Atmosphere-Biosphere Exchange of CO₂ and O₃ in the Central Amazon Forest

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Measurements of vertical fluxes for CO₂ and O₃ were made at a level 10 m above the canopy of the Amazon forest during the wet season, using eddy correlation techniques. Vertical profiles of CO₂ and O₃ were recorded continuously from above the canopy to the soil surface, and forest floor respiration was measured using soil enclosures. Nocturnal respiration of CO₂ by the forest ecosystem averaged 2.57 kgC/ha/h, with about 85% from the forest floor. During the daytime, CO₂ was taken up at a mean rate of 4.4 kgC/ha/h. Net ecosystem uptake of carbon dioxide increased with solar flux by 0.015 (kgC/ha/h)/(W m⁻²), corresponding to fixation of 0.0076 moles CO₂ per mole photons (about 0.017 moles CO₂ per mole of absorbed photons at photosynthetically active wavelengths). The relationship between net ecosystem exchange and solar flux was virtually the same in the Amazon forest as in forests in Canada (Desjardins et al., 1982, 1985) and Tennessee (Baldocchi et al., 1987a,b). The relatively high efficiency for utilization of light (about 30% of the theoretical maximum) and the strong dependence of net CO₂ uptake on solar flux suggest that light may significantly regulate net ecosystem exchange and carbon storage in the tropical forest.

Deposition rates of O₃ to the Amazon forest were estimated for the dry season from mass balance in the planetary boundary layer [Gregory et al., 1988; Browell et al., 1988; Kirchhoff et al., 1988]. Deposition rates at night were obtained by Kaplan et al. [1988] using measured vertical gradients of O₃ within and above the canopy and vertical exchange coefficients derived from fluxes and gradients of NO. Deposition rates for O₃ to the Amazon forest were estimated for the dry season from mass balance in the planetary boundary layer [Gregory et al., 1988; Browell et al., 1988; Kirchhoff et al., 1988]. Deposition rates at night were obtained by Kaplan et al. [1988] using measured vertical gradients of O₃ within and above the canopy and vertical exchange coefficients derived from fluxes and gradients of NO. The lack of direct information on trace gas exchange over tropical forests makes it difficult to determine the factors that regulate gas fluxes and to assess the role of tropical forests in the global atmosphere-biosphere system.

We present in this paper the first eddy correlation measurements of O₃ deposition and CO₂ exchange over a tropical forest. The eddy correlation method has the virtue of being direct and non-intrusive, and results may be obtained continuously over extended periods. The experiment was conducted at Ducke forest reserve near Manaus, Brazil as part of the NASA/INPE ABLE2b mission during the wet season of 1987. Fluxes and budgets of heat and water vapor, and momentum have been studied previously at this site by Shuttleworth et al., [1984a] and Fitzjarrell et al. [1988].

Fluxes of CO₂ and O₃ have been measured by eddy correlation over a variety of other vegetation types using either tower or aircraft platforms, e.g. Verma and Rosenberg, [1976]; Ohtaki, [1980]; Desjardins et al., [1982]; Alvo et al., [1984]; and Baldocchi et al. [1987a,b] for CO₂ over paddy field and forest; Wesely et al. [1978, 1981]; Lenschow et al. [1981, 1982]; and Droppo, [1985] for O₃ over forest, water, and other surfaces. Hicks and his
coworkers [e.g., Hicks and McMillen, 1988; McMillen, 1988] and Denmead and Bradley [1985, 1987] have contributed important recent advances in the application of eddy correlation measurements to forests. These studies provide the background required to design a measurement strategy for tropical rain forests, including precautions needed to make measurements in nonideal terrain using sensors with imperfect response functions and noise.

We also made continuous measurements of mixing ratios for CO$_2$ and O$_3$ at eight altitudes above and within the canopy. The profiles provide measurements of storage in the canopy layer. Canopy storage contributes a significant part to the net ecosystem exchange at certain times of day, particularly for CO$_2$.

The results define the diurnal variation of rates for gas exchange between the forest and the atmosphere, and provide information on the factors that regulate gas fluxes. We examine the elements that control atmosphere-biosphere exchange using a canopy resistance model similar to that used by Hicks and coworkers to describe deposition of O$_3$, SO$_2$, and NO$_2$ to vegetated surfaces such as maize or oak-hickory forest [Baldocchi et al., 1987; Hicks et al., 1987; Meyers and Baldocchi, 1988]. The model analysis indicates that atmospheric and biospheric processes are both important in limiting deposition of reactive species to the tropical forest.

2. EXPERIMENT

The experiment was conducted at the Reserva Florestal Ducke, 25 km northeast of Manaus, Amazonas, Brazil, between April 22 and May 8, 1987. Vegetation and climatology for the site have been described in detail by Shettleworth et al. [1984a,b] and Roberts et al. [1990]. The main tree canopy extends about 30 m above ground with some emergent trees to 35 m. Foliage is present at all levels, though vegetation density is highest in the upper portion of the canopy and near the ground. Diurnal variations of temperature and specific humidity deficit were strong at top of the canopy, ranging from 22 to 30°C and -0 to 8 g/kg (night-to-day) respectively. Diurnal variations of temperature and humidity were very small near the ground and the soil temperature was almost constant at 25°C. Mean cloudiness is about 0.6 in the dry season and 0.7 in the wet season [Raisenson, 1976].

