2$  and water-soluble N species in gas and aerosol phase are significantly enhanced when widespread biomass burning takes place during the dry season, resulting in high  
20 N deposition rates. The contribution of the dry N deposition to the total N deposition decreased substantially from the dry (biomass burning) season to the wet season. The estimated total (dry + wet) N deposition to this tropical pasture site is  $7.3\text{--}9.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$ , whereof  $2\text{--}4.5 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  are attributed to dry N deposition and  $\sim 5.3 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  to wet N deposition. Thus, dry deposition may contribute on average 30% to the total N deposition. It is expected that  $2.7\text{--}6.8 \text{ kgN ha}^{-1} \text{ yr}^{-1}$  are net (re-)emitted from the  
25 pasture site, mainly in the form of  $\text{NH}_3$ . The largest uncertainties in our estimates are (i.) the epicuticular pH and (ii.) the ratio of  $\text{NH}_4^+$  and  $\text{H}^+$  concentration in the apoplastic

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fluid ( $\Gamma$ ). These quantities strongly control the  $\text{NH}_3$  canopy compensation point concentration and, hence, the estimated bi-directional  $\text{NH}_3$  flux. In this study, low values of (i.) the epicuticular pH (4–4.5) and (ii.) the ratio of  $\text{NH}_4^+$  and  $\text{H}^+$  concentration in the apoplastic fluid ( $\Gamma=100\text{--}200$ ) were assumed. The latter can be justified by the low soil N status of the pasture, and, in combination with a low epicuticular pH, the daytime net emission and nighttime net deposition pattern of the  $\text{NH}_3$  flux found in temperate latitudes could be reproduced. Our results suggest that – regardless of considering net deposition of  $\text{NH}_3$  or bi-directional  $\text{NH}_3$  exchange – the contemporary net N deposition to tropical ecosystems predicted by global CTMs may be underestimated at least by a factor of two. Up to now, approximately 15% of the original Amazonian rainforest has been deforested and was mostly converted to cattle pastures. Our N deposition estimate is suggested to be representative for these areas, featuring comparable land use patterns and microclimates. N deposition in these regions may therefore be comparable to moderately polluted urban regions in e.g., North America (Munger et al., 1998; Tarnay et al., 2001).

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**Table 1.** Specifications of the instrumentation for the measurement of trace gases, aerosol species and (micro)-meteorological quantities at FNS during LBA-SMOCC 2002 (all heights are above ground).

Parameter/position/ height	Time resolution	Technique or sensor	Model, manufacturer	Detection limit/ precision
NH <sub>3</sub> , HNO <sub>3</sub> , HONO (5.3 m)	20–60 min <sup>(1)</sup>	Wet-annular denuder (WAD), IC, FIA <sup>(2)</sup>	ECN, Petten, Netherlands	≤0.015 ppb (3σ) for acids, ≤0.118 ppb (3σ) for NH <sub>3</sub>
Aerosol NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> (5.3 m)	20–60 min	Steam-Jet Aerosol Collector (SJAC), IC, FIA	ECN, Petten, Netherlands	≤0.015 ppb (3σ) for anions, ≤0.118 ppb (3σ) for aerosol NH <sub>4</sub> <sup>+</sup>
NO concentration (10 m)	5 min	Gas-phase chemilumi- nescence	Model 42C TL (trace level), Thermo Environ- ment Instruments Inc., USA	0.05±0.025 ppb
NO <sub>2</sub> concentration (10 m)	5 min	Catalytic conversion of NO <sub>2</sub> to NO by molybdenum con- verter (at 325°C), gas phase chemiluminescence	Model 42C TL (trace level), Thermo Environment Instru- ments Inc., USA	0.05±0.025 ppb
O <sub>3</sub> concentration (10 m)	5 min	UV absorption	Model 49C Thermo Environment Instruments Inc., USA	1±0.5 ppb
Air temperature (Met 1, 0.5 m and 5 m)	1 min	Pt-100 Ω resistance sensor	MP-103A-CG030-W4W Rotronic, Switzerland	±0.1 K
Relative humidity (Met 1, 0.5 m and 5 m)	1 min	Capacitive sensor	MP-103A-CG030-W4W Rotronic, Switzerland	±1.5%
Surface wetness (Met 1)	1 min	Surface wetness grids at soil surface	237 WSG, Campbell Scientific Ltd., UK	–
Global radiation flux (Met 1, 5 m)	1 min	Pyranometer sensor	LI200SZ (LI-COR, Lincoln, Nebraska, USA)	< ±3%
Eddy covariance; three dimen- sional wind and temperature fluctuations (Met 2, 4 m)	10 Hz	3-D ultrasonic anemometer	Solent 1012R2, Gill Instruments, UK	±1.5%
H <sub>2</sub> O mixing ratio (Met 2, 4 m)	10 Hz	Infrared closed-path absorp- tion	IRGA LI-COR 6262 (LI-COR, Lincoln, Nebraska, USA)	±1%
Shortwave radiation in and out (Met 2, 8.5 m)	1 min	Pyranometer sensor	Kipp & Zonen Pyranometer CM 21	±2%
Longwave radiation in and out (Met 2, 8.5 m)	1 min	Pyranometer sensor	Kipp & Zonen Pyrgeometer CG	±3%

