Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes
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Chapter 13

Cycling of NO_x in Tropical Forest Canopies

Daniel J. Jacob and Peter S. Bakwin

Nitrogen oxides (NO_x = NO + NO_2) play a central role in the chemistry of the troposphere. They regulate the photochemical production of ozone and the abundance of the hydroxyl radical (OH), which is the main oxidant for a number of trace gases including methane. Sources of NO_x to the troposphere include fossil fuel combustion, biomass burning, biogenic emissions from soils, and lightning (Logan, 1983; Table 1). Atmospheric oxidation of NO_x takes place on a time scale on the order of 1 day and produces nitric acid which is removed by deposition; this deposition is a major source of nitrogen and acidity to terrestrial ecosystems.

Simulation of NO_x is currently a top priority in the development of global models for atmospheric chemistry (Brost et al., 1988; Levy and Moxim, 1989). However, as shown in Table 1, the size of the biogenic source is a serious uncertainty. Biogenic emissions could dominate the budget of NO_x over the continental tropics, where soil NO_x fluxes are high and anthropogenic emissions are relatively low (Johansson et al., 1988; Johansson and Sanhueza, 1988; Jacob and Wofsy, 1988, 1990). Proper accounting of this source requires consideration not only of the magnitude of soil NO_x emissions (Davidson, this volume), but also of the fraction of those emissions that is lost by deposition to vegetation during transport from the soil to canopy top. The latter effect has been so far neglected in the construction of atmospheric source inventories, but we will argue here that it can reduce considerably the export of NO_x from forested canopies (by about a factor of 4). As a result, current global estimates of the biogenic source of NO_x to the atmosphere may be seriously exaggerated.

BIOSPHERE-ATMOSPHERE EXCHANGE OF NO_x

The biosphere is both a source and a sink for atmospheric NO_x. Microbes in soils emit NO_x (mainly as NO), while vegetation scavenges NO_x (mainly as NO_2). The mechanisms for NO_x deposition to vegetation have been reviewed recently by Johansson (1989). The principal route appears to be uptake of NO_2 by the plant stomata, followed by reduction to nitrite at the mesophyll and assimilation via

Daniel J. Jacob and Peter S. Bakwin • Department of Earth and Planetary Sciences and Division of Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts 02138.

Table 1. Global source inventory for NO_x in the troposphere[a]

Source	NO_x (Tg of N $year^{-1}$)
Fossil fuel combustion	21 (14–28)
Biomass burning	12 (4–24)
Soil emissions	8 (4–16)
Lightning	8 (2–20)
Atmospheric oxidation of NH_3	1–10
Oceans	< 1
Stratospheric input	< 1
Total	25–99

[a] Data from Logan (1983). Numbers are best estimates and possible ranges.

nitrite reductase (Rogers et al., 1979). Uptake of NO is negligibly slow compared to uptake of NO_2. Johansson (1989) stressed the need to consider the balance between soil emissions of NO on the one hand and NO_2 deposition to vegetation and to the ground on the other hand in assessing the flux of NO_x between the biosphere and the atmosphere. Indeed, measurements in polluted regions have documented net downward fluxes of NO_x to vegetation, due to the uptake of NO_x advected from anthropogenic sources upwind (Delany and Davies, 1983; Delany et al., 1986).

We wish to examine how the biosphere-atmosphere exchange of NO_x over tropical forests should be treated in regional and global models for atmospheric chemistry. These models generally use the top of the canopy as the lower boundary. The biogenic source of NO_x in the model is defined by the ventilation flux, F_v (molecules per square centimeter per second), of biogenic NO_x at canopy top, viz.:

$$F_v = \alpha E_{NO} \quad (1)$$

where E_{NO} is the soil emission flux of NO (molecules per square centimeter per second) and α is an "export efficiency" ($0 \leq \alpha \leq 1$) representing the fraction of NO_x emitted by soil that is ventilated to the atmosphere above the canopy. Estimates for α will be presented below. The ventilation flux, F_v, is balanced by a downward flux, F_d (molecules per square centimeter per second), of NO_x from the atmosphere to the canopy, which is usually expressed in terms of a deposition velocity, V_d (centimeters per second):

$$F_d = V_d(NO_x) \quad (2)$$

where (NO_x) is the concentration of NO_x (molecules per cubic centimeter) immediately above the canopy. Estimates for V_d will also be presented below. The net upward flux of NO_x at canopy top (i.e., at the lower boundary of the model) is the difference $F_v - F_d$.

Rapid chemical cycling between NO and NO_2 takes place inside a forest canopy (Fig. 1; Table 2). NO is oxidized to NO_2 by O_3 subsiding from aloft and by