An aluminum scaffolding tower of 45 m height served as the main platform for the experiment. The flux measurements of CO$_2$ and O$_3$ were acquired at 39 m on the tower, about 9 m above the canopy top. A fast response single-axis sonic anemometer (Campbell Scientific Inc.) was mounted at the end of a beam extending about 3 m from the tower [Fitzjarrald et al., this issue]. Operation of this instrument and associated measurements of heat and momentum flux at several altitudes are discussed by Fitzjarrald et al. [1988, and this issue].

A Teflon tube of 3/8" outside diameter (8 mm i.d.) was attached to the beam above 30 cm from the anemometer, opening downwards and protected by a small plastic funnel to avoid aspirating rain. Ambient air for analysis of CO$_2$ and O$_3$ was drawn through the Teflon tube at a total flow rate of 25 standard liters per minute, small enough to avoid interference with the measurement of vertical wind velocity. Most of the air flow was bypassed just upstream of the analytical instruments, with 2.5 L/min drawn through the CO$_2$ analyzer and 0.84 L/min through the O$_3$ analyzer (Monitor Labs, model 8410). A BINOS non dispersed IR analyser was used for the CO$_2$ flux measurements. The instrument electronics were modified to give rapid response (90% response time ~0.3 s), so that the experimental response time was limited by time required to flush the 25 mL sample cell (0.6 s) and cold trap (~0.3 s, see below). A pressure of about 650 torr was maintained in sample and reference cells, and calibrations were carried out at this pressure. The modified CO$_2$ instrument exhibited an artificial modulation at about 2 Hz, but this narrow band, high frequency component did not correlate with vertical velocity or contribute to CO$_2$ fluxes (cf. next section).

Air passed through a thermoelectrically cooled glass volume filled with glass beads before entering the CO$_2$ analyzer, establishing constant temperature and dew point (5°C). Liquid water was drained through an opening at the bottom of the volume by drawing off an air flow of 0.3 L/min. This arrangement assured that fluxes do not have to be corrected for density variations due to fluctuations of temperature or water vapor in the sample cell [Webb et al., 1980].

The O$_3$ analyzer (Monitor Labs, Model 8410) detects chemiluminescence of the reaction of O$_3$ with C$_2$H$_4$. It was modified for rapid response by Gregory et al. [1983, 1988], attaining a 90% response time of 0.8 seconds. Calibration of the instrument was checked in the field by comparing with O$_3$ concentrations measured by the Dasibi Model 1003AH O$_3$ analyzer at 41 m height [Bakwin et al., this issue (a), (b)]. Instrument response was extremely stable during the course of the experiment.

Raw data for w (the vertical wind speed), CO$_2$, and O$_3$ were acquired 10 times per second using a PDP 11/73 computer system and were recorded on floppy diskettes. Spectra, cospectra, and co-variances of w, CO$_2$, and O$_3$ were calculated later. Data were taken in parallel at 1 second intervals by a Campbell Scientific Da-atalogger. The datalogger stored readings for 20-min periods, then removed the mean for each sensor and computed variances and covariances, accounting for time delays between instruments rounded to the nearest 1 second [Fitzjarrald et al., this issue].

Time delays between the chemical and the vertical wind signals were estimated in the field by blowing breath into the tubing inlet (for CO$_2$) and by turning on and off an ozone generator (Hg vapor lamp) placed near the inlet (for O$_3$). The estimated delays, 8.1±0.1 s for CO$_2$ and 10.2±0.1 s for O$_3$, were used in flux calculations throughout the experiment. These values were confirmed by computing lagged covariances from the raw data as discussed below.

Concentration profiles for CO$_2$ and O$_3$ were obtained by sequential sampling at eight altitudes (0.02, 3, 6, 12, 19, 27, 36, 41 m) through fixed 1/4-inch OD Teflon tubes. The inlets of the top five levels were attached to rods extended about 1 m from the tower, while inlets of the lower three levels were attached to a tree about 15 m from the tower in order to avoid influence of human activity around the base of the tower. A manifold of solenoid valves was used to switch between inlet tubes for air sampling, from lowest to highest, with a dwell time of 4 min at each level.

Concentration profiles for O$_3$ were measured using a Dasibi 1003-AH ozone analyzer described by Bakwin et al. [this issue (a), (b)]. The measurements of CO$_2$ profiles were made with a Beckman 865 nondispersed infrared analyzer. Because of the variable lengths of the sampling tubes, cell pressures in the analyzer varied from 580 to 600 torts according to the altitude being sampled. Calibrations were carried out at several pressures approximately every 2 hours. A cooler, identical to that used in the fast-response instrument, conditioned sample air and standards to constant temperature and dew point. Carbon dioxide concentra-tions were calculated by interpolating between consecutive gain factors and zeros, and were corrected for pressure effects. Profiling procedures were controlled, and data recorded, by an HP-3421A data acquisition/control system and an HP-85 computer.

Soil emissions of CO$_2$ were measured at seven locations near the base of the micrometeorological tower using Teflon coated aluminum enclosures. The enclosures were made in two parts: round collars 16.4 cm deep and 24.8 cm diameter placed a few
centimeters into soil, and tops 19 cm high. Each top had two holes, 1.5 cm in diameter, one connected to 1/4-inch Teflon tube leading to gas analyzers and the other one open to the air. The air inside the enclosure was mixed gently by an aluminum paddle driven by a battery powered motor at 120 rpm. The collars were inserted in the soil at least 2 days prior to the measurements and most were left undisturbed throughout the experiment. Samples were taken continuously at a flow rate of 300 mL/min using the Beckman CO2 analyzer immediately after a top was put on the collar. Carbon dioxide emissions were calculated from the rate of increase of CO2 concentration inside the chamber.