<sup>(1)</sup> 20 min: dry season (12–13 September), 40 min: transition period (7–31 October), 60 min: wet season (1–14 November)

<sup>(2)</sup> IC: ion chromatography, FIA: flow injection analysis

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**Table 2.** Summary of trace gas and aerosol mixing ratios<sup>(\*)</sup> during the dry season (12–13 September), the transition period (7–31 October) and the wet season (1–14 November) at FNS during LBA-SMOCC 2002.

Species	Dry season				Transition period				Wet season			
	m (ppb)	P 0.25 (ppb)	P 0.75 (ppb)	n (1)	m (ppb)	P 0.25 (ppb)	P 0.75 (ppb)	n (1)	m (ppb)	P 0.25 (ppb)	P 0.75 (ppb)	n (1)
NO	0.09	0.07	0.15	372	0.09	0.07	0.17	295	0.12	0.07	0.13	229
NO <sub>2</sub>	4.54	2.85	6.46	630	1.78	1.23	2.56	697	1.07	0.82	1.76	268
O <sub>3</sub>	24.3	11.76	34.87	826	25.59	15.91	32.95	781	14.74	10.77	19.39	316
NH <sub>3</sub>	1.81	1.10	2.91	298	1.06	0.5	1.74	236	0.55	0.38	0.85	60
HNO <sub>3</sub>	0.16	0.10	0.25	317	0.06	0.03	0.13	210	0.06	0.04	0.08	52
HONO	0.12	0.08	0.27	323	0.07	0.05	0.09	315	0.06	0.04	0.07	139
Aerosol NH <sub>4</sub> <sup>+</sup>	1.01	0.73	1.51	291	0.54	0.33	0.85	267	0.47	0.32	0.62	66
Aerosol NO <sub>3</sub> <sup>-</sup>	0.34	0.17	0.61	297	0.09	0.06	0.15	282	0.06	0.04	0.07	33

<sup>(\*)</sup> m: median, P 0.25: 0.25 percentile, P 0.75: 0.75 percentile, n: number of determined data points above the limit of detection (for aerosol species PM 2.5 and bulk measurements were included). NO<sub>x</sub>/O<sub>3</sub> data were synchronized to the WAD/SJAC data, i.e. one data point is available for each gas and each aerosol measurement of the WAD/SJAC).

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**Table 3.** Ranges of surface resistances  $R_c$  for  $\text{HNO}_3$  and HONO for daytime and nighttime used to estimate flux scenarios at FNS during LBA-SMOCC 2002.

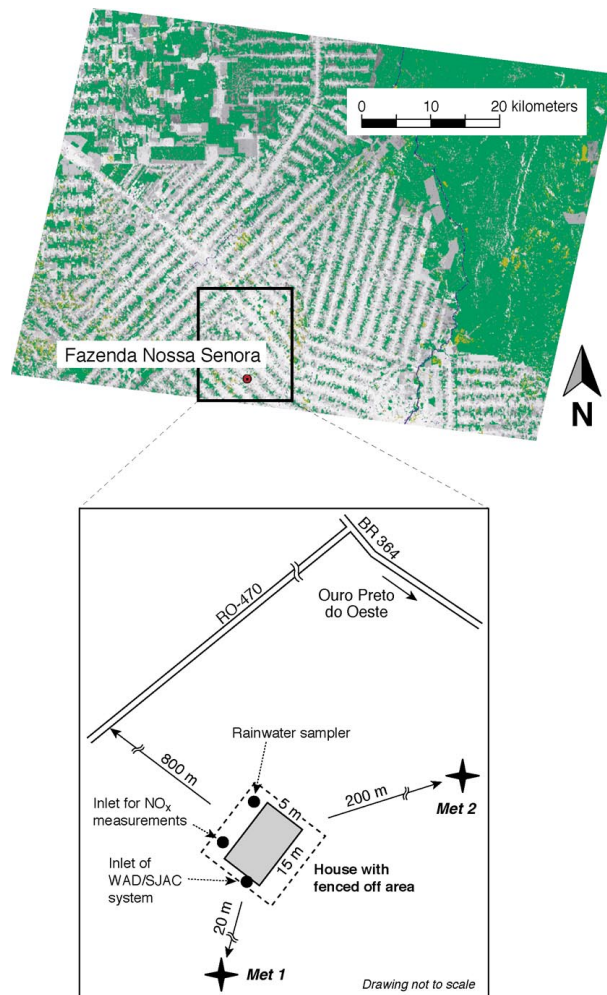
Scenario		$R_c(\text{HNO}_3)$ [s m <sup>-1</sup> ]	$R_c(\text{HONO})$ [s m <sup>-1</sup> ]
Day	high	1	50
	low	50	200
Night	high	1	15
	low	15	100

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**Fig. 1.** Location of the LBA-SMOCC measurement site “Fazenda Nossa Senhora Aparecida” (FNS) in Rondonia, Brazil.