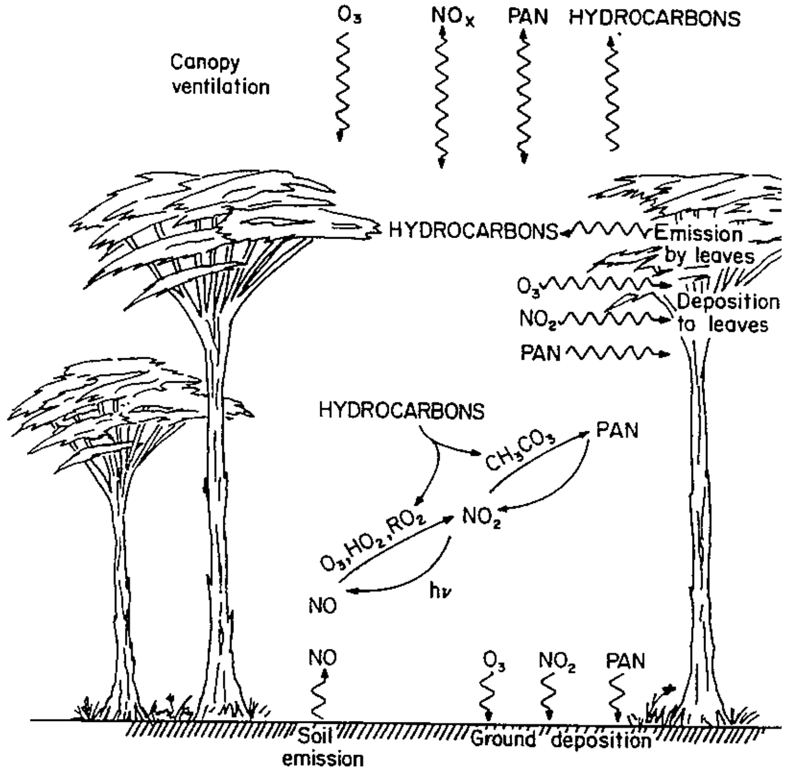

Figure 1. Chemical cycling of NO_x in a forest canopy.

peroxy radicals produced within the canopy from decomposition o hydrocarbons (e.g., isoprene and terpenes). The oxidation of NO takes time scale of minutes, less than typical time scales for canopy ventilation (et al., 1990). In the daytime NO_2 is photolyzed back to NO, and a equilibrium between NO and NO_2 is established where the NO_2/NO mo of order unity. At night there is no mechanism for reaction of NO_2 back that NO may be quantitatively converted to NO_2.

The NO_x budget inside the canopy is complicated by conversion $CH_3C(O)OONO_2$ (peroxyacetylnitrate, abbreviated as PAN). This con driven by CH_3CO_3 (peroxyacetyl) radicals generated locally from phot oxidation of biogenic hydrocarbons (Jacob and Wofsy, 1990). The lifetin against thermal decomposition back to NO_2 is relatively short at the ten found in tropical forest canopies (e.g., 35 min at 300 K), so that a equilibrium may be established between NO_2 and PAN. Dependin efficiency of PAN deposition to vegetation and to the ground, the equilibrium could affect the export of biogenic NO_x out of the canopy.

Table 2. Important reactions cycling NO_x inside a forest canopy

Reaction	Rate constant (cm^3 molecule^{-1} s^{-1} or s^{-1})
$NO + O_3 \longrightarrow NO_2$ or O_2	$2.2 \times 10^{-12} e^{-1,430/T}$ [a]
$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$	5.6×10^{-3} [b]
$O_3 + h\nu \xrightarrow{H_2O} 2\,OH + O_2$	4.3×10^{-6} [b,c]
Hydrocarbons + $OH \xrightarrow{O_2} RO_2$	$2.5 \times 10^{-11} e^{409/T}$ [d]
$NO + RO_2 \longrightarrow NO_2 + RO$	$4.2 \times 10^{-12} e^{180/T}$
$RO + O_2 \longrightarrow R'CHO, R'O_2, HO_2$	Fast[e]
$NO + HO_2 \longrightarrow NO_2 + OH$	$3.7 \times 10^{-12} e^{240/T}$
$CH_3COCHO + h\nu \xrightarrow{2O_2} CH_3CO_3 + HO_2 + CO_2$	8.4×10^{-4} [b,f]
$NO_2 + CH_3CO_3 \longrightarrow CH_3C(O)OONO_2$	4.7×10^{-12}
$CH_3C(O)OONO_2 \longrightarrow NO_2 + CH_3CO_3$	$1.95 \times 10^{16} e^{-13,543/T}$

[a] T is temperature in units of K.
[b] Photolysis rate constant at noon at canopy top, computed at the equator with a Rayleigh scattering code assuming 30% opaque cloud cover overhead, an O_3 column of 7.1×10^{18} molecules cm^{-2}, and a canopy albedo of 0.1. The photolysis rate constants inside the canopy are reduced because of extinction of light by leaves; correction factors are given in the text.
[c] For P_{H_2O} = 24.7 mb.
[d] Oxidation of hydrocarbons by OH produces organic peroxy radicals (RO_2). The rate constant is strongly dependent on hydrocarbon type; the value shown here is for oxidation of isoprene.
[e] Depending on the nature of the RO radical, products from this reaction may include HO_2, organic peroxy radicals, aldehydes, ketones, and dicarbonyls.
[f] Model calculations by Jacob and Wofsy (1990) indicate that this reaction (where methylglyoxal is produced from oxidation of isoprene) accounts for ≈ 90% of CH_3CO_3 production in the Amazon forest canopy.

The data base of NO_x flux measurements is limited, due in part to the difficulty of measuring NO_x concentrations accurately (Johansson, 1989). In particular there are at this time no reliable data for NO_x fluxes over forest canopies. Ideally, a field experiment designed to study the biosphere-atmosphere exchange of NO_x over a forest should include the following measurements: (i) soil emission fluxes of NO, (ii) turbulent fluxes of NO_x at canopy top, (iii) concentrations of trace gases inside and just above the canopy (NO, NO_2, O_3, PAN, and isoprene are key species), (iv) leaf and ground resistances to deposition, and (v) rates of vertical mass exchange within the canopy and at canopy top. The data set collected during the NASA/ABLE-2B expedition to the Amazon forest in the wet season of 1987 (Harriss et al., 1990) comes closest at this time to meeting the above requirements. As part of this expedition, extensive data were collected from a 40-m-high tower erected in a terra firme forest 20 km northeast of Manaus, Brazil. Trace gas concentrations at high altitudes were measured by aircraft. We will see below that these data afford important constraints on the export of biogenic NO_x out of the Amazon forest canopy.

