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TROPOSPHERIC OZONE MEASUREMENTS AT THE BRAZILIAN ANTARCTIC STATION

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Tropospheric ozone measurements are described from observations made at the Brazilian Antarctic Station Comandante Ferraz (62.1°S, 58.4°W). Ozone measurements at the surface were made almost continuously during several years, using ultraviolet absorption photometers. In the upper troposphere, ozone concentrations were obtained using balloon sondes, launched in the summer of 1991 and between March and October, 1992. Surface ozone concentrations show strong seasonal variations each year. The minimum monthly average occurs in February, 11.7 ppbv (parts per billion by volume) and the maximum in July, 29.6 ppbv. There is no apparent diurnal variation. Sporadic fast decreases in ozone are associated with synoptic scale perturbations during front passages, when the ozone mixing ratio may drop by 10-20 ppbv for about 6 hours or more. The ozonesonde data show a well-defined local mixing layer. The ozone mixing ratio does not change at the upper boundary of the mixing layer, indicating little or no photochemical activity. The mixing ratio follows a vertical distribution with a small positive gradient of about 2.5 ppbv/km.

MEDIDAS DE OZÔNIO NA TROPOSFERA DA ESTAÇÃO ANTÁRTICA BRASILEIRA *Descrevem-se medidas de ozônio na troposfera observadas na Estação Brasileira Comandante Ferraz (62.1°S, 58.4° W). As medidas de ozônio de superfície foram feitas quase que continuamente durante vários anos, usando fotômetros de radiação ultravioleta. Na troposfera superior, as concentrações de ozônio foram medidas usando sondas de ozônio lançadas em balão, numa campanha do verão de 1991, e em outra realizada entre março e outubro de 1992 (inverno). A cada ano, as concentrações de ozônio de superfície mostram intensas variações sazonais. A média mensal mínima foi observada em fevereiro, 11,7 ppbv (partes por bilhão por volume), e a máxima em julho, 29,6 ppbv. Não existe variação diurna regular. Rápidos decréscimos esporádicos de concentração de ozônio são associados a perturbações de escala sinóptica durante passagens de frentes, quando a razão de mistura do* O_3 *pode ter uma queda de 10-20 ppbv durante 6 horas ou mais. As sondagens mostram uma camada de mistura bem definida. A razão da mistura do ozônio não se altera no limite superior da camada de mistura, o que parece indicar falta de atividade fotoquímica. A razão de mistura segue uma distribuição vertical com um pequeno gradiente positivo de 2,5 ppbv/km.*

INTRODUCTION

The Brazilian Antarctic station Comandante Ferraz has been established at King George (62.1°S, 58.4°W), one of the South Shetland islands near the top of the Antarctic Peninsula. King George island houses also at least seven other stations of different countries, but closer contact is kept with the Chilean base Marsh, which offers the facility of an air strip. The Brazilian Antarctic station was established after 1982, when the Brazilian Antarctic Program was created (CIRM PROANTAR Program), with logistic support of the Brazilian Air Force and Navy. The objective of the program is to carry out scientific projects to study the Antarctic region. One of the research themes is the Antarctic atmosphere.

This report describes ozone measurements in the troposphere of Ferraz station: surface ozone measurements, and ozone profiles obtained from balloon borne ozonesoundings.

DATA DESCRIPTION AND TECHNIQUES

The air sampling facility for ozone measurements operates from a separate building (metallic container) that has been assembled at Punta Plaza, Ferraz station, at a distance of about 500 m from the main building. Power supply is provided by an electric power line coming from the station diesel generation plant. A cone shaped aluminum foil protects the air inlet teflon tubing (length 3 m, diameter, 1/4") from rain and snow.

The surface ozone measurements were made with a calibrated ozone photometer, which provides ozone mixing ratios every 15 seconds. The technique and previous results have been described, for example, in Kirchhoff (1988a), Kirchhoff and Silva (1989), Kirchhoff (1989), Kirchhoff and Rasmussen (1990), Kirchhoff and Pereira (1986), and Kirchhoff (1988b). Surface ozone measurements at Ferraz station were started during the summer of 1984-85. During 1989, 1990 and 1991, it was possible to maintain the monitoring activities during the whole year, including the winter period.

The sounding equipment uses a modern phase shift automatic directional antenna (manufactured by AIR Inc.), which receives radiosonde and ozonesonde signals at 1680 MHz. The sondes use digital transmission. During ascent, the sondes can make an average of about 60 observations per km, including temperature, pressure, relative humidity, temperature of the sensor, battery voltage, and ozone. For a typical sounding height of 25 km, this represents the collection of about 9000 data points.

