Emission of Nitric Oxide (NO) From Tropical Forest Soils and Exchange of NO Between the Forest Canopy and Atmospheric Boundary Layers

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Emissions of NO from soils in the Amazon rain forest were measured at 66 locations (224 measurements) using an enclosure technique, and continuous vertical profiles of NO and O_3 were measured between the ground and 41-m altitude. Fluxes of NO averaged 8.9 (±1.5) x 10^9 molecules cm^{-2} s^{-1} from the dominant (yellow clay) soils of the region, with larger fluxes (33.7 (±6.5) x 10^9 molecules cm^{-2} s^{-1}) observed from adjacent white sand soils. Fluxes from clay soils were lower by more than a factor of 5 than fluxes observed during the dry season at a nearby site. Low soil emission rates were reflected in lower concentrations of NO at the top of the forest canopy in the wet season, only 30-50 pptv (parts per trillion by volume) during the daytime. The measured fluxes are consistent with chemical mass balances for NO within the forest canopy, calculated from the NO and O_3 profiles taken at night, and with observations of NO between 150 and 5000 m altitude (A. L. Torres and K. R. Hooks, unpublished manuscript, 1989). Measurements of NO emission rates from soil plots fertilized using $NaNO_3$, NH_4Cl or sucrose indicated that a reductive pathway (denitrification) may have been primarily responsible for production of the NO released by both clay and sand soils.

1. INTRODUCTION

Nitric oxide (NO) and nitrogen dioxide (NO_2) play key roles in regulating atmospheric concentrations of ozone (O_3) and hydroxyl radical (OH), the principal agents for atmospheric oxidation of a large number of compounds [Levy, 1972; Crutzen, 1979; Logan et al., 1981; World Meteorological Organization, 1985], and are precursors of nitric acid, a major component of acid deposition [Galloway and Likens, 1981].

There are few measurements of the flux of NO_x (NO and NO_2) from soils, confined largely to temperate and subtropical regions (for review, see Galbally [1985]). Using existing data on NO_x fluxes from soils in temperate areas, Logan [1983] estimated that soils contribute approximately 15% of the global NO_x source. Two studies indicating large fluxes of NO from tropical forest soils have since been published. Delmas and Servant [1987] reported a mean NO flux of about 9.0 x 10^{10} molecules cm^{-2} s^{-1} from the soil of a primary tropical moist forest in the Ivory Coast on two days during the dry season. During ABLE 2A Kaplan et al. [1988] measured an average NO flux of 5.2 (±1.7) x 10^{10} molecules cm^{-2} s^{-1} from an undisturbed tropical forest soil in Brazil. These fluxes are 2-30 times larger than reported for vegetated, unfertilized soils in other climatic zones [Galbally and Roy, 1978; Johansson and Granat, 1984; Slemr and Seiler, 1984; Anderson and Levine, 1987; Williams et al., 1987]. Johansson et al. [1988] reported much lower NO fluxes from soils of a tropical cloud forest in Venezuela, where dry season emission rates ranged from <0.9 to 8.6 x 10^9 molecules cm^{-2} s^{-1}.

Emissions of NO in tropical areas could be especially important to atmospheric chemistry. Photochemical reactions proceed most efficiently at low latitudes, due to greater solar UV flux and high atmospheric H_2O content. Ecosystems in the humid tropics are characterized by rapid biological processes and high productivity leading to the emission to the atmosphere of many photochemically active trace gases [e.g., Crutzen et al., 1985; Harriss et al., 1988; Harriss et al., this issue]. Since tropical areas are being developed for human use at an accelerating rate, it is important to acquire data on the undisturbed system to allow quantification of potential impacts on the atmosphere [Fearnside, 1982; Crutzen, 1985; McElroy and Wofsy, 1986].

The data of Delmas and Servant [1987] and Kaplan et al. [1988] indicate the potential importance of tropical forest soils as a source for NO_x. However, the measurements represent limited spatial and temporal scales ($\approx 10^4$ m^2 and 1 month during the dry season, respectively, for the Kaplan et al., [1988] study) Monthly rainfall may vary by a factor of 5 or more in the central Amazon Basin between the wet and dry seasons [Franken and Leopoldo, 1984]. Soil characteristics such as texture, moisture regime and nutrient availability vary markedly within tropical forest regions [e.g., Stark, 1971; Jordan et al., 1982; Vitousek and Sanford, 1986; Goreau and deMello, 1985] and may affect NO_x emissions [Slemr and Seiler 1984; Johansson and Granat, 1984; Williams et al., 1987; Anderson and Levine, 1987]. Previous studies did not examine the fate of nitrogen oxides after emission from the soil; a significant fraction of NO_x from soils may not escape from the forest canopy. Quantification of the atmospheric effects of soil emissions requires knowledge of the chemical and physical processes that affect these gases within the forest canopy.

This paper reports measurements of NO emissions from tropical forest soils in Brazil during the NASA/Instituto de Pesquisas Espaciais Amazon Boundary Layer Experiment (ABLE 2B), using chamber and vertical profile (chemical mass balance) methods, and examines atmosphere/biosphere exchange of nitrogen oxides in the forest canopy. Wet season conditions prevailed during the measurement period (April-May, 1987) and the data show generally lower fluxes than found by Kaplan et al. [1988] during the dry season for similar soils at a nearby site. An experiment in which plots were amended with various fertilizers ($NaNO_3$, NH_4Cl, and sucrose) indicated that reduction of oxidized precursors such as NO_3^- (denitrification) may have been primarily

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responsible for soil NO emissions at this site, as was also found during the dry season [*Kaplan et al.*, 1988]. Data for NO fluxes and concentrations are combined with measurements of total reactive nitrogen oxides (NO_y) in a companion paper [*Bakwin et al.*, this issue] to show that the forest canopy is a net sink for NO_y during the wet season despite the proximate source of NO from the soil. Forest vegetation helps to maintain low ambient concentrations of NO_x and NO_y, and thus plays an important role in regional photochemistry [*Jacob and Wofsy*, this issue].

