

OZONE MEASUREMENTS IN THE TROPOSPHERE OF AN AMAZONIAN
RAIN FOREST ENVIRONMENT

V. W. J. H. Kirchhoff

Instituto de Pesquisas Espaciais, Ministério da Ciência e Tecnologia
São José dos Campos, São Paulo, Brazil

E. V. Browell and G. L. Gregory

NASA Langley Research Center, Hampton, Virginia

Abstract. Ozone concentration profiles from the ground to above the stratospheric peak have been obtained, for the first time, in an equatorial rain forest environment near Manaus (3°S 60°W). We have described in detail the average ozone profile in the troposphere, the observed variations, and a major biomass-burning event that occurred near the end of the experiment. The average ozone mixing ratio at 1000 mbar was 13 parts per billion by volume (ppbv), increasing to 45 ppbv at 500 mbar. From 500 mbar upward, in the free troposphere, the mixing ratio stays roughly constant. The peak O₃ concentration occurs at 20 mbar (26.6 km) reaching 4.4×10^{12} molecules cm⁻³. The values in the troposphere are much lower than results from the low-latitude Atlantic coast. The average gradient below 1000 m in Manaus is twice as large. The diurnal variation is strongest near the surface, decreasing upward. Close to the surface the ozone gradient is largest in the early morning, decreasing toward noon. A significant pollution (burning) event, near the end of the experiment, was responsible for large changes in ozone concentrations, which increased first in the lower troposphere but eventually reached the free troposphere as well.

1. Introduction

The ozone data to be described were obtained in a tropical environment. Tropospheric chemistry in the tropics is more active, as described below, and is important to the global atmosphere in many aspects, for example, to the long-lived constituents which can be transported via the Hadley cell to higher latitudes.

1.1. Importance of Sampling Region

The equatorial rain forest of the Amazon Basin is the largest of its kind on Earth. On Brazilian territory alone, it occupies an area of about 3 million square kilometers and is therefore, in addition to its strong regional influence, important on a global scale as well. This Amazonian environment occupies a large area of low latitudes. Here the driving force of atmospheric chemistry, ultraviolet radiation, is much larger than elsewhere, and one can anticipate much stronger production and loss

processes. In the spectral range between 300 and 305 nm, for example, the UV intensities are expected to be about 75% more intense in the tropics, assuming typical observed total ozone contents of 0.35 atm cm for mid-latitudes, and 0.28 atm cm for low latitudes. Thus the driving force for atmospheric chemistry should be stronger. In addition, the direct sunlight power density is obviously also larger in the tropics, and one may expect an atmosphere that is much more active in terms of vertical motions.

1.2. Ozone in the Tropics

There has been some progress in recent years toward understanding ozone in the tropics [Fishman et al., 1979, 1986; Kirchhoff et al., 1981, 1983; Crutzen, 1985; Crutzen et al., 1985; Delany et al., 1985; Sanhueza et al., 1985; Logan and Kirchhoff, 1986], but many basic interesting aspects remain unexplored (for example, UV measurements are unavailable, as well as attenuation studies within the forest canopy) and many questions remain unanswered (for example, climatological aspects, longitudinal gradients, etc.).

Measurements of ozone concentrations over the Amazon forest were first performed in 1979 and 1980, during aircraft expeditions in the dry season, with a special interest in studies of biomass burnings [Crutzen et al., 1985; Delany et al., 1985]. Higher concentrations of ozone were reported over the cerrado region of central Brazil, in the mixing layer. The present paper adds to that original data set, reporting also about local time variations and perturbations, in addition to the average profile.

Ozone interacts with many constituents of the atmosphere. One of the most reactive molecules of the troposphere is the result of ozone photolysis, the hydroxyl radical OH, which has its production favored in the tropics because of larger UV intensities and larger water vapor concentrations [Crutzen, 1985]. This molecule will start important oxidation chains, for example, the oxidation of methane (CH₄), carbon monoxide (CO), and isoprene (C₅H₈). These processes may, under certain circumstances, produce ozone in the presence of the nitrogen oxides NO and NO₂.

The rain forest of the tropics may represent a source for several constituents of the atmosphere, some of which are ozone precursors (CO, CH₄, NO). A large number of nonmethane hydrocarbons (NMHC) are produced in the forest [Zimmerman et al., 1978], especially isoprene, which is directly involved in the photochemistry

Copyright 1988 by the American Geophysical Union.

Paper number 88JD03490.
0148-0227/88/88JD - 03490\$05.00

of CO and O₃ [Rasmussen and Khalil, 1988]. The plains flooded by the large Amazon River and its tributaries are expected to be an important source for CH₄ [Harriss et al., 1982; Crill et al., 1988], while the forest soil may be a sink for CH₄ [Keller et al., 1983].

It has been shown that NMHC are reactive species [Roberts et al., 1983; Brewer et al., 1984; Levine, 1984; Greenberg et al., 1985; Rasmussen and Khalil, 1985], which may be responsible for the destruction of ozone [Killus and Whitten, 1984; Crutzen et al., 1985]. On the other hand, larger than expected emission rates of nitrogen oxides (N₂O, NO) have been measured in the forest area [Keller et al., 1983; Anderson and Levine, 1986; S. C. Wofsy, unpublished preliminary report on Amazonian atmospheric studies, 1984]. Thus the oxidation of NMHC (in particular C₅H₈) and resulting secondary products, including CO, in the presence of NO_x, could photochemically produce ozone [Chameides and Walker, 1973, 1976; Fishman et al., 1979; Crutzen, 1979; Fehsenfeld et al., 1983], in which case, the forest would act as a source of ozone. Besides the natural emissions from the forest, biomass burning in the cerrado or in forest areas would obviously represent additional sources for ozone.

The time constants involved in these ozone generation processes vary considerably, depending on the relative concentrations of some key constituents. In clean air environments not influenced by surface vegetation, the lifetime of ozone is quoted at about 2 weeks [Logan, 1985]. In the presence of biomass burnings, the production time constant may be of the order of hours [Delany et al., 1985; Fishman et al., 1986], and in the equatorial rain forest the whole diurnal variation at the ground may be the result of photochemical production [Jacob and Wofsy, 1988].

Ozone is destroyed when brought in contact with solid surfaces, owing to its high reactivity. This makes the ground a sink for ozone; a downward flux of ozone is always penetrating the ground. The more effective the sink, the larger the flux. Lenschow et al. [1982]

noticed an increase of the downward ozone flux over a pine forest, and Gregory et al. [1986] also described an Amazonianlike environment as an ozone sink. This paper also gives evidence showing larger ozone fluxes in the measurement area near Manaus.

1.3. Aim of Work

This work is the result of a large bi-national field expedition to the Amazon forest, which took place in July-August of 1985 with the participation of some 50 Brazilian and American scientists. The main objective was to study the lower atmosphere of the equatorial rain forest, with emphasis on the atmospheric chemistry. The expedition was carefully planned [McNeal et al., 1983] and was called the Amazon Boundary Layer Experiment (ABLE). The first expedition to Manaus was named ABLE 2A. Data were obtained from the ground and on board NASA's Electra aircraft. The measurement campaign lasted for about 30 days.

This paper describes ozone measurements in the troposphere above the equatorial rain forest near Manaus (3°S, 60°W). Other papers describe surface ozone measurements, and ozone distributions across the Amazon Basin [Kirchhoff, 1988; Gregory et al., 1988]. The ozone profiles of this analysis have been obtained from the launching of 14 ozonesondes near Manaus. In addition, profiles obtained on board NASA's Electra aircraft, near the site of the ozonesonde launches, will be used to complement our analysis.