The ozonesonde is of the ECC (Electrochemical Concentration Cell) type (Komhyr, 1969; Komhyr and Harris, 1971). This sounding technique has been used extensively in the tropics by Kirchhoff et al. (1991), and elsewhere by Oltmans and Komhyr (1976, 1986). It uses an iodine/iodide redox cell, where two platinum electrodes are immersed in neutral buffered iodide solution of different concentrations in the cathode and anode. This provides an internal small voltage difference which allows a current to flow between the electrodes, when air containing ozone is pumped into the cathode. The electrical signal is then converted to partial pressure of ozone. Balloons of 1200 and 2000 g were used. The major difficulty during launch are the strong surface winds in Antarctica. By the time the balloon reaches heights of 15-20 km, the range to the balloon is already 100-150 km, which is the limit for the radiosonde transmitter. For many of our soundings, the transmitted signals were lost before the balloon reached heights of 20-25 km.

The soundings for 1992 are listed in Table 1. They include launches before and during the period of the formation of the Antarctic ozone hole (Stolarski, 1988) in the stratosphere. The results of stratospheric ozone will be described elsewhere. In the summer of 1991 another set of sondes were launched as shown in Table 2.

Table 1. Ozonesonde launches from Ferraz station in 1992 for studies in the troposphere.

Lançamentos de ozoniossondas da estação Ferraz em 1992 para estudos na troposfera

#	DATE	TROPOPAUSE HEIGHT(mb)	TROPOPAUSE TEMP.(c)	MIXING HEIGHT(mb)	WINDS
1	27 MAR	320	-51.3	790	S,SW
2	28 MAR	222	-59.5	800	SW
3	04 APR	220	-63.1	640	SW,W
4	21 APR	206	-61.0	800	SW,W
5	11 MAY	200	-70.0	950	U
6	13 MAY	U*,220	-58.0	850	W,NW
7	10 JUN	250	-65.0	850	W,NW,N
8	20 JUN	U,350	-53.0	790	SW,W
9	29 JUN	280	-68.0	800	SE,S
10	07 JUL	205	-67.8	700	SW,W
11	19 JUL	240	-69.5	900	SW,W
12	28 JUL	200	-64.0	680	SW
13	05 AUG	180	-73.0	700	W
14	07 AUG	240	-69.5	800	SW,W
15	11 AUG	300	-59.5	850	W
16	13 AUG	172	-74.6	U,650	W
17	16 AUG	200	-72.0	800	SW,W
18	18 AUG	200	-74.0	850	W,NW
19	22 AUG	250	-64.5	700	W,NW
20	23 AUG	200	-67.0	850	W
21	25 AUG	300	-64.0	840	SW,W
22	30 AUG	260	-67.0	850	SW,S
23	04 SEP	U,200	-68.0	U,900	W,NW,N
24	06 SEP	U,300	-56.0	U,900	S,SW
25	10 SEP	U,200	-65.0	U,900	U
26	15 SEP	300	-59.5	820	SW,W
27	25 SEP	200	-70.5	850	SW,S
28	29 SEP	243	-61.9	850	E,NE-S,SW
29	03 OCT	240	-70.0	800	W

∗ designates a tropopause not well-defined.

Table 2. Ozonesonde lauches from Ferraz station in 1991 for studies in the troposphere.
Lançamentos de ozoniossondas da estação Ferraz em 1991 para estudos na troposfera.

#	DATE	TROPOPAUSE HEIGHT(mb)	TROPOPAUSE TEMP.(c)	MIXING HEIGHT(mb)	WINDS
1	17 JAN*	290	-48	600	N,NW
2	19 JAN*	310	-55	700	NW
3	21 JAN	900	-52	U	S,SE
4	22 JAN	300	-54	590	NW
5	23 JAN	250	-58	800	NW
6	25 JAN	340	-47	800	U
7	26 JAN	290	-55	810	W
8	29 JAN	300	-52	810	W
9	31 JAN	240	-54	790	W
10	02 FEB	350	-49	800	W
11	03 FEB	210	-61	950	U
12	05 FEB	300	-48	750	S,SE
13	06 FEB	300	-48	700SW	SW
14	07 FEB	240	-58	800	U

* Only radiosonde data.

RESULTS AND DISCUSSION

Temperature

The temperature profile in the Antarctic region does not follow the general pattern of decreasing temperatures in the troposphere, followed by increasing temperatures in the stratosphere, as is the case in the tropics and mid latitudes.

Fig. 1 shows four temperature profiles, two of which have well-defined tropopauses and two others for which it is not obvious where the tropopause is. To avoid overlapping, curve 4, for April 04, 1992, was plotted adding +5°C to all data points; to curve 2, for August 23, 1992, -7°C were added, and for curve 1, for July 28, 1992, -15°C were added. The different symbols were plotted at a rate of only one every 15 data points.