2. STUDY AREA

The measurements were carried out at the Ducke Forest Reserve, 40 km North of Manaus, Brazil, between Apil 15 and May 10, 1987. The site was occupied by terra firma forest with an average canopy height of about 30 m, with emergents to 35 m. Measurements of profiles for atmospheric NO and O_3 were carried out using a 43 m high tower located on top of a small hill. Chamber measurements of NO fluxes were made at several sites on the clay-textured soil (yellow Oxisol) near the tower (sites A, F, and T) and on the hill slope ≈750 m from the tower (site B), and on the sandy soil of the campina about 1500 m west of the tower near the base of the hill (site C). The sandy soil was covered by a dense root mat. The clay soil is the dominant soil type in the area [*Food and Agriculture Organization*, (FAO), 1971; *Vitousek and Sanford*, 1986]. More detailed site descriptions can be found in papers by *Stark*, [1971], *Roberts et al.* [1990], *Keller et al.* [1988], and *Livingston et al.* [1988].

3. EXPERIMENTAL METHODS

3.1. Chamber Measurements

One week or more prior to the initiation of flux measurements small square (10 x 10 cm and 15.3 cm high) and larger round (24.8 cm diameter and 16.4 cm high) collars were driven about 5 cm into the ground at each study site. A flux measurement was made by placing a fitted top on a collar and sampling the head space continuously for about 10 min, with a sample flow rate of 200-300 cm^3/min STP. Square tops were 15.3 cm high, the round collars were fitted with either a flat top or a 19.0 cm high top. Tops and collars were made of aluminum coated with FEP Teflon. A 1.5 cm diameter hole in each top served as an air inlet and a 4 mm ID Teflon outlet tube ran from the chamber to the NO analyzer (Figure 1). Mixing of the chamber air was accomplished using an aluminum impeller driven at 120 rpm by a battery operated motor mounted outside the chamber. Nitric oxide flux was calculated from the initial rate of concentration increase in the chamber. There was no evidence of any systematic differences between fluxes measured using the large round or small square chambers. Systematic variation of sample flow rate established
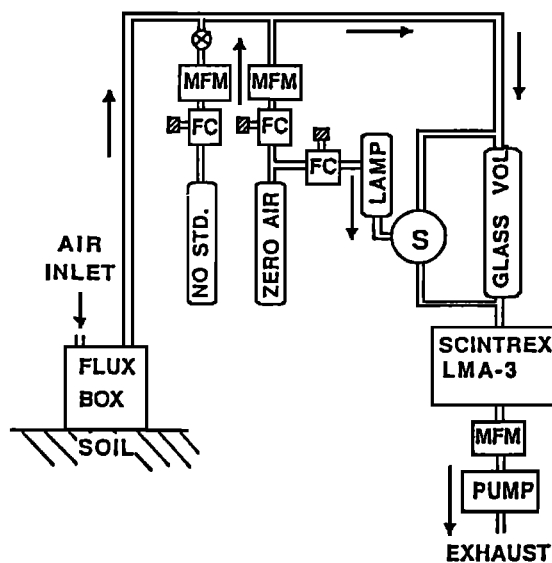

Fig. 1. Experimental design for the chamber measurements of NO flux. FC, flow control valve; MFM, mass flow meter [MKS Instruments, Inc.], S, three-way valve.

that flux values were independent of flow rate for the values adopted here.

Sites were selected to give maximum information about the spatial and temporal variability of NO fluxes while simultaneously allowing a time-resolved fertilization experiment to be carried out. In most cases, 3 x 6 m plots were equally divided into eight sectors. Within each of six randomly selected sectors a collar was emplaced, using five small square collars and one large round collar. One to four plots were located within about 20 m of each other at several sites on the clay and sandy soils (Table 1). For the fertilization experiments individual subplots within some of the plots were treated with $NaNO_3$, NH_4Cl (50 kg N ha^{-1}) or sucrose (500 kg C ha^{-1}) dissolved in 1 L of distilled water. Distilled water was added to control plots. Flux measurements were made 0.5, 2.5, and 4.5 hours after application of the fertilizer and then at various intervals on subsequent days.

Chamber air was analyzed for NO concentration using a Scintrex LMA-3 luminol-based NO_2 analyzer modified for NO analysis as described by *Bakwin et al.* [this issue]. Conversion of NO to NO_2 was accomplished by reaction with about 500 ppbv O_3 in a 300 cm^3 glass volume just upstream of the detector (Figure 1). Ozone was generated using a "Pen-ray" type Hg vapor lamp (UVP, San Gabriel, California) to irradiate a stream of "zero" air flowing at 30 cm^3/min STP. The instrument was zeroed between each flux measurement by switching the O_3 addition point to downstream of the reaction volume. In this configuration NO was

TABLE 1. Field Sites for NO Flux Measurements by the Chamber Method Including Fertilizer Treatments at Each Site

Site	Number of Plots	Total Number of Collars	Fertilizations (Plot No. Treatments)
A (clay)	4	24	A-I: NO_3^-, NH_4^+, sucrose
			A-II: NO_3^-, sucrose
B (clay)	2	12	none
F (clay)		8	none
T (clay)	1	8	none
C (sand)	3	18	C-I: NO_3^-, NH_4^+, sucrose
			C-II: NO_3^-, NH_4^+, sucrose

not oxidized to NO_2 but the background signal due to O_3 remained constant. The total flow rate through the instrument was about 1000 cm^3/min STP. It was necessary to keep the air flow through the chamber to a minimum in order to avoid disturbing the soil air and thereby possibly inducing NO emission [Kaplan et al., 1988]. Therefore 700-800 cm^3/min STP of "zero" air was added to 200-300 cm^3/min STP of air drawn from the chamber. Calibration was by standard addition of a small flow of NO standard (1 ppmv NO in N_2) to sample air. Flows were measured using MKS mass flow meters (MKS Instruments, Inc., Burlington, Massachusetts) powered by lead-acid batteries.