2. Results

A total of 14 ozonesondes of the electrochemical concentration cell (ECC) type (see Table 1) were launched in the period from July 19 to August 2 from the Ducke forest preserve, located some 30 km north of Manaus. The ozonesonde is a chemical sensor which produces an electrical current proportional to the ozone concentration of the air sample that is bubbled through the cathode/anode assembly of the sensor [Komhyr, 1969; Barnes et al., 1985]. The sensor is coupled to a normal radiosonde and launched

TABLE 1. Ozone Soundings in Manaus During the 1985 ABLE Campaign

Date	Time of		Burst		Notes	
	Launch, UT	Burst, UT	Height, km	Pressure, mbar		
1	19 JUL 85	1358	1551	35.5	5.2	Morning
2	22 JUL 85	1556	1736	34.2	6.3	Morning
3	23 JUL 85	1509	1634	30.2	11.4	Morning
4	24 JUL 85	1900	2043	38.4	3.4	Afternoon
5	25 JUL 85	1345	1525	36.7	5.2	Morning
6	26 JUL 85	1516	1702	35.5	5.1	Morning, Natal
7	27 JUL 85	1337	1519	35.4	5.2	Morning
8	29 JUL 85	2036	2221	35.5	5.2	Afternoon
9	30 JUL 85	2030	2228	34.6	5.7	Afternoon
10	31 JUL 85	0001	0158	33.2	7.1	Night
11	31 JUL 85	2050	2250	31.0	10.0	Afternoon
12	01 AUG 85	1315	1514	35.3	5.5	Morning
13	01 AUG 85	1952	2151	36.9	4.4	Afternoon
14	02 AUG 85	1940	2126	35.8	5.2	Afternoon

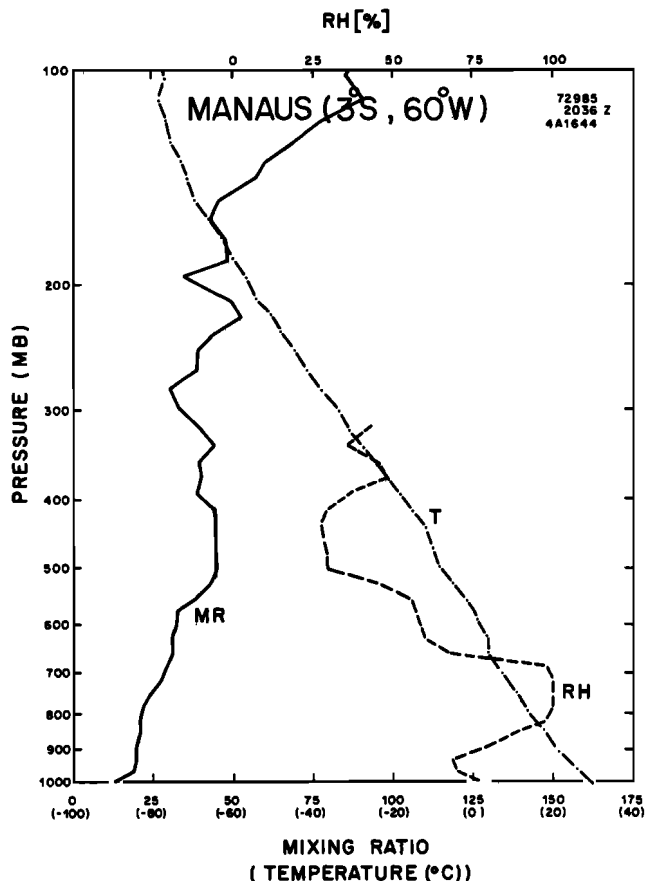


Fig. 1. Typical result of an ozone sounding in the troposphere, showing temperature, T; O_3 mixing ratio, MR; and relative humidity, RH.

on a slightly larger balloon. A ground-based receiver records all radiosonde parameters plus the in situ ozone measurements.

Measurements in the troposphere and stratosphere are normally recorded, but the emphasis in this paper is on the troposphere. In the stratosphere it is interesting to note that of the 14 soundings a total of 10 reached 6 mbar (34.7 km), two went up to 5 mbar (36 km), one sounding reached the 4-mbar level (37.4 km), and one reached 3.5 mbar (38.3 km). The stratospheric peak is rather broad, with maximum concentrations of $4.4 \times 10^{12} O_3$ molecules cm^{-3} at 20 and 25 mbar (between 25.1 and 26.5 km). It should also be noted that each sonde was individually calibrated in the Wallops Island laboratory (courtesy of Arnold Torres, NASA) to compensate for the lower pump efficiency of the commercial sondes at higher altitudes [Torres and Bandy, 1978]. The same launching technique used at Natal [Logan and Kirchhoff, 1986] was used for the forest soundings.

A normal sounding consists basically of temperature, relative humidity, and ozone partial pressure data. A typical sounding with results between 1000 and 100 mbar is shown in Figure 1, where T is temperature, RH is relative humidity, and MR is the ozone mixing ratio in parts per billion by volume (ppbv). This data was obtained from sonde 4A-1644, flown on July 29, 1985, at 1636 LT. The example in Figure 1 shows an ozone

mixing ratio roughly increasing at a constant rate from the ground to about 500 mbar staying roughly constant above this level, but with considerable structure in the free troposphere. The temperature does not show much variability from day to day, contrary to the relative humidity, which shows large variations. The accuracy and precision of the ECC sensor have been analyzed by Torres and Bandy [1978], Barnes et al. [1985], and Hilsenrath et al. [1986].

2.1. Average O_3 Profile

A simple average for the 14 Ducke ozonesonde soundings is shown in Figure 2. The horizontal bars represent the standard deviation from the mean. Also shown in Figure 2, for comparison, is the Natal average. The Natal (6°S, 35°W) data is part of a comprehensive data base which includes over 150 ozone soundings started in 1978 [Kirchhoff et al., 1981, 1983; Kirchhoff 1984; Logan 1985; Logan and Kirchhoff, 1986]. A total of 11 soundings were available for the same short period of the year as the Ducke data. The average temperature profiles for Ducke (dashed curve) can also be seen in Figure 2, showing the tropopause at about 100 mbar (16.5 km). The data have been plotted at selected pressure levels, shown on a log scale. Note that the corresponding height levels are shown on the right-hand scale which is not linear.

The vertical structure in the ozone data is similar at the two stations. In the atmospheric layer between the surface and about 500 mbar, or 5.9 km, the ozone mixing ratio increases at a relatively constant rate of approximately 6 ppbv km^{-1} . For the average Ducke profile the mixing ratio is about 13 ppbv at the surface and 45 ppbv at 500 mbar (5.9 km). Above 500 mbar the ozone mixing ratio stays roughly constant, up to about 200 mbar (12.4 km). Above 200 mbar the transition from tropospheric to stratospheric ozone takes place, and therefore the large gradients of Figure 2. Several sublayers can be identified with measurements of finer resolution.