Total incident solar radiation was routinely monitored by a pyroheliometer at a site 2 km away from the micromet tower (O. Cabral, unpublished data, 1989). We retrieved solar flux data from chart records for 50 days in April and May 1987; the data were digitized, rectified, and converted to incident flux using the manufacturer's calibration.

3. VERIFICATION OF FLUX DATA

The vertical flux of a scalar, such as CO2 or O3, can be viewed as an imbalance between the quantity of scalar transported across a horizontal plane by air parcels moving up and down. The time averaged vertical flux $F$ may be represented by

$$F = \frac{1}{T} \int_{0}^{T} w'(t)c'(t+\Delta t) dt$$

where $T$ is the averaging interval, and $\Delta t$ is the delay time between the measured signals for vertical velocity, $w$, and concentration, $c$. The primes in (1) denote deviations of $w$ and $c$ from their respective running means computed over intervals of length $T$. The sensors for $w$ and $c$ must be sensitive enough and respond rapidly enough to resolve small deviations at the frequencies important for turbulent transport. Averaging intervals ($T$) must be sufficiently short to resolve atmospheric variations in flux but sufficiently long to obtain statistical significance. A period of 20 min to 1 hour is often chosen to obtain an effective average over a large number of eddies, while allowing observations of the change in the flux with time [Lumley and Panofsky, 1964].

The observed signals are affected by instrumental artifacts (baseline drift and noise) that may produce errors in the computed flux. Exposure and orientation of the anemometer may also affect the quality of flux determinations. Shuttleworth et al. [1984a] and Fitzjarrald et al. [1988, and this issue] have demonstrated previously the validity of eddy flux measurements for momentum, heat and water vapor at this site. We examine here in detail the accuracy of the tracer fluxes determined by the Datalogger, which constitute the main components of our data set (only a few hours of raw O3 data were acquired by the PDP system due to logistical problems.) Three sources of error will be examined: (1) errors in delay times used by the Datalogger, (2) instrumental zero drift and selection of data averaging interval, and (3) statistical imprecision associated with fluctuation of transport rates and with aliasing of high-frequency noise from the sensors.

Time delays of 8 s for CO2 and 10 s for O3 were used by the Datalogger throughout the experiment. Lagged covariances between $w$ and CO2 and between $w$ and O3 were calculated using 10 Hz PDP data to investigate the sensitivity of computed fluxes to deviations from the assumed values. The magnitude of the covariance of $w'$ and $c'$ should be maximum at the correct delay time. Examples of the covariance as a function of delay time are shown in Figures 1a and 1b, in which optimal correlations were found at 8.5 s between $w$ and CO2 and 10.2 s between $w$ and O3, in good agreement with estimates made in the field.

Cross correlation functions similar to that shown in Figure 1 were calculated for other periods. The delay times obtained from these correlation functions vary only a few tenth seconds from one period to another. As indicated in Figure 1, an error in the time delay of 0.1 s would introduce an error in flux of about 1 percent for both CO2 and O3, small compared to other sources of error.

Instrumental zero drift represents low frequency noise. It can be a serious source of error if zero drift occurs for both $w$ and $c$ signals and averaging does not effectively remove its contribution to the flux estimate. The fluxes were calculated from the Datalogger measurements by subtracting 20-min means from $w$ and $c$, then performing the integral in (1). In order to assess the magnitude of errors introduced by the Datalogger algorithm, we computed fluxes of CO2 and O3 using 10 Hz raw data, for a series of running mean intervals from 1.7 to 20 min. Results (Figures 2a and 2b) indicate that the computed flux is independent of the averaging interval for intervals between 6 and 20 min. The computed flux declines for intervals less than 5 minutes. When 20-
min grand means were removed from signals averaged for the 16-min period (1400-1640) on May 2, 1987, fluxes were at most 15% different from those computed by subtracting the 6 min running mean (see Figure 2). These results were typical of other time intervals, as indicated by Figure 4 (discussed below). The small errors associated with zero drift reflect stable instrument performance in environmental conditions that varied little during the period of experiment. We conclude that subtraction of running mean over intervals between 6 and 20 min, or a grand mean over a 20-min period, provide flux estimates consistent to better than 15% for most intervals.

Statistical errors in estimates of the mean flux are associated with temporal variation of the vertical flux and with instrumental noise produced by fast response chemical sensors. Statistical imprecision is usually the largest source of error for a flux estimate in a single 20-minute interval, typically at least 10% under ideal conditions [Wesely and Hart, 1985]. The errors in a given period depend on the variances of \( w \) and \( c \), and on the signal-to-noise ratio of each measurement [Lenschow and Kristensen, 1985].

Figures 3a-3c show power spectra for \( w \), CO\(_2\), and O\(_3\) sensors, computed using a Fourier transform of 10-Hz data for a 140-min interval in the afternoon. The spectra for CO\(_2\) and O\(_3\) have significant power at high frequencies that is not observed in the spectrum for \( w \). However Figures 3d and 3e show that the cospectra of \( w \) with CO\(_2\) and O\(_3\) show no significant contributions from fre-
Figures 4a and 4b show hourly averaged CO₂ fluxes derived by the Datalogger (squares) and fluxes derived by analysis of 10 Hz data (+ connected by lines) for the intervals when both systems were operating. Fluxes derived from 10 Hz data vary smoothly over periods of several hours. The fluxes obtained from the Datalogger were scattered about the smooth lines, but the magnitude and diurnal variation of fluxes derived from the 10 Hz data are well reproduced. Errors for hourly averaged fluxes are in most cases less than -20% of peak values. Comparison of hourly fluxes from the Datalogger to those computed from 10 Hz data (Figure 4c) indicates a regression ($r^2=0.66$) with a slope very close to 1 and with zero intercept. The residual standard error is 1.9 kgC/ha/h, with no systematic trend in the residuals.

