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14. Abstract/Notes

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Acima de todas as leis, a Lei do Amor.

GROUND BASED OZONE MEASUREMENTS IN AN EQUATORIAL RAINFOREST

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ABSTRACT

Ozone concentrations have been measured in Manaus (3^{o}S, 60^{o}W) during NASA's ABLE expedition of July 1985. Diurnal variations of surface ozone were measured using UV surface ozone sensors, and 14 ozonesondes were launched to obtain vertical profiles of ozone in the troposphere and stratosphere. The diurnal variations are rather strong. At night it is not uncommon to obtain zero mixing ratios, diurnal values being around 10-20 ppbv, maximizing around 13 L.T. Tropospheric mixing ratios are much lower than at Natal (6^{o}S, 35^{o}W), and the mixing ratio gradient close to the ground is more than twice as large as at Natal.

Introduction

The northwest region of Brazil is covered by an extensive equatorial rainforest which represents a unique tropical ecosystem in which the huge Amazon river and its tributaries define the Amazon basin. This ecosystem can be important as a potential source or sink for several atmospheric gases. For example, the forest itself can contribute as a sink for methane (Keller et al. 1983) and as a source in the production of a number of other hydrocarbons (Zimmerman et al. 1978), nitrous oxide (Keller et al. 1983; Wofsy, 1984), and methane can be produced in swamp areas (Harriss et al. 1982) which can be found abundantly in the Amazon basin. It should also be noted that the Brazilian Amazon alone occupies about 3 million square kilometers, which makes its possible effects on the atmosphere important on the global scale as well.

Stratospheric ozone concentrations being lower with decreasing latitude, make the U.V. intensities that reach the troposphere larger in the tropics. Also, the solar radiation flux is larger in the tropical belt because of the relative Sun-Earth position. These features make the tropical atmosphere the one most effectively driven by solar energy, and chemical reactions can become much more active in the tropics than at mid latitudes. Under those circumstances, most of the OH radical is probably produced in this region (Crutzen, 1985) by U.V. dissociation of ozone followed by the reaction of $O(^1D)$ with water vapor, and since OH is a very reactive molecule, a chain of secondary reactions is immediately started, among which oxidation of methane (CH_4) and carbon monoxide (CO). This process in turn may produce ozone under certain circumstances, and in the troposphere this appears to be an important source for O_3 production in the presence of the nitrogen oxydes NO and NO_2 (Fishman et al. 1979).

Despite the obvious interest in making observations in this low latitude region, relatively few ozone measurements have been made in the tropics. The available data, however, have shown apparently

contradicting results. While at Panama, $9^{o}N$ (see Fishman et al. 1979), the ozone in the troposphere has mixing ratios of the order of 10 ppbv with no consistent and obvious seasonal variations, the more recent Natal, $6^{o}S$, data (Kirchhoff et al, 1981; Kirchhoff et al. 1983) show relatively large ozone averages with very large seasonal variations in the whole troposphere (Kirchhoff, 1984; Kirchhoff and Logan, 1985). The reasons for these differences in the O_3 behavior are not well known yet. There is strong evidence, however, indicating that nearby ecosystems and local environmental characteristics may have a strong influence on the composition and behavior of the atmosphere. It has been postulated (Delany et al. 1985; Crutzen et al, 1985) from airplane measurement expeditions that burnings in the campo cerrado region of central Brazil can contribute as a source to a number of gases of the atmosphere. These additional gases, including CO, may then be transported to other regions, and CO and CH_4 can be oxidized by OH to produce O_3. For a better evaluation of burnings in the cerrado and/or burnings of deforested areas of the Amazon region and their effects on atmospheric trace gases, as suspected from the previously mentioned aircraft and Natal measurements, it is evidently essential to obtain direct information on the natural Amazonian trace gases and their time variations. Ozone variations at the surface have recently been reported from the Venezuelan tropical savannah (Sanhueza et al. 1985) showing results very similar to our own data from Cuiaba ($15.6^{o}S$, $56.1^{o}W$). Previous data on surface ozone (Oltmans, 1981) in the Pacific Ocean tropical region have shown only very small diurnal variations, of at most 4 to 5 ppbv. This paper describes ground based ozone measurements made at Manaus during the NASA-GTE-ABLE field expedition of July-August 1985. The NASA Global Tropospheric Experiment (GTE) is described by McNeal et al. (1983).

Results

Surface ozone measurements were made in Manaus at the Ducke forest preserve owned by the Instituto de Pesquisas da Amazônia (INPA). The buildings of the preserve, and thus the potential

measurement sites, are distributed along a hill. There is a clearing at the top of the hill where meteorological parameters are routinely measured, being an open area of about 100 x 50 m, which has a simple one room construction with no air-conditioning. This site has been called the Met site, and we designate it as sampling site 1. In this building we have installed sensor 1, a strip chart recorder, and a cassette device for magnetic data recordings. The air samples were taken from the top of the roof through a 4 m long teflon tubing of 6 mm internal diameter. This instrument was maintained at this site throughout the field campaign, from July 11 to August 3, 1985. Measurements at additional sites were also performed with a second ozone analyser, sensor 2, starting at the Ducke preserve's administration building, another open area, downhill, designated as sampling site 2, from which site the ozonesondes were launched. Data were taken between July 16 and 29, with the aim of obtaining the ozone diurnal variation at the site where the ozonesondes were chosen to be launched. This site had the advantage of having an air-conditioned room, where the ozone calibration laboratory was installed. The air sample was also taken from the top of the roof, first, and later from a tree branch close to the building, using a 6 m long teflon tubing also of 6 mm internal diameter. This instrument was later moved to sampling site 3, located at the bottom of the hill. The last sampling site, number 4, was directly in the forest, on the top of the hill and beyond sampling site 1. The instrument was powered from a long cable and sheltered in a tent from which other measurements were performed, including NO, aiming to obtain simultaneous O_3 data.

The surface ozone measurements were made using ultraviolet absorption cell photometers. One of these, sensor 1, came from our own laboratory in São José dos Campos, whereas a second unit was kindly made available to us by Arnold Torres (NASA, Wallops Island). This second instrument, sensor 2, was recently calibrated and adjusted in the Wallops Island laboratory. It was used in Manaus first to make comparisons with sensor 1, and second, to make surface ozone

measurements around site 1, where sensor 1 made continuous measurements throughout the field campaign (July 11 to August 3).

