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Ozone Measurements in Amazonia: Dry Season Versus Wet Season

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The concentration of atmospheric ozone was measured in the Amazonian rain forest. Observations were made almost continuously at the surface, and in addition, 20 ozone profiles were obtained in the troposphere and stratosphere. These ozone measurements were part of a field expedition to the Brazilian Amazon region, the ABLE 2B mission, a joint American-Brazilian effort to measure local concentrations of several species relevant to atmospheric chemistry. The time period of this expedition was April–May 1987, during the local wet season. For the surface ozone data the measurement technique used was UV absorption. Ozone profiles were obtained with electrochemical concentration cell sondes, launched on balloons. The major site of operation was set up near Manaus (3°S, 60°W). The results are presented and compared with a previous dry season experiment. Surface ozone mixing ratios show diurnal variations that have maxima in the daytime and minima at night. The diurnal maximum at noontime, considered very low (12 ppbv) in the dry season was even lower in this wet season period (6 ppbv). A significant difference can be seen between clearing and forest data, and between different height levels above the surface, showing the existence of a large positive gradient of ozone with height. The ozone profiles in the troposphere show that there is less ozone not only at the surface but in the whole troposphere, with the wet season average showing between 6 and 12 ppbv less ozone. This difference is much smaller in the stratosphere, where there is slightly more ozone in the region of the peak, during the wet season. An isolated shower or thunderstorm in the dry season could produce transient ozone variations (mixing ratio increases or decreases) that were not observed in the wet season.

INTRODUCTION

The Amazon Boundary Layer Experiment (ABLE) was planned to obtain in situ atmospheric chemistry data at certain important sites of the globe [*McNeal et al.*, 1985] using ground-based and aircraft-borne instruments. The first ABLE expedition to Amazonia took place in July–August 1985 during the rain forest dry season. The ABLE 2A mission was described by *Harriss et al.* [1988]. Ozone measurements for that experiment were described by *Kirchhoff* [1988*a*], *Kirchhoff et al.* [1988], *Browell et al.* [1988], and *Gregory et al.* [1988]. In a similar way, the ABLE 2B mission [*Harriss et al.*, this issue] measured important atmospheric constituents in Amazonia during the wet season, April–May 1987. These ABLE missions were large binational expeditions, a result of cooperative efforts between the Brazilian Institute for Space Research (Instituto de Pesquisas Espaciais, or INPE) and the American National Aeronautics and Space Administration (NASA). The objective was to study the lower atmosphere of the equatorial rain forest with emphasis on the atmospheric chemistry. Measurements were made from the surface and from NASA's Electra aircraft. Some of the many atmospheric species measured at the surface were O_3, CO_2, NO_x, sulphur species, and CO and from the aircraft were O_3, CO, CO_2, aerosols, NO, and PAN. Several important experiments in meteorology were also made [*Martin et al.*, 1988; *Garstang et al.*, 1988; *Scala et al.*, this issue; *Greco et al.*, this issue]. Ozone measurements from the aircraft are reported by *Browell et al.* [this issue] and *Gregory et al.* [this issue].

Ozone has important characteristics in the tropics that are of interest from a global atmospheric chemistry perspective [*Crutzen*, 1987; *Kirchhoff*, 1988*a*; *Logan and Kirchhoff*, 1986]. More recently, ozone has received further attention because of its greenhouse effect characteristics. There is evidence that tropospheric ozone has increased its average concentration [*Logan*, 1985; *Oltmans and Komhyr*, 1986; *Bojkov*, 1986, 1988; *Feister and Warmbt*, 1987], as have other greenhouse gases such as N_2O, CH_4, and chlorofluorocarbons (CFCs) [*Rasmussen and Khalil*, 1986]. It appears that among the minor contributors to the greenhouse effect, ozone represents the fastest growing component (J. Fishman, private communication, 1988). Also, because of its toxicity, increases of tropospheric ozone are a major concern for growing corps [*Heck et al.*, 1982, 1984].

Previous Measurements

It appears that the first ozone measurements in Amazonia were made from an aircraft, in two expeditions organized by the National Center for Atmospheric Research (NCAR) in 1979 and 1980, during the dry season, with a special interest

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in studying biomass burning [*Crutzen et al.*, 1985; *Delany et al.*, 1985; *Greenberg et al.*, 1984]. It was observed that ozone concentrations were rather high in comparison to measurements in marine environments, and that CO and O_3 were layered in the mixing layer. This was the first field experiment that showed the biomass-burning impact on the chemical composition of the lower atmosphere in Amazonia.

Ozone measurements have also been reported for the African equatorial region [*Cros et al.*, 1987, 1988]. They showed a behavior similar to that at Brazilian sites, as well as to measurements in Asia [*Tsuruta et al.*, 1988; *Ogawa and Komala*, 1988], and the Venezuelan savannah [*Sanhueza et al.*, 1985]. The concentrations are generally lower at low latitudes over the ocean [*Winkler*, 1988; *Oltmans*, 1981; *Oltmans and Komhyr*, 1986], where the shape of the diurnal variation is different than that over the continents. This is due in part to the much slower loss rate that ozone has over water, making the downward flux of ozone smaller by as much as a factor of 10 or more over wet surfaces than over soil [*Wesely et al.*, 1981].

Tropospheric ozone measurements in Brazil were started in 1978 by a collaborative effort between INPE and NASA. Two balloon ozonesondes have been launched per month from Natal (6°S, 35°W) [*Kirchhoff et al.*, 1981, 1983; *Kirchhoff*, 1984; *Logan and Kirchhoff*, 1986], and sporadic rocket campaigns were carried out [*Barnes et al.*, 1987]. Continuous surface ozone measurements were started in 1986 at Cuiabá (16°S, 58°W), and later also at Natal (6°S, 35°W, and Fortaleza (4°S, 38°W) [*Kirchhoff and Nobre*, 1986], as well as field expeditions [*Kirchhoff*, 1988*a*; *Kirchhoff et al.*, 1988]. Because of the importance of biomass burning, CO measurements using grab sampling and chromatographic techniques were also started [*Kirchhoff and Marinho*, 1989, this issue]. In this paper we will concentrate on the ABLE 2B results.

Objective of Paper

The aim of this report is to describe recent ozone measurements taken in the Amazonian rain forest environment, during the wet season, revealing interesting new aspects of the regional atmospheric chemistry. Ozone measurements obtained at the surface by several instruments are used to describe the ozone mixing ratio at different sites, and their time variations. Ozone profiles were also obtained and are used to describe the upper troposphere and stratosphere. Besides a comprehensive description of these results, the major differences in comparison to a previous dry season experiment are stressed.

RESULTS

Measurement Techniques

Surface ozone measurements were made using the ultraviolet (UV) absorption technique. The air sample containing ozone is injected into an absorption cell. A UV light beam that is directed through the length of the cell, is measured before and after it emerges from the cell. From the attenuation of the UV light, it is possible to calculate the ozone mixing ratio. Commercially available instruments can make the measurements automatically, providing a new ozone measurement in about 20 s. Four of these instruments were available for measuring surface ozone during most of the time of the experiment. They were carefully intercalibrated and referred to a secondary ozone standard instrument provided by Torres, traceable to NBS standards [*Barnes et al.*, 1985]. The accuracy of such instruments at low concentrations is typically 1 ppbv (parts per billion by volume). The measurement precision for a single measurement is typically 1–2 ppbv.

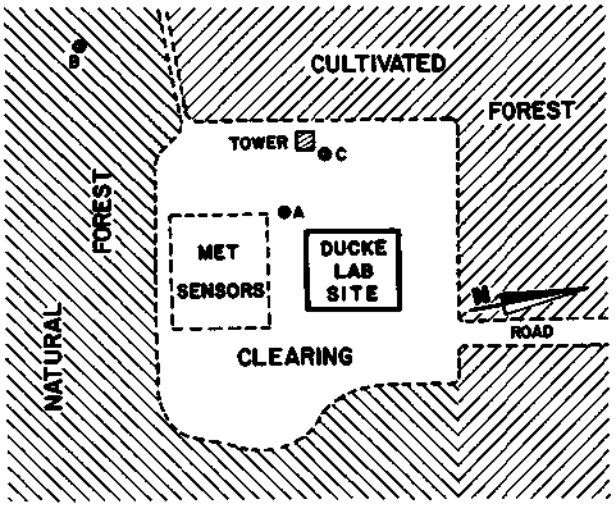

Fig. 1. The ozone measurement sites at Ducke forest preserve located about 30 km north of Manaus. Surface ozone measurements were made from point A (in the clearing) and point B (inside the forest). Measurements at different heights were made from point C. The size of the clearing is about 100 × 100 m.