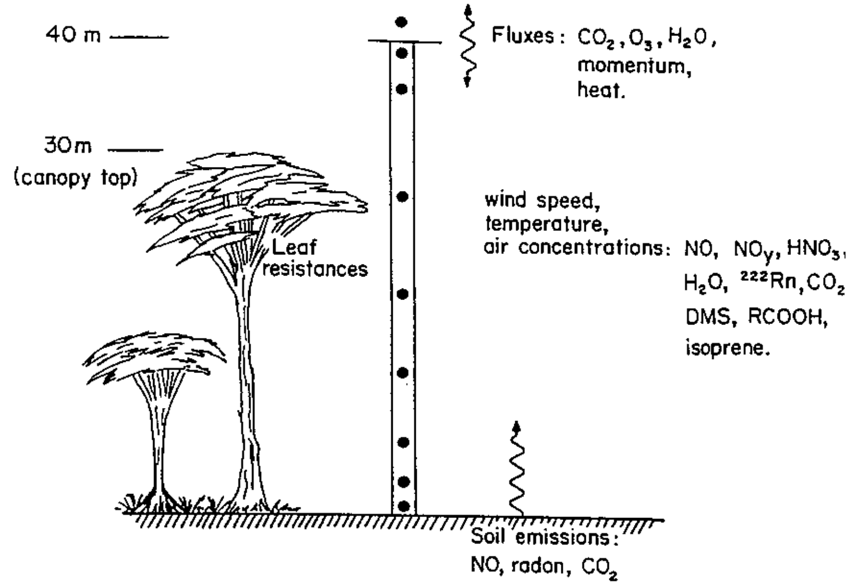

Figure 2. Ensemble of measurements made at the Ducke Forest Reserve, 20 km northe Manaus, Brazil, during the ABLE-2B expedition in April–May 1987. Fluxes and air cc trations were measured from a 40-m-high tower erected through the forest canopy.] were measured at the top of the tower by the eddy correlation method. Air concentr. were measured at several altitudes, indicated by the solid circles. Soil emissions measured using static (closed) chambers. Leaf resistances were measured by Roberts (1990) during earlier expeditions at the site. Further details on investigators and metho given by Harriss et al. (1990).

OBSERVATIONAL CONSTRAINTS ON THE NO_x BUDGET IN THE AMAZON FOREST CANOPY

Overview of the ABLE-2B Data

Figure 2 gives an overview of the measurements available from the ABI tower site. The forest canopy was 30 m high, with emergents up to 35 m and area index of 7 (the leaf area index is the total leaf area per unit area of air col counting only one side of leaf; it is a dimensionless measure of vegetation loac Soil fluxes of NO from the predominant clay soils averaged 8.9×10^9 mole cm^{-2} s^{-1} with no significant diurnal variation (Bakwin et al., 1990b). Conce tions of NO inside the canopy decreased sharply with altitude (Fig. 3), refle the emission from soil and the rapid oxidation to NO_2 (Bakwin et al., 19 Maximum concentrations of NO were observed at night when canopy ventil was restricted and O_3 concentrations were near zero. Aircraft measurements a to 300 m altitude indicated NO concentrations of 12 ± 7 parts per trillic volume (ppt), much lower than inside the canopy.

Concentrations of NO_y, representing the sum of all reactive nitrogen o

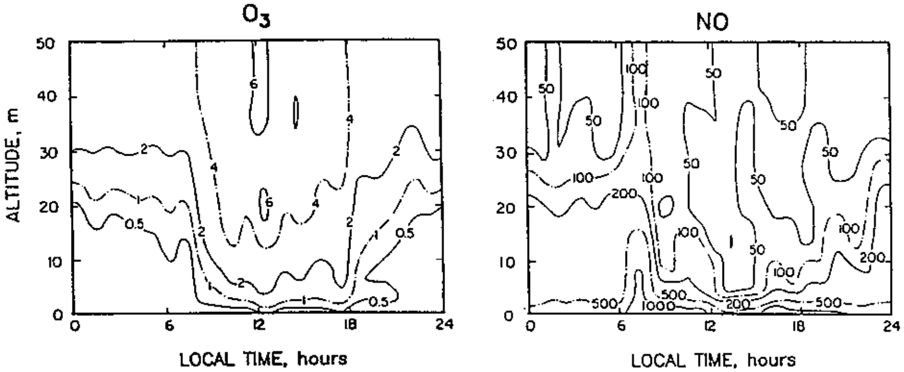

Figure 3. Average concentrations of O_3 and NO measured at the ABLE-2B tower site as a function of time of day. Units are parts per billion by volume (ppb) for O_3 and parts per trillion by volume (ppt) for NO.

(including NO_x, HNO_3, PAN, and other organic nitrates), were measured at 19 and 39 m altitude by Bakwin et al. (1990a) (Fig. 4). Values at 19 m averaged 400 ppt with little diurnal variation; values at 39 m were slightly higher, implying a net downward flux of NO_y to the canopy. The principal components of NO_y were not clearly identified. Concentrations of HNO_3 were only 20 to 50 ppt (Talbot et al., 1990), and concentrations of PAN measured from aircraft at 100 to 300 m altitude were less than 20 ppt (Singh et al., 1990). Concentrations of NO_2 were not measured. Model calculations (Jacob and Wofsy, 1990) suggest that NO_2 could have accounted for most of the NO_y in the canopy at night, but not in the daytime.