The diurnal variations of surface ozone observed in Manaus are quite different from those found in the Pacific region, reported by Oltmans (1981) for Hawaii and Samoa. In Manaus the phase of of the diurnal variation is synchronized to the solar zenith angle, the maximum occurring around noon, whereas in the Pacific the maximum is seen at about 8 hours of local time. Furthermore, the difference between maximum and minimum,is much larger in Manaus, being of the order of 12 ppbv for the average shown.

Figure 1 shows the average diurnal variation obtained for site 2, in terms of ozone mixing ratio as a function of local time (L.T.). The vertical bars are the standard deviation from the hourly means, and therefore represent the day to day variability of the data in the July period. The ozone mixing ratio decreases to values close to zero at night. This feature has been consistent for the majority of diurnal periods observed. The daytime maximum for individual days is reached around noon or one to two hours later, when the mixing ratio reaches values between about 7 and 30 ppbv. The ozone concentrations increase right after sunrise and decrease before sundown.

It appears that such a behavior of surface ozone mixing ratios, decreasing to such extremely low values at night, has never been described in the literature before. As mentioned, this behavior was observed on most of the observation days except during the first days of August, when appreciable amounts of ozone were observed even at night, as will be discussed later (Figure 4). It appears also that at the end of the experiment the whole troposphere had considerable more ozone than at the beginning (Figure 6).

Very low boundary layer ozone values have also been measured by Routhier et al. (1980) during the May 1978 airplane survey over the latitude range between 2^{o}N and 13^{o}S, but his latitudinal ozone

trough was not seen in their 1977 O_3 data of the Gametag project, and may therefore be considered a sporadic event, not at all comparable with the cyclic diurnal character observed in the Amazon basin. It should also be noted that the Gametag results as well as results obtained earlier and summarized by Routhier et al (1980) implied a region of minimum free troposphere ozone concentration between 0 and 20^{o}S, but later flights have not seen such a minimum (Gregory et al. 1985). In any case, comparisons from latitudinal surveys should be made with caution since very large seasonal variations have been observed even at very low latitudes (Logan and Kirchhoff, 1986; Logan, 1986).

There is considerable variability of the ozone mixing ratio during sunlit hours. Figure 2 shows in detail the diurnal variations of four consecutive days in mid July. A thunderstorm caused the strong and fast increase at 6 L.T. on July 19. A rather pronounced minimum can be seen around noon on July 19 and 20. The variability is indicated by the vertical bars of Figure 2, showing the standard deviations of the 15 m averages. Is appears that the variability is mainly caused by turbulent air mass motion in a region where the ozone mixing ratio has a rather strong height gradient (see Figure 5).

Several changes in the position of the air sample inlet have been made to make sure the daytime variability was not a result of the position of the sample line. The initial idea was to sample the freely moving air of the clearing and, therefore, it seemed logical to sample air from the top of the roof. It turned out that the roof material would heat up considerably during sunlit hours which could affect the air inlet tube fixed some 50 cm above the roof. Therefore, air samples were also collected by fixing the line on nearby tree branches, but this made no evident difference in the collected data.

To further illustrate the uniqueness of the Manaus ozone data we show diurnal variations of the ozone mixing ratio at other ecosystems in Figure 3. The largest daytime value, the largest day-night variation, and the highest ozone diurnal mean is obtained in the downtown area of São José dos Campos(23.2°S, 45.9°W), a city of about 350,000 inhabitants. This data probably includes a considerable fraction of ozone produced by pollution products. The variation for Cuiaba, a remote site in the Brazilian savannah region, is somewhat in between the city results and the Manaus data. The savannah results are believed to represent a clean atmosphere during a period when no biomass burnings were observed. And finally we also show measurements from the Antarctic region (62°S, 60°W), which have no diurnal variation, apparently owing to the absence of local sources and sinks. This appears to be the opposite to the Manaus results, where extremely strong sources or sinks are active. In the case of ozone a very effective sink, fortunately identified and measured simultaneously with ozone, is a rather large production of nitric oxide in the forest. Large amounts of NO at night act as loss factors for ozone by the reaction

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

During the daytime, the above reaction is not terminal anymore, since sunlight can dissociate the NO_2 molecule

$$NO_2 + h\nu \rightarrow NO + O$$

and followed by the fast reaction

$$O + O_2 + M \rightarrow O_3 + M$$

the ozone molecule is regenerated during sunlit hours.

The ozone variations in the forest openings seem to be similar to the variations observed under the forest canopy. This is

shown in Figure 4, where we compare the observations from site 1, the clearing, with the data taken directly in the forest, site 4. The absolute values in the forest are generally lower than those in the clearing, but the variations seem to be rather well correlated. Since meteorological data within the forest indicate stable air conditions under the canopy, it is not clear at present, how the above correlation is accomplished.

It should be pointed out that the variations recorded between July 31 and August 3 are not the variations that one would expect on the basis of the average variation recorded on the previous days. Two independent elements of evidence point to the fact that the behavior in the troposphere, as far as ozone is concerned, was different on the mentioned last days of the experiment. Ozone was more abundant in the whole troposphere, indicated in Figure 6, and at the surface there was some ozone, much more than usually, present at night (Figure 4). An "ozone front", or even more generally, a "dirt front" may have passed by Manaus in this time period. It would have been much more difficult, if not impossible, to detect any correlation between the clearing and the forest, had the diurnal variation during this period benn well behaved. But the many short time scale variations that took place at both sites make it clear, despite the data gap, that a good degree of correlation was present.

A strong gradient of the ozone mixing ratio is observed close to the surface, as well as a corresponding gradient of NO. The largest differences are observed below 6 m height. The case shown in Figure 5 is an average for 4 measured profiles. It reinforces our interpretations made earlier for the ozone diurnal variation, specially the observed oscillations. Even on a larger vertical scale, from about the 900 mb level downwards, the mixing ratio gradient for the Manaus average is much larger than that for Natal, which appears to point again to the much larger ozone sink in Manaus. As can be seen from Figure 7, the sonde results show a gradient more than twice as large in Manaus, close to the ground.