Interferences to the LMA-3 NO analysis include NO_2, O_3, and peroxyacetylnitrate (PAN). None of these species are expected to be produced by the soils studied, and ambient levels of these reactive species were expected to rapidly decline to zero in the enclosure [Anderson and Levine, 1987]. A buildup of any of these species in the flux box would have been observed as an increase in the instrument signal in the zeroing mode, when NO was not being detected. No such drift of the zero level was seen. Flux measurements using the modified LMA-3 were checked against measurements using a TECO-14A O_3-chemiluminescence NO detector (Thermo Environmental, Hopkinton, Massachusetts) in the lab and field, with excellent results, confirming that these soils do not emit significant levels of interfering species. The LMA-3 has the advantage of being portable and requiring low power. Further, the LMA-3 features a fast response and high sensitivity, allowing NO fluxes to be calculated from the first few minutes of data following enclosure. The minimum detectable flux was about 1 x 10^9 molecules cm^{-2} s^{-1} for a 10 min. experiment.

3.2. Profile Measurements

Profile measurements of NO and O_3 were obtained through the forest canopy at eight heights, 0.02, 3, 6, 12, 19, 27, 36, and 41 m. The NO concentrations were determined using a TECO-14A O_3-chemiluminescence detector modified to increase sensitivity and stability (detection limit 40 pptv (parts per trillion by volume), for 2-min average). Ozone was measured using a Dasibi 1003-AH UV photometer and by a chemiluminescence instrument using C_2H_4 (Monitor Labs, model 8410). Experimental details are given by Bakwin et al. [this issue]. An estimate for the NO flux was obtained from nighttime profiles of NO and O_3 [Parrish et al., 1987; Kaplan et al., 1988]. The one-dimensional mass balance equation for NO in a layer of thickness h is

$$\frac{\partial}{\partial t}(\int_0^h [NO]dz) + F_h - F_o = \int_0^h (P-L)dz \qquad [1]$$

where F_h and F_o are the NO fluxes across the upper boundary and the soil-air interface respectively, P and L are the chemical production and loss rates for NO within the layer, z is height, and t is time. At night $P \approx 0$ (i.e., no NO production by photolysis of NO_2). Reaction with O_3 should be the dominant sink for NO so that (1) reduces to

$$F_o - F_h = \partial/\partial t(\int_0^h [NO]dz) + \int_0^h k[NO][O_3]dz \qquad [2]$$

where k is the rate constant for reaction of NO with O_3. If the concentration of NO above height h (41 m) is sufficiently small, then F_h may be neglected and (2) gives the NO emission rate from the soil averaged over an area which influences the NO profile ($\approx 10^4$ m^2).

Equation (2) represents the NO soil flux as a balance between the total amount of NO stored in the canopy layer and the homogeneous loss of NO by reaction with O_3, the first and second terms on the right-hand side of (2) respectively. Both terms on the right hand side of (2) may be determined from the profile measurements, allowing calculation of F_o - F_h. The result represents a lower limit of the soil flux, F_o: other chemical processes (e.g., deposition on leaves, oxidation by organic peroxy radicals) may remove NO, also F_h may not be negligible.

4. RESULTS

4.1. Chamber Measurements on Unfertilized Plots

Figure 2 presents approximate probability distribution functions [see Keller et al., 1983] for NO flux measurements from unfertilized collars on the clay and sandy soils. The points represent daily means of measurements from a particular collar. Data from the same collar taken on different days are considered independent. An exception was made for site F, which was sampled intensively for 3 days: only the overall mean for each collar was used to avoid giving undue weight to this site. The 116 points on these plots represent a total of 224 individual flux measurements from 66 different collars (49 on clay soil and 17 on sandy soil). The distributions in Figure 2 are strongly non-Gaussian (normal distributions would be represented by a straight line on these plots). There are a small number of measurements with flux values much higher than the median, a distribution similar to those found by Keller et al. [1983, 1986] for N_2O emissions from soils in similar environments.
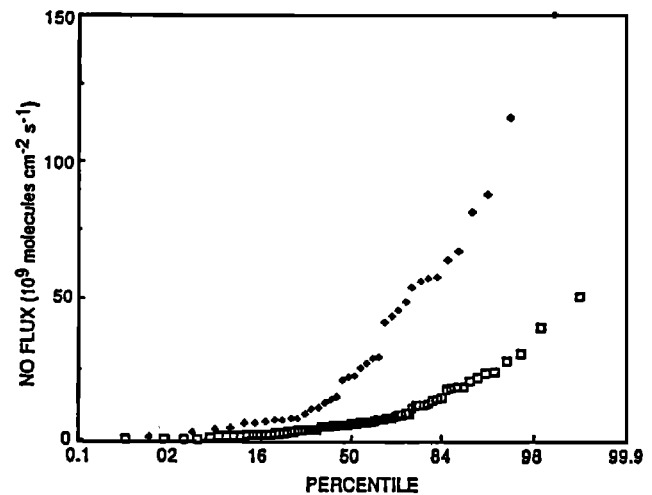

Fig. 2. Approximate probability distribution functions of NO flux measurements by the chamber method. The flux is plotted against the estimated probability $[P_i=[i-1/2]/N]$ of finding a flux smaller than the flux F_i where i is the rank in the set of observations of number N. Points represent daily means of multiply sampled collars [see text]. Open squares indicate data from clay soil sites, solid diamonds show sandy soil sites.