In situ measurements of ozone in the troposphere and stratosphere were made using the electrochemical concentration cell (ECC) sonde [*Komhyr*, 1969; *Barnes et al.*, 1985]. This is a small lightweight ozonesonde that is coupled to a regular meteorological radiosonde launched on balloons. In general, the measurements are only made on ascent, with the balloon reaching heights of up to 10 mbar. This ECC sonde 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. The pumping element of this sensor has a lower efficiency at higher altitudes [*Torres and Bandy*, 1978] starting at about 60 mbar. Because of this, each of the 20 sondes launched in Manaus during the ABLE 2B mission had been calibrated in the Wallops Island laboratory (courtesy of A. Torres, NASA). The accuracy and precision of these sondes have been analyzed by *Torres and Bandy* [1978], *Barnes et al.* [1985], and *Hilsenrath et al.* [1986].

Site Description

The measurement site was at the Ducke forest preserve, some 30 km north of Manaus (3°S, 60°W). This is the same general area used for the ABLE 2A experiment. A sketch of the site can be seen in Figure 1. The Ducke lab site, also called the Met site, was the center for the carbon monoxide measurements [*Kirchhoff and Marinho*, this issue] and the ECC telemetry receiver. The surface ozone measurements were made at point A (1.5 m above the surface), at point C next to a metallic antenna tower (15 m above the surface), and at point B. Points A and C measured inside of the clearing, while point B measured inside of the forest, in the

TABLE 1. Summary of Surface Ozone Data Measured at Ducke Forest Reserve Between April 8 and May 11, 1987 (GTE/ABLE 2B Campaign)

Measurement Type	Site	Date	Maximum Concentration, ppbv
Surface	Ducke Forest, clearing	April 8 to May 11	5.7
Tower			
5 m	Ducke Forest, clearing	April 14–15	—
7 m	Ducke Forest, clearing	April 16–28	6.7
15 m	Ducke Forest, clearing	April 28 to May 11	6.9
Surface	downtown Manaus, INPA	April 23 to May 6	6.1
Surface	inside forest	May 6–11	3.7

Surface refers to 1.5 m above ground. Maximum concentrations occurred around noon, several days average.

southern part of the site, where the forest showed few signs of human modification. In contrast, the northern part of the site had signs of reforestation with many trees grown for botanic studies. The ECC sondes were launched from an area between points A and C.

Surface Ozone Data

A summary of the surface ozone data measured at Ducke preserve during the wet season of 1987 is shown in Table 1. Also shown in this table are the maximum daytime ozone concentrations observed, which were between 3.7 and 6.9 ppbv. This is much smaller than typical daytime values observed at any other Brazilian sampling site [*Kirchhoff*, 1988*b*] and certainly much smaller than any from the U.S. sites, described by *Logan* [1985, 1987]. But as shown in the previous experiment in Amazonia [*Kirchhoff*, 1988*a*], the concentrations of O_3 during the dry season were only about 12–15 ppbv, then considered surprisingly low for a continental site.

The typical diurnal variation of the ozone mixing ratio on four consecutive days is shown in Figure 2. Measurements for three different conditions are shown for May 7–10: the mixing ratio at the 15-m level of the tower (point C in Figure 1, not to be confused with the Micro-Met tower, several kilometers inside the forest), the surface results obtained at point A, and a third one from the inside of the forest (point B in Figure 1). The concentrations are all shown in ppbv and local time (LT) is UT-4 hours. Evidently, the major characteristics are similar at the three different sampling points: all show daytime maxima around noon, with very low concentrations at night. In the forest, they are zero during most of the nights observed. The daytime maximum concentrations are rather small in comparison with ozone mixing ratios observed elsewhere. A concentration gradient is present near the surface, making the concentrations larger at greater heights from the surface. The concentrations observed inside of the forest are the smallest. This general behavior has also been observed in the previous experiment, but the magnitudes were larger. The large ozone increase at 0100 LT on May 10 was an isolated perturbation.

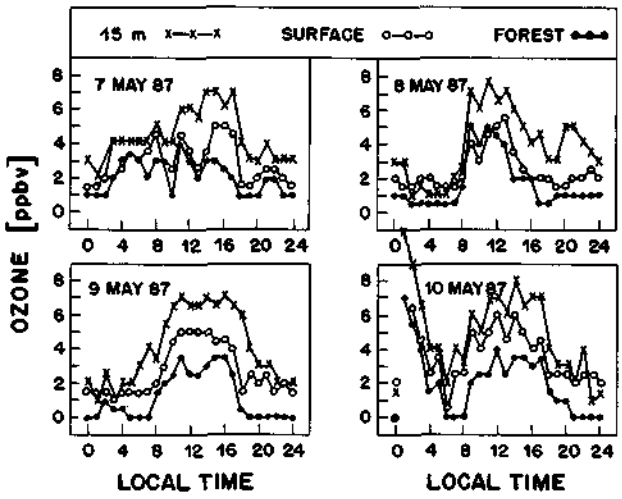

Fig. 2. Typical diurnal variations of ozone obtained on four consecutive days in May 1987 at the forest preserve.

The diurnal variation described above seems to be characteristic for continental sites [*Oltmans*, 1981; *Kirchhoff*, 1988*b*]. The marine sites that receive air masses from over the oceans do not show any consistent diurnal variation, as in the case of Natal (6°S, 35°W), or have a variation caused by special characteristics of the local winds as in Hawaii [*Oltmans*, 1981; *Oltmans and Komhyr*, 1986]. In part, this different behavior may be caused by different levels of NO_x concentrations [*Chameides and Stedman*, 1977]. In addition, at sites that show diurnal variations, the amplitude of the diurnal variation decreases with height [*Harrison et al.*, 1978; *Broder et al.*, 1981], which appears to indicate the importance of the lower boundary, the surface, and being at least coresponsible for imposing a diurnal variation. Since the surface usually represents a solid (liquid) body where ozone can be destroyed on contact, the surface acts as a sink. This sink acts, in association with the local winds and vertical air motions, to destroy ozone. The time constant for this destruction depends on the surface reactive characteristics, and the effective contact that the air makes with the surface. It may vary between minutes, as in the case of the interactions in Amazonia, with strong sink (large vertical fluxes [*Kirchhoff*, 1988*a*]) and excellent effective contact, caused by strong turbulence, characteristic of that region, or the time constant may also be several hours, as in the case of the Natal data, caused essentially by the small downward ozone flux [*Wesely et al.*, 1981] over marine environments.

The average diurnal variation obtained during the experiment is shown in Figure 3. The average is shown as well as the minima and maxima observed during the experiment. It shows that concentrations of ozone higher than 12 ppbv were not observed during this wet season campaign in

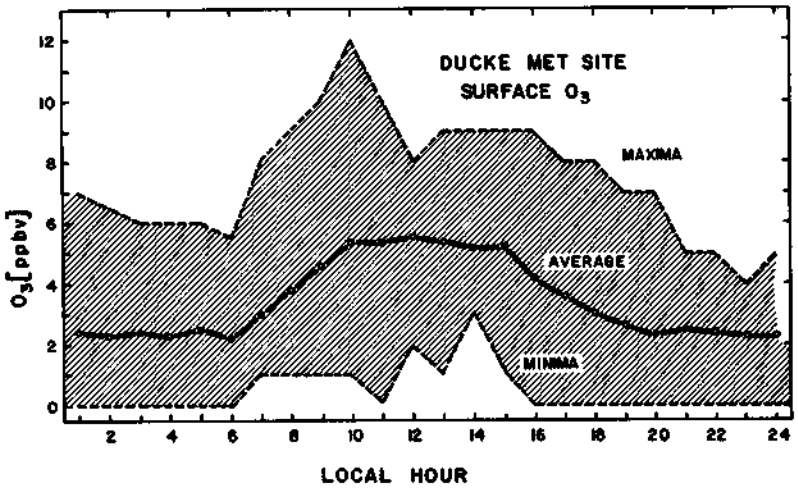

Fig. 3. Overall ozone average diurnal variation obtained for the experiment. The maxima and minima are also shown. The standard deviation in the daytime is typically 1.6 ppbv.