The tropospheric total ozone content had a slight decrease between July 19 and 26, but then it increased showing a maximum at the last day of sounding, August 2. The height integral of ozone from the ground to 100 mb is shown in Figure 6. This variation in the whole troposphere seen by the ozonesondes seems to be consistent with the different behavior observed in the surface ozone data at site 1, between July 31 and August 2, when appreciable ozone concentrations were observed even at night, as shown previously in Figure 4.

The ozone mixing ratio in the troposphere follows a vertical pattern also observed at other stations. In the boundary layer our results are about 10 ppbv less than those of Crutzen et al. (1985). The best data sample to be used for comparison seems to be the Natal ($6^{o}S$, $35^{o}W$) data, where we have launched some 150 ozonesondes from 1978 to the present. There is no other tropical station with a comparable data base. Up to about 500 mb there is a considerable mixing ratio gradient, increasing the mixing ratio by more than a factor of 2 for the larger Natal data set. For the average Manaus profile shown in Figure 7, the mixing ratio is about 13 at the surface and 45 ppbv at 500 mb. Above 500 mb, the ozone mixing ratio stays roughly constant up to about 200 mb. It is apparent that the vertical profiles of ozone measured in Manaus have a remarkable similarity to the Natal data in terms of the vertical structure, but the absolute values in Manaus are smaller, as already noted. Higher than expected O_3 concentrations at Natal have been ascribed to subsidence (Logan and Kirchhoff, 1986). This result may be related to vertical motions owing to large scale circulation cells, characteristic of the region. 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. While Manaus is almost in the center of the upward moving branch of the Walker circulation cell, Natal is close to the high pressure side of the subsiding branch. We intend to investigate this further, including in this discussion the ozone profiles measured on board the aircraft.

Discussion

The three major results of this paper seem to be the diurnal variation of surface ozone concentrations, the low concentrations observed in the upper and lower troposphere, and the apparent correlation between surface ozone variations under the forest canopy and the forest clearing. In what follows we concentrate on discussing the diurnal variation of surface ozone.

The observed pattern of the diurnal variation in surface ozone concentrations in Manaus is similar to that observed at other continental sites, where sources and sinks are operative (Broder et al. 1981); Harrison et al. 1978; Lenschow et al. 1981; Fehsenfeld et al. 1983). Roughly, this pattern shows smaller O_3 concentrations at night, and larger values during the day. Exceptions are the observations of Oltmans (1981) in the Pacific Ocean region, and absence of diurnal variations in the polar regions. But observations at $40^{o}N$ by Oltmans (1981) and Fehsenfeld et al. (1983), and our own measurements in the Brazilian Savannah and downtown areas, confirm in general the description of the diurnal variation pattern. What is new, however, for the Manaus data, is the strong effect of a local ozone sink which makes the concentrations become vanishingly small at night. This strong surface ozone sink at Manaus seems to be a large surface emission of NO. Colleagues from the University of Harvard have measured large near surface concentrations of NO, between 500 and 700 pptv, decreasing upwards (Steven Wofsy, private communication). These values seem to be much larger than those observed at other sites, (Kelly et al. 1980; Kley et al. 1981) and may therefore be responsible for the removal of ozone, at night, by the recation

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

During the day, of course, this sink is inoperative, since in daylight the NO_2 molecule is easily dissociated by

$$NO_2 + h\nu \rightarrow NO + O$$

and the oxygen atom can produce ozone again in the fast three body production

$$O + O_2 + M \rightarrow O_3 + M \ .$$

Actually the NO sink effect for ozone at night is probably not the only reason for the low O_3 values observed. A stable layer of air develops, in general, close to the surface at night, which inhibits mixing. Therefore, ozone rich air, often injected from above, cannot replenish the O_3 lost in the stable layer by the photochemical sink, and the ozone concentration must decrease at night.

The daytime variations seem to be much more difficult to interpret. Let us concentrate on the daytime increase of surface ozone and the early afternoon decrease of O_3 concentrations at the surface, as is indicated by the Manaus data. In the early morning we have again a dynamic effect, the disruption of the stable surface layer established during the night, and the onset of mixing. This process of the formation of the so called dry convective boundary layer continuously increases the height of the mixing layer, reaching about its maximum of about 1000 m close to 12 hs of local time (Mike Garstang, private communication). Thus, in the time interval between early morning and noon, ozone from ever higher levels is mixed into the boundary layer with an expected O_3 concentration increase. What seems to be difficult to explain with this dynamic effect alone is the other side of the daytime variation, the O_3 concentration decrease after the noon maximum. At or even after a couple of hours after noon, there should be still plenty of mixing, and the photochemical surface sink is still inoperative. It appears, therefore, that some other mechanism not yet considered, must be responsible for the production of the ozone maximum, being also responsible for the concentration decrease closely after reaching the near noon maximum.

The difficulty with the photochemical interpretation is that photochemistry should be effective only in polluted environments, and the Manaus area must be considered, a priori, a clean air environment. From previous work (Fehsenfeld et al. 1983) and a much larger data base than ours, it has been established that the diurnal variation is small in two cases. For winter conditions, that is, when the solar energy input is small, and for "clean air" conditions. The first case probably never applies to the Manaus data, but the second may. The photochemical production of ozone is strongly dependent on the amount of odd nitrogen oxides present, roughly $NO_x = NO + NO_2$. For NO_x concentrations less than 600 pptv, the data of Fehsenfeld et al. (1983) show minimum nocturnal values of 35 ppbv, and maximum values of 45 ppbv. The daytime maximum is rather flat between about 7 and 15 L.T., when the average concentration decreases until 20 L.T., reaching the nocturnal minimum. This condition should represent clean air conditions. For polluted air a steady increase and decrease of ozone concentrations in the daytime can be seen in Fehsenfeld's data, and their interpretation is that only dynamics is operative in the first case, but that photochemistry dominates in the second one.