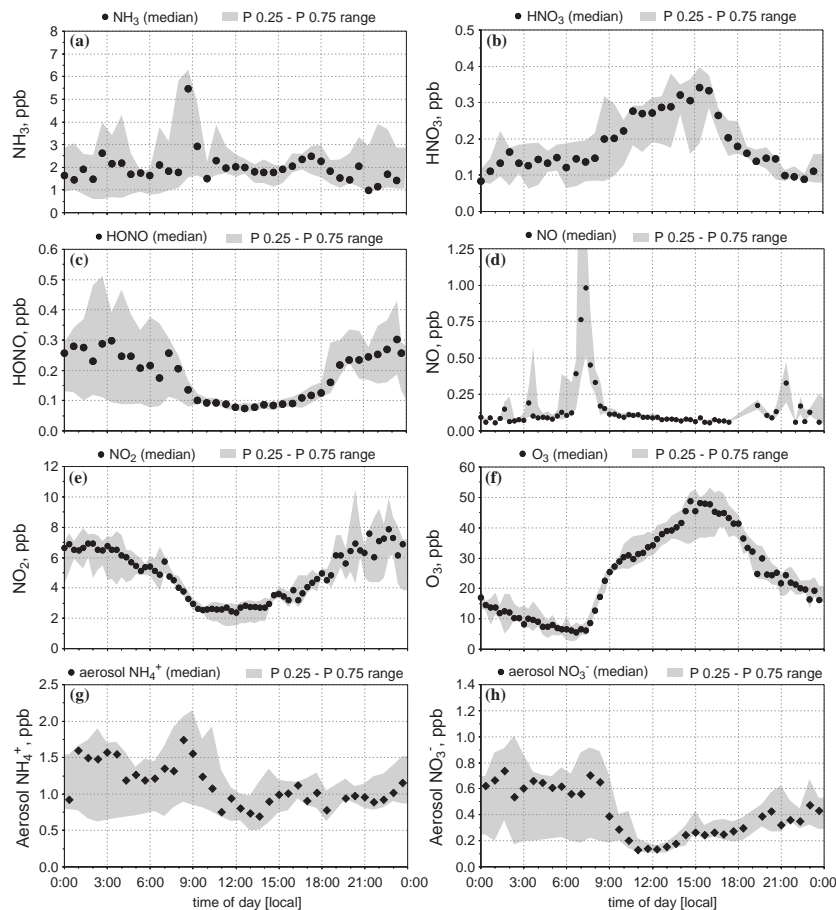
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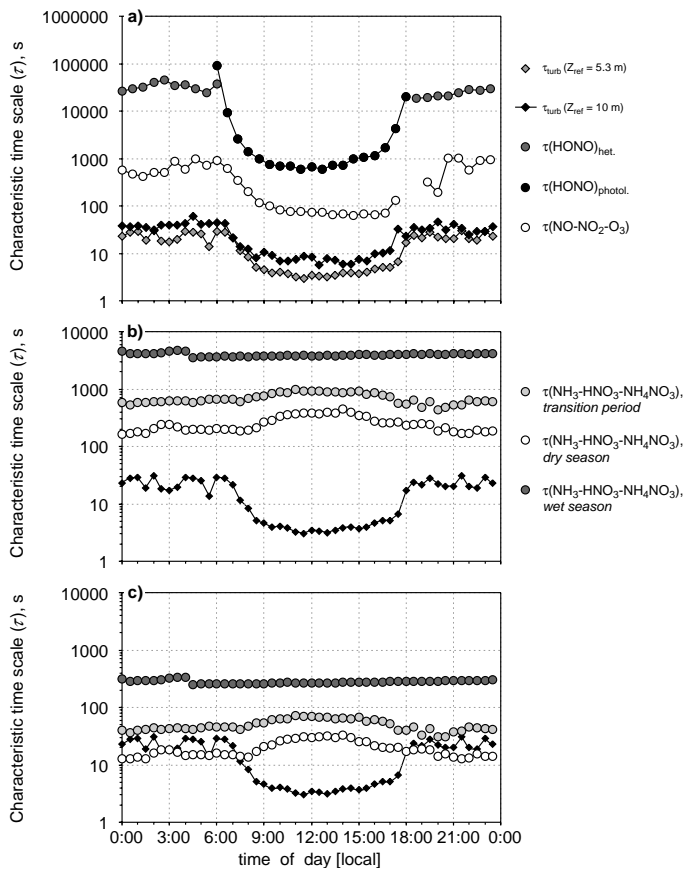


**Fig. 2.** Diel variations of (a)  $\text{NH}_3$ , (b)  $\text{HNO}_3$ , (c)  $\text{HONO}$ , (d)  $\text{NO}$ , (e)  $\text{NO}_2$ , (f)  $\text{O}_3$ , (g) aerosol  $\text{NH}_4^+$  (PM 2.5) and (h) aerosol  $\text{NO}_3^-$  (PM 2.5) measured during 12–23 September 2002 (dry season, biomass burning) at FNS during LBA-SMOCC 2002. Symbols and grey shading represent medians and interquartile ranges (0.25 to 0.75 percentiles), respectively.