Amazonia. This average is about one half of that observed during the dry season experiment.

For comparison with the other sampling points, Figure 4 shows the surface average and those computed for the tower at 15 m, and in the forest. Typical standard deviations for these measurements are 0.3 ppbv. One ppbv more ozone is seen at 15 m compared with that at the surface, during sunlit hours. At night there seems to be no difference between the surface and 15-m data sets. This seems to suggest that both sampling points belong to the same stable layer, which is isolated from the surface at night. The concentrations inside the forest are considerably lower than the clearing values both at night and daytime hours. It appears that this is due not only to a vertical loss flux of ozone but, in addition, horizontal movement that also produces plenty of contact of the air with the leaves adding a loss factor that is absent in the clearing. In addition, since the forest soil emits NO [*Jacob and Wofsy*, this issue; *Bakwin et al.*, this issue (*a*, *b*), ozone could be depleted from the lower layers, where it is more difficult for the UV light to reach.

It was clear from the CO data set obtained at the same site [*Kirchhoff and Marinho*, this issue] that the CO data showed larger variability during April than during May. This was not so obvious from visual inspection of the ozone data. However, subtracting the diurnal average obtained in both periods, it became apparent that slightly larger ozone values were seen in April. The hourly differences are shown in Figure 5. No significant difference exists between the nighttime data, which seems consistent with photochemical production of excess ozone in the daytime. For April, larger concentrations for carbon monoxide and larger concentrations for ozone were seen, compared with May. For the daytime period between 1200 and 1400 LT, the monthly averages and standard deviations for April and May are 108.0 ± 5.5 and 102.0 ± 5.0 for carbon monoxide, and 5.8 ± 0.3 and 4.7 ± 0.3 for ozone.

Concurrent observations of carbon monoxide and ozone have been used previously to demonstrate photochemical activity in the troposphere [*Fishman et al.*, 1979, 1980] when higher carbon monoxide concentrations are positively correlated with higher ozone values. Since the carbon monoxide concentrations usually decrease with height while ozone concentrations increase, simple vertical transport would not produce positive correlations. The theoretical work of *Jacob and Wofsy* [1988] clearly indicated photochemical activity in Amazonia, but carbon monoxide measurements were not made at the surface during the ABLE 2A mission. The observations of concentration increases or decreases in both ozone and carbon monoxide seem to be direct observational evidence in favor of a link between CO and O_3, made possible, perhaps, by chemical reactions and UV radiation.

Figure 6 shows the results of surface ozone measurements in the downtown area of Manaus. An ozone sensor was installed at the INPA complex, in Manaus, near the so-called guest house. Although city pollution was not our major concern, it was instructive to have an idea of the magnitude of ozone concentrations generated there. It should be noted that just walking or driving through Manaus convinces one that this remote city has high levels of pollution. A few air samples taken at random for analysis of carbon monoxide showed concentrations of several ppmv, as high as those of downtown São Paulo. The record of ozone at the INPA site was rather complex. On most days the ozone mixing ratio behaved similar to the data obtained in the forest. This set of days has been taken together to obtain an average diurnal variation, as shown in Figure 6. It is much lower than one

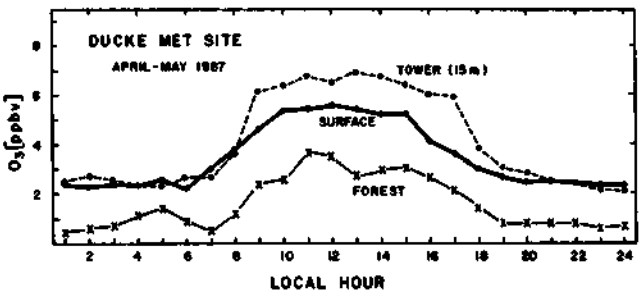

Fig. 4. Comparison of the surface average and the average concentrations obtained inside of the forest and at 15 m above the surface. In the daytime, the standard deviations of these averages are about 0.3 ppbv.

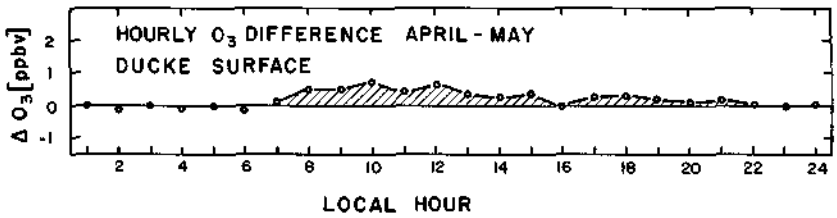

Fig. 5. Hourly differences of ozone concentrations between April and May 1987. The standard deviations in the daytime are 0.3 ppbv.

might expect, with a daytime maximum practically identical to the forest value (Table 1). On the other hand, 3 days of this measurement set showed completely different behavior, with very large ozone outbreaks. This is also shown in Figure 6, for April 24 and 26 and May 2. Nearly 50 ppbv of ozone were observed on April 24 at 1400LT, and 25 ppbv on May 2, a little later in the day, 1600–1800 LT, with a sharp decrease just after 1800 LT. On April 26, another large value, nearly 18 ppbv, was observed in the daytime, at 1300 LT. These large values disappeared at night, consistent with photochemical ozone production in excess NO_x, consuming ozone in the dark period. None of these events had any obvious correlated variations in the forest area.

No other constituents were measured in the city area. If the NO_x concentrations were large, however, ozone concentrations would be strongly dependent on the relative cloudiness, much more in the city area, where production rates could be fast, than in the forest, where NO_x levels would probably be much lower. It is interesting to note that model studies show the inclusion of molecular scattering and surface reflections has a tendency to increase the calculated ozone mixing ratio in the whole troposphere [*Thompson*, 1984]. Turning again to the forest data sets, the ABLE 2B results are compared in Figure 7 with the ABLE 2A data. The hourly concentrations of ozone are subtracted, dry season minus wet season. The differences are larger during daytime hours and negative in the nighttime hours, consistent with photochemical activity.

Tropospheric Ozone

As mentioned, ozone was measured in situ by ozonesondes of the ECC type. A summary of the soundings made during the 1987 ABLE 2B campaign at Ducke Forest Reserve is shown in Table 2. A total of 20 sondes were launched successfully from the forest clearing shown in Figure 1, between April 16 and May 10, 1987. The flight duration of each sonde varied from 38 to 125 min. Six flights were made in the morning hours, 13 during the afternoon, and one at night. Thirteen of the sondes reached heights above 30 km. The average tropospheric abundance, that is, the ozone integral from the surface to 100 mbar, was 19.2 Dobson units (DU), which amounts to 7.3% of the overall tropospheric and stratospheric content of 264 DU. The total ozone content expressed in DU, when divided by 100, represents the thickness of an equivalent ozone layer in millimeters, when compressed at STP. Further details of the average behavior are given in Table 3.

Two typical ozone profiles, in terms of mixing ratios, are shown in Figure 8. Note the tendency for ozone to increase with height in the lower 3–5 km. In this height region the ozone gradient is about 6 ppbv/km, a value close to the 20-profile average, but much smaller than the gradient near the surface, which is an order of magnitude larger based on results of the measurements at 15 m. Above about 5–6 km the gradient vanishes, and the ozone concentration remains roughly constant, but with strong structure, which makes the mixing ratio vary by about 8 ppbv. This general behavior is similar to results obtained previously [*Logan and Kirchhoff*, 1986; *Kirchhoff et al.*, 1988], except for the ozone gradient between the surface and about 6 km, which is typically larger during the dry season.