The Manaus data is, of course, not entirely comparable to the $40^{o}N$ data discussed above. There are, however, some points that can help for a better interpretation. For example, the amplitude of the day-night transition is about the same at Manaus and $40^{o}N$, about 10 ppbv, in the clean air case. But the Manaus data do not appear to favor either a slow day-night transition as would be expected for photochemical production, neither an always relatively fast transition around sundown, as would be expected if only dynamics is important. There are clear cases in which slow decreases can be seen after the noon maximum, and there are also cases when very fast concentration variations are observed between day and night.

The small ozone concentrations observed in Manaus would favor the hypothesis of negligible photochemical production. Is should be noted, however, that the NO concentrations observed in Manaus were

Summary

We describe the first ground based ozone measurements made in the Brazilian Equatorial Rainforest. Surface ozone measurements were made continuously during the experiment and 14 ozonesondes were launched. The results can be summarized as follows:

1 - Diurnal variation - Surface ozone concentrations at Manaus show a strong diurnal oscillation between almost zero ppbv at night and about 12 ppbv during the day, with considerable day-to-day variability of the daytime maximum, which occurs at about noon. The diurnal average is much lower than values measured at other environments.

2 - Correlation between clearing and forest - Simultaneous ozone measurements made under the canopy and in a nearby forest clearing show a good degree of correlation, with the implication that some mechanism of surface-canopy exchange is operative.

3 - Troposphere O_3 profiles - The ozone concentration at Manaus was much lower than at Natal, not only at the surface but also in the whole troposphere.

Acknowledgements

We thank Arnold Torres for continuing support. The O_3 measurements within the forest and the O_3 profiles close to the ground were performed in collaboration with Steven Wofsy, Warren Kaplan and Mike Keller. We also thank José Alves and Isa Silva for their work in Manaus and their continuing interest, and Y. Sahai, E. Pereira, and L. Molion for useful discussions.

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Figure Captions

Figure 1. Average diurnal variation of surface ozone measured in Manaus.

Figure 2. Surface ozone mixing ratios in a sequence of 4 days.

Figure 3. Comparison of the ozone diurnal variation in different environments.

Figure 4. Comparison of ozone variations in the forest and in the clearing, between 31 July and 03 August 1985.

Figure 5. Ozone and nitric oxide profiles close to the ground.

Figure 6. Time variation of the tropospheric ozone content at Manaus.

Figure 7. Average vertical profile of ozone at Manaus and comparison with the Natal data.

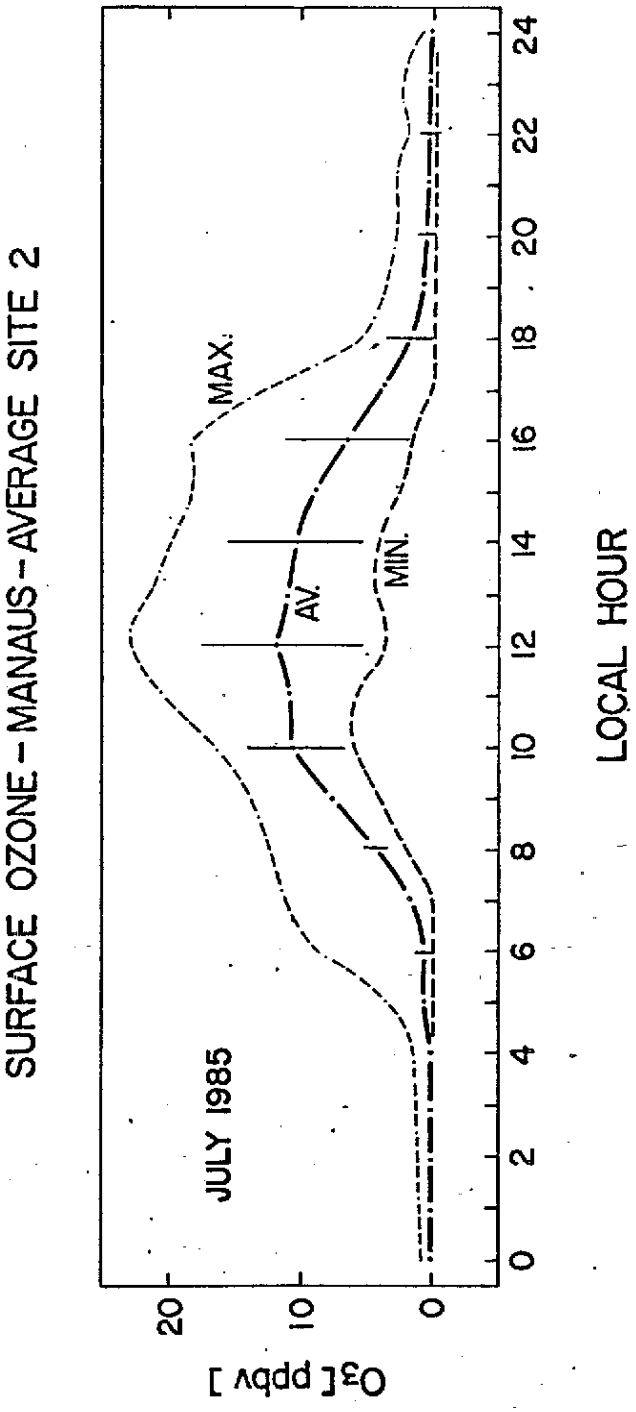

Fig. 1 - Average diurnal variation of surface ozone measured in Manaus.