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**Fig. 3.** Diel variation of characteristic turbulent time scale  $\tau_{turb}$  for the reference heights  $Z_{ref}=10$  m and  $Z_{ref}=5.3$  m in comparison to **(a)** chemical time scale of the NO-NO<sub>2</sub>-O<sub>3</sub> triad ( $\tau(\text{NO-NO}_2\text{-O}_3)$ ), daytime HONO photolysis ( $\tau(\text{HONO})_{photol.}$ ) and heterogeneous HONO formation at night ( $\tau(\text{HONO})_{het.}$ , dry season only), **(b)** upper estimate of equilibration time scales for the NH<sub>3</sub>/HNO<sub>3</sub>/NH<sub>4</sub>NO<sub>3</sub> system ( $\tau(\text{NH}_3\text{-NO}_3\text{-NH}_4\text{NO}_3)$ ) ( $\alpha=0.1$ ,  $\text{PM}_{inorg.} \leq 20\%$ ) and **(c)** lower estimate of  $\tau(\text{NH}_3\text{-NO}_3\text{-NH}_4\text{NO}_3)$  ( $\alpha=1$ ,  $\text{PM}_{soluble} \leq 60\%$ ) at FNS during LBA-SMOCC 2002. Except for  $\tau(\text{HONO})_{het.}$ , data from all seasons were used.

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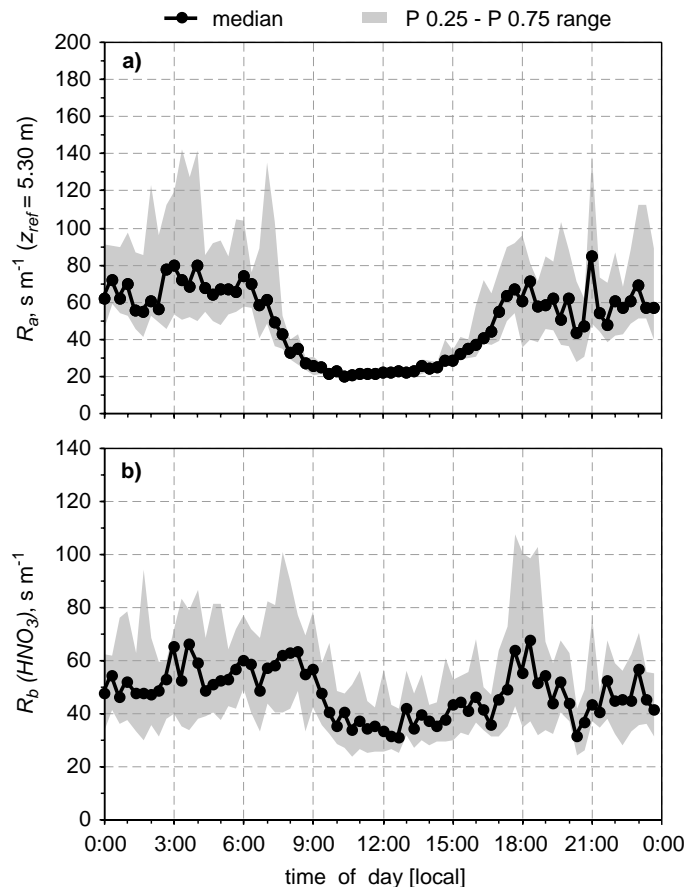
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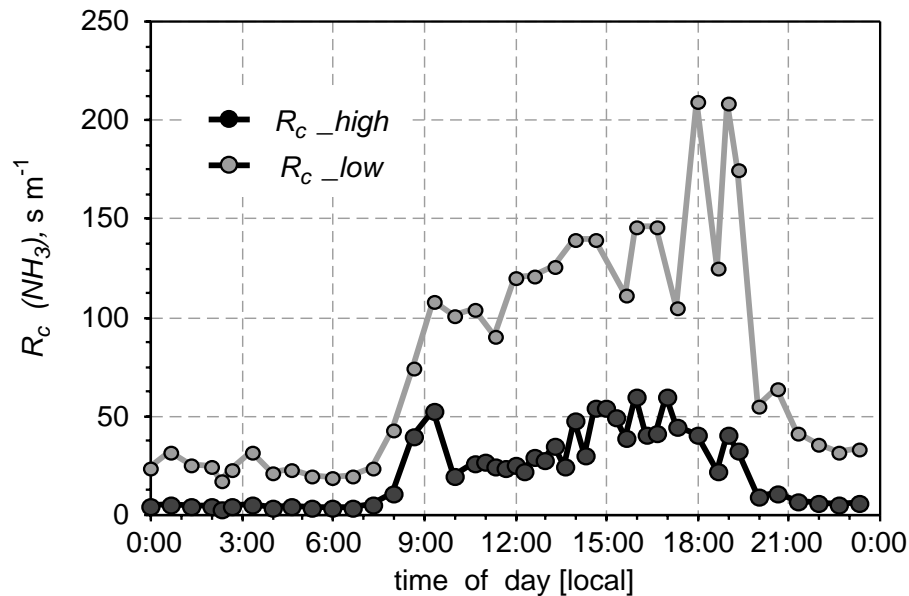