The mean NO fluxes for the clay and sandy soils (±95% confidence interval calculated by the "bootstrap method" of Efron and Tibshirani [1986]) were 8.9 (±1.5, n=78) x 10^9 molecules cm^{-2} s^{-1} and 33.8 (±6.5, n=38) x 10^9 molecules cm^{-2} s^{-1}, respectively. Mean values are insensitive to the treatment of multiply sampled plots: nearly identical results are obtained if multiple samples from the same collar are considered independent or if daily means

are used. The standard deviations were 8.0×10^9 molecules $cm^{-2} s^{-1}$ and 24.4×10^9 molecules $cm^{-2} s^{-1}$, respectively. The large coefficients of variation indicate substantial temporal and spatial variability.

Figures 3a and b show time courses of NO flux from particular collars on clay and sandy soils, respectively, and Figure 3c shows a time history of rainfall amount at the tower (L. Molion, unpublished data, 1988). Fluxes at site A (Figure 3a) display no apparent relationship to rainfall, but are characterized by large transient variations. The data from site C (Figure 3b) appear to show an effect of rain. Small fluxes were measured at this site during an initial wet period. Fluxes from each collar were highest following a dry period which lasted at least 2 days, and then declined gradually with subsequent rainfall.

Most of the flux measurements reported here were made during the daylight hours. To investigate the possibility of a diel variation in NO flux site F was established near the base of the tower and sampled intensively from the evening of May 7 to the night of May 9, 1987. No rainfall occurred during this interval. The

results, presented in Figure 4, show no clear diel pattern. This is as might be expected considering that the soil surface temperature at this site was virtually constant at 25-26°C (S. Trumbore, unpublished data, 1988) and studies in temperate areas have found that diel trends in NO emissions are controlled primarily by temperature [Slemr and Seiler, 1984; Johansson and Granat, 1984; Anderson and Levine, 1987; Williams et al., 1987].
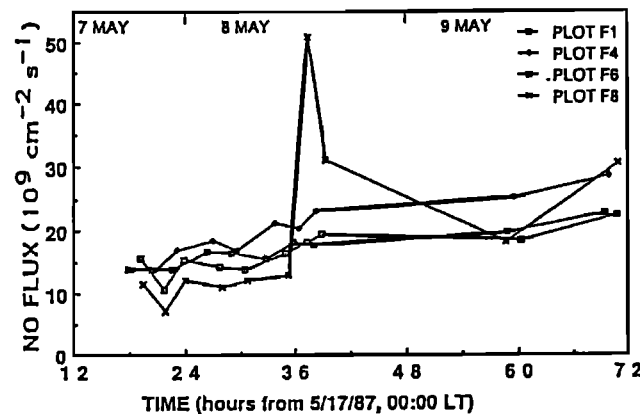
Fig. 4. Results of a diurnal study of NO emissions from clay soil (May 7-9, 1987). Results from each collar are plotted separately, only four of the eight collars sampled are shown.

An interesting feature of the data in Figure 4 is the spike in the NO flux observed from collar F8 at 13:30 on May 8, 1987. The NO flux increased at that site by a factor of 4 in just over 2 hours. The flux determination at 15:15 confirmed the increase, although by that time the flux had decreased to about 60% of the maximum. Similar short term transient increases are typical of NO emissions from other collars on the clay soil but were not observed on the sandy soil (Figure 3).

The mean (±95% confidence interval) of the NO fluxes at site F was 21.0 (±1.9, n=80) x 10^9 molecules $cm^{-2} s^{-1}$, more than a factor of 2 higher than the mean for the other clay soil sites. High values at site F could reflect natural spatial variation or could result from disturbance in the vicinity of the tower. The area immediately surrounding the collars had been cordoned off approximately 1 month prior to the initiation of these measurements, however the tower has seen frequent use since it was erected in 1983 [e.g., Shuttleworth et al., 1984; Roberts et al., 1990]. These data were included in the overall mean NO flux reported above; the result would have been smaller by about 20% if these data were omitted.

4.2. Fertilization Experiments

In all four fertilization experiments the addition of NO_3^- caused a large and immediate increase in the NO flux (Figure 5). Increases of five-fold to 150-fold were measured just 30 min. after application of the fertilizer, and the maximum response was always seen at this earliest time point. Other fertilized plots and control plots showed no pronounced increase in NO flux, except for one NH_4^+ fertilized plot at site C which showed a response similar to that of the NO_3^- fertilized plots.

4.3. Nocturnal Vertical Profiles

Simultaneous vertical profiles of NO and O_3 concentrations through the forest canopy were obtained on eight nights in late
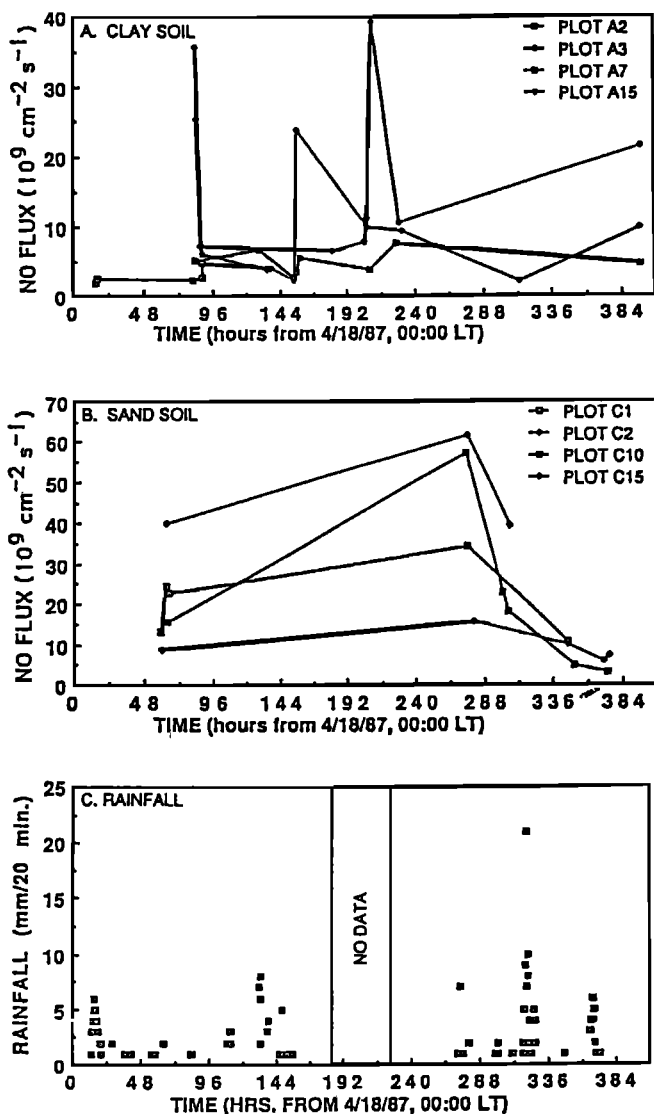