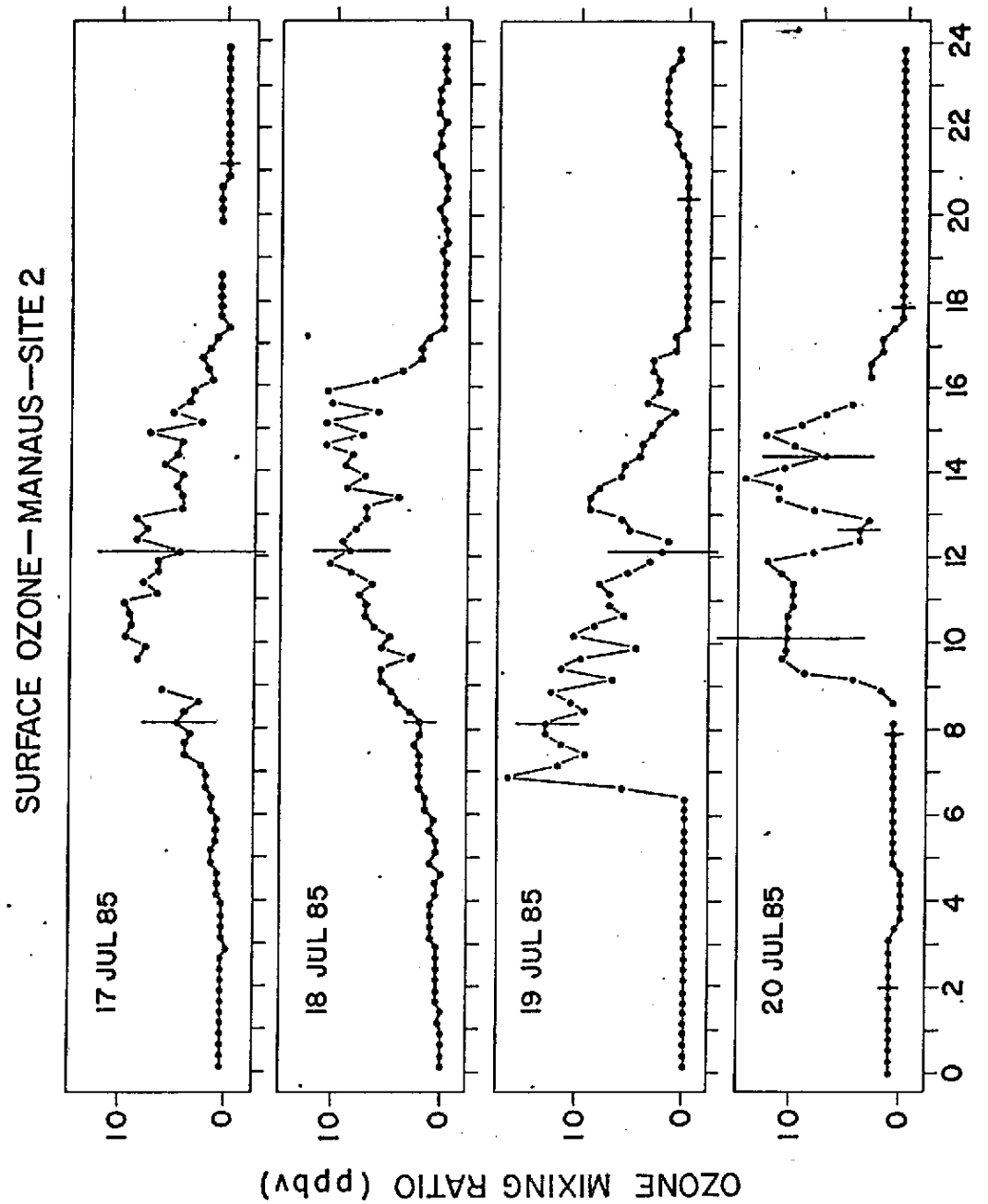

Fig. 2 - Surface ozone mixing ratios in a sequence of 4 days.

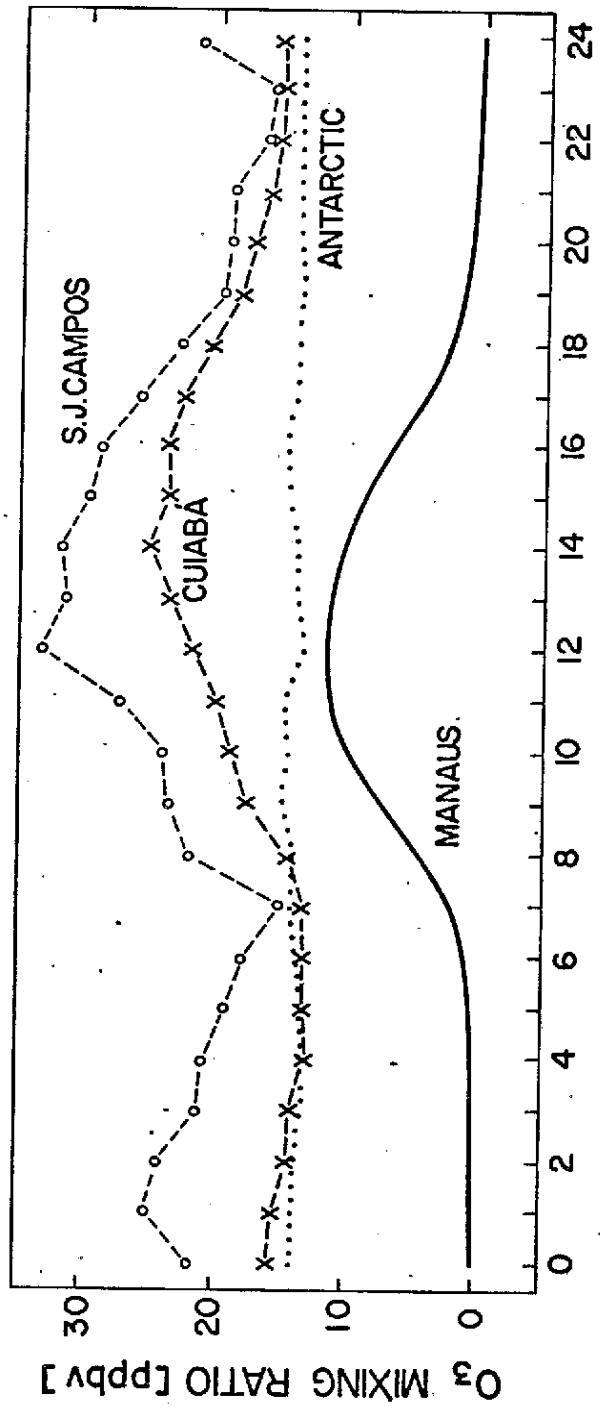

Fig. 3 - Comparison of the ozone diurnal variation in different environments.