**Fig. 4.** Diel variations of (a) turbulent resistance ( $R_a$ ) and (b) quasi-laminar boundary layer resistance ( $R_b$ ) exemplary for  $\text{HNO}_3$  at FNS during LBA-SMOCC 2002. Symbols and grey shading represent medians and interquartile ranges (0.25 to 0.75 percentiles), respectively. Data from all seasons were used.

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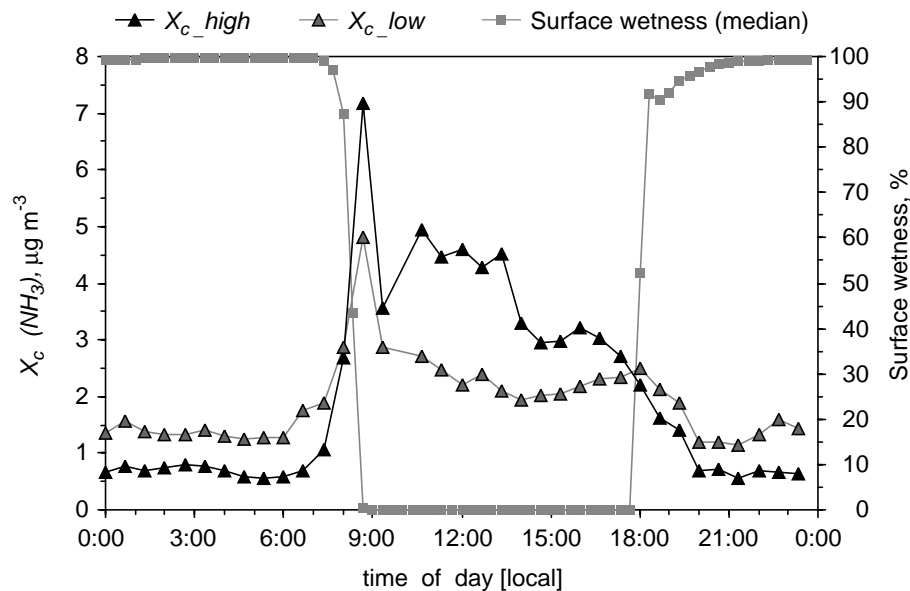
**Fig. 5.** Median diel variation of the estimated lower (low) and upper (high) bulk surface resistance  $R_c(\text{NH}_3)$  (sum of the parallel resistances  $R_s(\text{NH}_3)$  and  $R_d(\text{NH}_3)$ ) at FNS during LBA-SMOCC 2002. Data from all seasons were used.

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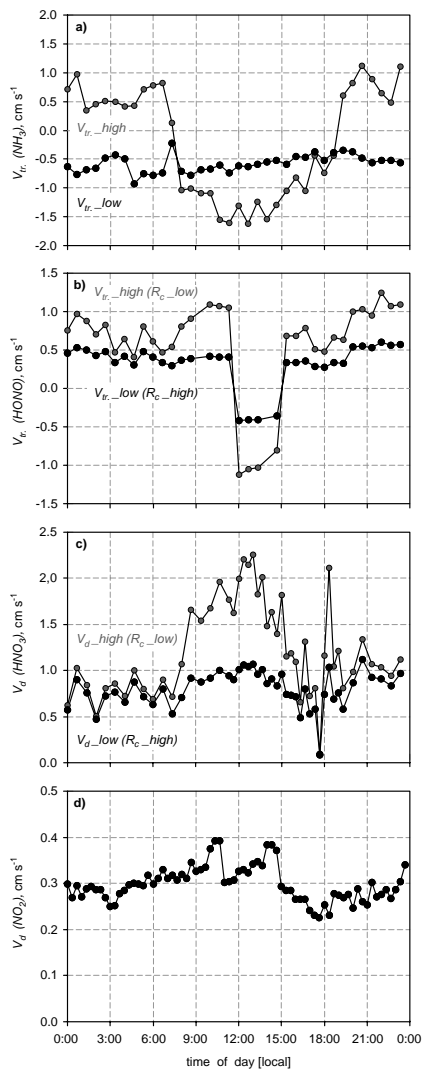
**Fig. 6.** Median diel variation of the simulated lower (low) and upper (high)  $\text{NH}_3$  canopy compensation point  $X_c(\text{NH}_3)$ , and the median diel variation of the measured surface wetness, shown exemplarily for a period during the dry season (12–23 September) at FNS during LBA-SMOCC 2002. For details about low and high estimates, see text.