The comparison of the average profiles obtained in the dry and wet seasons is shown in Figure 9. Note that these seasonal periods are compared for different years. The surface ozone measurements also show that the ozone values are much lower, compared with the dry season results, in the whole troposphere. It was shown [*Kirchhoff et al.*, 1988] that the ozone profile for the 1985 data set had

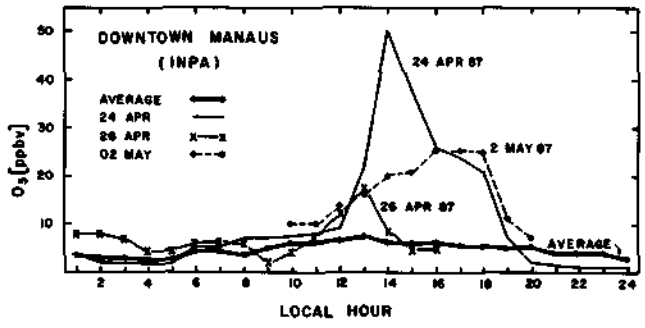

Fig. 6. Ozone concentrations obtained in the downtown area of Manaus.

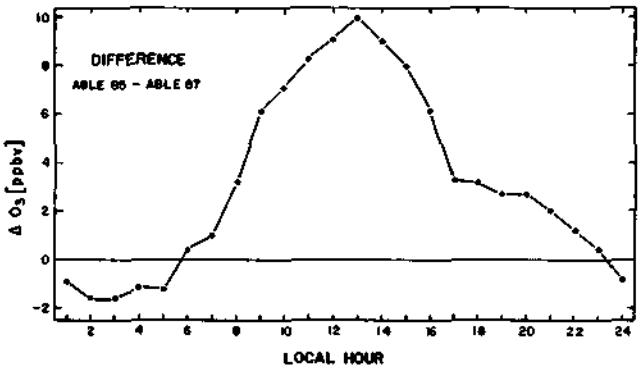

Fig. 7. Hourly ozone concentration differences between the ABLE 2A (1985) and ABLE 2B (1987) experiment (dry and wet season, respectively).

TABLE 2. Summary of ECC Ozone Soundings During the 1987 GTE/ABLE 2B Campaign at Ducke Forest Reserve

Date in 1987	Launch, LT	Flight Duration, min	Burst Height, km	Burst Pressure, mbar	Tropospheric Abundance, DU	Comment
April 16	1523	101	33.6	7.0	21.2	morning
April 17	1728	90	31.5	9.5	18.9	afternoon
April 19	1430	67	22.5	32.5	21.4	morning
April 22	0114	60	19.7	57.9	19.2	night
April 22	1948	112	31.4	9.6	33.3	afternoon
April 23	1847	88	31.1	9.9	40.2	afternoon
April 24	1953	111	33.1	7.6	21.3	afternoon
April 26	2048	45	16.1	105.0	22.4	afternoon
April 27	2025	46	17.1	80.9	20.1	afternoon
April 28	1556	99	33.6	7.0	15.0	morning
April 29	1945	107	33.1	7.6	22.7	afternoon
May 2	1828	114	32.7	7.9	19.8	afternoon
May 5	1958	125	37.6	4.0	21.0	afternoon
May 6	1534	85	31.7	9.3	20.3	morning
May 7	1927	86	27.9	16.0	26.4	afternoon
May 8	1550	38	14.4	146.0	29.8	morning
May 8	1921	99	35.8	5.2	30.0	afternoon
May 9	1502	92	31.0	10.2	23.6	morning
May 9	1908	58	19.3	62.3	29.7	afternoon
May 10	1605	95	32.2	8.7	24.4	afternoon

The tropospheric abundance is defined here as the O_3 integral from the surface to 100 mbar, in Dobson units. LT = UT − 4 hours. 1 DU = 2.7×10^{16} molecules cm^{-2}.

TABLE 3. Average Ozone Sounding Results for Amazonia During the ABLE 2B Campaign

Pressure, mbar	Height, km	Soundings	Temperature, K	Humidity, %	O_3 Concentration		
					nbar	cm^{-3}	ppbv
1000	0.6	20	297.4	68.2 (20)	11.5	0.28	11.5
900	1.3	20	291.9	80.1 (20)	14.3	0.35	15.8
850	1.8	20	288.9	78.1 (20)	15.6	0.39	18.4
800	2.7	20	284.3	72.6 (20)	16.8	0.43	21.0
700	3.9	20	278.4	59.8 (20)	17.1	0.44	24.4
600	5.3	20	270.9	55.0 (15)	16.9	0.45	28.2
500	6.9	20	261.7	56.4 (14)	14.8	0.41	29.6
400	8.1	20	253.6	40.3 (13)	13.8	0.39	34.5
350	9.2	20	245.9	41.2 (11)	11.7	0.34	33.4
300	10.4	20	236.4	39.3 (4)	10.3	0.32	34.5
250	11.8	20	224.7		8.3	0.27	33.4
200	13.5	20	210.6		8.3	0.28	41.5
150	14.8	20	200.2		8.3	0.30	55.1
125	16.0	18	193.3		9.4	0.35	75.4
100	17.2	17	192.5		14.6	0.54	145.9
80	18.2	17	196.7		24.0	0.88	299.7
70	19.0	16	199.2		36.2	1.31	516.5
60	20.0	15	203.9		54.4	1.92	906.3
50	21.2	15	209.7		81.3	2.79	1626.7
40	22.3	15	213.9		106.2	3.58	2654.8
35	23.2	15	217.4		124.4	4.13	3554.1
30	24.4	14	221.2		142.6	4.65	4752.6
25	25.8	14	226.1		158.0	5.04	6319.1
20	26.9	14	229.5		162.9	5.12	8143.9
17.5	27.8	13	233.0		152.4	4.72	8707.7
15	29.0	13	235.0		125.7	3.86	8879.5
12.5	30.4	13	237.7		98.5	2.99	7877.5
10	31.9	10	240.5		75.1	2.26	7508.0
8	33.2	4	243.2		60.0	1.79	7496.9
7	34.2	4	243.4		50.0	1.49	7146.4
6	36.0	1	240.9		19.9	0.60	3316.7
5	37.6	1	240.9		17.2	0.51	3440.0

For the relative humidity, the number of data points is shown in parentheses. The O_3 concentration is given in terms of partial pressure in nanobars, of density in 10^{12} cm^{-3}, and of mixing ratio in ppbv.

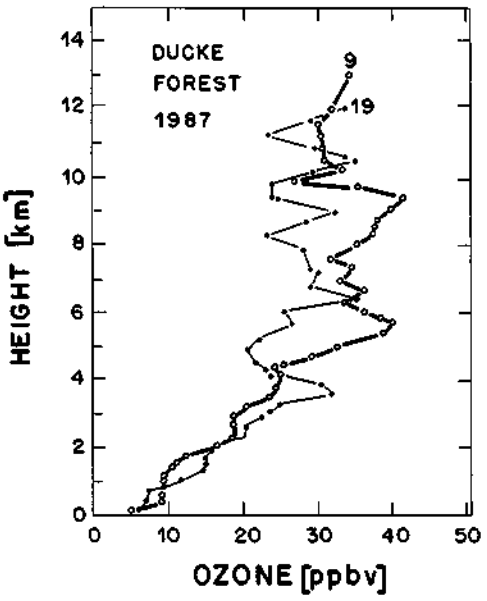

Fig. 8. Typical vertical ozone profiles obtained in the Amazonian wet season on April 19 and May 9, 1987. Notice the O_3 gradient in the lower 4–6 km, and then roughly a constant mixing ratio in the upper troposphere.

mixing ratios smaller than the Natal average. Ozone concentrations measured in equatorial India are also larger than the Amazonian concentrations, in the lower troposphere [*Subbaraya and Jayaraman*, 1987], but this comparison may be biased by differences in the sounding systems.