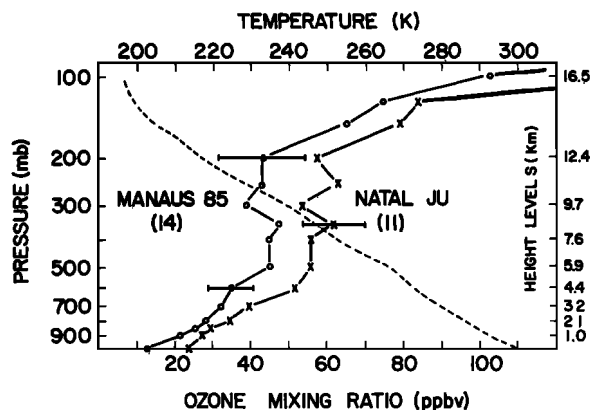


Fig. 2. Average tropospheric ozone profile measured at Manaus (and Natal, for comparison). A total of 14 soundings were performed at Manaus. For the same time period of the Ducke preserve data, 11 soundings at Natal were available. The dashed line shows the average temperature profile.

These layers and the ozone behavior in them, are discussed in detail in the companion papers.

The lower ozone densities shown by the Ducke data in Figure 2, in comparison with the Natal data, seem to be the consequence of the stronger sink role of the forest area, as described in papers by Kirchhoff, [1988], Gregory et al. [1988], and Browell et al. [1988]. Close to the surface, the mixing ratio gradient for Ducke is, in fact, more than twice as large as that for Natal. This gradient, however, is time dependent, as shown partly by the surface ozone data and also by the aircraft O_3 data [Gregory et al., 1988]. Stronger gradients are seen in early morning, as compared to the noon profile.

2.2. Variability

Variations of the ozone mixing ratio have been observed on time scales of hours and days. There is a strong diurnal variation at the surface [Kirchhoff, 1988], with decreasing intensity at higher altitudes, observed by the sondes and by the airplane measurements [Gregory et al., 1988]. It appears that above about 900 mbar (1000 m) the amplitude of the diurnal variation is less than 10% of the variation at the surface.

The time distribution of our soundings is shown in Figure 3, in the upper panel. There are eight soundings representative of the morning period (including the nocturnal case) and six launchings were made in the afternoon period. Obviously we do not have enough data for a precise statistical analysis, but the available data seem to be consistent in showing lower concentration gradients in the afternoon period. The average gradients for these two periods are shown in the lower part of Figure 3, where the morning gradient is equal to $10.5 \text{ ppbv km}^{-1}$ and the afternoon gradient is 6.3 ppbv km^{-1} . The gradients are shown relative to a normalized mixing ratio at 1 km.

Typical variability from flight to flight is shown in Figure 4. The soundings launched on July 30 (set A) and August 1 (set B) were separated by only a few hours. The ozone mixing ratio is shown as a function of pressure. For July 30 the dots show a sounding at 1630 LT (2030 UT) and a

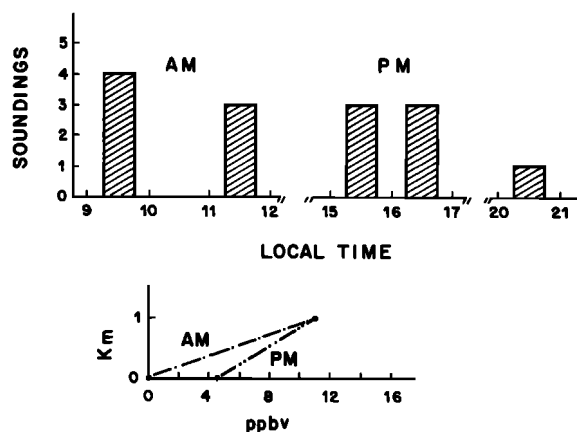


Fig. 3. Time distribution of the soundings and profiles obtained for the morning and afternoon periods.

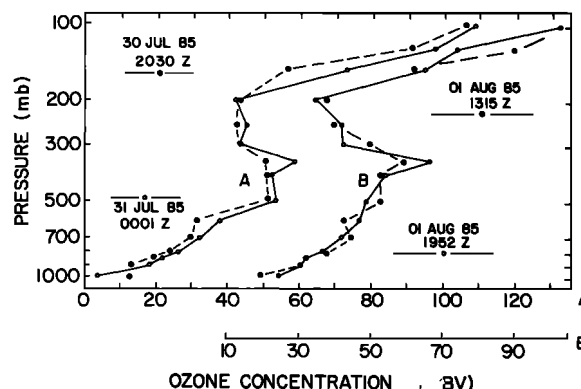


Fig. 4. Comparison of ozone soundings in the daytime for August 1 and during the nighttime on July 30.

nocturnal case made at 2001 LT (0001 UT). A morning sounding at 0915 LT (1315 UT) and the subsequent afternoon launch of 1552 LT (1952 UT) are also shown in Figure 4. This should give an idea of the variability of the measurements. For July 30, at night, and for August 1, in the early morning, the mixing ratio gradient in the mixed layer is much larger than that observed closer to midday. Note that, for simplicity, only a few points are shown in Figure 4, but many more were actually sampled.

The day-to-day variability is shown in Figure 5 in terms of the ozone concentration integral in the troposphere, between 1000 and 100 mbar. This tropospheric abundance corresponds to about 10% of the total ozone column content. Except for the values obtained in August, the day-to-day variability of tropospheric ozone content in July was not very large, only about 1 in $7.3 \times 10^{17} \text{ molecules cm}^{-2}$. This was a period of very clean air, especially in the first 20 days of July, as can be deduced from several meteorological and chemical variables. This picture changed completely in the first week of August. Many chemical constituents that were monitored during ABLE 2A showed concentration increases, for example, NO [Torres and Buchan, 1988], CO [Sachse et al., 1988], and several hydrocarbons (R. A. Rasmussen, private communication 1986) as well as ozone concentrations at the ground [Kirchhoff, 1988] and the present results in the troposphere.

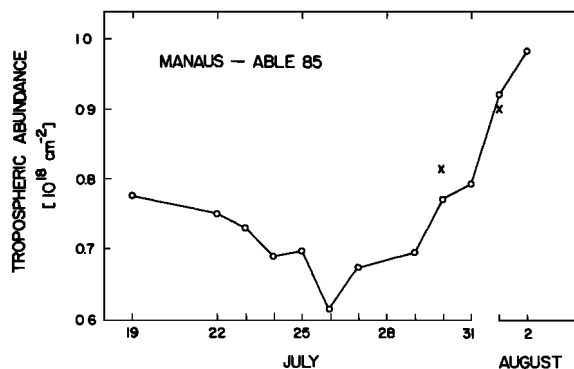


Fig. 5. Time evolution of ozone concentrations integrated through the troposphere.

2.3. Biomass-Burning Event

A number of agricultural fires and associated biomass burnings were seen in satellite images over equatorial Brazil [Setzer and Pereira, 1986] in early August. As shown, ozone concentrations increased and higher levels of NO and CO were also reported.

It is believed that tropospheric ozone may originate from the stratosphere [Junge, 1962] and that the injection of stratospheric ozone into the troposphere occurs in sporadic bursts [Danielsen and Mohnen, 1977; Crutzen, 1979; Browell et al., 1987]. It has also been recognized, more recently, that chemical activity in the troposphere can, in fact, introduce significant sources and sinks which in turn affect local concentrations [Chameides and Walker, 1973, 1976; Fishman and Crutzen, 1977; Crutzen, 1979; Crutzen et al., 1985; Logan and Kirchhoff, 1986]. One may question therefore whether the observed ozone increases are introduced from the stratosphere or produced locally in the troposphere. It should be noted, however, that the Manaus region is not known as a subsidence area, and therefore stratospheric injections should be unlikely.