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**Fig. 7.** Median diel variation of simulated lower (low) and upper (high) transfer velocity  $V_{tr}$  for bi-directional surface atmosphere exchange of **(a)**  $\text{NH}_3$ , **(b)**  $\text{HONO}$ , and deposition velocity  $V_d$  for **(c)**  $\text{HNO}_3$  and **(d)**  $\text{NO}_2$  at FNS during LBA-SMOCC 2002. Data from all seasons were used, except for  $V_{tr}(\text{HONO})$ , which only represents results from the dry season, since negligible small upward  $\text{HONO}$  fluxes were predicted during transition period and wet season.

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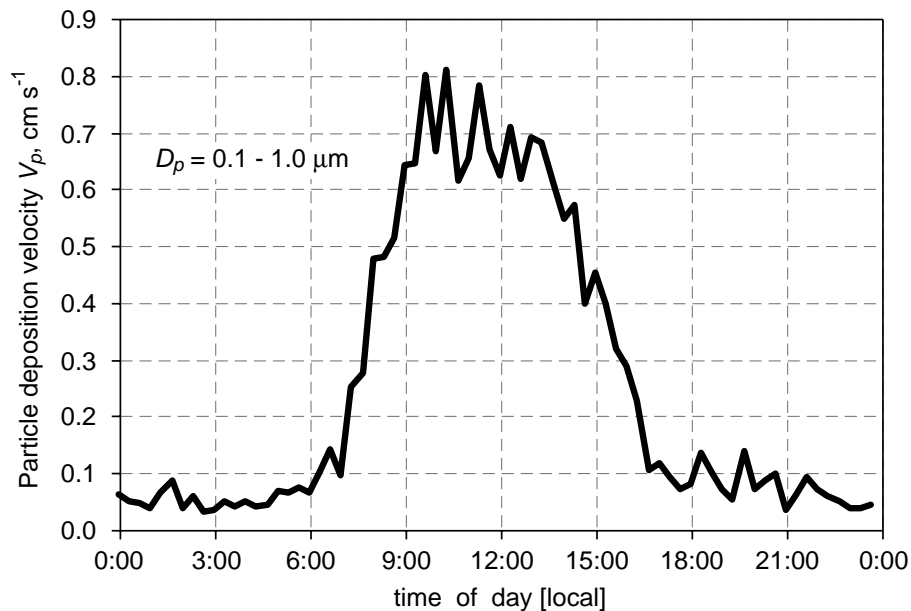
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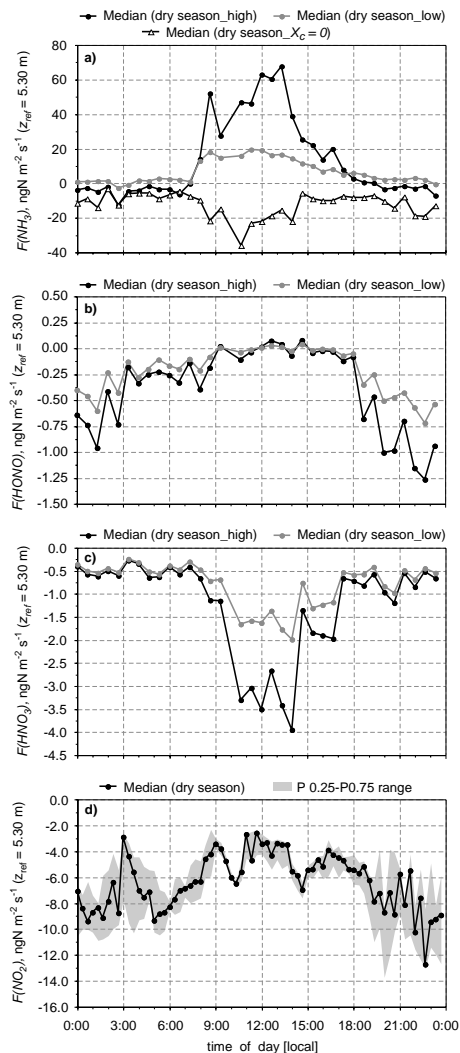
**Fig. 8.** Median diel course of the particle deposition velocity  $V_p$  using the empirical parameterization derived by Wesely et al. (1985) for aerosol particles with  $D_p=0.1-1 \mu\text{m}$  at FNS during LBA-SMOCC 2002.