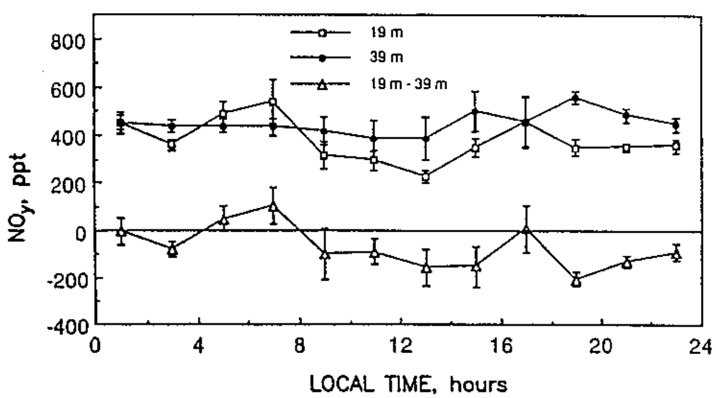

Figure 4. Average concentrations of NO_y measured at the ABLE-2B tower site as a function of time of day at 19 and 39 m altitude. Figure adapted from Bakwin et al. (1990a).

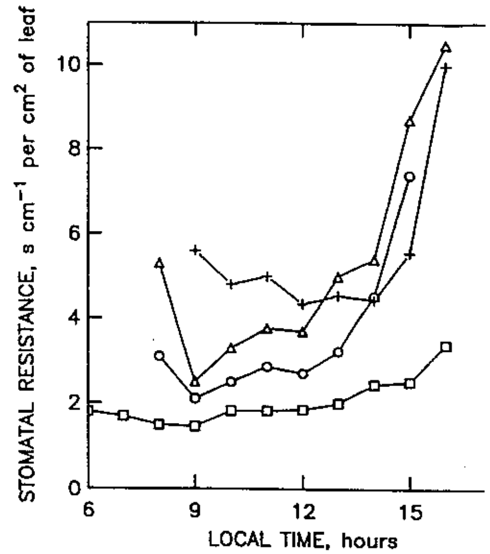

Figure 5. Average stomatal resistances measured at the ABLE-2B tower site as a function of time of day for four species present at different altitudes. Symbols: □, *Piptadenia suaveolens* at 33 m; ○, *Naucleopsis glabra* at 17 m; △, *Gustavia angusta* at 8 m; +, *Scheelea* sp. at 0 to 3 m. Figure adapted from Roberts et al. (1990).

Organic nitrates subsiding from aloft were probably the major contributor daytime NO_y.

Concentrations of O_3 within the canopy (Fig. 3) were very low compare values commonly observed in surface air (Logan, 1985), reflecting the r deposition of O_3 to the forest vegetation. Deposition velocities of O_3 measured m altitude averaged 1.8 cm s^{-1} in the daytime (Fan et al., 1990), a factor of 2 hi than typical values observed over mid-latitudes forests (Lenschow et al., 1982 night the deposition velocities for O_3 were lower but still substantial (averagin cm s^{-1}).

Deposition of O_3, NO_2, and other gases to vegetation is thought to take p primarily at the stomata of leaves (Hicks et al., 1987). Stomatal and boun (leaf-atmosphere) resistances to water vapor transfer were measured at the tc site by Roberts et al. (1990) during expeditions in 1983 to 1985 which prece ABLE-2B. The boundary resistances were always small compared to the ston resistances. The stomatal resistances were themselves quite low (Fig. 5), consis with observations in other tropical forests (J. Roberts, personal communicat 1989), and presumably reflecting the high insolation and the availability of w Lowest values for the stomatal resistances were observed for trees in the u canopy; these increased gradually from mid-morning to mid-afternoon, possibl a result of water stress.

The low stomatal resistances of the Amazon forest vegetation, together the high leaf area index, indicate the potential for rapid uptake of trace gases. can derive the stomatal resistances to uptake of a particular gas by using measured values for water vapor and scaling by the ratio of molecular diffusivi

Fan et al. (1990) explained their observed daytime deposition velocities for O_3 during ABLE-2B by using a standard leaf resistance model (Hicks et al., 1987) constrained with the stomatal resistance data of Roberts et al. (1990). The deposition of O_3 observed at night (when the stomata were closed) suggests that significant O_3 uptake took place also at the outer (cuticular) surfaces of leaves (Fan et al., 1990).

A key variable regulating the export of biogenic NO_x out of the canopy is the canopy ventilation rate. Much of the canopy ventilation at the ABLE-2B site occurred by episodic large-scale downdrafts flushing the entire canopy (Fitzjarrald and Moore, 1990; Fitzjarrald et al., 1990). This ventilation mechanism is typical of forest environments in general (Gao et al., 1989) and cannot be properly described with standard mixing-length models for atmospheric turbulence. Vertical mass exchange rates during ABLE-2B can nevertheless be constrained quite well by using the observed vertical distributions and fluxes of three chemical tracers: radon-222, CO_2, and O_3 (Trumbore et al., 1990; Fan et al., 1990). Radon-222 is a particularly useful tracer as it is released at a relatively constant and uniform rate by the soil, and it is removed from the atmosphere solely by radioactive decay (half-life, 3.8 days). Trumbore et al. (1990) used the radon-222 and CO_2 data from ABLE-2B to derive air residence times (τ) within the 0–40-m column of 5.5 h at night and ≤ 1 h in the daytime. Sharp vertical gradients of radon-222 concentration were observed in the lowest 2 m above ground, but above that altitude the concentrations were relatively uniform.

A Box Model for the Amazon Forest Canopy

The ABLE-2B data place some important constraints on the export of biogenic NO_x from the forest to the atmosphere. These constraints can be expressed in a simple way with a steady-state box model for the 0–40-m air column, including no explicit chemistry. In the next section we will present a more detailed process-based model which includes temporal and vertical resolution, as well as a full description of photochemistry; we will see that results from the box model capture to a good approximation the main features of the complicated model. The upper boundary of the box model is chosen at 40 m because the canopy ventilation times (τ) given by Trumbore et al. (1990) are defined with respect to that altitude. We define "biogenic NO_x" as the NO_x supplied to the 0–40-m column by soil emission, in contrast to "atmospheric NO_x" supplied to the column from aloft.