A closer look at our data shows that the ozone density increase was not limited to the mixing layer or the higher levels of the boundary layer, but also occurred in the free troposphere. Figure 6 shows five ozone profiles obtained after July 25. On July 26 the free troposphere had the lowest O_3 concentrations. On July 29 the largest increase occurred at 400 mbar (7.6 km) and 500 mbar (5.9 km). On July 30 the increase is even larger at 400 and 500 mbar, while not much change can be seen below 600 mbar (4.4 km). A large increase below 400 mbar can be seen by August 1, followed by a strong increase above the 500-mbar level the next day, August 2.

To further investigate the origin of the ozone increases in the troposphere, we show in Figure 7 the tropospheric ozone content and its time evolution, divided in three layers. The lower layer, from 1000 to 600 mbar, a middle layer from 600 to 300 mbar, and an upper layer, from 300 to 100 mbar. The ordinates show relative ozone

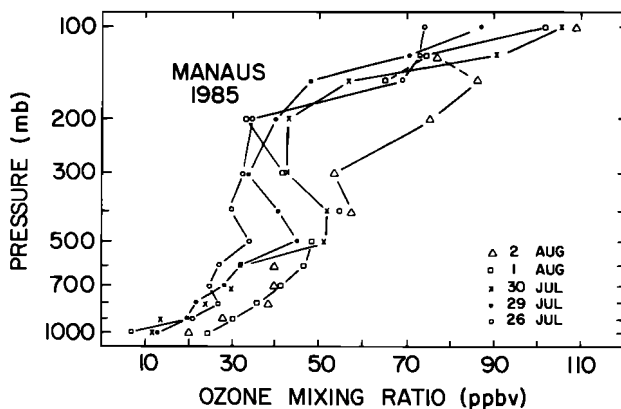


Fig. 6. Time evolution of ozone concentrations for selected profiles to show the changing of the ozone concentrations, presumably due to biomass-burning effects.

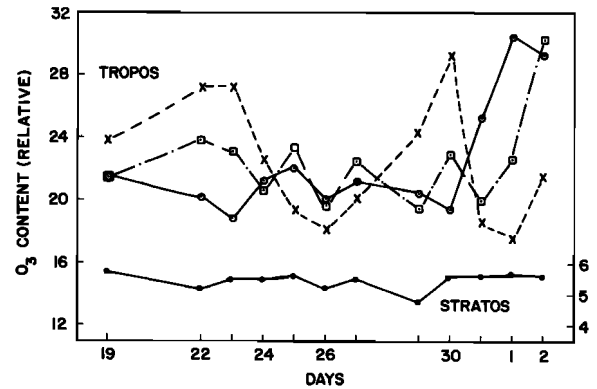


Fig. 7. Relative ozone content in three tropospheric layers defined between 1000 and 600 mbar (dots in circles), 600 and 300 mbar (crosses and dashed curve), and 300 and 100 mbar (dots in squares). Also shown is the stratospheric abundance.

contents in these layers. It can be seen that the increase in ozone occurs first in the middle layer, then in the lower layer, and finally in the higher layer. The time delay for changes in adjacent layers is of the order of 1.5 days. It seems therefore that the ozone increase did not start in the region closest to the tropopause, as one would expect for stratospheric injections.

Since all ozonesondes launched during this experiment have reached heights equivalent to 10 mbar or higher, it is possible to follow the variation of the stratospheric ozone content, that is, the ozone concentration integral from 1000 to 10 mbar. The variations are rather small, that is, less than one standard deviation (except the minimum on July 29) and almost constant during the tropospheric high at the end of the period. The tropospheric variations, instead, are at least as large as two standard deviations. From the examination of ozone and moisture variations, it is clear that there is no negative correlation, which would indicate subsidence of air masses.

The ozone concentration increase in the troposphere can also be observed in the ozone data collected on board the NASA aircraft. We have analyzed those profiles collected near the Ducke site. A total of four profiles with data below 3.5 km were available close to the forest preserve from the collection of DIAL (Differential Absorption Laser) data (for a description of the lidar technique and details of the measurement procedures, see Browell et al. [1988]). We do not have an ideal time sequence of profiles to detect a well-defined trend, but it is apparent that profiles obtained before July 30 show lower concentrations, as shown by the plot of Figure 8a. The numbers close to the profiles indicate the last days of July or the first days of August of 1985. Figure 8b shows five profiles from aircraft spirals made close to the Ducke site when ozone concentrations were measured by a chemiluminescent technique [see Gregory et al., 1988]. Again, profiles before July 30 show less ozone than those obtained afterwards. This tendency is consistent with the other data sets.

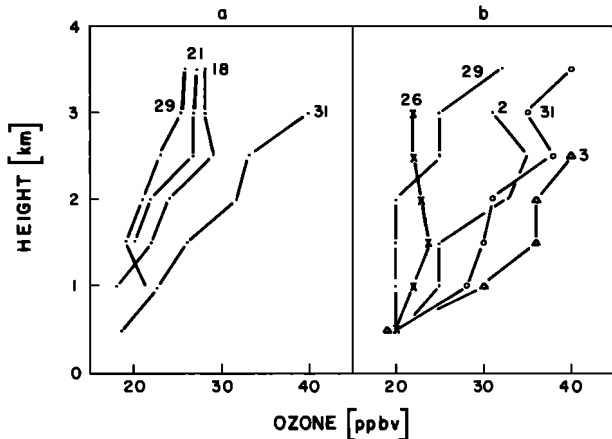


Fig. 8. (a) Profiles obtained via the DIAL instrument and (b) profiles measured by a chemiluminescent technique, both on board the NASA aircraft. They illustrate much higher concentrations of O_3 in the troposphere after July 30.

3. Discussion

3.1. Average Profile and Variations

The mixing layer is generally defined as the lower layer of the troposphere, where mixing is so strong that long-lived constituents would have a constant mixing ratio with height. This feature is actually used by Kirchhoff [1988], Browell et al. [1988], and Gregory et al. [1988] to define the mixing layer depth, close to 1.6 km. This threshold cannot be well identified in the ozone soundings. In terms of an average profile, however, a much more consistent threshold occurs at about 500 mbar (5.9 km). Below this height the mixing ratio of ozone decreases, whereas above this level the mixing ratio stays roughly constant.

Ozone concentrations in the whole troposphere of the Atlantic coast show a very strong seasonal variation. There is a factor of 2 between the April-May minimum and the September-October maximum [Logan and Kirchhoff, 1986]. It is therefore pertinent to ask, when comparing the Duce data to the Natal data, if we are comparing the same seasonal periods. This is not an easy task if we take into account the very different circulation patterns close to Natal and Duce. While Natal is practically always in a regime of atmospheric subsidence, Duce is usually close to the upward moving branch of the Walker circulation cell.

The effect of vertical motions on the concentration of ozone has been observed previously by Wolff et al. [1977], while Kelly et al. [1980] noticed very low levels of NO_x coincident with subsidence. The mean precipitation rates for the area of Manaus and Natal show an in-phase relationship. But owing to the prevailing wind direction in the lower troposphere, which is easterly, any air mass from central Brazil should reach Manaus before it reaches Natal. This should cause a phase delay in the ozone concentration seasonality between Manaus and Natal, even if the source for the ozone seasonal increase is the same for both

locations, namely, burnings in the savannah regions of central Brazil. Since the minimum average precipitation rate of the savannah region occurs during June-July-August (for example, for Cuiabá (16°S, 57°W) the average is less than 1 mm day⁻¹, this period (with the addition of a small time delay of perhaps a few days) could well represent the season of maximum ozone in Manaus. This result would imply, of course, that the small concentrations of ozone measured at Duce during this experiment may be expected to be even smaller during the other seasonal periods.