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**Fig. 9.** Median diel courses of estimated lower (low) and upper (high) surface-atmosphere trace gas exchange fluxes for: **(a)**  $\text{NH}_3$ , **(b)**  $\text{HONO}$  and **(c)**  $\text{HNO}_3$ . Bi-directional  $\text{NH}_3$  flux scenarios were complemented by a net deposition scenario ( $X_c(\text{NH}_3)=0$ ). The median flux of **(d)**  $\text{NO}_2$  is estimated using  $R_c$  values from Kirkman et al. (2002) and is presented with interquartile ranges (0.25 to 0.75 percentiles). Medians have been calculated exemplarily for a period during the dry season (12–23 September) at FNS during LBA-SMOCC 2002.

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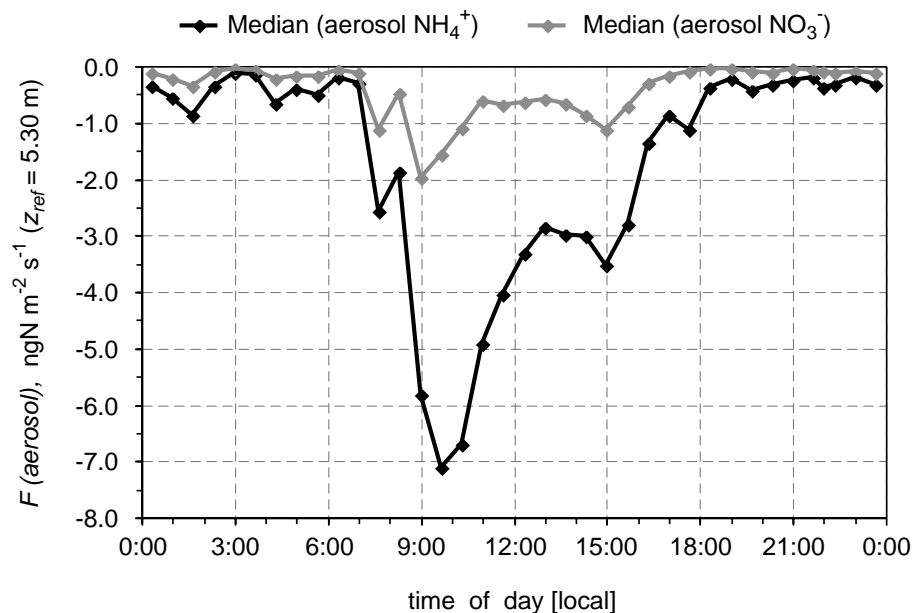
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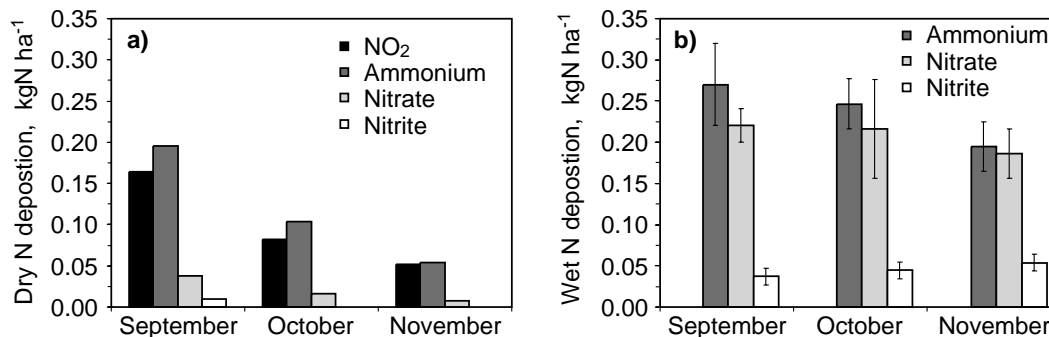
**Fig. 10.** Median diel courses of inferred deposition fluxes of aerosol  $\text{NH}_4^+$  and aerosol  $\text{NO}_3^-$  shown exemplarily for a period during the dry season (12–23 September) at FNS during LBA-SMOCC 2002.

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**Fig. 11.** Monthly estimates of **(a)** dry N deposition of NO<sub>2</sub>, total ammonium (aerosol NH<sub>4</sub><sup>+</sup> + NH<sub>3</sub>), total nitrate (aerosol NO<sub>3</sub><sup>-</sup> + HNO<sub>3</sub>) and nitrite (HONO) (averages of lower and upper estimates are shown, except for NH<sub>3</sub> which represents an average of all three estimates (cf. Fig. 9a) and **(b)** wet N deposition of ammonium, nitrate and nitrite (error bars represent measurement uncertainties) for September (dry season, biomass burning), October (transition period) and November (wet season, clean conditions) at FNS during LBA-SMOCC 2002.