The influence of aliasing by the Datalogger algorithm was further examined by computing CO₂ and O₃ fluxes from PDP data sampled once per second to simulate data collection by the Datalogger. Mean fluxes and standard deviations are shown in Table 1 along with the corresponding fluxes from the Datalogger. The errors introduced by the low sampling rate are evident. The coefficient of variation for O₃ flux is smaller than that for CO₂, reflecting the higher signal-to-noise ratio of the ozone measurement. Nevertheless, fluxes averaged over eight intervals from the Datalogger and the PDP agree closely for both O₃ and CO₂, consistent with our analysis of errors for the techniques.

Data were obtained for various time intervals on 12 days, and for each hour we have from the Datalogger 19-29 (mostly 27), 20-min intervals for CO₂, and 24 20-min intervals for O₃. According to the analysis of errors outlined above, random errors in hourly mean values for the whole experiment, due to statistical variance, removal of means, etc., should be less than 5% of daily maxima for most hours of the day. As we shall see below, bias in the data due to variations of natural conditions (cloudiness, wind speed) and by flooding of the anemometer during rainstorms may introduce larger errors in defining mean values for the experimental period.

4. CARBON DIOXIDE FLUX AND NET ECOSYSTEM PRODUCTIVITY

A characteristic diurnal pattern was observed for CO₂ flux (12 days of data) and a very similar pattern was observed for O₃ (partial data for 6 days), as shown in Figure 5. Concentrations above and within the canopy exhibited marked diurnal patterns (Figure 6). The mean daily minimum for CO₂ above the canopy was 340 ppm at midday, 7-8 ppm lower than the mean value observed at 3 km altitude from the Electra aircraft [R. Harriss and S. Wofsy, unpublished data, 1989]. The mean daily maximum at canopy top, more than 370 ppm, was observed as CO₂ accumulated in the forest boundary layer before sunrise. Variation of total CO₂ content between 0 and 39 m height is related to the fluxes at the top and bottom boundaries, and to production and loss within the column, by

$$
\frac{d}{dt} \int c(z)dz + F_{39m} = F_{soil} + F_{leaf} + F_{net}
$$

where $F_{soil}$ is the rate of emission by soils, $F_{leaf}$ is the integrated rate of emission by leaves, and $F_{39m}$ is the upward flux at 39 m. The influence of horizontal advection is assumed to be negligible on average. The left-hand side in (2), the net ecosystem exchange (NEE), can be computed using measurements of vertical concentration profiles and flux at the top of the tower.

Figure 5 compares the diurnal variations of storage ($\int_{0}^{39m} c(z)dz$) with the measured mean fluxes ($F_{39m}$). Diurnal changes in storage terms were significant for the budget of CO₂, but not for O₃. Storage terms were particularly important during the early morning hours, when CO₂ respired at night is used for photosyn-
thesis while simultaneously being exhausted from the forest to the developing atmospheric mixed layer.

The maximum uptake of CO₂ by the forest system occurred around noontime, on average about 9.3 kgC/ha/h. Mean daytime (6-18 hours) NEE for CO₂ was about -4.4 kgC/ha/h, with greater uptake observed before noon (-5.0 kgC/ha/h) than in the afternoon (-3.8 kgC/ha/h). The flux of CO₂ from the forest floor averaged 2.22 kgC/ha/h, with little variation according to time of day (Figure 7). The nighttime mean value for NEE was 2.57 kgC/ha/h, also with little variation through the night (Figure 5a).

The morning/evening (am/pm) ratio for CO₂ uptake (1.31) was virtually the same as the am/pm ratio for incident solar flux (see Figure 8), reflecting greater cloudiness for afternoon sampling intervals: the mean solar flux was 460 W m⁻² in the morning and 360 W m⁻² in the afternoon (am/pm=1.28). Neither the asymmetry nor the magnitude of the solar irradiance were typical of the 50 days in April and May 1987, for which we obtained solar flux data: average values for the solar flux in the morning and afternoon were 320 W m⁻² and 325 W m⁻², respectively (am/pm=0.99). Intervals with flux data are evidently biased to-
FIG. 4. (continued)

TABLE 1. Fluxes of CO2 and O2 Recorded by the Datalogger and Calculated from the PDP data

<table>
<thead>
<tr>
<th>Time</th>
<th>CO2</th>
<th>O2</th>
<th>Mean (kg C/ha/h)</th>
<th>Std (10^11 molecules/cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1420</td>
<td>-5.29</td>
<td>-3.75</td>
<td>0.47</td>
<td>-2.53</td>
</tr>
<tr>
<td>1440</td>
<td>-5.54</td>
<td>-3.29</td>
<td>0.39</td>
<td>-3.18</td>
</tr>
<tr>
<td>1500</td>
<td>-6.02</td>
<td>-5.39</td>
<td>0.33</td>
<td>-3.73</td>
</tr>
<tr>
<td>1520</td>
<td>-4.73</td>
<td>-7.24</td>
<td>0.89</td>
<td>-4.82</td>
</tr>
<tr>
<td>1540</td>
<td>-6.89</td>
<td>-5.55</td>
<td>1.33</td>
<td>-4.05</td>
</tr>
<tr>
<td>1600</td>
<td>-3.15</td>
<td>-2.41</td>
<td>0.34</td>
<td>-1.53</td>
</tr>
<tr>
<td>1620</td>
<td>2.69</td>
<td>-4.74</td>
<td>0.31</td>
<td>-3.68</td>
</tr>
<tr>
<td>1640</td>
<td>-5.68</td>
<td>-4.64</td>
<td>0.34</td>
<td>-1.53</td>
</tr>
<tr>
<td>Mean</td>
<td>-5.12</td>
<td>-4.63</td>
<td>0.55</td>
<td>-3.37</td>
</tr>
<tr>
<td>Standard</td>
<td>1.50</td>
<td>1.50</td>
<td>1.04</td>
<td>1.28</td>
</tr>
</tbody>
</table>

* Mean flux calculated for the interval by sampling 10Hz data at 1 Hz and computing 10 values of the flux.
† Standard deviation.

wards sunny periods, a consequence of repeated failures of the sonic anemometer during rain storms.