Besides the comparison between the Natal and Duce averages there was one occasion at which a nearly simultaneous sounding was made. This is shown in Figure 9. For July 26 the sounding at Natal took place at 1310 UT, and at Duce the sounding was at 1516 UT. For this day, the difference in ozone concentrations between the two stations was not very large in the boundary layer but was considerable in the free troposphere. At 600 mbar, for example, the concentration at Natal was 56 ppbv, when it was 29 ppbv at Duce. There is a significant difference in the free troposphere, with Natal showing more ozone than Duce. It may be argued that the ozone concentrations in the free troposphere at Duce should be smaller, as explained later, but large day-to-day variations have also been observed at Natal [Logan and Kirchhoff, 1986], and therefore a sporadic event can not be ruled out completely for the Duce data. However, the comparison between the averages at both sites suggests that indeed the concentrations at Natal should be expected to be larger. One might expect that the whole troposphere, boundary layer, and free troposphere should have less ozone in Amazonia, owing to the much more active role of meteorological updrafts and downdrafts. These would force faster exchange and stronger mixing, with more effective contact of the air with the ground, thus representing a much stronger sink than other environments.

3.2. Vertical Fluxes

One of the major goals of the Manaus expedition was to obtain vertical fluxes of chemical constituents. It is worthwhile therefore to discuss ozone fluxes in some detail.

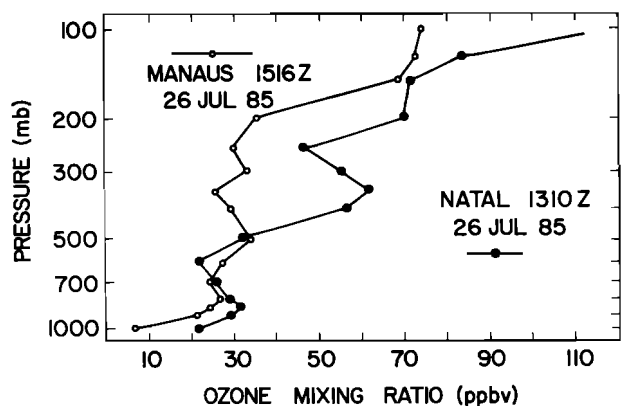


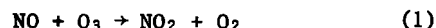
Fig. 9. Comparison of a simultaneous ozonesounding at Natal and Manaus.

The vertical ozone flux in the lower troposphere has a strong turbulent nature, which means that on very short time scales the flux may be upward; while at other short time periods it may be directed downwards. The net effect of this turbulent flux, however, is a downward average mean. This is the value that one wants to determine and possibly use in homogeneous modeling, where the downward flux would have its nature closer to a laminar flow. This characteristic is explored by the eddy correlation technique, which measures ozone concentrations and vertical velocities at very short time intervals in order to determine the vertical flux [Wesely et al., 1978, 1981; Lenschow et al., 1981, 1982; Droppo, 1985]. The vertical flux of ozone has been estimated in the past from the measurements of ozone profiles and by assuming that the eddy diffusivity for ozone is equal to the eddy diffusivity for momentum [Regener, 1957; Junge, 1962], when values between 0.87 and 2.5×10^{11} ozone molecules $\text{cm}^{-2} \text{s}^{-1}$ were obtained.

The interest in establishing the vertical ozone flux is to know the strength of the surface sink and to understand how the uptake of ozone by the soil or vegetation operates. It is known that large fluxes incident on crops can be harmful, with crop losses occurring above certain thresholds [Heck et al., 1982]. The mean ozone flux is always directed downwards which defines any type of surface as a sink for ozone. But different types of surface can destroy different amounts of ozone and, to complicate things, there is a temporal variation in flux as well. This is shown in the field campaign of Wesely et al. [1978], who measured the ozone flux over a maize field using eddy correlation. Flux values between 2.5 and $15 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ were measured, but the average was below $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. It is interesting to note that the ozone flux seems to be quite reduced over wet surfaces (water, snow [Wesely et al., 1981]), when fluxes are below values of $1.2 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. On the basis of these results we may not, however, expect smaller ozone fluxes in the Manaus area during the next ABL mission, which is planned to take place in the wet season, because the effective surface area is in fact represented by the plant foliage and the plant growth activity is expected not to be much different than it was for the present experiment (D. H. Lenschow, private communication, 1986).

In what follows we describe two different methods to calculate the ozone flux, independent from each other. The vertical ozone flux entering the surface can be calculated from the simultaneous NO and O_3 profile measurements, made in the lower 30 m. The O_3 profile data close to the ground were obtained in collaboration with Kaplan et al. [1988], who describe the method in detail. If one can assume that there is no local production of NO in this shallow layer, as expected at night, the loss of NO by chemical reaction with O_3 , integrated over the layer, should equal the upward flux of NO from the ground. The integral should be evaluated from ground to infinity, but, since the NO profile has such a strong gradient (see Figure 7, of Kirchhoff [1988]) the approximation used should be adequate. Since the concentration profiles of

both O and NO were measured, knowing the reaction rate k , for the reaction



to be $1.8 \times 10^{-14} \text{ cm}^{-3} \text{ s}^{-1}$, the NO emission is calculated to be, for an average of four measurement profiles, equal to $5.0 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$. This is the number of NO molecules necessary to be emitted from the ground to restore those molecules removed by reacting with ozone. Knowing the NO flux, we calculate the O_3 flux by first calculating K , the eddy diffusion coefficient, commonly defined in the diffusion equation [Hunten, 1975; Droppo, 1985]

$$\phi = -K \left[\frac{dn}{dz} + \frac{n}{H} \right] \quad (2)$$

where ϕ is the vertical flux, n is the diffusing species density, H is the atmospheric pressure scale height, and z is height. In the case of large gradients, the derivative term of the above equation is much larger, and therefore the coefficient K may be obtained by dividing the NO flux by the NO density gradient, which gives $K = 3.3 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$. Since the ozone profile is also known, we use again the diffusion equation to find the ozone flux: $\phi(\text{O}_3) = 1.1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Note that it is not necessary to know the sources or sinks for ozone to obtain this flux. It is also important to note that this O_3 flux is much larger than the NO flux emitted from the surface, and therefore the downward ozone flux that enters the ground is not triggered by the NO + O_3 reaction alone. It does not mean, on the other hand, that this reaction is unimportant in producing, for example, the observed diurnal variation. (Wofsy has reconsidered his NO values, lowering the flux by a factor of 2; see Kaplan et al. [1988]).

It is interesting to note that the values just obtained for K and ϕ do vary from place to place and, apparently, in time as well [Lenschow et al., 1982]. Precise measurements of these parameters by Droppo [1985] give for K averages of 4.27×10^3 and $6.98 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ for 2 days in 1982, at a height of 2.05 m. Our calculation of $K = 3.3 \times 10^3$ seems therefore to be of the correct order of magnitude. The same cannot be said about the ozone flux. Droppo finds much smaller values for his field experiment in Illinois, the ozone flux being of the order of only $3.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. This is of the same order of magnitude as values previously cited, at least 3 times smaller than the Ducke flux. It should be noted that Lenschow et al. [1982], using eddy correlation techniques to measure the vertical ozone flux, found a large increase of this parameter when their instrument was flown over a pine forest area.