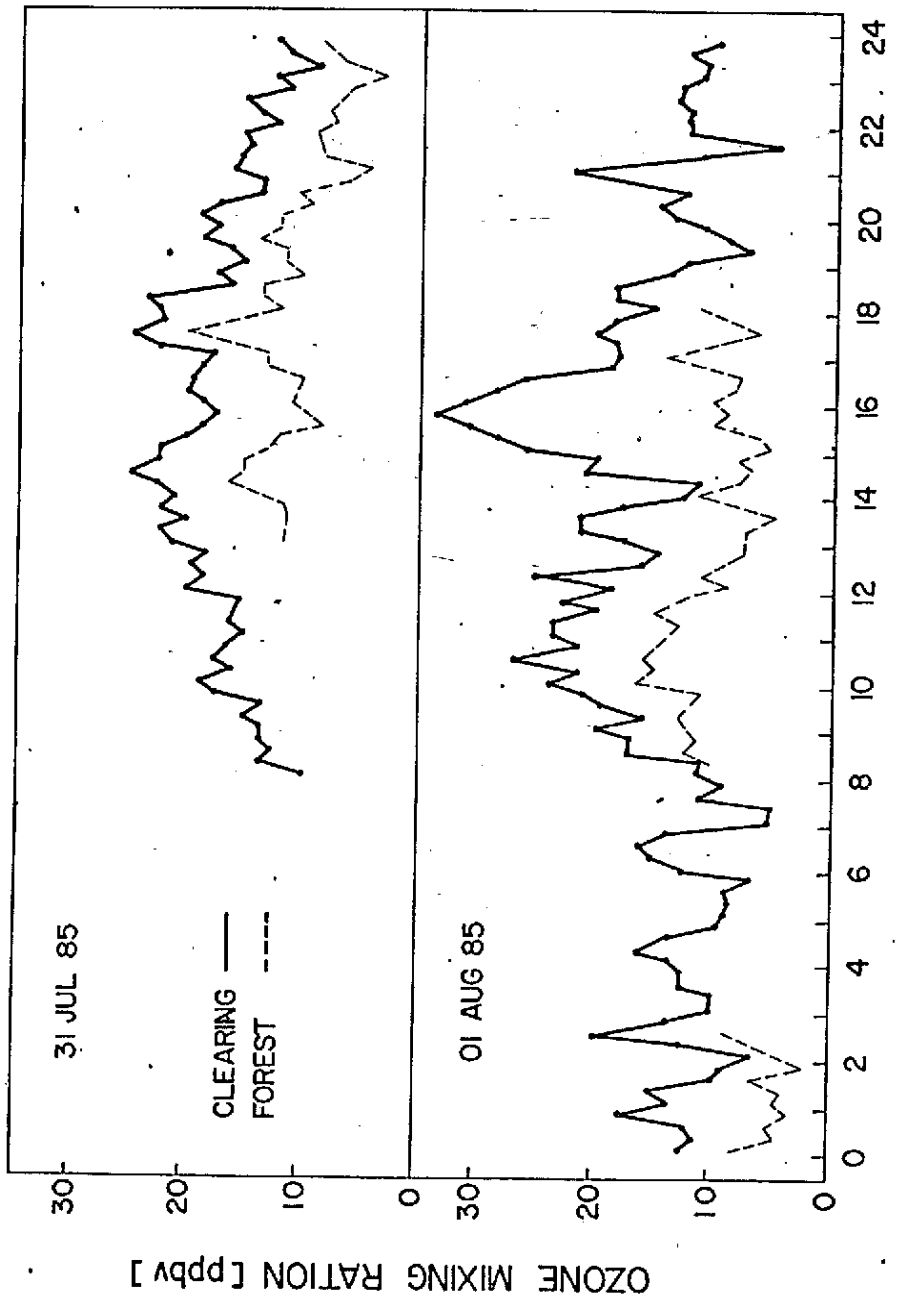

Fig. 4a - Comparison of ozone variations in the forest and in the clearing, for 31 July to 01 August 1985.

