SURFACE BOUNDARY LAYER EXCHANGE OF NITRIC OXIDE, NITROGEN DIOXIDE, AND OZONE OVER A BRAZILIAN PASTURE

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1. INTRODUCTION

The measurement of the species of the NO_2–NO–O_3 triad is necessary for studying and making inferences on the air–surface exchanges at the landscape scale. The fast chemical reactions of nitric oxide (NO) with ozone (O_3) or peroxyl radicals, which form nitrogen dioxide (NO_2), and the reverse photodissociation of NO_2 during the day (<400 nm), occur on time scales of minutes. The same time scales apply for turbulence mixing at the surface. Secondly, 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. 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.

This work was conducted as part of the LBA-EUSTACH project (*European Studies on Trace Gases and Atmospheric Chemistry* within the *Large-Scale Biosphere-Atmosphere Experiment in Amazonia*) over a cattle pasture in Rondônia. Measurements were performed during both the LBA-EUSTACH-1 and LBA-EUSTACH-2 campaigns, 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.

2. EXPERIMENTAL

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. In

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order to determine ecosystem-representative NO_2 and O_3 deposition fluxes for both the LBA–EUSTACH-1 and -2 periods, an inferential method (multi-resistance model) was applied to measured ambient NO_2 and O_3 concentrations using observed quantities of turbulent transport. 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 during both campaigns.

2.1 Site Description

The measurement site was located on the commercial cattle ranch *Fazenda Nossa Senhora Aparecida* (FNS), which is situated in Rondônia, Brasil on the fringe of the Amazon basin. The land cover consists of a homogenous sward of *Brachiaria brizantha* (A. Rich.) Stapf cattle pasture grass. The original forest was cleared in 1977.

2.2 Monitoring of ambient trace gas concentrations

During the LBA-EUSTACH-1 and -2 campaigns, concentrations of NO, NO_2, and O_3 were measured at 3.5 m above ground using commercial gas-phase chemiluminescence and spectrometric analyzers (Thermo Environmental Instruments Inc.) [see *Kirkman et al.*, in press]
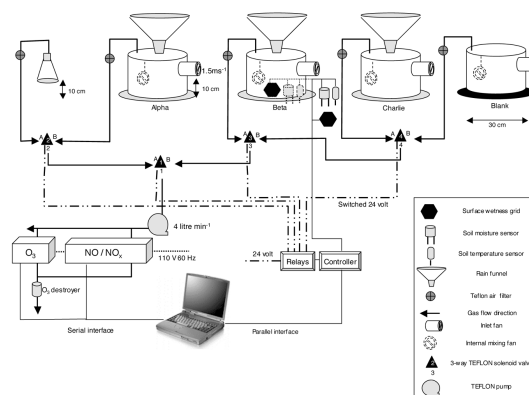

Figure 1: Dynamic chamber system.

2.3 Dynamic chamber system

A second set of identical NO, NO_x, and O_3 analyzers was applied to a dynamic chamber system. This system comprised three chambers sealed to the surface. Ambient air flow through the chambers was controlled and air inside the chamber was continuously mixed to prevent concentration gradients. A fourth "blank" chamber, closed at the bottom, was employed for *in situ* quantification of chemical reactions and chamber wall deposition effects. A sample inlet for measurement of ambient NO, NO_2, and O_3 concentrations was positioned close to the inlet of one of the chambers.

2.4 Inferential method for determining NO_2 and O_3 fluxes

Dry deposition fluxes of NO_2 and O_3 depend on surface uptake characteristics, surface concentrations, and turbulent transfer conditions close to the surface. Chamber NO_2 and O_3 fluxes are generally not representative for ambient field conditions. In order to correct for this, we applied an inferential method based on the "big leaf multiple resistance approach" [*Hicks et al.*, 1977], where surface resistances inside and outside the chambers were assumed to be similar.

$$F(j) = C(j) / R_{tot}(j) \qquad (1)$$

where $C(j)$ is the ambient mixing ratio of the trace gas compound j at the reference height and $R_{tot}(j)$ a gas transfer resistance. Correspondingly, $R_{tot}(j)$ is split into a series of partial resistances,

$$R_{tot}(j) = R_a + R_b + R_c(j) \qquad (2)$$

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 R_a and R_b inside the chamber was determined experimentally. 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

$$R_c(NO_2) = C(NO_2)_{chamber} / F(NO_2)_{chamber} - R_{aero,chamber} \qquad (3)$$

$$R_c(O_3) = C(O_3)_{chamber} / F(O_3)_{chamber} - R_{aero,chambe} \qquad (3)$$

According to eq. (2), 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 representative turbulent resistances (R_a) and molecular-turbulent boundary-layer resistances (R_b) were estimated according to *Hicks et al.* [1987].