Figure 9 shows the hourly mean NEE for CO2 observed at Reserva Duque, plotted against the incident solar radiation at the Embrapa site 2 km away. Carbon dioxide is taken up with reduced quantum efficiency at the higher irradiance levels. A least squares fit of the data to the functional form

\[ \text{NEE} = c_1 + \frac{c_2 \cdot S}{c_3 + S} \]

where NEE is the net ecosystem exchange for CO2 and S is the incident solar flux, gave \( c_1 = 4.1 (±1) \) kg C/ha/h, \( c_2 = 18.4 (±3.8) \) kg C/ha/h, and \( c_3 = 411 (±1) \) (Wm²), \( (r^2 = 0.90) \). The average half-saturation value for the forest system \( (c_2) \) is higher than the daytime mean of 389 W/m², implying that the system is light limited: net daily carbon fixation should vary with daily insolation.

Analysis of airborne flux data for the Larose forest in Canada [Desjardins et al., 1985] gave a relationship remarkably close to that found here for the Amazon forest. They fit a line to uptake data as a function of solar irradiance, obtaining a slope of \(-0.014\) (kg C/ha/h)/(W m⁻²) and an intercept of about \(1.2\) kg C/ha/h. If we treat the Amazon data the same way (see the dotted curve in Figure 9), we obtain a slope of \(-0.015\) (kgC/ha/h)/(W m⁻²) and intercept of \(2.2\) kgC/ha (\( r^2 = 0.86 \)). The coefficient for carbon uptake observed in a Tennessee forest by Baldocchi et al. [1987a] was about \(-0.028\) kgC/ha/h (W m⁻² of PAR), and since PAR accounts for about half of the solar flux [Campbell, 1977; Odum et al., 1976], the variation of NEE with solar flux also corresponds to about \(-0.014\) kgC/ha/h (W m⁻²).

The maximum quantum yield for photosynthesis in leaves of \( C_3 \) species is about 0.06 mole CO2 fixed per mole photons at 25°C and intercellular concentrations of CO2 and O2 of 230 ppm and 21%, respectively [Farquhar et al., 1980]. The mean coefficient for CO2 uptake by the Amazon forest, 0.015 (kgC/ha/h)/(W m⁻²), is equivalent to a quantum yield of 0.0076 mole CO2/mole photons, using the conversion factors given by Campbell [1977]. The albedo over the Amazon forest was estimated by Shuttleworth et al. [1984a] to be about 12%, and if PAR is assumed to account for 50% of solar irradiance, the quantum yield for absorbed PAR at the mean irradiance level is about 0.017 mole CO2/mole photons. This is 30% of the theoretical maximum. For irradiance levels between zero and 200 W/m², the carbon fixation rate increases by about 0.051 moles of CO2 for each additional mole of absorbed photons in the PAR spectrum; the marginal quantum yield for
CO₂ uptake at low light levels is therefore nearly equal to the maximum expected for C₃ plants.

The remarkable coincidence of results for boreal, temperate, and tropical forests strongly suggests that, in a forest with well-developed canopy and adequate water, available PAR controls net ecosystem uptake of carbon, at least over short time periods. Light saturation effects are not dominant because the forest is optically deep, and most of the leaves function at light levels below saturation and at temperatures within limiting values. The high efficiency for utilization of light by well-watered forest ecosystems is
consistent with this view. It might be possible to use the coefficient for NEE versus solar flux as a diagnostic tool, i.e., if a system were significantly less efficient, another limiting factor (e.g., water) might be suspected.

Net daily uptake of CO₂ was observed to be 0.93 kgC/ha/h for the period of experiment, representing a significant imbalance between carbon fixation and mineralization. This imbalance is a function of the sampling bias toward sunny intervals. The 12-hour-mean solar flux for intervals with flux data exceeded the 50-day mean by 90 W m⁻², equivalent to stimulation of CO₂ uptake by 0.67 kgC/ha/h (averaged over 24 hours) according to the results in Figure 9. We would expect therefor that, over the 50 days in April and May for which we have solar data, net uptake of CO₂ would be only 0.25 kgC/ha/h, close to the detection limit for this experiment.

The small residual uptake of CO₂ during the wettest months, 0.25 kgC/ha/h, corresponds to a globally significant flux of carbon, more than 1.2x10¹² kgC/yr over the 5x10⁶ km² of the Amazon Basin. This flux may be balanced in part by emissions of volatile hydrocarbons. Zimmerman et al. [1988] estimated that emissions of isoprene and terpenes should account for 0.010 and 0.002 kgC/ha/h during the dry season, respectively, based on extensive measurements in the planetary boundary layer. Jacob and Wofsy [1988] obtained similar results for isoprene (0.016 kgC/ha/h) using a photochemical model and aircraft observations of isoprene concentrations. Emissions of reactive terpenoid hydrocarbons alone may thus account for 5–6% of the estimated net carbon uptake. Carbon monoxide [Kirchhoff et al., this issue], methane, and particulate and dissolved organic carbon are also exported from the forest, and may account for much of the remainder.