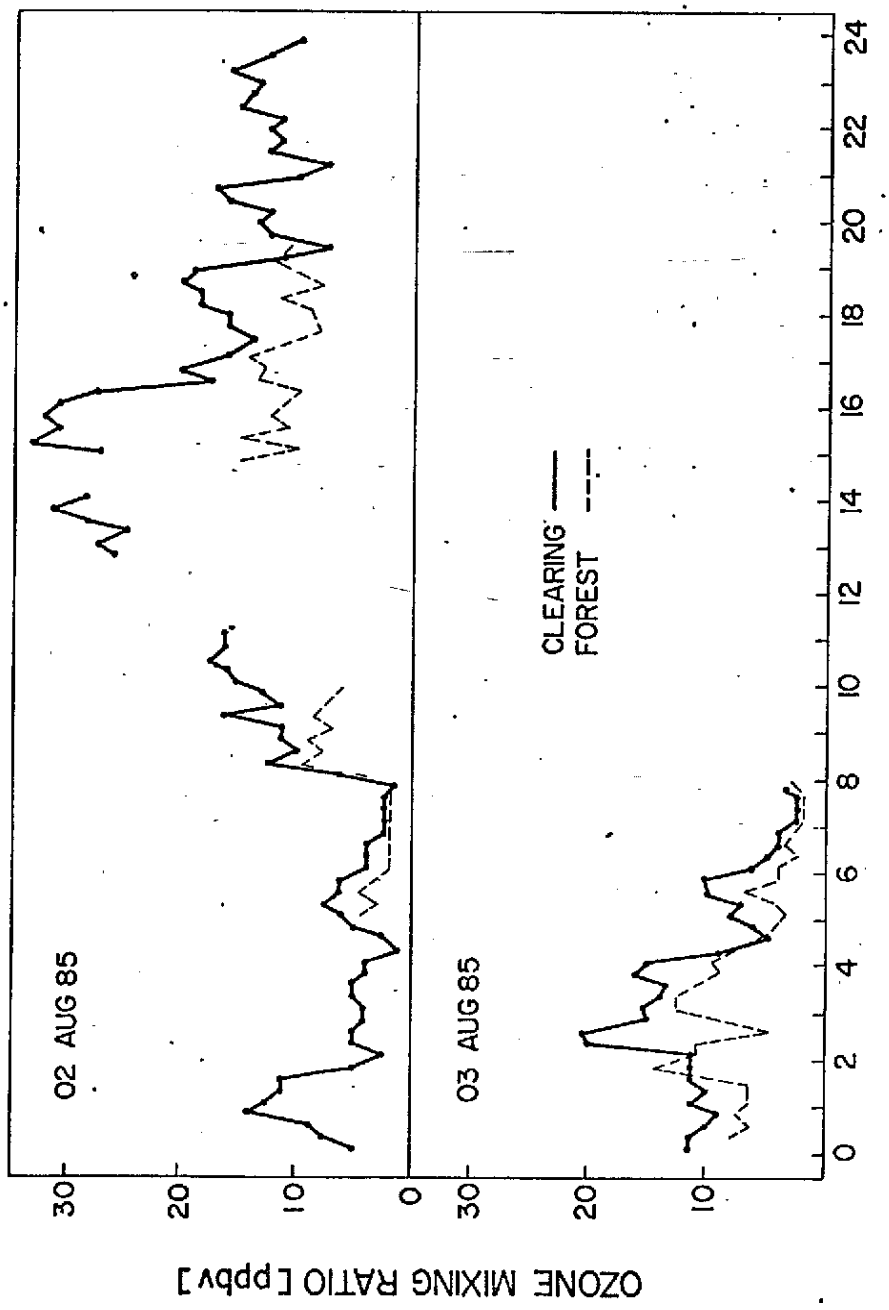

Fig. 4b - Comparison of ozone variations in the forest and in the clearing, for 02 August to 03 August 1985.

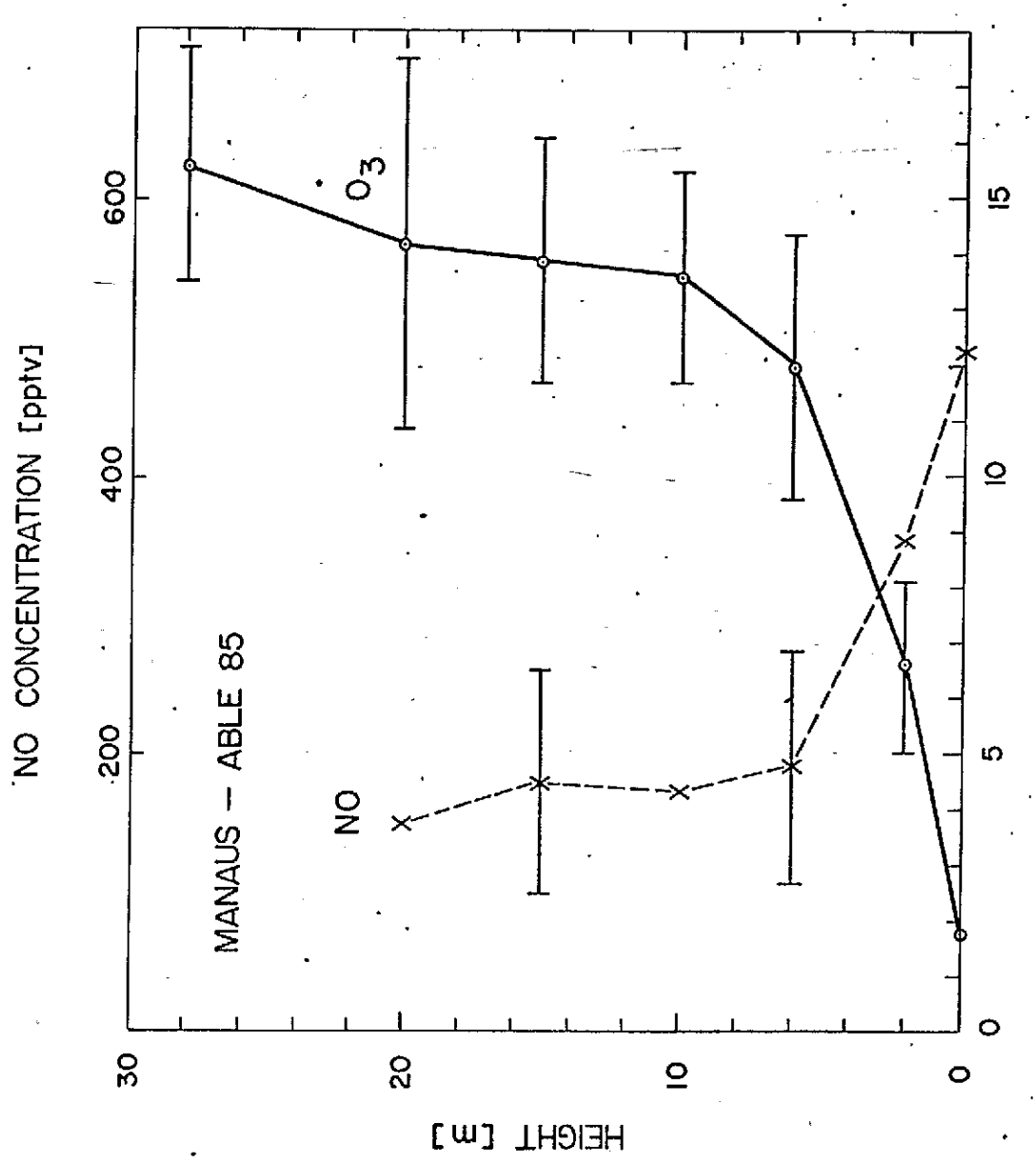

Fig. 5 - Ozone and nitric oxide profiles close to the ground.