The second method to obtain the flux will estimate the ozone sink strength at the surface, based only on the observations of the ozone data. Our results, as well as those of Galbally [1968], Lenschow et al. [1981], Broder et al. [1981], and Gregory et al. [1988], show that the diurnal variation of the ozone mixing ratio has a tendency to be strongest at the surface, becoming smaller upwards, until it may be considered

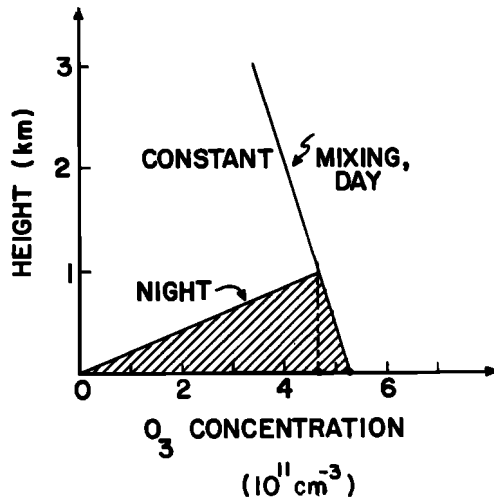


Fig. 10. Sketch of the amount of ozone that must be removed (added) by the vertical ozone flux.

negligible at about a height of 1 km. It is observed that the largest variation in terms of removal or addition of ozone occurs near dusk or dawn.

The vertical flux of ozone close to the surface may have a considerable diurnal variation as well [Wesely et al., 1978], being maximum around noon and approaching zero at night, when strong inversion layers are active. The largest flux divergence, however, must take place around dusk and dawn, when the largest variations in ozone concentration are observed. We will use this argument to estimate the sink strength. Transforming the average measured mixing ratio information into number densities, the change between nocturnal and diurnal profiles is as shown sketched in Figure 10, where the hatched area corresponds to the amount of ozone that must be removed between the daytime and the nighttime regions. The question we want to address is how strong must the surface sink be in order to remove the hatched area ozone content of Figure 10. With typical values observed at Ducke, as shown in Figure 10, and assuming that the transition from day to night is accomplished in about 3 hours (a reasonable average on the basis of our observations), the corresponding removal rate should be $2.4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Thus again, we arrive at a sink strength value of the order of $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$.

3.3. Biomass Burning

The effect of biomass burnings has been investigated in detail by Crutzen et al. [1985]. There are numerous small agricultural developments in the Manaus area, but large areas in the north of the State of Mato Grosso, south of Manaus, are among the ones most subject to forest clearing for agricultural developments. The normal procedure for disposing of the cut vegetation is to burn it. Extremely large areas can be set on fire at times and can be identified from satellite images. The heat produced by these fires is likely to start a localized dry convection cell. Gases produced in these fires [Crutzen et al., 1979; Delany et al., 1985] can

therefore be added to high levels in the atmosphere.

From our observations of several burning events, it appears that the effect of the fires has a development that can be divided in two stages. In the first stage, when the dry vegetation is first set on fire, there is an enormous amount of heat released, which starts an upward draft cell through which the heated air ascends through the troposphere. It is uncertain how high this heated air can reach in the troposphere. (Normal dry convection is estimated by Chatfield and Harrison [1976] to reach 2-3 km). For cells generated by intense fires, this height could perhaps reach much higher levels in the free troposphere, but it probably depends on the intensity of the fire and other meteorological conditions. In any case, this first stage of the fire development should be responsible for the direct injection of burning products into the higher levels of the troposphere. In the second stage of the fire development, the events continue at a much slower rate. The extreme heat liberated in the first stage has dissipated. The burning is characterized now by the production of dense smoke clouds, which can no longer ascend to very high levels but which can be transported horizontally for long distances, since their lifetime is rather long. It appears that this sequence of events has been observed at Ducke with our ozonesonde measurements, as shown in Figures 6, 7, and 8.

The ozone concentration increase described earlier seems to indicate that the first perturbation of the background ozone profile over Ducke, noticed in the middle layer (lower free troposphere), is the result of pollutants injected directly into the free troposphere over the areas of strong heat sources, possibly by direct vertical upward injection of the dry convection type. Winds of this height region were able to transport the higher ozone concentrations to the Ducke preserve site before the major plume of the boundary layer did, reaching the preserve only on August 1 and later reaching also the much

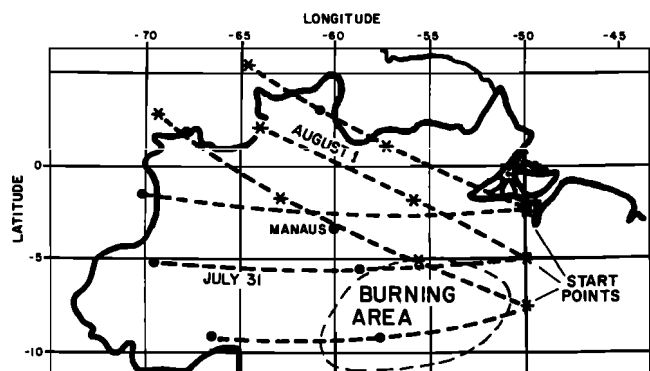


Fig. 11. The northern map of Brazil showing the Manaus area and air mass trajectories in the mixed layer. The curves with black dots are representative for the initial "clean" period. The curves with stars occurred starting August 1 and show the transport of biomass-burning products to the Manaus area.

higher levels of the free troposphere on August 2, through mixing in the convective cloud layer. This evidence seems to indicate that gases from intense biomass burnings can not only enter those atmospheric layers affected by local meteorology, but can in fact penetrate the free troposphere.

It must be added that an alternative cause for the O_3 concentration increase may have been a completely different mechanism, that is, direct stratospheric injection, which our one-dimensional observations could not see. This possibility, however, seems unlikely, since the Manaus area is a region known for ascending air motions, as mentioned earlier. Besides, a concentration increase was also seen in other constituents, especially CO [Sachse et al., 1988] and NO [Torres and Buchan, 1988], which seem to point to a burning origin.

In Figure 11 we show the northern part of the map of Brazil, between longitudes -45° and -75° and latitudes $+5^\circ$ to -10° . There are basically two points of interest: the city of Manaus (and Ducke preserve), at $3^\circ S$, $60^\circ W$, and the so-called burning area, identified from satellite images, where the largest concentration of biomass burnings occurred. This area is sketched around $8^\circ S$, $55^\circ W$.

Figure 11 shows air mass trajectory calculations for two periods, one starting July 31 and the other starting August 1 (courtesy A. Setzer). These trajectories have been calculated from interpolations of radiosonde data and are representative of mixed layer air. Calculations start at longitude -50° and three latitudes: -2.5° , -5.0° , and -7.5° . The three curves, showing basically east-west trajectories, have been calculated starting at July 31, at 1200 UT. The distance between two black dots corresponds to a time interval of 12 hours. The trajectory stretches from east to west. This is the usual trajectory of mixing layer air in this region of Brazil (A. Setzer, private communication, 1986). During the first two thirds of the Ducke experiment, this kind of trajectory was dominant; that is, air from the burning area (sketched in Figure 11) did not reach Manaus.

A very different air mass trajectory is obtained starting the next day, August 1. With starting points exactly the same as in the previous case, the air mass trajectories now develop from the southeast to the northwest. The distance between stars corresponds to a 12-hour travel time, as before. From Figure 11 it is clear that now, products from the burning area can be brought directly to the Manaus and Ducke area, in agreement with our previous discussion.