The day-to-day variability of the ozone mixing ratio may be considerable, as shown in Figure 10. Two cases are shown: profiles for April 24, 26, and 27 showing relatively small changes of ozone from one profile to the other, and the case for April 21, 22, and 23 when very large changes are observed; especially from April 21 to 22. These changes are not limited to certain layers of the troposphere, but the increases are distributed rather uniformly throughout the troposphere, which may indicate that the observations were

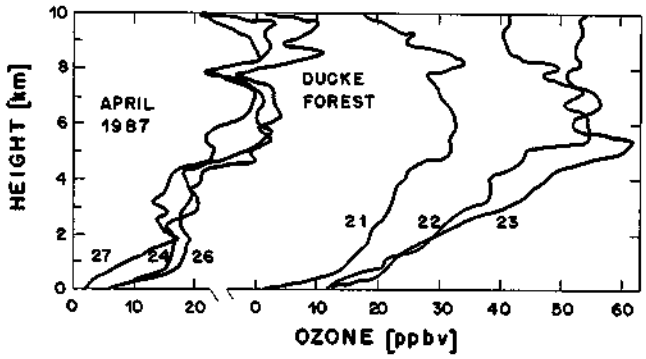

Fig. 10. The variability from day to day may be relatively small as for the soundings of April 24, 26, and 27 but may be large in some cases, as for April 21, 22, and 23, 1987.

made in a different air mass. Large-scale transport and air mass trajectories are discussed in a later section.

Figure 11 shows sequential profiles, from one day to the next, when the vertical structure is very clear. It has been argued previously, for the Natal data [*Logan and Kirchhoff*, 1986], that the vertical structure in the upper troposphere is a real characteristic and not the lack of precision of the ozone sensor. When the air mass is not changed during a second measurement, as seems to be the case for April 28 and 29, the sonde shows the vertical structure almost as a duplicate from the previous day. Only small displacements of the major peaks or valleys can be seen. The meteorological group of ABLE 2B has classified these as more active days, with well-defined squall lines and plenty of rain. This stronger dynamic activity may be partly responsible for the strong vertical structure.

It is important to note that there is considerable horizontal structure as well. This can be seen in detail by the ozone height-time cross sections observed by the airborne differential absorption lidar (DIAL) system [*Browell et al.*, 1988], which measures ozone by remote sensing the lower atmosphere. The Amazonian wet season surveys using this technique will be reported elsewhere [*Browell et al.*, this issue]. Here we want to describe the horizontal and vertical irreg-

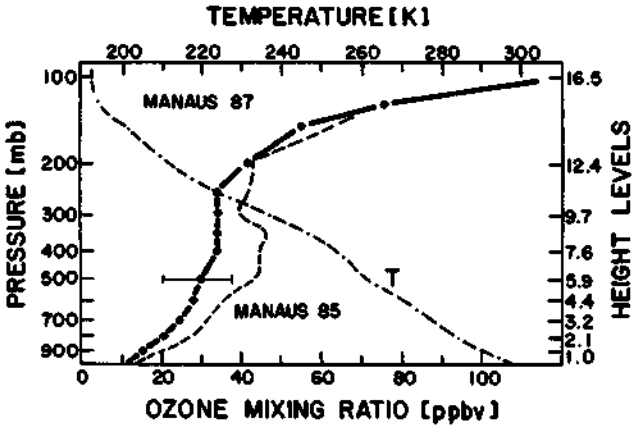

Fig. 9. The average wet season profile obtained in 1987 (dash-dot line) compared with the dry season 1985 average profile (dashed line). The average temperature profile for 1987 is also shown. Note that the height levels are given on a nonlinear scale. The horizontal bar represents typical data variability of one standard deviation.

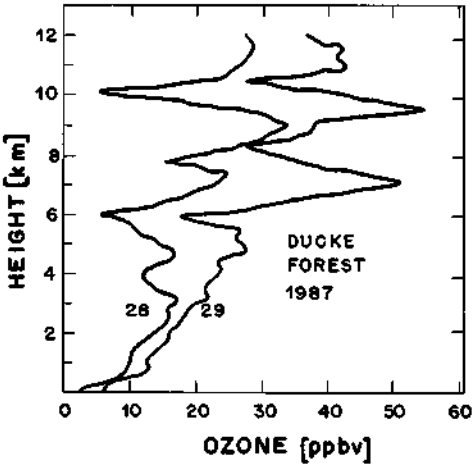

Fig. 11. The vertical structure is well pronounced in some cases as shown for April 28, 1987. This structure is relatively long lived, as can be seen for the next day, when the structure remained almost identical.

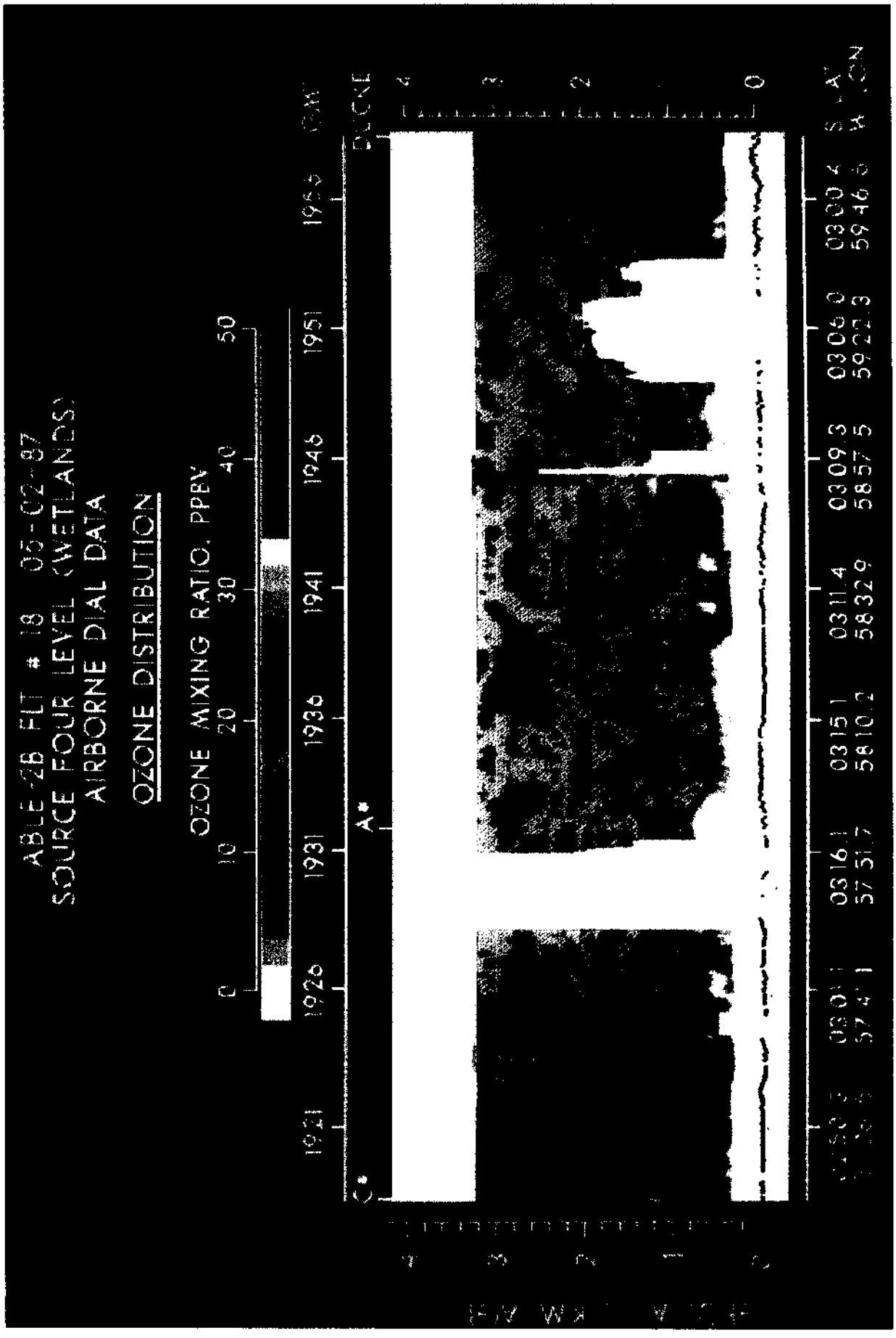

Plate 1. Ozone mixing ratio cross section for May 2, 1987, near Ducke forest showing the existence of strong horizontal and vertical irregularities.