The response of NEE to variations in solar irradiance suggests that important shifts in global carbon storage could be induced by changes in the distribution of cloudiness, due for example to climate fluctuations such as the El Nino-Southern Oscillation. If cloud cover increased by 10%, (insolation decreased by about 35
Fig. 9. The NEE of CO₂ versus insolation. Our measurements (squares) and curvilinear regression (solid line) are shown, along with a linear fit (dotted line) compared in the text with the treatment of boreal forest data by Desjardins et al. [1985].

Fig. 10. Diurnal variation of ozone deposition velocity (cm s⁻¹) measured in the Amazon forest.

W m⁻²) we might expect net release of 0.25 kgC/ha (24-h basis) or about 1.2x10¹² kgC/yr. Although this is only a factor of 4 smaller than the annual release from fossil fuel burning, it represents loss of only about 0.5% of the standing biomass [Medina and Klinge, 1983] per year and might be sustained for a significant period. A decrease of cloud cover might stimulate carbon storage, although enhanced evaporation might induce stress that counteracted the influence of higher solar flux.

5. FACTORS CONTROLLING O₃ DEPOSITION

The daytime (0700-1700 LT) fluxes of O₃ to the forest canopy averaged 2.3x10¹¹ molecules cm⁻² s⁻¹, a rather large value considering the low O₃ concentrations at canopy top (=6 ppb). Mean nighttime fluxes (1700-0700 LT) were lower by more than a factor of 10, 2.2x10¹⁰ molecules cm⁻² s⁻¹, while O₃ concentrations at canopy top were lower by only a factor of 2. Uptake of O₃ by vegetation is evidently much more efficient during the daytime than at night. The daytime O₃ fluxes are about a factor of 6 lower than the mid-morning average estimated by Gregory et al. [1988] for the dry season. This difference can be explained in part by larger O₃ concentrations in the planetary boundary layer (PBL) during the dry season, about 20 ppb in the daytime [Gregory et al., 1988].

The O₃ flux Fₜ at altitude z may be assumed proportional to the concentration [O₃](z) at that altitude [Galbally and Roy, 1980], where the proportionality constant defines the deposition velocity Vₜ:

\[ Fₜ = [O₃](z)Vₜ \]  

We show in Figure 10 the hourly mean variation of Vₜ at 39-m altitude, computed from the hourly mean eddy correlation fluxes and O₃ concentrations. Deposition velocities averaged 1.8 cm s⁻¹ in the daytime (0700-1700 LT) and 0.26 cm s⁻¹ at night (1700-0700 LT). The daytime deposition velocities are at the high end of values previously reported for vegetation surfaces [Galbally and Roy, 1980; Sehmel, 1980]. In particular, Lenschow et al. [1982] measured a deposition velocity of 1.0 cm s⁻¹ over a Gulf Coast pine forest, using the eddy correlation technique. It appears that O₃ uptake by the Amazon forest is particularly efficient compared to other environments. Possible factors determining this rapid uptake are the high density of vegetation, the high temperature and humidity (favoring stomatal opening), and rapid turbulent transport at canopy top. These various factors are examined below.

The downward flux of O₃ measured at 39 m reflects contributions from deposition to vegetation and to the ground, and chemical reactions in the air column between zero and 39 m. Chemical reactions are negligible contributors to the flux in the daytime when the ozone flux is large [Jacob and Wofsy, this issue], but at night the contribution from reaction with NO emitted by soil is significant [Bakwin et al., this issue (a), (b). The flux Fₜ₉ₚm can be written as:

\[ Fₜ₉ₚm = \int_{0}^{39m} \frac{[O₃]}{R_L(z)} dL(z) + \int_{0}^{39m} k[NO][O₃]dz + \frac{[O₃](1)}{R_g} \]  

where z₉ₚₐₚ = 30 m is the top of the canopy, R_L(z) is the leaf resistance to deposition per square centimeter of leaf area, L(z) is the leaf area index between z and z₉ₚₐₚ, k is the rate constant for the reaction NO + O₃, and R_g is the resistance to deposition at the ground based on the O₃ concentration ([O₃](1)) at 1 m altitude. The leaf resistance R_L can be decomposed into contributions from leaf-atmosphere boundary (Rₐ), stomatal (Rₛ), mesophyllic (Rₘ), and cuticular (R_c) resistances, as follows [Meyers and Baldocchi, 1988]:

\[ R_L = \frac{1}{R_a} + \frac{1}{D_aR_c} + \frac{1}{D_cR_m} \]  

where D and D_a are the molecular diffusivities for O₃ and water vapor, respectively. The term representing reaction with NO is not strictly correct in the daytime, since some of the product NO₂ may photolyze, but the term is negligible except at night.