As previously mentioned, the application of the inferential method is strictly valid for non-reactive 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. However, the "nonreactive" flux-resistance relationship can also be applied as a sufficient proxy in the case of reactive trace gases if "slow chemistry" is prevalent [*Villá-Guerrau de Arellano & Duynkerke,* 1992] (i.e., if characteristic chemical reactions times are much larger than corresponding turbulent transport times). Following *Villá-Guerrau de Arellano & Duynkerke* [1992], the characteristic time of turbulent transport (τ_{turb}) was calculated by

$$\tau_{turb} = k \, (z_{ref} + z_0) \, (\sigma_w^2/u^*)^{-1} \qquad (4)$$

The overall characteristic time scales for the NO–NO_2–O_3 triad (τ_{chem}) are given by the combination [*Lenschow*, 1982] of $\tau_{NO} = (k_{13} [O_3])^{-1}$, $\tau_{NO2} = k_{12}^{-1} = j(NO_2)^{-1}$, and $\tau_{O3} = (k_{13} [NO])^{-1}$, with the reaction constants $k_{12} = j(NO_2)$ (s^{-1}) and $k_{13} = 2 \times 10^{-12}$ exp(−1400/T) (cm^3 molecules^{-1} s^{-1}) for the reactions,

$$NO_2 + h\nu \rightarrow NO + O_3 \qquad (5)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (6)$$

The NO_2 photolysis rate $j(NO_2)$ was calculated from global radiation data using a relationship derived from simultaneous measurements of global radiation and the NO_2 photolysis rate at a nearby forest site during LBA-EUSTACH-1 and -2. Monitored NO, NO_2, and O_3 concentrations and micrometeorological data were used to calculate mean diel variations of τ_{turb} and τ_{chem} for the LBA-EUSTACH-1 and -2 periods. Turbulent transport times were generally found to be at least one order of magnitude faster than chemical reaction times (Fig. 2).
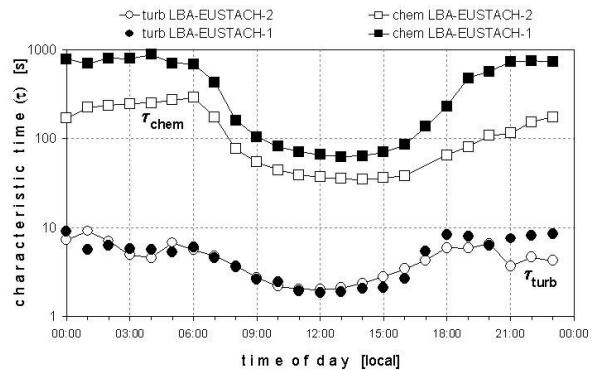

Figure 2. Chemical and turbulent characteristic times scales

3. RESULTS AND DISCUSSION

For all trace gas fluxes, the micrometeorological convention of negative downward fluxes and positive upward direction was adopted.

3.1 Surface resistances of NO_2 and O_3

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 (Fig. 3). 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. However, these data only reflect the nights with relatively high wind speeds that passed the rejection criteria. 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} (Fig. 3). Ozone canopy resistances were significantly higher during daytime (106 s m^{-1}) than night 65 s m^{-1}. The gradient and dynamic chamber derived $R_c(O_3)$ values during the dry–wet period showed reasonable agreement, with daytime medians of 141 s m^{-1} and 106 s m^{-1}, respectively. 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, because of higher wind speeds. Daytime total resistances, determined by the gradient method, ($R_a + R_b + R_c(O_3)$) for both the wet–dry and dry–wet periods also showed little seasonal difference, such that corresponding O_3 deposition velocities ($v_d(O_3) = R_{tot}(O_3)^{-1} = [R_a + R_b + R_c(O_3)]^{-1}$) were within 10% of each other during 1999.