4. Conclusion

Ozone concentrations were obtained in the troposphere and stratosphere of Ducke forest preserve in Amazonia, from 14 ozonesonde launches. These ozone data are the first set of in situ tropospheric-stratospheric results obtained in the Brazilian rain forest. We have described in detail the average ozone profile in the troposphere, the observed variations, and a major biomass-burning event that occurred near the end of the experiment.

The Amazonian concentrations are smaller than those obtained at another low-latitude station,

but the features of the ozone profile are similar. The average profile shows an increase in mixing ratio up to 500 mbar, at a rate of about 6 ppbv km^{-1} , and then an approximately constant mixing ratio extends up to 200 mbar. The combined effect of a larger effective surface area, represented by the abundant foliage, and larger mixing, represented by the stronger convective activity in the Manaus area, produces a more efficient surface sink for ozone, which is probably responsible for a tropospheric ozone content that is smaller at Ducke than at Natal.

Toward the end of the experiment an increase of the ozone concentration was observed. After examination of individual ozone profiles and dividing the troposphere in three layers, it appears that the concentration increase did not come from above, that is, from the stratosphere. The increases start in the middle and lower layers of the troposphere, eventually reaching also the upper troposphere. This conclusion is in direct agreement with air mass trajectory calculations and simultaneous increases in CO and NO. While a sporadic stratospheric O_3 injection cannot be ruled out completely, given the one-dimensional character of our observations, it seems much more probable that the O_3 increase was produced photochemically, following a large biomass-burning event.

We calculate the downward ozone flux to be of the order of $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, that is, much larger than fluxes determined previously for different environments.

Acknowledgments. We greatly appreciate and thank Arnold Torres for his long-standing interest and unselfish support. The simultaneous NO and O_3 measurements were made in collaboration with Steven Wofsy, Warren Kaplan, and Mike Keller. We thank Robert Harriss and Jim Hoell for their coordination efforts of ABLE and their support during and after the ABLE expedition to Manaus. At the Ducke preserve we had the support of Francisco da Silva and the INPA staff. We have benefited from discussions with Jennifer Logan, Jack Fishman, Enio Pereira, Charles Martin, David Fitzjarrald, and Donald Lenschow. We also thank David McDougal, for technical support, and A. Setzer, for the trajectory analysis. INPA Director Herbert Schubart has helped us to overcome some of the extreme difficulties of working in the jungle. The field work of José Alves and Isa Silva as well as the coordination efforts in Manaus by Aduino Motta and Luiz Molion are greatly appreciated.

References

- Anderson, I. C., and J. S. Levine, Relative rates of nitric oxide and nitrous oxide production by nitrate, denitrifiers, and nitrate respirers, *Appl. Environ. Microbiol.*, **51**, 938-945, 1986.
- Barnes, R. A., A. R. Bandy, and A. L. Torres, ECC ozonesonde accuracy and precision, *J. Geophys. Res.*, **90**, 7881-7888, 1985.
- Brewer, D. A., M. A. Ogliaruso, T. R. Augustsson, and J. S. Levine, The oxidation of isoprene in the troposphere: Mechanism and model calculations, *Atmos. Environ.*, **18**, 2723-2744, 1984.

- Broder, B., H. U. Dütsch, and W. Graber, Ozone fluxes in the nocturnal planetary boundary layer over hilly terrain, Atmos. Environ., **51**, 1195-1199, 1981.
- Browell, E. V., E. F. Danielsen, S. Ismail, G. L. Gregory, and S. M. Beck, Tropopause fold structure determined from airborne lidar and in situ measurements, J. Geophys. Res., **92**, 2112-2120, 1987.
- Browell, E. V., G. L. Gregory, R. C. Harriss, and V. W. J. H. Kirchhoff, Tropospheric ozone and aerosol distributions across the Amazon Basin, J. Geophys. Res., **93**, 1431-1451, 1988.
- Chameides, W., and J. C. G. Walker, A photochemical theory of tropospheric ozone, J. Geophys. Res., **78**, 8571-8760, 1973.
- Chameides, W., and J. C. G. Walker, A time dependent photochemical model for ozone near the ground, J. Geophys. Res., **81**, 413-420, 1976.
- Chatfield, R., and H. Harrison, Ozone in the remote troposphere: Mixing versus photochemistry, J. Geophys. Res., **81**, 421-424, 1976.
- Crill, P. M., K. B. Bartlett, D. I. Seebacher, R. C. Harriss, J. O. Wilson, J. Melack, L. Lesack, and S. MacIntyre, Tropospheric methane from an Amazonian floodplain lake, J. Geophys. Res., **93**, 1564-1570, 1988.
- Crutzen, P. J., The role of NO and NO₂ in the chemistry of the troposphere and stratosphere, Annu. Rev. Earth Planet. Sci., **7**, 443-472, 1979.
- Crutzen, P. J., The role of the tropics in atmospheric chemistry, in The Geophysiology of Amazonia, edited by R. E. Dickinson, pp. 107-130, John Wiley, New York, 1986.
- Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollock, and W. Seiler, Biomass burning as a source of atmospheric gases CO, H₂, N₂O, NO, CH₃Cl, and COS, Nature, **282**, 253-256, 1979.
- Crutzen, P. J., A. C. Delany, J. Greenberg, P. Haagenson, L. Heidt, R. Lueb, W. Pollock, W. Seiler, A. Wartburg, and P. Zimmerman, Tropospheric chemical composition measurements in Brazil during the dry season, J. Atmos. Chem., **2**, 233-256, 1985.
- Danielsen, E. F., and V. Mohnen, Project DUSTSTORM: Ozone transport, in situ measurements and meteorological analysis of tropopause folding, J. Geophys. Res., **82**, 5867-5877, 1977.
- Delany, A. C., P. Haagenson, S. Walters, A. F. Wartburg, and P. J. Crutzen, Photochemically produced ozone in the emission from large-scale tropical vegetation fires, J. Geophys. Res., **90**, 2425-2429, 1985.
- Droppo, J. G., Jr., Concurrent measurements of ozone dry deposition using eddy correlation and profile flux methods, J. Geophys. Res., **90**, 2112-2118, 1985.
- Fehsenfeld, F. C., M. J. Bollinger, S. C. Liu, D. D. Parrish, M. McFarland, M. Trainer, D. Kely, P. C. Murphy, D. L. Albritton, and D. H. Lenschow, A study of ozone in the Colorado Mountains, J. Atmos. Chem., **1**, 87-105, 1983.
- Fishman, J., and P. J. Crutzen, A numerical study of tropospheric photochemistry using a one-dimensional model, J. Geophys. Res., **82**, 5897-5906, 1977.
- Fishman, J., S. Solomon, and P. J. Crutzen, Observational and theoretical evidence in support of a significant in situ photochemical source of tropospheric ozone, Tellus, **31**, 432-436, 1979.
- Fishman, J., P. Minnis, and H. G. Reichle, Jr., Use of satellite data to study tropospheric ozone in the tropics, J. Geophys. Res., **91**, 14,451-14,465, 1986.
- Galbally, I., Some measurements of ozone variation and destruction in the atmospheric surface layer, Nature, **218**, 456-457, 1968.
- Greenberg, J. P., P. R. Zimmerman, and R. B. Chatfield, Hydrocarbons and carbon monoxide in African savannah air, Geophys. Res. Lett., **12**, 113-116, 1985.
- Gregory, G. L., et al., Air chemistry over the tropical forest of Guyana, J. Geophys. Res., **91**, 8603-8612, 1986.
- Gregory, G. L., E. V. Browell, and L. S. Gahan, Boundary layer ozone: An airborne survey above the Amazon Basin, J. Geophys. Res., **93**, 1452-1468, 1988.
- Harriss, R. C., D. I. Seebacher, and F. P. Day, Methane flux in the Great Dismal Swamp, Nature, **247**, 673-674, 1982.
- Heck, W. W., O. C. Taylor, R. Adams, G. Bighan, J. Miller, E. Preston, and L. Weinstein, Assessment of crop loss from ozone, J. Air Pollut. Control Assoc., **32**, 353-361, 1982.
- Hilsenrath, E., et al., Results from the balloon ozone intercomparison campaign (BOIC), J. Geophys. Res., **91**, 13,137-13,152, 1986.
- Hunten, D. M., Vertical transport in atmospheres, in Atmospheres of Earth and the Planets, edited by B. M. McCormack, pp. 59-72, D. Reidel, Hingham, Mass., 1975.
- Jacob, D. J. and S. C. Wofsy, Photochemistry of biogenic emissions over the Amazon forest, J. Geophys. Res., **93**, 1477-1486, 1988.
- Junge, C. E., Global ozone budget and exchange between stratosphere and troposphere, Tellus, **14**, 363-377, 1962.
- Kaplan, W. A., S. C. Wofsy, M. Keller, and J. M. da Costa, Emission of NO and deposition of O₃ in a tropical forest system, J. Geophys. Res., **93**, 1389-1395, 1988.
- Keller, M., T. J. Goreau, S. C. Wofsy, W. A. Kaplan, and M. B. McElroy, Production of nitrous oxide and consumption of methane by forest soils, Geophys. Res. Lett., **10**, 1156-1159, 1983.
- Kelly, T. J., D. H. Stedman, J. A. Ritter, and R. B. Harvey, Measurements of oxides of nitrogen and nitric acid in clean air, J. Geophys. Res., **85**, 7417-7425, 1980.
- Killus, J. P., and G. Z. Whitten, Isoprene: A photochemical kinetic mechanism, Environ. Sci. Technol., **18**, 142-148, 1984.
- Kirchhoff, V. W. J. H., Are northern hemisphere tropospheric ozone densities larger? Eos Trans. AGU, **65**, 449, 1984.
- Kirchhoff, V. W. J. H., Surface ozone measurements in Amazonia, J. Geophys. Res., **93**, 1469-1476, 1988.
- Kirchhoff, V. W. J. H., Y. Sahai, and A. G. Motta, First ozone profiles measured with ECC sondes at Natal (5.9°S, 35.2°W), Geophys. Res. Lett., **8**, 1171-1172, 1981.
- Kirchhoff, V. W. J. H., E. Hilsenrath, A. G. Motta, Y. Sahai, and R. A. Medrano-B.,