The ventilation flux (F_v) of biogenic NO_x through the top of the 0–40-m air column is given by:

$$F_v = \frac{\Delta Z}{\tau}(NO_x) \quad (3)$$

where (NO_x) is the concentration in the column and $\Delta Z = 40$ m. Replacing in equation 1, we obtain an expression for the export efficiency α of biogenic NO_x out of the canopy:

$$\alpha = \frac{(NO_x)}{E_{NO}}\frac{\Delta Z}{\tau}$$

where E_{NO} is the soil emission flux. Although (NO_x) was not measure ABLE-2B, an upper limit is imposed by the NO_y concentrations shown in Fi $(NO_y) \approx 400$ ppt implies that biogenic $(NO_x) < 400$ ppt. At night when $\tau \approx$ h, this upper limit on biogenic (NO_x) places a severe constraint on α. Insertin average observed value $E_{NO} = 8.9 \times 10^9$ molecules cm^{-2} s^{-1} into equatio and converting (NO_x) to units of molecules per cubic centimeter (1 ppt $= 2.4$ 10^7 molecules cm^{-3}), we find $\alpha < 0.22$. In the daytime, by contrast, the NO_y afford no constraint on α; replacing $\tau = 1$ h into equation 4 yields the useless r $\alpha < 1.2$. Most of the NO_y in daytime was contributed by non-NO_x specie opposed to nighttime (see Overview of the ABLE-2B Data, above). The upper l $(NO_x) < 400$ ppt, is evidently not sufficiently stringent to constrain α ir daytime.

An estimate for α in the daytime can, however, be derived from the depos flux of biogenic NO_x to vegetation. Let R (seconds per centimeter) be the tota resistance to NO_2 deposition per square centimeter of air column, and let (NO the concentration of biogenic NO_2 in the 0–40-m column. The deposition flu biogenic NO_x is given by $(NO_2)/R$ and represents the balance between the emission flux, E_{NO}, and the ventilation flux, F_v:

$$\frac{(NO_2)}{R} = E_{NO} - F_v$$

By combining equations 3 through 5 we obtain:

$$\alpha = \frac{1}{1 + \dfrac{\tau\,(NO_2)}{R\Delta Z(NO_x)}}$$

The ratio $(NO_2)/(NO_x)$ in daytime is of order 0.7 (see below). An upper limit can be estimated by assuming that deposition of NO_2 is restricted to the stomata. We then decompose R as the sum of a boundary resistance (R_b), a stor resistance (R_s), and a mesophyllic resistance (R_m) placed in series (Hicks e 1987):

$$R = \frac{R_b + \beta R_s + R_m}{L}$$

Here $L = 7$ is the leaf area index, $\beta \approx 1.6$ is the ratio of the molecular diffusi of water vapor and NO_2, and R_b, R_s, and R_m are in units of seconds per centin per square centimeter of leaf. Assuming $R_m = 0$ (Wesely, 1989), mean value

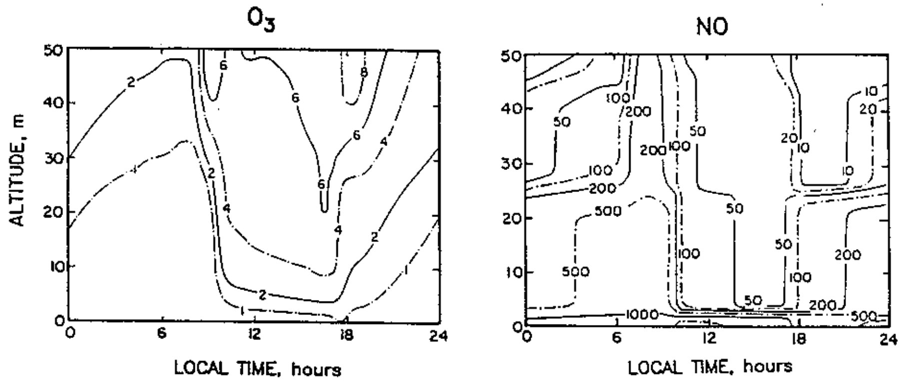

Figure 6. Concentrations of O_3 (ppb) and NO (ppt) simulated by the model of Jacob and Wofsy (1990), as a function of altitude and time of day. Results are in good agreement with observations (compare with Fig. 3). Figure adapted from Jacob and Wofsy (1990).

R_b and R_s of 0.5 and 3 s cm^{-1} per cm^2 of leaf, respectively (Roberts et al., 1990), and τ = 1 h, we obtain α = 0.56. Averaging the daytime and nighttime results yields a 24-h mean value of $\alpha \leq 0.39$. It appears therefore that only a small fraction of NO emitted by soil is exported to the atmosphere above the canopy.

ONE-DIMENSIONAL MODEL OF NO_x CYCLING IN THE AMAZON FOREST CANOPY

The box model presented above suffers from obvious flaws, in particular the assumption of uniform NO_x concentrations and the neglect of deposition to the ground and to the cuticles of leaves. An improved estimate of the NO_x budget in the Amazon forest canopy can be obtained by using the one-dimensional process-based model of Jacob and Wofsy (1990). This model was developed to simulate the atmospheric chemistry observed during the ABLE-2B expedition; it has proven successful at reproducing various observations from tower and aircraft, in particular the NO and O_3 concentrations inside the canopy (Fig. 6). The full model extends from the ground to 2,000 m altitude and includes (i) vertical transport rates constrained by observations for radon-222, O_3, and CO_2; (ii) detailed photochemistry describing the oxidation of biogenic hydrocarbons and the cycle of reactive nitrogen oxides; and (iii) biosphere-atmosphere exchange regulated by local vegetation density, leaf resistances, insolation, and temperature.