We approximate the integrals in (4) by subdividing the atmosphere between zero and 39 m into discrete layers of uniform vegetation density and uniform O₃ concentration:

\[ Fₚ₉ₚₐₚ = \sum_i \frac{[O₃]_i\Delta L_i}{R_{L_i}} + \sum_i k[NO][O₃]_i\Delta z_i + \frac{[O₃](1)}{R_g} \]  

where [O₃]_i, [NO]_i, and R_{L_i} represent quantities averaged over layer i, ΔL_i is the leaf area index of the layer, and Δz_i is the layer...
thicknes. Inspection of canopy architecture and of vertical O3 concentration profiles suggests a subdivision of the canopy into 3 layers: 0-2 m (layer 1), 2-20 m (layer 2), and 20-30 m (layer 3). Layer 1 consists of undergrowth with high vegetation density and low light levels, layer 2 consists mainly of tree trunks and has the lowest vegetation density, and layer 3 includes the crowns of trees, which intercept most of the incoming light. The atmosphere above the canopy, between 30 and 39 m, is described as a fourth layer (\Delta L = 0), where O3 may be consumed at night by reaction with NO. The concentrations of NO and O3 used in (4) are the mean values measured at the site as a function of time of day [Bakwin et al., this issue (a), (b)]. The ground resistance \( R_g \) is approximated as the aerodynamic resistance between 0 and 1 m obtained from CO2 and radon data (\( R_g = 1 \text{s/cm}^{-1} \) at night, and 2.5 s cm\(^{-1}\) in the daytime [Trumbore, 1988]). The surface resistance of the ground is assumed negligible.

The leaf area index of the forest canopy was not measured during the ABLE2B experiment, but previous irradiance measurements at the site [Shuttleworth et al., 1984a] indicate that about 1.4% of the light at canopy top reaches the ground between 0900 and 1000 LT (the time of day when cloudiness is least frequent). Assuming a uniform angular distribution of leaves, corresponding to an extinction coefficient of 0.5 normalized to leaf area index [Verstraete, 1987], we find that the light penetration observed by Shuttleworth et al. [1984a] corresponds to a leaf area index of 7 (taking into account the correction for zenith angle, \( \theta = 38^\circ \) at 0930 LT). We assume (1,2,4) as the distribution of leaf area index in the canopy, where the notation refers to leaf area index in (layer 1, layer 2, layer 3) of the canopy from bottom to top; sensitivity calculations will be conducted with distributions (1,1,5) and (1,3,3).

The leaf resistances \( R_{\text{leaf}} \) can be computed from knowledge of the individual contributing resistances in (5). Leaf-boundary (\( R_b \)) and stomatal resistances (\( R_s \)) were measured at the site by Roberts et al. [1989]. Values for \( R_b \) varied with altitude, from 1.7 s/cm near the ground to 0.3 s/cm at canopy top; values for \( R_s \) varied both with altitude and time of day, reflecting stomatal response to illumination and other parameters. The minimum stomatal resistance in mid-morning at canopy top was about 1.5 s/cm. We adopted average values of the resistances measured by Roberts et al. [1989] for each layer and time of day. Mesophyllic resistances were assumed negligible [Wesely, 1989]. A uniform cuticular resistance \( R_c = 10 \text{s/cm}^{-1} \) was adopted, as determined from observed O3 flux at night. The total leaf resistances for each layer, \( R_{\text{Total}} \), are significantly lower in the daytime than at night, as shown in Table 2, due to opening of the stomata during the day.

We compare in Figure 11 the O3 fluxes computed from (4) to the observed values. Reasonable agreement is found throughout the day. Deposition to the upper canopy (20-30 m) accounts for about 75% of the total flux, due to the high vegetation density in that layer and the low stomatal resistances. The distribution of leaf area index in the canopy has only a small effect on the computed flux: the 24-hour average flux is 11% higher with the (1,1,5) distribution, and 11% lower with the (1,3,3) distribution. The agreement between observed and computed fluxes at night reflects mainly the adjustment of the cuticular resistance to 10 s cm\(^{-1}\), a value much lower than previously estimated for deciduous forests [Meyers and Baldocchi, 1988; Wesely, 1989]. Despite this relatively low cuticular resistance, the daytime flux is still much higher than the nighttime flux because of the lower leaf resistance in the upper canopy (factor of 4) and the higher O3 concentration at 39 m (factor of 2) during the day. The decrease in the flux from morning to afternoon can be explained by an increase in stomatal resistance (Table 2), associated with partial stomatal closure caused most likely by water stress [Roberts et al., 1990].

Our analysis shows that the daytime removal of O3 by vegetation can be computed using observed stomatal resistances. Generalization of this approach to other environments is however hampered by the scarcity of data for stomatal resistances. A number of models have been proposed to predict the functional dependences of stomatal resistances on environmental variables, for various vegetation types; a particularly elaborate model has been proposed by Baldocchi et al. [1987a, b] which includes the effects of photosynthetically active radiation, temperature, vapor pressure deficit, and leaf water potential. Figure 12 shows stomatal resistances calculated using the model of Baldocchi et al. [1987a, b], adopting environmental data for the Amazon forest and model parameters for stomatal response derived by these authors for an oak forest. Water vapor deficits were computed from data on air temperature and humidity. Leaf water potential was assumed to remain high throughout the day. Computed stomatal resistances agree well with observations, except near the ground where the model does not predict sufficient stomatal area at the low ambient light intensity. The model successfully simulates the increase in resistance between morning and afternoon, indicating good representation of the effect of water deficit.
The factors regulating the flux of O₃ to the forest may be elucidated by studying the sensitivity of the O₃ flux to values for canopy surface resistance or rate of vertical transport, using the one-dimensional photochemical model of Jacob and Wofsy [this issue]. The model simulates meteorologically undisturbed conditions observed frequently even during the wet season, with diurnal growth and decay of a well-defined mixed layer. Deposition to leaves and ground is treated with the multi-layer model presented above, and vertical transport is described by a series of aerodynamic resistances extending from the ground to the top of the planetary boundary layer (2000 m). A fixed concentration is at the upper boundary adopted from observations at 2500 m for each constituent (25 ppb for O₃).