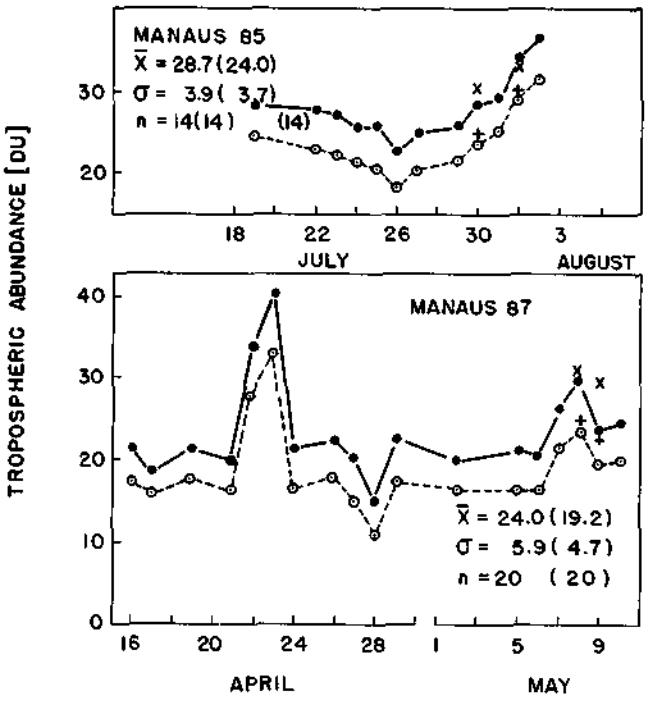

Fig. 12. Time sequence of the tropospheric abundance variation for the dry and wet season experiments. The solid lines use 100 mbar for the upper boundary, the dashed lines 200 mbar. The overall mean, standard deviation, and number of soundings are shown (within parentheses for the 200-mbar top).

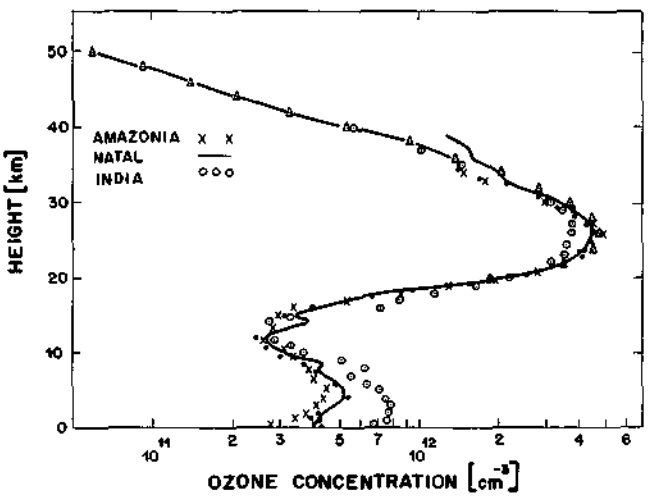

Fig. 13. Low-latitude ozone profile. Crosses represent the Amazonian data, continuous line represents Natal data for the period March–April from several years of soundings, and circles show results obtained in India. Triangles show the average of a rocket campaign made in April 1985 at Natal. Dots represent a sounding average of eight launches in the March–April 1985 period.

ularities of the ozone distribution observed near Ducke forest.

A good example on the size and extent of the horizontal and vertical ozone concentration irregularities is shown in Plate 1. It illustrates the ozone cross section below about 3.2 km near Ducke forest in the afternoon of May 2, 1987. The absence of data in the gaps observed between 1928 and 1931 UT, and two more starting at 1945 and 1949 UT, is caused by clouds. The section observed after 1931 UT shows irregularities in the horizontal and vertical directions varying between light blue (18 ppbv) and green/dark green (23 ppbv) between 3.2 and 1.5 km. The sizes of these irregularities are about 300–500 m in the vertical and several kilometers in the horizontal direction. Below about 1.5 km the irregularities vary between red (5 ppbv) and light blue (15 ppbv). This shows that measurements made at slightly different locations may show differences in ozone concentrations between 5 and 10 ppbv, when such irregularities are present. These irregularities, which appear to be associated with convection activity, were also observed during the dry season experiment. In another case (not shown) for May 7, the general distribution of ozone near Ducke is much more uniform than in Plate 1. There is, however, one striking isolated spot of an ozone maximum, at a height of 1.6 km near Ducke, at 1400 UT. It takes only a 3-min flight, or a few kilometers, for the ozone to drop from its 38 ppbv maximum to the background value of 16 ppbv.

One can define the tropospheric abundance, that is, the total ozone integrated in the troposphere. The top of the troposphere can be defined at 100 mbar, the tropopause, or somewhat lower, at 200 mbar for example, below the strong ozone gradient between troposphere and stratosphere. Figure 12 shows the time variation of the tropospheric O_3 abundance for the dry season and wet season experiments. The full lines use 100 mbar for the upper boundary, the dashed lines, 200 mbar. There seems to be no systematic variation for 1987, while in 1985 a minimum was reached on July 26. The mean, error bar, and number of soundings are shown, and in parentheses, the values calculated for the 200-mbar top are shown. For the dry season a real ozone increase with time occurred between July 26 and August 3. For the 1987 data set, no systematic trend can be seen. There is a short period of 2 days, however, April 22 and 23, that has much larger abundances with larger ozone values in the whole troposphere (Figure 10). Most soundings in 1987 fell within the 18–27 DU interval, with only the April 23 sounding standing out at the high side. A possible relationship to air mass transport is discussed in a later section. On days when more than one sounding was made, plus and cross symbols are used in Figure 12 to indicate the ozone integral.

Stratospheric Profiles

A composite stratospheric-tropospheric profile for low latitudes is shown in Figure 13, with results for different sites and different techniques. The different symbols represent averages of several soundings: crosses represent the Amazonian ABLE 2B data, and the continuous line shows Natal data for the period March–April, accumulated over several years of soundings at Natal. The triangles show the average result of a rocket experiment made in April 1985 at Natal [*Barnes et al.*, 1987]. The black dots represent eight ECC soundings from Natal in the period March–April 1985. Typical standard deviations for these averages are largest in the lower troposphere, about 0.5×10^{11} cm^{-3}. Around the ozone peak it is about 10% of the concentration.

As shown previously for the tropospheric average profile comparison, the wet season results (crosses) represent smaller concentrations in most of the troposphere, in comparison with the Natal results, obtained in the same seasonal period. There is almost no difference in the lower strato-

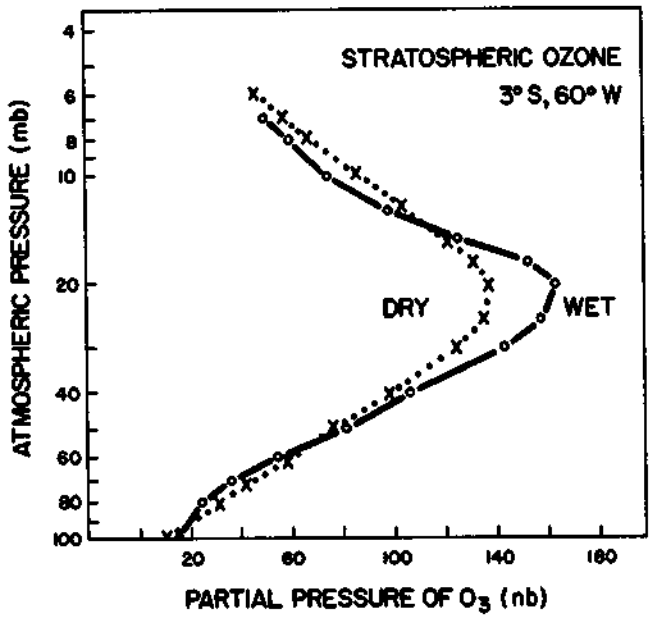

Fig. 14. Average stratospheric ozone comparison between dry (dots-crosses) and wet seasons (dash–open circles) in Amazonia from the ECC data.

sphere, but around the peak, the concentrations of the rain forest data are slightly larger. In the upper stratosphere a smaller amount of data points is available, but the differences seem to be within the measurement variability.