Fig. 3. Nitric oxide flux or rainfall rate versus time: (a) clay soil, (b) sandy soil, (c) rainfall rate (L. Molion, unpublished data, 1988). Rainfall data are missing for the period indicated and for the afternoon of April 21, on which there was a heavy thunderstorm.
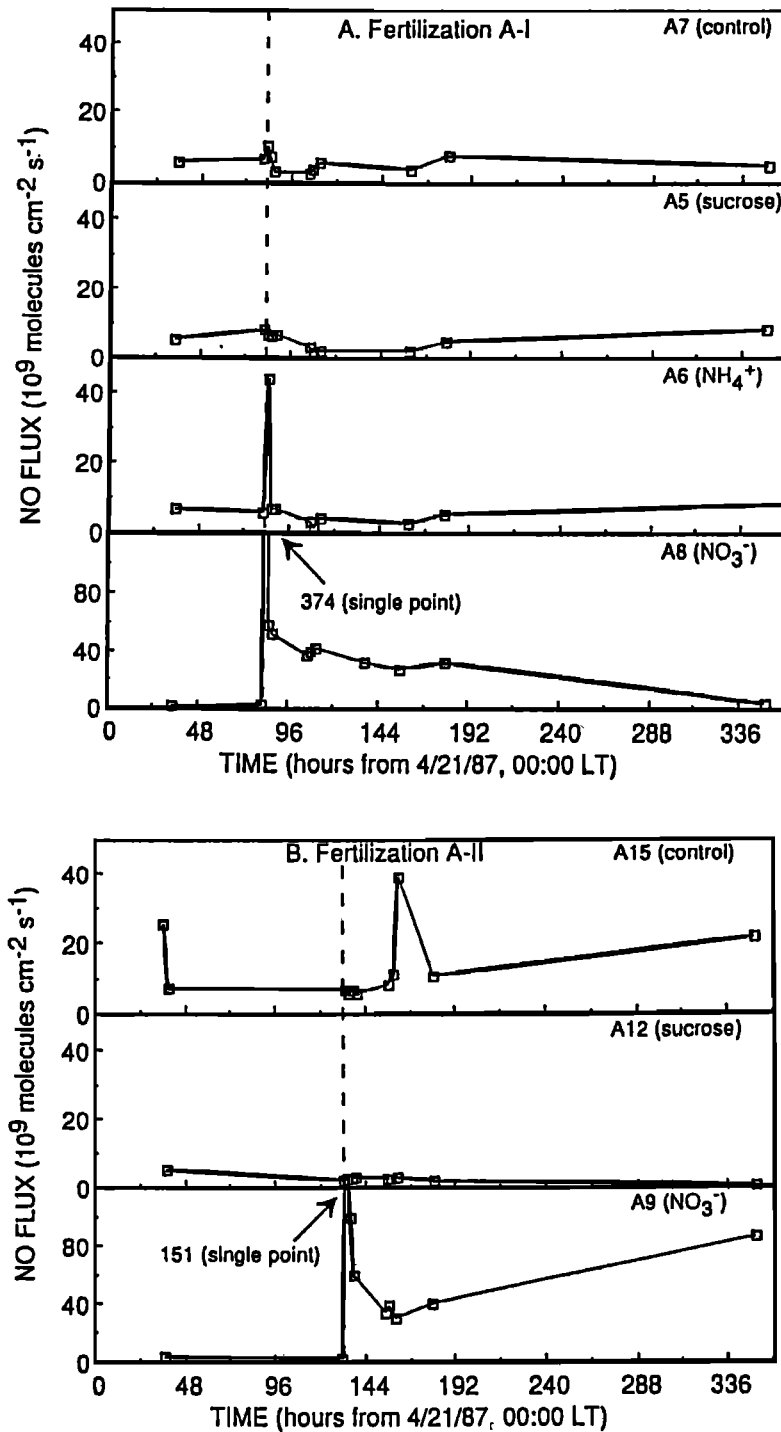
Fig. 5. Results of the fertilization experiments summarized in Table 1: (a) A-I, (b) A-II, (c) C-I, and (d) C-II. Symbols correspond to fertilizer treatments as indicated. Dashed line indicates time of fertilizer application.