Results of model runs are summarized in Table 3. The 24-hour average O₃ flux to the canopy computed using "standard" model parameters [Jacob and Wofsy, this issue], 1.07x10⁻¹⁵ molecules cm⁻² s⁻¹, agrees well with observed values. Photochemical production and loss rates for ozone are significant throughout the column [Jacob and Wofsy, this issue] despite the very low levels of NOₓ; however the net effect of photochemistry is small due to cancellation of net production at low altitudes by net loss at higher levels. Net O₃ loss, due mainly to deposition to the canopy, is only partly balanced by supply from the free troposphere (flux at 2500 m), leading to decay of the ozone column with a time constant of about 2.5 weeks. We believe that ozone is replenished episodically by deep mixing of the troposphere in convective storms [Gregory et al., this issue], indicating an important role for deep convection in supplying ozone to the lower atmosphere.

The factors regulating the O₃ flux were assessed by imposing arbitrary changes to the values adopted for leaf area distributions and for rates for turbulent transport (see Table 3) in this model. Increasing the leaf area index by a factor of 2 increased the flux to the canopy by 12%, decreasing by a factor of 2 decreased the flux by 16%. Results were more sensitive the rate of vertical transport: increasing Rₚ by a factor of 2 throughout the boundary layer decreased the ozone flux by 30%, decreasing Rₚ by 2 increased flux by 40%. The response to Rₚ reflects changes in the concentration of ozone just above the canopy top, i.e. changes in the gradient of O₃ in the "mixed" layer. We conclude that the flux of O₃ to the Amazon forest is significantly limited by the rate of supply from the free troposphere, although the canopy surface resistance also has an effect. Note that the average concentration of O₃ in the boundary layer is regulated largely by the upper boundary condition imposed in the model, implying an important connection between O₃ deposition fluxes and global-scale processes that determine ozone concentrations in the middle troposphere.

6. CONCLUSIONS

The net ecosystem exchange of CO₂ in the tropical forest undergoes a well-defined diurnal variation driven by the input of solar radiation. A curvilinear relationship was found between solar irradiance and uptake of CO₂, with net CO₂ uptake at a given solar irradiance equal to rates observed over forests in other climate zones. Uptake during the day was on average closely balanced by release at night, with soils accounting for more than 90% of nocturnal respiration.

The carbon balance of the system appeared to be very sensitive to cloud cover on the time scale of the experiment. The global importance of carbon storage in the tropics has long been recognized...
TABLE 3: Ozone Budgets over the Amazon Forest

<table>
<thead>
<tr>
<th>NO</th>
<th>O3 flux at 2500 m</th>
<th>O3 flux at canopy top</th>
<th>Photochemical production</th>
<th>dO3/dt</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.6</td>
<td>5.9(10)</td>
<td>9.9(10)</td>
<td>-2.5(9)</td>
<td>-4.25(10)</td>
</tr>
<tr>
<td>12.9</td>
<td>6.6(10)</td>
<td>1.10(11)</td>
<td>-6.5(8)</td>
<td>-4.46(10)</td>
</tr>
<tr>
<td>14.5</td>
<td>4.9(10)</td>
<td>8.4(10)</td>
<td>-2.6(9)</td>
<td>-3.76(10)</td>
</tr>
<tr>
<td>14.0</td>
<td>2.9(10)</td>
<td>6.9(10)</td>
<td>-1.0(10)</td>
<td>-5.0(10)</td>
</tr>
<tr>
<td>13.6</td>
<td>1.0(11)</td>
<td>1.4(11)</td>
<td>2.3(9)</td>
<td>-2.77(10)</td>
</tr>
</tbody>
</table>

Results from simulations using the model of Jacob and Wofsy [1990], using values of canopy leaf area index (LAI) and aerodynamic resistances (Rg) from their standard model as well as higher and lower values of LAI. All results shown as 24-hour averages. NO and O3 concentrations represent mean values between 30 and 2000 m, in ppv and ppbv respectively. Photochemical production is given as the column integral between 30 and 2000 m, in molecules cm^-2 s^-1. Fluxes and column time derivative are also given in molecules cm^-2 s^-1. The expression 5.6(10) denotes 5.6x10^10.

With leaf area distribution (2,4,8).

With all aerodynamic resistances from the ground to 2500 m are multiplied or divided by a factor of 2.

Averaged between 30 and 2500 m.

Column loss rate between 30 and 2500 m.

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Gregory, G. L., C. H. Hodge, and E. A. Edahl, Jr., Laboratory evaluation of [e.g., Houghton et al., 1985], and present results suggest that global carbon storage might be affected by changes in insolation associated with tropical climatic fluctuations such as the ENSO.

The forest was an efficient sink for O3 during the day. A large flux was observed (2.3x10^11 molecules cm^-2 s^-1) despite low ambient concentrations (~6 ppbv) at canopy top. The high deposition velocity for O3 during the day (1.8 cm s^-1 at canopy top) appeared to reflect the large stomatal area available in the dense foliage of the tropical forest.

Rapid deposition of O3 over the Amazon forest, combined with the absence of significant net photochemical production and close coupling to the middle troposphere, suggest that the Amazon forests could be a significant sink for global ozone during the wet period (typically 9 months of the year). This sink for O3 is not observed during the dry season, because photochemical production of O3 is enhanced by higher levels of NOx, derived from higher soil emissions and from biomass burning [Crutzen et al., 1985; Jacob and Wofsy, 1988; Andreae et al., 1988]. Deforestation and colonization of the Amazon Basin could dramatically alter regional, and perhaps global, budgets for O3, by simultaneously decreasing the potential for deposition and increasing rates for photochemical production.

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