We consider here a truncated model domain, extending from 0 to 40 m altitude only, with fixed concentrations at 40 m as upper boundary conditions. The domain is subdivided into four grid cells (Table 3); cells 1 to 3 are in the canopy (0 to 30 m), and cell 4 is above the canopy (30 to 40 m). Each cell is assumed to be individually well mixed and exchanges air with adjacent cells by turbulent diffusion. The

Table 3. Structure of the Jacob and Wofsy (1990) model for the Amazon forest canopy[a]

Grid cell no.[b]	Atmospheric column[b] (m)	Leaf area index[c]	Exchange velocity at grid cell top[d] ($cm\ s^{-1}$)	
			0900–1600	1600–0900
1	0–2	1	0.13	0.4
2	2–20	2	2	0.5
3	20–30	4	15	1
4	30–40	0	2	0.2

[a] The model is one-dimensional in the vertical and simulates concentrations and fluxes of chemically reactive trace gases in the air column between 0 and 40 m altitude. The top of the forest canopy is at 30 m altitude.

[b] The atmosphere extending from 0 m (ground level) to 40 m altitude is subdivided into four grid cells (1 through 4), which are assumed to be individually well mixed and to exchange mass with adjacent grid cells.

[c] The leaf area index in each grid cell measures the local density of vegetation (square centimeters of leaf area per square centimeter of air column, counting only one side of the leaf). The sum of leaf area indices for all grid cells is 7 and represents the total leaf area index of the canopy.

[d] The exchange velocities define the rates of turbulent mass transfer between grid cells, as given by equation 8 in the text. We distinguish between a daytime regime (0900 to 1600 local time) when turbulence is vigorous and a nighttime regime (1600 to 0900 local time) when vertical motions are suppressed.

upward vertical flux, $F_{i,j}$ (molecules per square centimeter per second), of spe
i through the top of grid cell j is given by:

$$F_{i,j} = V_j \left[\frac{n_{i,j}}{N_j} - \frac{n_{i,j+1}}{N_{j+1}} \right] \frac{N_j + N_{j+1}}{2}$$

where V_j (centimeters per second) is an exchange velocity, $n_{i,j}$ (molecules per cu centimeter) is the concentration of species i in cell j, and N_j (molecules per cu centimeter) is the air density in cell j. The exchange velocities measure the inten of turbulence and are specified to fit the observed concentrations and vertical flu of radon-222, O_3, and CO_2 (Table 3). The residence time in the 0–40-m model column for an inert tracer emitted at the ground is 0.6 h at noon and 5.0 h midnight, consistent with the radon-222 data of Trumbore et al. (1990).

Upper boundary concentrations for the model at 40 m are specified fr ABLE-2B observations. Very low concentrations of NO_x and PAN are imposed a m in order to suppress the downward flux of atmospheric NO_x and thus isolate from F_d. The simulations are iterated to a diurnal steady state, i.e., to a solut where concentrations show no net change over a 24-h cycle. The time scale to re this steady state is less than 1 day, and hence we believe it to be a g approximation of atmospheric conditions.

The total leaf area index of the canopy (L = 7) is apportioned among the th canopy grid cells (0 to 30 m) as shown in Table 3. Half of the total leaf area is in upper canopy. Extinction of light by vegetation is computed by treating the can as a grey absorber and assuming a uniform angular distribution of leaves. The canopy optical depth at any altitude is then equal to half the leaf area index of the vegetation overhead (Verstraete, 1987). The resulting insolation near the ground at noon (θ = 13°C) is only 2.8% of the value at canopy top; the optical depth of the vegetation has thus a major effect on photochemical rates (in particular NO_2 photolysis).

Natural hydrocarbons (mainly isoprene and acetaldehyde) are emitted by vegetation in each grid cell at a rate dependent on vegetation density, temperature, and insolation, as described by Jacob and Wofsy (1990). The hydrocarbon emission fluxes peak in the upper canopy at noon; 24-h average emission fluxes at canopy top are 9.1×10^{10} molecules cm^{-2} s^{-1} for isoprene and 4.0×10^9 molecules cm^{-2} s^{-1} for acetaldehyde. Deposition of O_3, NO_2, and other reactive species is simulated in each grid cell using equation 7, with additional terms to describe deposition to the ground and to the leaf cuticles. For O_3 and NO_2 we assume R_m = 0, cuticular resistances of 10 s cm^{-1} per cm^2 of leaf (Fan et al., 1990), and resistances to deposition at the ground of 2 s cm^{-1} in the lowest grid cell (Johansson et al., 1988; Wesely, 1989). Values of R_b and R_s are taken from Roberts et al. (1990) and vary with altitude and time of day (see Fig. 5).

Figure 7 shows the main pathways for NO_x cycling within the 0–40-m air column at noon and at midnight. The NO_x budget reflects largely a balance between soil emissions of NO, deposition of NO_2, and ventilation. Conversion of NO_2 to PAN turns out to be a minor process; the concentrations of PAN inside the canopy at noon are only ≈ 10% those of NO_2, and the upward flux of PAN at 40 m is only 4% that of NO_x. Production of PAN is inhibited by the optical thickness of the canopy, which suppresses the photochemical decomposition of biogenic hydrocarbons and hence the source of CH_3CO_3 radicals.