April and early May 1987. Examples of observed profiles are shown in Figure 6. Ozone concentrations were very low, generally only 3-6 ppbv (parts per billion by volume) above the canopy, and concentrations decreased sharply in descent through the canopy, to near zero ppbv at the ground. High concentrations of NO were observed near the ground, reflecting the soil source. Concentrations of NO near the detection limit of the TECO-14A (about 40 pptv for a 2-min average) were usually observed at the top of the tower. The volumetric loss rate of NO was on average nearly uniform with height from 10 m to the top of the tower, about 1×10^5 molecules cm^{-3} s^{-1}

Figure 7 shows values for individual terms in (2) calculated from data for the nights of April 22, 23, and 24, 1987. The chemical loss term usually dominated and was not correlated with the storage term. Occasionally the storage term became dominant, as was observed between about 2100 on April 22 and 0030 on April 23, when two events occurred which abruptly removed NO from the canopy. The large negative values of the storage term in Fig-
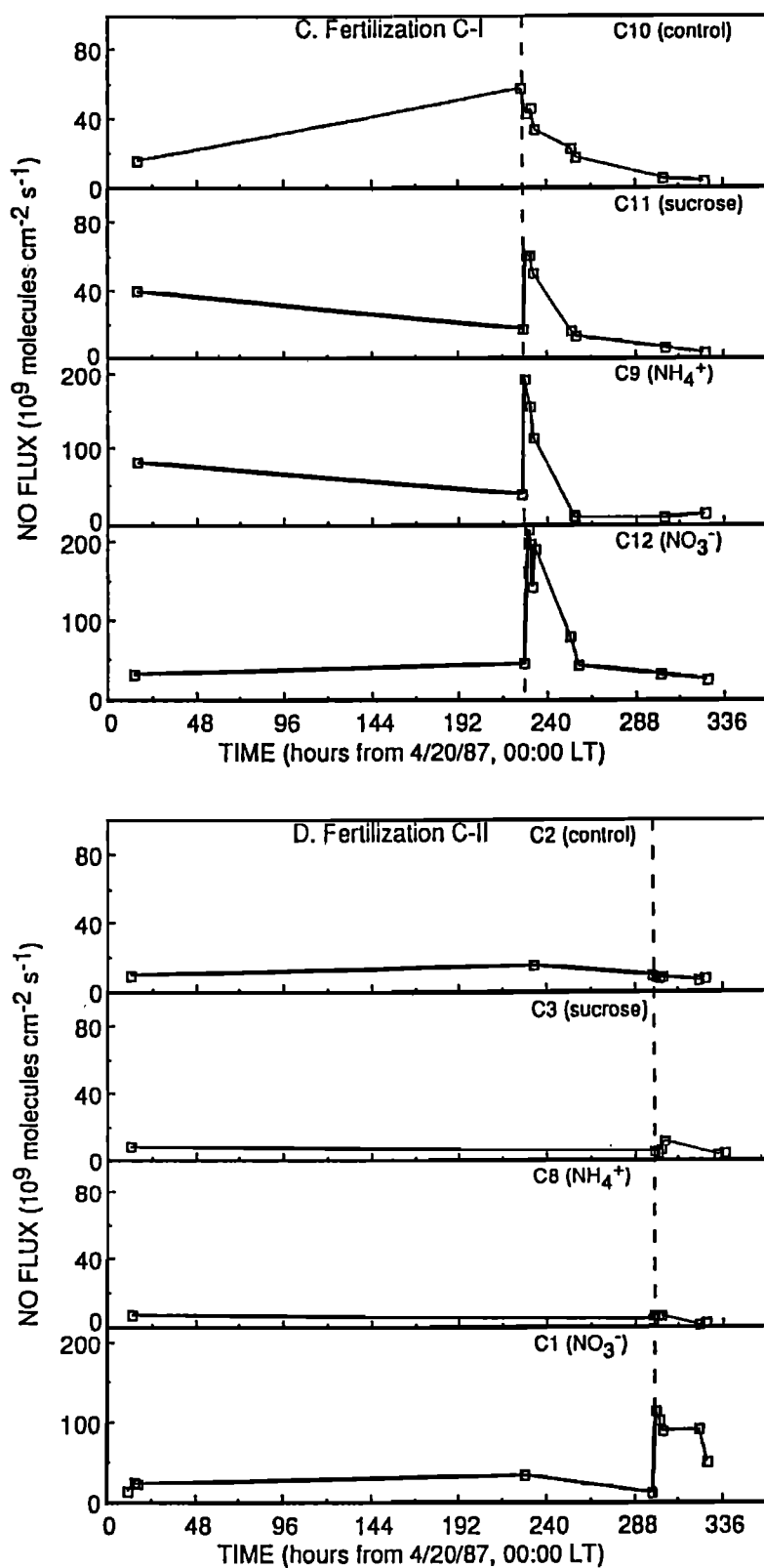
Fig. 5.   (continued)

ure 7a reflect these events. These events most likely represent in-stances of intrusion of low-NO air into the canopy from above [see *Fitzjarrald et al.*, this issue]. Despite such events, on average the amount of NO within the canopy changed little during the night, so the mean of the storage term was generally small. For all eight nights the mean value for F_o - F_k (±95% confidence inter-val) calculated using (2) was 5.1 (±0.9, n=108) x 10^9 molecules cm^{-2} s^{-1}. The mean for the chemical loss term alone was 4.6 (±0.6) x 10^9 molecules cm^{-2} s^{-1}. Hence inclusion of the storage term changed the mean calculated NO soil flux by only about 10%. The differencing required to compute the storage term in-creased the variance somewhat. Because of the extremely low O_3
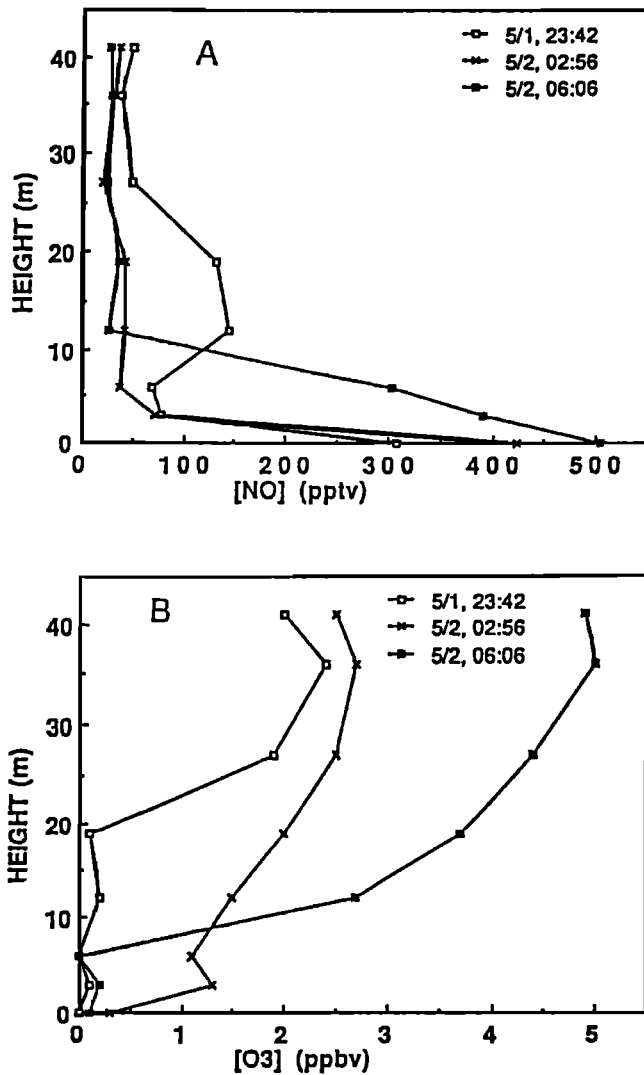
Fig. 6. Example nighttime profiles of (a) NO and (b) O_3.