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: (a) stomatal, cuticular and mesophyllic uptake, (b) soil uptake, and (c) uptake into solution of wet surfaces. The lower nighttime $R_c(O_3)$, when plant stomata are expected to be closed, is possibly due to a nighttime uptake of O_3 via stomata and/or foliar cuticle by the *B. brizantha* grass species. The similar day– and nighttime $R_c(NO_2)$ values indicates that the same holds true for $R_c(NO_2)$. Surface wetness might also significantly alter the surface resistances of less soluble trace gases like NO_2 and O_3, which was detectable by 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 these wet nights as opposed to nights when no condensation occurred. Therefore, nighttime $R_c(NO_2)$ and $R_c(O_3)$ 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.

3.2 NO, NO_2 and O_3 fluxes and NO_x budget

NO soil emission fluxes were extremely low during the dry–wet period (0.65 ng N m^{-2} s^{-1}). They were 9 times lower than old-growth rainforest 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.

During LBA-EUSTACH-2, NO_2 and O_3 concentrations were considerably elevated above those measured during LBA-EUSTACH-1 at FNS due to dry season biomass burning. NO_2 concentrations were a factor three higher during the dry–wet transition season resulting in deposition fluxes six times larger than those of the wet–dry period (–3.93 versus –0.7 ng N m^{-2} s^{-1}). Ozone concentrations were equally elevated during the dry–wet period with deposition $F(O_3)$ fluxes twice as large (–6.11 nmol m^{-2} s^{-1} or 0.13 µg m^{-2} s^{-1}) during the dry–wet in contrast to the fluxes (–2.75 nmol m^{-2} s^{-1} or 0.29 µg m^{-2} s^{-1}) during the wet–dry season.

Due to higher soil moisture in the wet season, which limits NO production and inhibits soil diffusion, it is assumed 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. However, during the dry–wet season, the surface of FNS removed up to 7 times more NO_2 from the atmosphere than was emitted as NO. This constitutes a net NO_2 sink of 0.73 kg N ha^{-1} yr^{-1}, which is a factor 4 larger than the NO emitted from the soil (0.17 kg N ha^{-1} yr^{-1}) at FNS.
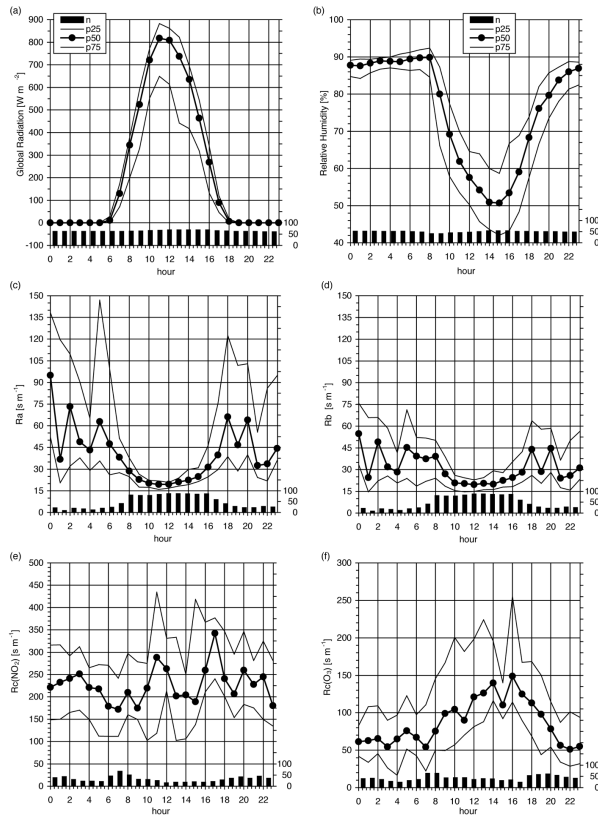
Figure 3: Diel (a) global radiation (W m^{-2}), (b) relative humidity (%), (c) R_a, (s m^{-1}) (d) R_b (s m^{-1}), (e) $R_c(NO_2)$ (s m^{-1}), and (f) $R_c(O_3)$ (s m^{-1}) first second and third quartiles for the dry-wet transition season during LBA-EUSTACH-2 (24 September to 27 October 1999). Bars indicate actual data counts used to derive the hour averages (solid points).

4.   CONCLUSION

The pasture FNS was a net NO_x (NO_x = NO + NO_2) sink during 1999. NO_2 and O_3 deposition velocities also varied little during the wet–dry and dry–wet seasons at FNS. However, deposition fluxes were a factor 6 larger during the dry–wet season due to the ambient concentrations.

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 this unusual diel pattern.

5.   REFERENCES

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