The NO_x concentrations in the canopy are higher at night than in the daytime, partly because of the higher resistance to NO_2 deposition and partly because of the lower canopy ventilation rate. At night NO is oxidized to NO_2 by O_3 and there is no conversion of NO_2 back to NO, so that NO_x reaching the top of the canopy is ≈ 90% NO_2. In the daytime, oxidation of NO is facilitated by the higher concentrations of O_3 (Fig. 6) and by the presence of peroxy radicals produced from the decomposition of isoprene (which account for about half of total NO oxidation). Photolysis of NO_2 maintains a daytime NO_2/NO_x ratio in the range 0.5 to 0.9 inside the canopy.

Inspection of Fig. 7 indicates that the uptake of NO_2 by vegetation is roughly evenly distributed with altitude and that the ground accounts for 30% of total deposition. The export efficiency (α) of NO_x out of the canopy is 0.39 at noon and 0.17 at midnight; the 24-h average value is 0.25. The lower value of α at night follows mainly from the restricted ventilation, which is only partially compensated by the higher resistance to deposition. The values of α obtained here are somewhat lower than in the box model described above, principally due to the inclusion of ground deposition.

Deposition to the Amazon forest of atmospheric NO_x supplied from aloft (equation 2) was investigated in a separate simulation in which we assumed zero

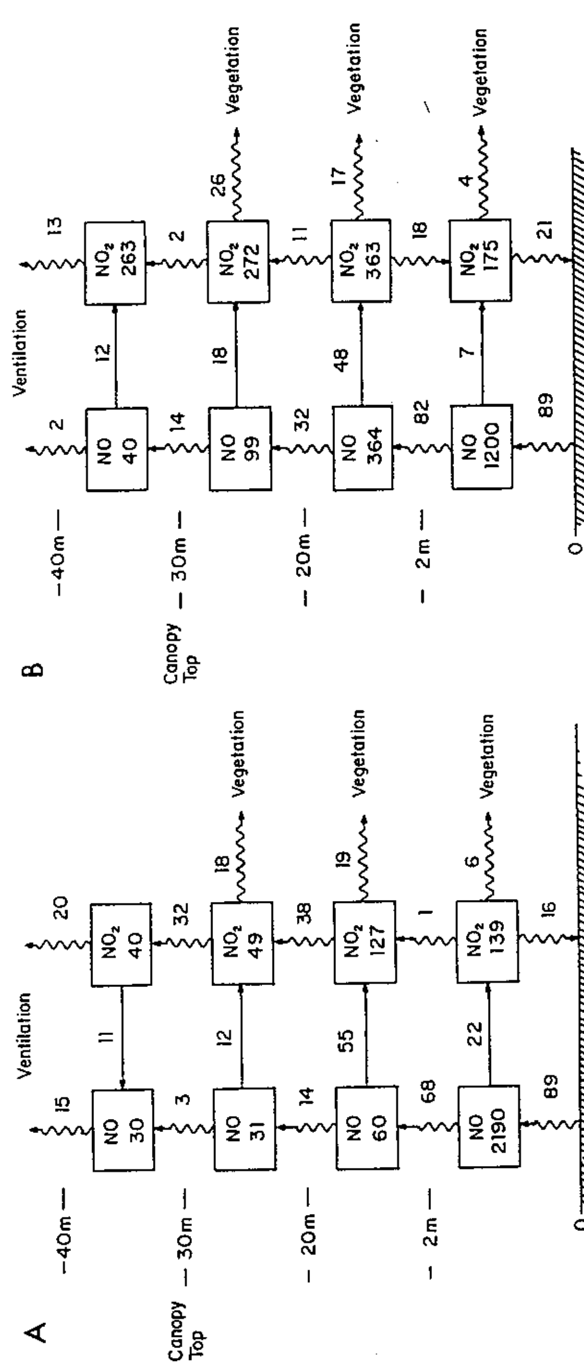

Figure 7. Cycling of biogenic NO_x in the Amazon forest canopy, as simulated by the model at noon (A) and at midnight (B). Concentrations in each grid cell (boxes) are in units of ppt. Fluxes and transformation rates per unit area of air column (arrows) are in units of 10^8 molecules cm^{-2} s^{-1}. Conversion factor: 10^8 molecules cm^{-2} s^{-1} ≈ 150 ppt m h^{-1}.

soil emissions of NO and a fixed NO_x concentration at 40 m of 26 ppt (taken from Jacob and Wofsy [1990]). We found deposition velocities (V_d) for NO_x at 40 m of 0.78 cm s^{-1} at noon and 0.13 cm s^{-1} at midnight; these values were insensitive to the speciation of NO_x assumed at 40 m because of the rapid chemical cycling between NO and NO_2. Over 70% of total deposition of atmospheric NO_x took place in the upper canopy (20 to 30 m).

EXTENSION TO OTHER TROPICAL FOREST ENVIRONMENTS

The fraction α of biogenic NO_x emitted by soil that is ventilated to the atmosphere above the forest (export efficiency) depends on a number of environmental variables including (i) the magnitude of soil emission, (ii) the O_3 concentration above the canopy, (iii) the leaf resistances to NO_2 and O_3 deposition, (iv) the canopy ventilation rate, and (v) the leaf area index. Figure 8 shows results from sensitivity simulations in which values for each of these variables were individually modified from the values used in the standard simulation described in the previous section. The range of perturbations was chosen to span the conditions likely to be encountered in tropical forests. The perturbations to R and τ were applied by multiplying all leaf and ground resistances, or all exchange velocities, by a given factor relative to the values in the standard simulation.