concentrations within the canopy at night (<3 ppbv, Figure 6b) the observed column loss of NO by reaction with O_3 is sensitive to uncertainties introduced by the resolution of the instrument used to measure O_3 (±0.5 ppbv for a 3-min average).

5. DISCUSSION

Fluxes of NO measured from the clay soils averaged 8.9 (±1.5) x 10^9 molecules cm^{-2} s^{-1}, about a factor of 6 lower than that found by Kaplan et al. [1988] on clay soils at a nearby site during the dry season of 1985. Rain events had no discernible effect on emissions from the clay soils. The NO emission rate from sandy soil was higher than from clay soils by nearly a factor of 4, and varied inversely with rainfall amount (Figure 3). Roberts et al. [1990] found that the matric potential of the 0-30 cm depth interval of clay soil at this site was small and relatively constant during the wet season (March-April) of 1985, although daily rainfall amount varied widely, indicating that this soil remains near saturation during much of the wet season. Dry season measurements showed generally larger and much more variable matric potential. It is therefore not suprizing that NO fluxes from the clay soil do not respond to rain events.

Rapid temporal variations were characteristic of NO fluxes

from clay (see Figures 3a and 4) but not the sandy soil, possibly reflecting subtle differences in microenvironment. Short term changes suggest that either the source of NO, or a strong sink for NO, was in the soil zone nearest the surface, since it is this zone that is most subject to the influence of varying environmental conditions.

The higher NO flux from sandy soil contrasted with the trend observed for N_2O flux by Matson et al. [this issue] who sampled in parallel with some of the measurements discussed here. Similarly, Goreau and de Mello [1985] found that N_2O fluxes from clay soils at Ducke Forest Reserve were nearly a factor of 3 higher than from sandy soils in the dry season. These comparisons indicate differences in processes that control the production and/or escape of NO and N_2O from these soils. Escape efficiency is probably much more important in regulating NO than N_2O flux due to the greater chemical reactivity of NO, so that the higher NO fluxes on the porous sandy soil could simply reflect better ventilation, even if the in situ production rate was lower. In support of this idea the ^{222}Rn study of Trumbore et al. [1990] showed that, during the period of our measurements, the gas exchange rate between the soil air space and the atmosphere (expressed as a bulk
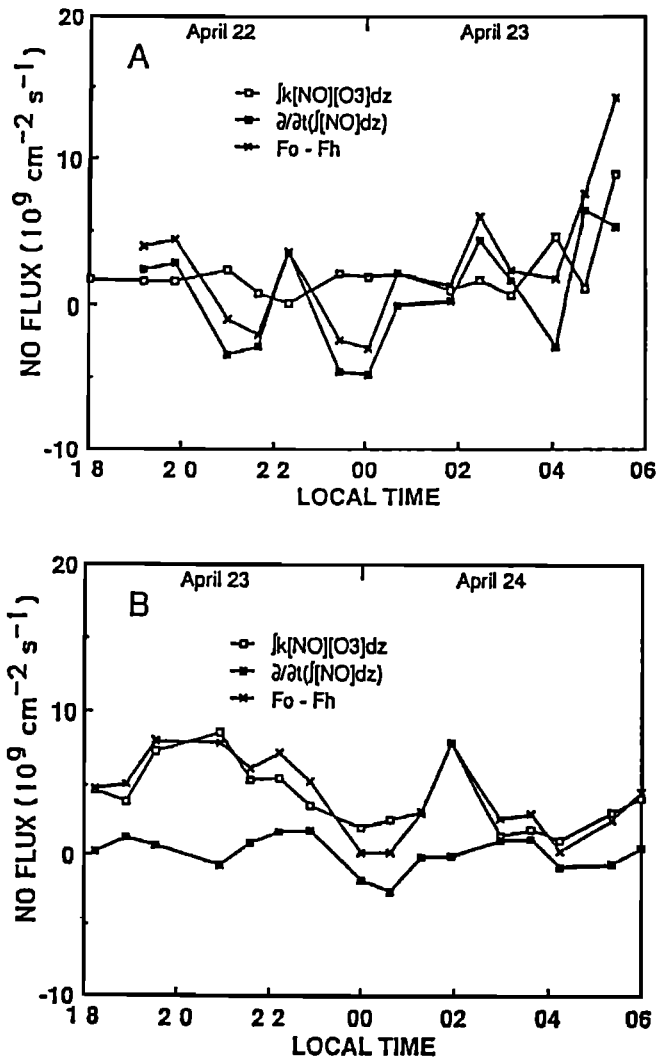

Fig. 7. Examples of terms in (2) for the nights of April 22, 23, and 24, 1987. Each point represents a single profile. Open squares = $\int_h k[NO][O_3]dz$, solid squares = $\partial/\partial t$ $(\int_h [NO]dz)$, and crosses = $F_o - F_h$.

diffusivity) was about 4 times larger for the sandy soil than for the clay soil.