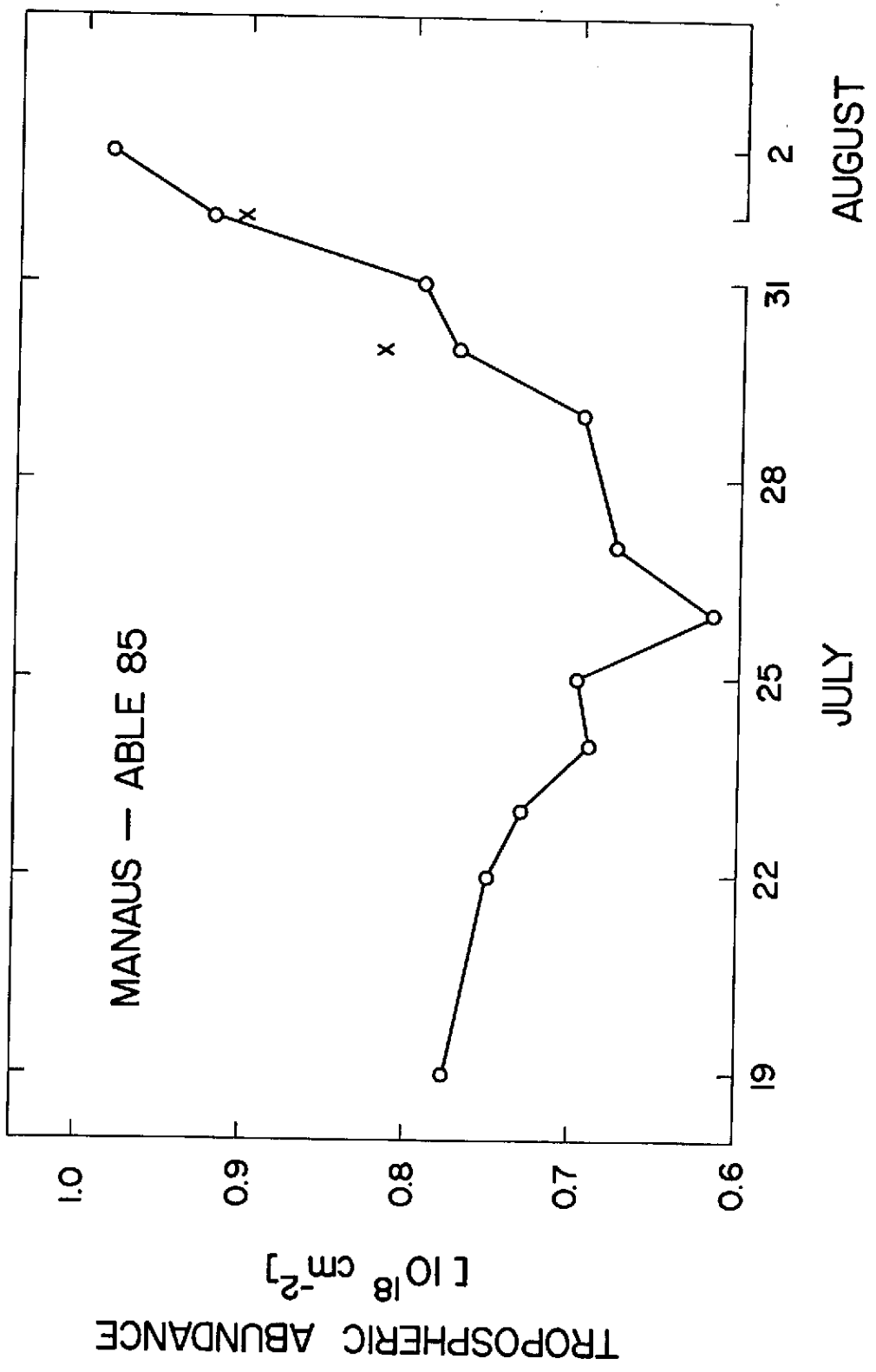

Fig. 6 - Time variation of the tropospheric ozone content at Manaus.

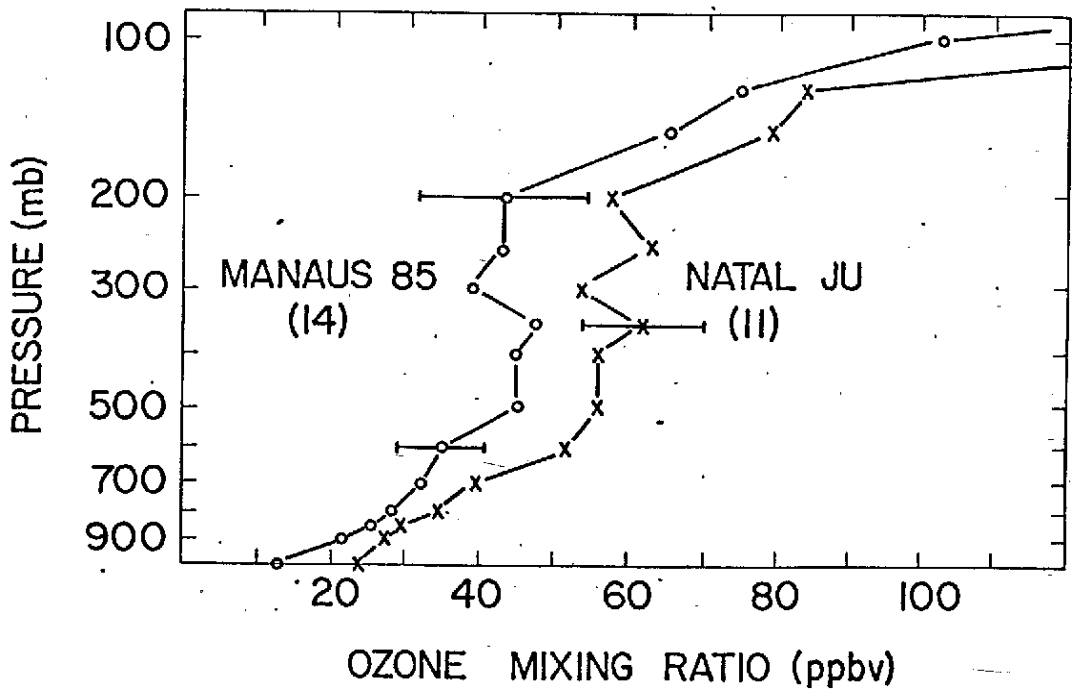

Fig. 7 - Average vertical profile of ozone at Manaus and comparison with the Natal data.

Aprovada pela Banca Examinadora

em cumprimento a requisito exigido para a obtenção do Título de Mestre em Ciência Espacial

Dr. Renê Adalid Medrano-Balboa — Presidente

Dr. Walter D.Gonzalez Alarcon — Orientador

Dr. Osmar Pinto Júnior — Co-Orientador

Dr. José Pantuso Sudano — Membro da Banca -convidado-

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Candidato: Odim Mendes Júnior

São José dos Campos, 18 de setembro de 1985