- Equatorial ozone characteristics as measured at Natal (5.9°S, 35.2°W), J. Geophys. Res., **88**, 6812-6818, 1983.
- Komhyr, W. D., Electrochemical concentration cells for gas analysis, Ann. Geophys., **25**, 203-210, 1969.
- Lenschow, D. H., R. Pearson, Jr., and B. B. Stankov, Estimating the ozone budget in the boundary layer by use of aircraft measurements of ozone eddy flux and mean concentration, J. Geophys. Res., **86**, 7291-7297, 1981.
- Lenschow, D. H., R. Pearson, Jr., and B. B. Stankov, Measurements of ozone vertical flux to ocean and forest, J. Geophys. Res., **87**, 8833-8837, 1982.
- Levine, J. S., Water and the photochemistry of the troposphere, in satellite sensing of a cloudy atmosphere: Observing the third Planet., edited by A. H. Sellers, pp. 123-166, Taylor and Francis, London, 1984.
- Logan, J. A., Tropospheric ozone: Seasonal behavior, trends, and anthropogenic influence, J. Geophys. Res., **90**, 10,463-10,482, 1985.
- Logan, J. A., and V. W. J. H. Kirchhoff, Seasonal variations of tropospheric ozone at Natal, Brazil, J. Geophys. Res., **91**, 7875-7881, 1986.
- McNeal, R. J., J. P. Mugler, Jr., R. C. Harriss, and J. M. Hoell, Jr., NASA Global Tropospheric Experiment, Eos Trans. AGU, **64**, 561-562, 1983.
- Rasmussen R. A., and M. A. K. Khalil, Atmospheric isoprene, Eos Trans. AGU, **66**, 39, 1985.
- Rasmussen, R. A. and M. A. K. Khalil, Isoprene over the Amazon Basin, J. Geophys. Res., **93**, 1417-1421, 1988.
- Regener, V. H., The vertical flux of atmospheric ozone, J. Geophys. Res., **62**, 221-228, 1957.
- Roberts, J. M., F. C. Fehsenfeld, D. L. Albritton, and R. E. Sievers, Measurements of monoterpene hydrocarbons at Niwot Ridge, Colorado, J. Geophys. Res., **88**, 10,667-10,678, 1983.
- Sachse, G. W., R. C. Harriss, J. Fishman, G. F. Hill, and D. R. Cahoon, Carbon monoxide in the atmosphere over the Amazon Basin during the 1985 dry season, J. Geophys. Res., **93**, 1422-1430, 1988.
- Sanhueza, E., K. H. Octavio, and A. Arrocha, Surface ozone measurements in the Venezuelan tropical savannah, J. Atmos. Chem., **2**, 377-385, 1985.
- Setzer, A. W., and M. C. Pereira, Detection of large biomass burning in the Amazon with satellite images, Eos Trans. AGU, **67**, 247, 1986.
- Torres, A. L., and A. R. Bandy, Performance characteristics of the electrochemical concentration cell ozonesonde, J. Geophys. Res., **83**, 5501-5504, 1978.
- Torres, A. L., and H. Buchan, Tropospheric nitric oxide measurements over the Amazon Basin, J. Geophys. Res., **93**, 1396-1406, 1988.
- Wesely, M. L., A. Eastman, D. R. Cook, and B. B. Hicks, Daytime variations of ozone eddy fluxes to Maize, Boundary Layer Meteorol., **15**, 361-373, 1978.
- Wesely, M. L., D. R. Cook, and E. M. Williams, Field measurement of small ozone fluxes to snow, wet bare soil, and lake water, Boundary Layer Meteorol., **20**, 459-471, 1981.
- Wolff, G. T., P. J. Liroy, G. D. Wight, R. E. Meyers, and R. T. Cederwall, An investigation of long range transport of ozone across the midwestern and eastern United States, Atmos. Environ., **11**, 797-802, 1977.
- Zimmerman, P. R., R. B. Chatfield, J. Fishman, P. J. Crutzen, and P. L. Hanst, Estimates on the production of CO and H₂ from the oxidation of hydrocarbon emissions from vegetation, Geophys. Res. Lett., **5**, 679-682, 1978.
- E. V. Browell and G. L. Gregory, Atmospheric Sciences Division, NASA Langley Research Center, Hampton, VA 23665.
- V. W. J. H. Kirchhoff, Instituto de Pesquisas Espaciais, Ministério da Ciência e Tecnologia, 12201 São José dos Campos, São José dos Campos, São Paulo, Brasil.

(Received August 28, 1987;
revised June 1, 1988;
accepted August 19, 1988.)