The seasonal variation of NO and N_2O emissions suggests that NO efflux from soils may be strongly modulated by physical processes controlling air exchange between the soil and atmosphere. The most important parameter for controlling the soil-atmosphere air exchange is probably the amount of connected air-filled pore space in the soil. Drier and coarser textured soils tend to be better ventilated and thus allow more NO to escape.

Fertilizer experiments provide additional information on processes that control NO production in these soils. Nitrate additions caused a large and immediate increase in the NO flux while sucrose additions did not. Only one out of the three of plots amended with NH_4^+ showed an increased NO flux following fertilization. Addition of NO_3^- stimulated large enhancements of NO emissions from soils at a nearby site during the dry season [Kaplan et al., 1988]. Laboratory studies show that NO and N_2O may be produced biologically by both denitrification [Payne, 1982; Anderson and Levine, 1986] and nitrification [Goreau et al., 1980; Lipschultz et al., 1981; Anderson and Levine, 1986], and abiologically by the decomposition of NO_2^- [Nelson and Bremner, 1970]. Both gases may be used as a substrate during denitrification [Payne, 1981]. Our results for the NO_3^- and sucrose additions indicate that a reductive process (i.e., denitrification) was primarily responsible for production of the NO released by both soils studied and that this process was nitrogen limited, but not carbon limited. If NO_2^- decomposition was the source of the NO produced from added NO_3^- it must have followed biological reduction of NO_3^- to NO_2^-. It is not clear whether oxidative processes (e.g., nitrification) play a role. An increase in the input of NO_3^- by dry or wet deposition, due to increased biomass or fossil fuel burning, could result in enhancement of the NO flux from these soils.

The mean flux $(F_o - F_h)$ calculated from nocturnal NO and O_3 concentrations was 5.1 (±0.9) x 10^9 molecules cm^{-2} s^{-1}, about 40% lower than the mean from chamber measurements. The profile method yields a lower limit to the soil emission rate if the upward NO flux through the top level (41 m) is not negligible (i.e., F_h is not zero) or if processes other than oxidation by O_3 remove NO within the canopy layer. Very low O_3 concentrations prevailed during the measurement period, providing a favorable setting for both of these processes. The relatively large value for F_h $(F_h/F_o \approx 0.4$, where F_o is taken as the mean soil emission rate from the chamber measurements) appears to reflect the long lifetime for NO, which allows significant quantities of NO to rise above the canopy at night. Detailed model calculations by Jacob and Wofsy [this issue] indicate that, at night, 80-90% of the NO emitted from the soil is converted to NO_2 by O_3 and, to a lesser extent, by HO_2 and organic peroxy radicals within the 0-41 m layer, a somewhat greater amount than indicated by the results presented here. Some of this NO_2 may be deposited back onto the canopy. For the full diurnal cycle the model indicates that the mean NO_x release to the atmosphere was only about 20% of the soil emission rate due to loss of NO_2 to the canopy. However, the uncertainties in the measurements and the model preclude a definative assessment. The analysis does not allow for deposition of NO to leaves. Nitric oxide may have been deposited to, or catalytically oxidized on, leaf surfaces. The uptake of NO by various natural and man made surfaces has been documented [Hill, 1971; Judeikis and Wren, 1978; Johansson, 1987; Kisser-Priesack et al., 1987] but, to our knowledge, estimates of NO removal rates by leaf surfaces have not been made.

Escape of NO is likely to be more efficient in the day than at night since air exchange between the canopy and the mixed layer is much faster during the day [Fitzjarrald et al., this issue]. In order to determine overall impact of the forest on the reactive nitrogen oxide (NO_y) budget of the tropical atmosphere, including the fate of NO emitted from the soil, the study reported on by Bakwin et al. [this issue] was undertaken. The results of that study indicate that the forest was a net sink for NO_y during the wet season. The role of the forest as a sink for NO_y is consistent with the observations of A. L. Torres and K. R. Hooks (unpublished manuscript, 1989) of NO levels in the mixed layer over Ducke and the surrounding area at or below the detection limit of their instrument ($\approx$10 pptv) except as could be attributed to pollution from the nearby city of Manaus. Conditions may have been quite different during the dry season when soil fluxes (52.3 (±1.7) x 10^9 molecules cm^{-2} s^{-1}) [Kaplan et al., 1988] and atmospheric levels of NO (25-65 pptv) [Torres and Buchan, 1988] were much higher.

The data suggest that the forest plays a major role in regulating the abundance of NO_x and NO_y in the tropical atmosphere, and that the forest functions very differently in the wet season than in the dry season. During the wet season low soil emissions of NO, efficient conversion of NO to other NO_y species, and deposition back to the forest, result in low concentrations of NO and NO_y in the lower atmosphere. These conditions should lead to slow or negative rates of photochemical oxidant formation [Crutzen, 1985; Jacob and Wofsy, this issue], consistent with the observation of low O_3 concentrations and a persistent increase with height through the boundary layer of O_3 concentration during the wet season [Fan et al., this issue; Browell et al., this issue; Gregory et al., this issue; Kirchhoff et al., this issue].

Higher concentrations of NO during the dry season reflect larger soil sources and possibly inputs from biomass burning [Torres and Buchan, 1988]. Enhanced NO_x concentrations lead to photochemical production of O_3 over the Amazon Forest [Crutzen et al., 1985; Jacob and Wofsy, 1988]. Modulations of oxidant concentrations in the tropical mixed layer by seasonally varying NO emissions from tropical forest soils and by uptake of reactive nitrogen oxides in the forest canopy may play an important role in global atmospheric chemistry and needs to be incorporated in global models.

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