Also shown for comparison in Figure 13 is an average profile, shown by circles, obtained from an experiment using balloon and rocket sondes in India (8°N), carried out during March [*Subbaraya and Jayaraman*, 1987]. The largest differences seem to occur in the lower troposphere. The ozonesondes used in India are also of the ECC type and are manufactured by the Indian Meteorology Department. It appears unlikely that the difference of more than a factor of 2 in the lower troposphere, shown in Figure 13, could be attributed to differences in the sondes. The peak ozone concentrations around 27 km are slightly less for the Indian results compared with the ABLE 2B data.

A more detailed comparison in the stratosphere between the dry and wet seasons in Amazonia is shown in Figure 14, where the concentrations are shown in terms of partial pressure. The peak ozone concentration is slightly larger in the wet period, but in terms of total ozone content, the comparison is 264 DU in the wet season against 258 DU in the dry season, a difference of only 2%. At 20 mbar the dry season average of 140 nbar has a standard deviation of about 4 nbar. One may conclude that the difference between dry and wet seasons is small but significant.

Discussion

Ozone Chemistry

Major aspects of the ozone photochemistry were developed many years ago [*Levy*, 1971, 1972; *Chameides and Walker*, 1973, 1976; *Wofsy*, 1976; *Crutzen*, 1979], but other aspects, more specific to the tropics, are of more recent interest [*Crutzen*, 1987]. One of these is biomass burning, but the direct effect of the forest on atmospheric chemistry has also become important [*Zimmerman et al.*, 1978, 1988; *Rasmussen and Khalil*, 1985, 1988; *Brewer et al.*, 1984]. Other theoretical aspects involving transport as well are discussed by *Chatfield and Harrison* [1976], *Levy et al.* [1985], and *Jacob and Wofsy* [1988, this issue].

Ozone interacts chemically with several constituents of the troposphere. The OH radical will start oxidation chains that are especially important for ozone in the tropics, where ozone can be produced in the lower atmosphere from the by-products of biomass burning. On the other hand, in the forest, bacterial activity in the soil can produce methane (CH_4), and the metabolism of the plants can produce isoprene (C_5H_8). The oxidation of C_5H_8 by OH produces carbon monoxide (CO), and the oxidation of CH_4 and CO by OH in the presence of the nitrogen oxides (NO_x = NO + NO_2) and UV light, may produce ozone. As shown by *Logan* [1985], the simplest O_3 production cycle starts with CO and OH,

$$CO + OH \rightarrow CO_2 + H$$

followed by three intermediate catalytic reactions, and the ozone production reaction, with the overall net effect

$$CO + 2O_2 \rightarrow CO_2 + O_3$$

Similar cycles may start with CH_4, C_5H_8, or higher order hydrocarbons, but for all of these, it is necessary that an adequate supply of NO_x and UV radiation be available. While one ozone molecule is formed for each carbon monoxide, the ozone production from CH_4 may be 3 times larger, and even more for the higher hydrocarbons.

The strongest perturbation that is observed in the concentration of atmospheric species in Amazonia, such as ozone and carbon monoxide, is the result of biomass burning. Large amounts of CO_2, CO, and NO are directly produced in such rural combustion processes [*Crutzen et al.*, 1979], and the subsequent oxidation of CO leads to substantial amounts of ozone. Cases were reported when biomass burning affected Amazonian data in ABLE 2A [*Kirchhoff*, 1988*a*; *Andreae et al.*, 1988; *Sachse et al.*, 1988; *Browell et al.*, 1988]. Much stronger events were documented by a previous aircraft expedition in the Amazon region described by *Crutzen et al.* [1985], *Delany et al.* [1985], and *Greenberg et al.* [1984]. The strength of the dry season is shown by measurements at Cuiabá (16°S, 58°W) [*Kirchhoff et al.*, 1989], where concentrations of CO and O_3 in the dry season are 4 and 7 times larger than the wet season concentrations. Outside of the direct biomass-burning area the magnitude of the seasonal variation is about a factor of 2.

In the absence of UV light, the loss factor for ozone in the atmosphere by its reaction with NO is quite different in wet and dry seasons. Using K = 27.7 ppm^{-1} min^{-1} for the reaction rate in

$$O_3 + NO \rightarrow NO_2 + O_2$$

and using O_3 = 10 ppbv, NO = 0.5 ppbv for the dry season, the loss rate becomes L = 8.3 ppbv/hour near the surface. Because of the strong vertical gradient of NO, this rate decreases rapidly with height, but near the surface it is certainly strong enough to affect the diurnal variation of ozone. For the wet season period, much lower concentrations for NO were observed (A.L. Torres and K. R. Hooks, Nitric oxide measurements over the Amazon Basin during

ABLE 2B, submitted to *Journal of Geophysical Research*, 1989). Using O_3 = 6 ppbv and NO = 0.05 ppbv, the loss rate becomes L = 0.5 ppbv/hour, 16 times less than the dry season value (the NO values are based on the work of *Torres and Buchan* [1988]). This is evidently not strong enough to remove the daytime maximum O_3, around 6 ppbv in a period of about 5 hours except, perhaps, inside the forest. Again this shows the importance of the surface sink for O_3 and the turbulent mixing of the lower atmosphere in the process of determining the diurnal variation of ozone near the surface.

The wet season data set did not show transients as observed in the dry season. Besides the regular or cyclic variations of ozone near the surface, two types of transient, short-lived variations were noticed during the dry season experiment: ozone increases associated with nearby thunderstorms and ozone decreases observed in the daytime, associated with localized shower activity. One of the events observed in clear association with strong thunder activity near the observation site, near 1900 LT, when normally the ozone concentration has decreased to the nocturnal lower values, had an ozone increase of about 12 ppbv probably produced by strong downdraft transport in a cumulonimbus cloud. The ozone increase lasted for only about 1 hour. Another type of transient observed several times in 1985 was a short-lived ozone decrease, during the daytime, when the ozone concentrations are normally highest. The decreases lasted only about 1 hour and all appeared in the 1200–1400 LT period. Their origin seems to be related to localized showers producing strong inversion layers, where the ozone not being restored could perhaps be destroyed by reaction with NO. As shown above, the loss rate of 8.3 ppbv/hour is consistent with the dips in mixing ratio, but evidently the surface sink may add to the ozone destruction. After the shower the inversion layer disappears, and mixing from above restores the observed ozone concentration.

None of the transients just described were observed in the wet season experiment. It seems that the main reason for the absence of noticeable transients is the fact that the sources of the events, thunderstorms, or showers were isolated features in the dry season period, point sources that would stand out strongly in an otherwise calm and steady atmosphere. An isolated strong downdraft at night will bring down air of much higher ozone mixing ratios, which however, cannot survive for long, given the nocturnal stability of the lowest atmospheric layer and the losses therein. The situation is similar for the shower events in the daytime. A localized shower can momentarily cool off the atmosphere, so that the resulting inversion layer blocks off mixing of ozone from above, simultaneously allowing ozone to be lost against surface contact and reactions with NO. For an atmosphere in the wet season there are perhaps hundreds of such showers, and therefore the effect is much more distributed, making a more uniform atmosphere in which the transient character disappears.

Large-Scale Transport

The central region of Brazil has a unique large-scale transport system. It is important to examine some of its features for better understanding of the possible effects of transport on the concentration of some of the atmospheric constituents. This review will be based in part on the analysis of 4 years of radiosoundings over South America (1969–1973 [*Sobral*, 1980]). Other meteorological aspects are discussed by *Scala et al.* [this issue] and *Greco et al.* [this issue].