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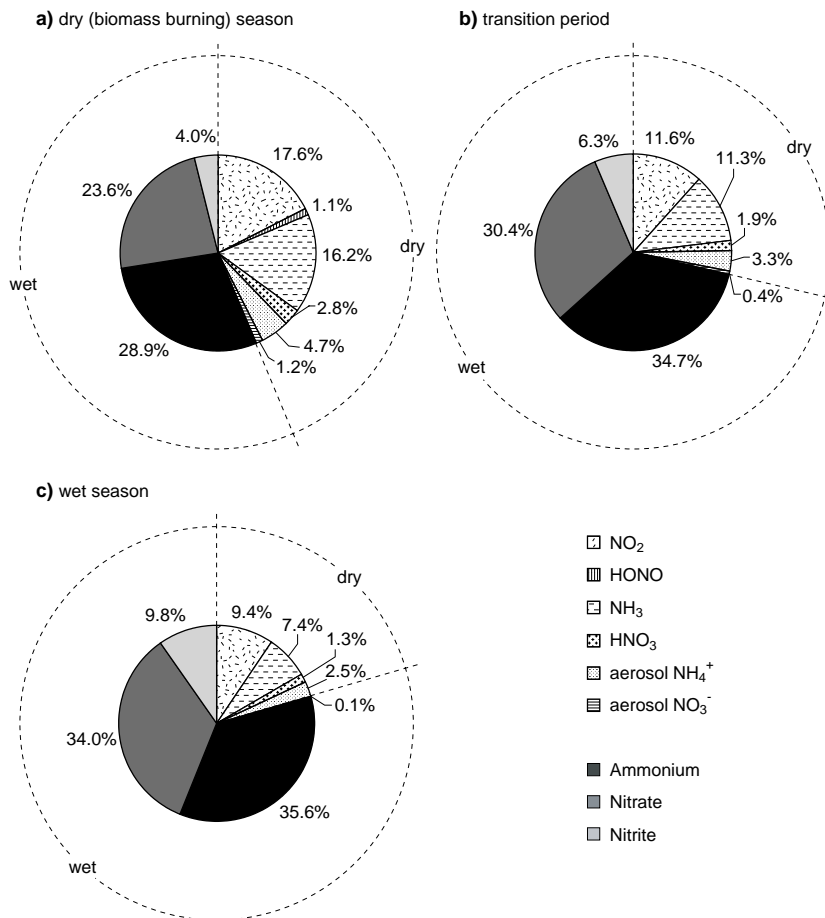
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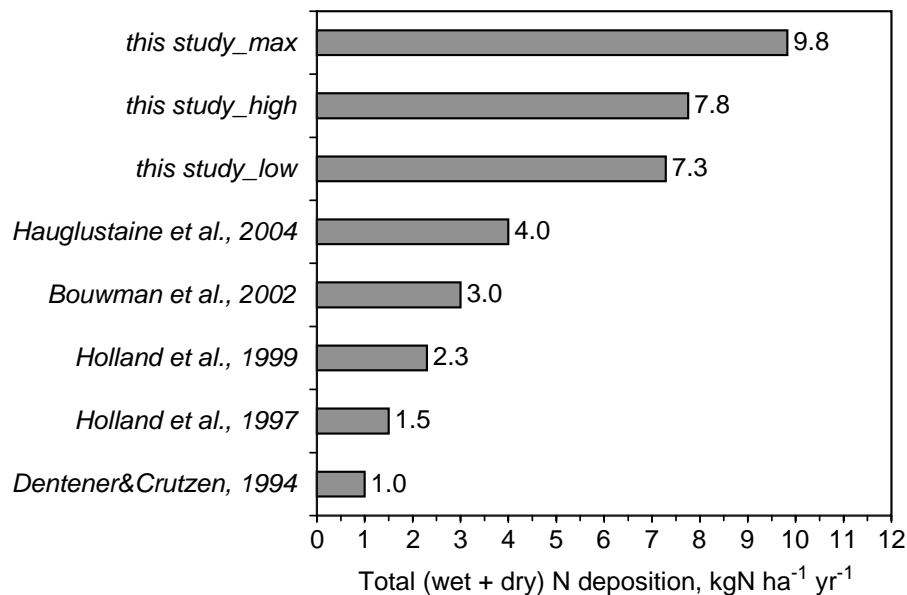


**Fig. 12.** Contribution of inorganic N compounds to the estimated total N deposition for **(a)** September (dry season, biomass burning), **(b)** October (transition period) and **(c)** November (wet season, clean conditions) at FNS during LBA-SMOCC 2002. Dry deposition of gaseous species is presented using averages of lower and upper estimates.

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**N deposition in the tropics**

I. Trebs et al.



**Fig. 13.** Comparison of the annual (dry + wet) N deposition predicted by global chemistry and transport models for the Amazon region with the annual (dry + wet) N deposition estimated in this study. “This study\_low” and “this study\_high” correspond to lower and upper flux estimates. “This study\_max” corresponds to the upper flux estimate, but considering  $\text{NH}_3$  to be net deposited ( $X_c(\text{NH}_3)=0$ , cf. Fig. 9a).

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