An increase in the O_3 concentration above the canopy increases the NO_2/NO_x ratio and hence the scavenging of NO_x by vegetation. At O_3 concentrations of >30 parts per billion by volume (ppb), the NO_2/NO_x ratio approaches unity through most of the canopy and a lower limit for α is reached which is dependent solely on the relative rates of NO_2 deposition and ventilation. An increase in NO emission, by contrast, decreases the NO_2/NO_x ratio and hence increases α. High soil fluxes of NO could result theoretically in complete titration of O_3 inside the canopy and consequently in very high values of α. However, it seems unlikely that titration of O_3 could ever occur since high soil fluxes of NO would foster photochemical production of O_3 in the atmosphere above the forest, thus increasing the supply of O_3 to the canopy from aloft. Such a situation was indeed encountered during the dry season ABLE-2A expedition, which operated from the same site as ABLE-2B (Harriss et al., 1988). Soil emission fluxes of NO in the dry season averaged 5.2×10^{10} molecules cm^{-2} s^{-1}, six times higher than in the wet season, but O_3 concentrations averaged $\approx$20 ppb at 40 m and 10 to 20 ppb inside the canopy (Kaplan et al., 1988). Model calculations for the dry season (Jacob and Wofsy, 1988) indicate that the concentrations of biogenic NO_x above the canopy were sufficiently high to promote photochemical production of O_3, explaining in part the relatively high O_3 levels (NO_x from biomass burning was an additional explanation). From the average dry season values for E_{NO} and O_3 concentrations we derive a 24-h mean α of 0.22, slightly lower than in the wet season (0.25).

Changes in the resistance to deposition, the canopy ventilation rate, or the leaf area index have remarkably little effect on α because of negative feedbacks. For example, an increase in the resistance to deposition hinders the uptake of NO_2 but also of O_3; it facilitates penetration of O_3 inside the canopy and hence increases the

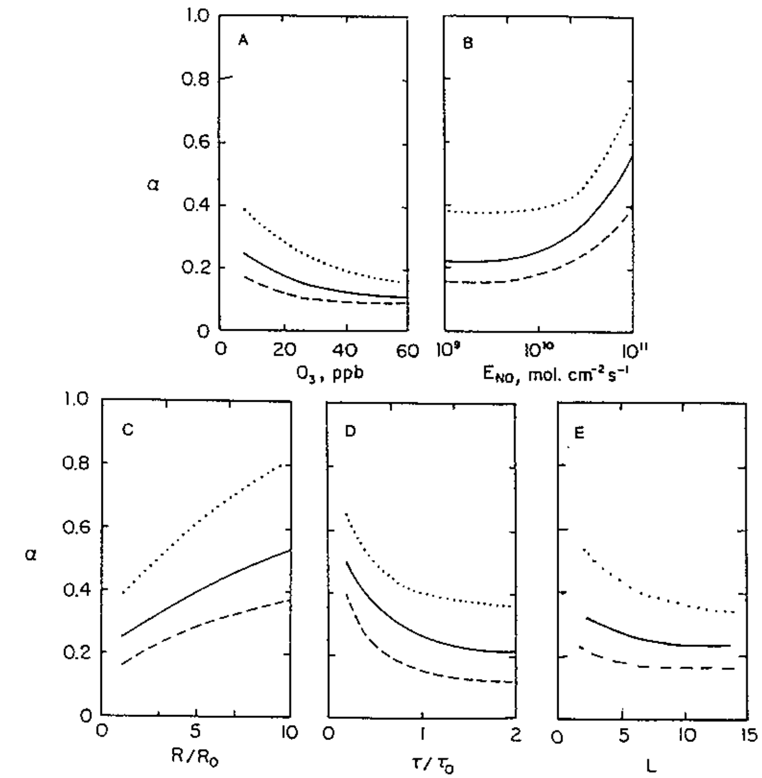

Figure 8. Export efficiency α of biogenic NO_x out of the forest canopy as a function of environmental variables. The export efficiency represents the fraction of NO_x emitted by soil that is exported to the atmosphere above the canopy. The environmental variables include (A) O_3 concentration at 40 m altitude, (B) soil emission flux of NO (E_{NO}), (C) total resistance to deposition (R), (D) residence time of air inside the 0–40-m column (τ), and (E) canopy leaf area index (L). The perturbations to R and τ are applied by multiplying the individual resistances and exchange velocities used in the standard simulation (corresponding to standard values R_0 and τ_0) by a given factor. The figure shows 24-h average values for α (solid line) and values at noon and midnight (dashed and dotted lines, respectively).

NO_2/NO_x ratio. Similar arguments can be made to explain the weak dependen of α on canopy ventilation rate and on leaf area index.

CONCLUSIONS

Results from a process-based model for the Amazon forest atmosphere indic that only 25% of biogenic NO_x emitted by soil is exported to the atmosphere ab the canopy (35% in the daytime, 17% at night). The balance is deposited vegetation during transport from the ground to canopy top. The deposited NO_x may be assimilated into the plant material, thus recycling nitrogen within the ecosystem. The role of the canopy filter in limiting the export of biogenic NO_x to the atmosphere appears to be important over a broad range of conditions encountered in tropical forest environments. Neglect of this effect in atmospheric chemistry models may lead to serious overpredictions of NO_x concentrations above tropical continents.

Extension of our results to non-forest canopies is difficult because canopy ventilation rates and leaf surface resistances may be vastly different. High soil emissions of NO have been observed from wet savannas (Johansson and Sanhueza, 1988) and from fertilized cropland (Williams et al., 1988), but the ventilation of such open canopies could be much faster than for tropical forests, and the seasonality of leaf activity would need to be considered. Open chamber flux measurements by Slemr and Seiler (1984) indicate lower NO emissions from grassland than from adjacent bare soil, suggesting uptake of NO_2 by grass. However, Johansson and Granat (1984) observed the same effect when using a static chamber where O_3 (and hence NO_2) should be depleted due to excess NO. More research is needed to explain these observations.

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