A large-scale transport pattern is determined in the troposphere over Brazil largely by two permanent features: easterly winds near the equator and westerly winds south of 25°S. In between, this wind system determines a region of anticyclonic motion (ACM), with its associated subsidence. In the lower troposphere this subsidence center is present over the northeast region of Brazil and is largely responsible for the drought characteristics of this region. Its location is frequently seen between latitudes 10° and 20°S and longitudes 30° and 45°W. This center of nearly circular motion can be easily identified from the construction of wind streamlines based on the radiosonde data mentioned. Its exact location has some seasonal and year-to-year variability. For the month of April the streamlines of the winds for the latitude of Manaus show a clockwise rotation from the surface to the upper height levels, which means that the center of anticyclonic motion is different for different heights, such that the subsidence is not exactly vertical but makes a certain angle with respect to the zenith. The center of ACM is displaced from the surface to higher altitudes, from northeast to southwest.

Air Mass Trajectories

Isentropic backward air mass trajectories have been calculated for specific events based on a special radiosounding campaign made during ABLE 2B. Sondes were launched every 6 hours from five Amazonian stations: Manaus (3°S, 60°W), Belém (1°S, 48°W), Boa Vista (2.6°N, 60.5°W), Vilhena (12.5°S, 60°W), and Tabatinga (3.5°S, 69°W). An example of the calculated trajectories is shown in Figure 15, when the starting point was at 1828 UT, for May 2, 1987. The general pattern of those trajectories is similar to the general streamline configuration mentioned before for the case of ACM and subsidence to the east.

So far, general features of large-scale transport and air mass trajectories have been discussed. The discussion will focus next on a specific case, shown in Figure 10. For April 22 and 23, a large increase of ozone concentrations was observed in the whole troposphere. From April 24 on, the concentrations were down again at normal values. Figure 16 shows the backward trajectories of the air masses at four different pressure levels: 950 (crosses), 850 (diamonds), 700 (triangles), and 500 mbar (squares), the same symbols and pressure levels of the previous figure. It is apparent that these trajectories are different from the general pattern discussed previously in Figure 15. Again the period of calculations is 48 hours and interpolations are obtained every 3 hours. The fact that the wind directions are the same at the different heights seems to indicate that during this period the ACM centers were aligned along the zenith direction, with subsidence being very nearly vertical. Our interpretation is that during this period the subsidence of air, with higher mixing ratios of ozone characteristic at the upper levels, was exceptionally efficient, causing a substantial increase in ozone concentrations at all lower height levels, as shown in Figure 10 for April 22 and 23. Besides this possibility, horizontal transport of an air mass of different origin must also be considered, as if for example, the air mass seen April 22 and 23 had been brought from some

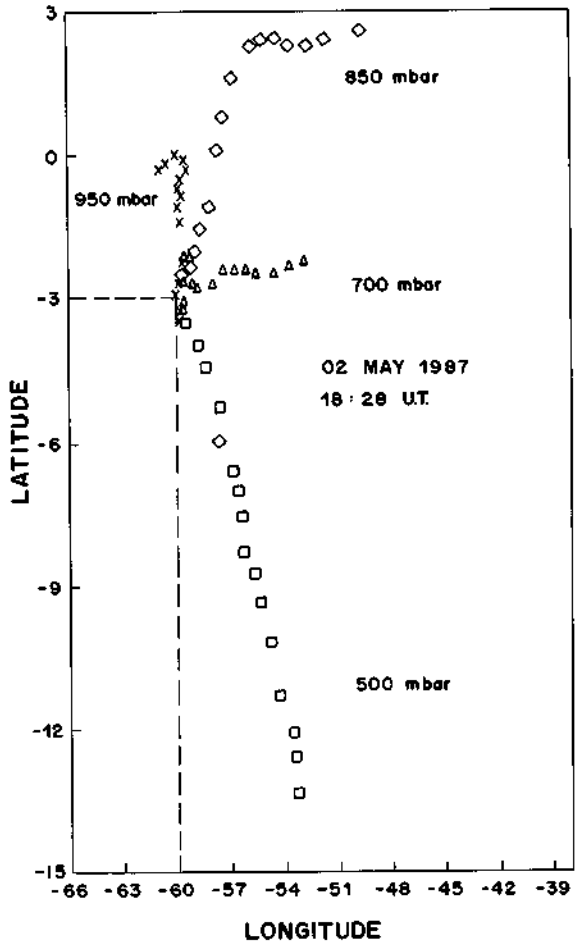

Fig. 15. Backward trajectories calculated for May 2, 1987, start time 1828 UT, start point 3°S, 60°W. The time period is 48 hours, at 3-hour steps.

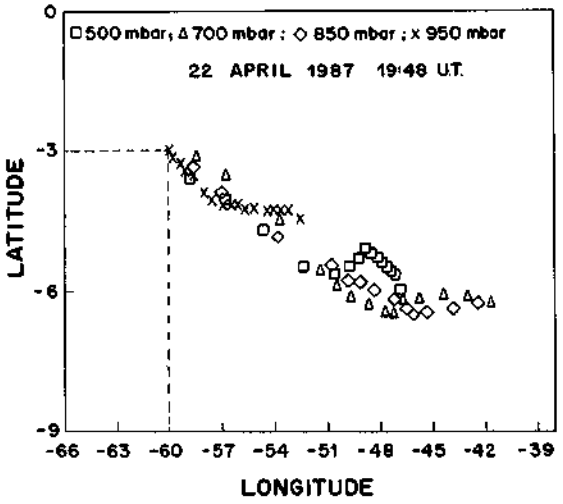

Fig. 16. Backward Trajectories calculated for April 22, 1987, start time 1948 UT, start point 3°S, 60°W. Four pressure levels are considered: 500, 700, 850, and 950 mb, as in Figure 15. The time period is 48 hours, at 3-hour steps.

nearby city, instead of from rural forest environments. This possibility seems to be very unlikely. Examination of air mass trajectories for other days, starting April 21, 23, and 24, indicates that they all represent air motions from the same general direction, that is, from the northeast of Brazil. No large pollution center can be found in this streamline. By April 26, the trajectories have recovered their general appearance of Figure 15. It seems therefore that strong subsidence caused the ozone increases on April 22 and 23.

SUMMARY AND CONCLUSIONS

Ozone concentrations were measured in a typical rain forest environment during the local wet season as part of a large field expedition. Observations were made almost continuously at the surface, and in addition, 20 ozonesondes were launched to obtain the vertical ozone profile. In comparison with a previous experiment which took place in the dry season, ozone concentrations were lower in the whole troposphere by nearly a factor of 2.

Ozone near the surface. A consistent variation of the ozone concentration near the surface was observed in the clearing, inside the forest, and 15 m above the surface. Ozone maximizes in the daytime around noon, and is minimum at night. This behavior is similar to the variations observed in the dry season, except that the amplitudes in the wet period are much lower, about 6 ppbv compared with 12 ppbv for the dry season. The ozone concentrations inside the forest were the smallest, 3.5 ppbv.

Ozone in the troposphere. Ozone concentrations in the mixed atmospheric layer and in the free troposphere were lower in the wet season than the dry season. Between 500 and 300 mbar, 10 ppbv less ozone were observed, and typical concentrations were about 40 ppbv.

Ozone in the stratosphere. A small but significant variation in the stratosphere was observed, the ozone peak being slightly larger (150 nbar) in the wet season than in the dry season (138 nbar), but this change represents only a variation of 2% in the ozone total content.

Acknowledgments. The ECC sondes were individually calibrated for pressure sensitivity by Arnold Torres, NASA, Wallops Island. We greatly appreciate his long-standing interest and support. We thank Robert Harriss and Jim Hoell for their coordination efforts of ABLE, and for support during and after the ABLE expedition to Manaus. At the Ducke preserve, we had the support of the INPA staff. Director Herbert Schubart helped us to overcome some of the extreme difficulties of working in the jungle. We have benefited from discussions with Daniel Jacob, Jack Fishman, and Steven Wofsy. The field work of José Alves, Francisco da Silva, Manoel dos Santos, as well as the coordination efforts in Manaus by Adauto Motta and Luiz Molion, are greatly appreciated.

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