Very sharp tropopauses can be seen for curves 3 and 4, followed by strong gradients of the ozone mixing ratios. Right after the temperature pause, the temperature increases with height for about 2-3 km, as is normally the case for the stratosphere, but then the temperature again starts to decrease with height.

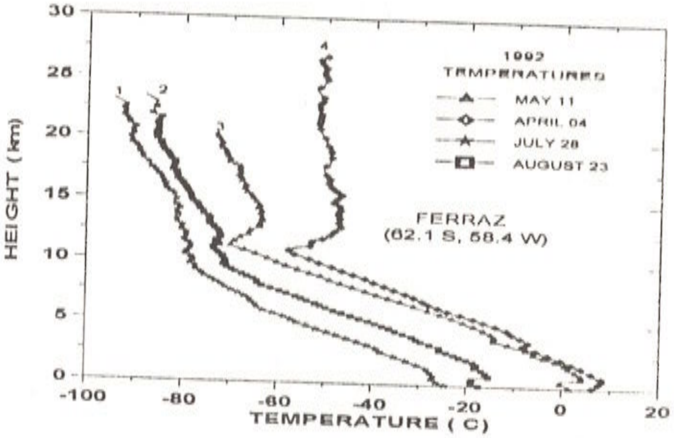

Figure 1. Atmospheric temperature profiles in Antarctica showing two cases where the tropopause is well-defined (May 11 and April 4) and two other profiles where the tropopause is not well-defined.

Perfis de temperatura da atmosfera Antártica mostrando dois casos em que a tropopausa é bem definida (maio 11 e abril 14) e dois casos em que a tropopausa não é bem definida.

In fall and winter periods, the lowest temperatures in the stratosphere were similar in magnitude to that of the tropopause. In the spring period, however, most soundings showed stratospheric temperatures much lower than the tropopause values. This is also the case for the July and August curves 1 and 2, shown in Fig. 1.

The tropopause height is an important parameter for ozone studies in the troposphere since it is at this boundary that the ozone mixing ratio suddenly starts to increase to its stratospheric value. At the Brazilian station Ferraz, the tropopause occurred mostly near 200-250 mb, as shown more exactly in Fig. 2. Of the 29 observations, 11 had the tropopause between 200 and 250 mb, and 10 cases were below 200 mb. The tropopause temperature was between about -60 and -70°C. As shown in Fig. 3, nine soundings observed tropopause temperatures between -65 and -70°C, and 8 cases observed temperatures between -60 and -65°C. The lowest temperatures in the stratosphere reached nearly -80°C.

Fig. 4 shows a plot of the pressure-height temperature pair for the tropopause. Normally, a higher tropopause should have a lower tropopause temperature, and vice-versa. Fig. 4 shows this, but with a large dispersion. The tentative linear fit shows a correlation coefficient of only 0.5, indicating a temperature drop with height of nearly -7°C/km (near the surface the adiabatic lapse rate is -9.8°C/km).

The lower troposphere shows a well-defined mixing layer in most of the soundings. The histogram of Fig. 5 shows that in 16 cases, the mixing layer height was observed between 900 and 800 mb. The mixing layer height is often visually defined by a temperature inversion, and/or a strong drop in humidity. This is shown in Fig. 6, for June 20, 1992. Ozone and humidity are shown as a function of height. The humidity shows a sharp drop, from about 95 to 45% at about 770 mb or 1.8 km, indicating the end of the mixing layer and beginning of the planetary boundary

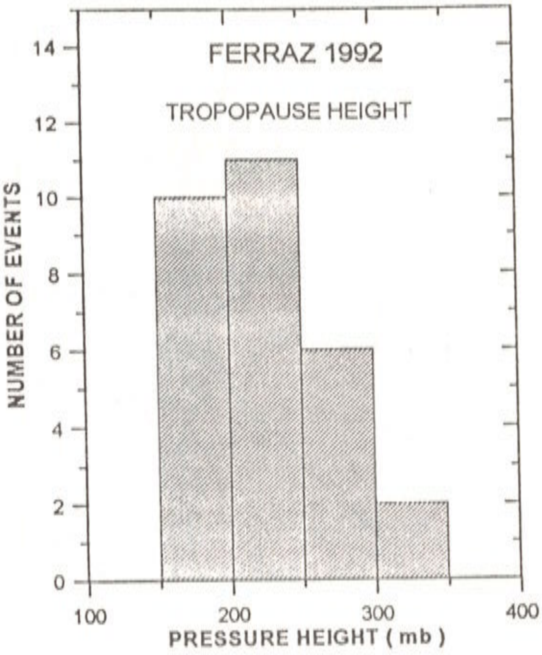

Figure 2. Histogram showing the pressure height of the tropopause at Ferraz station.

Histograma mostrando a altura em pressão da tropopausa na estação Ferraz.

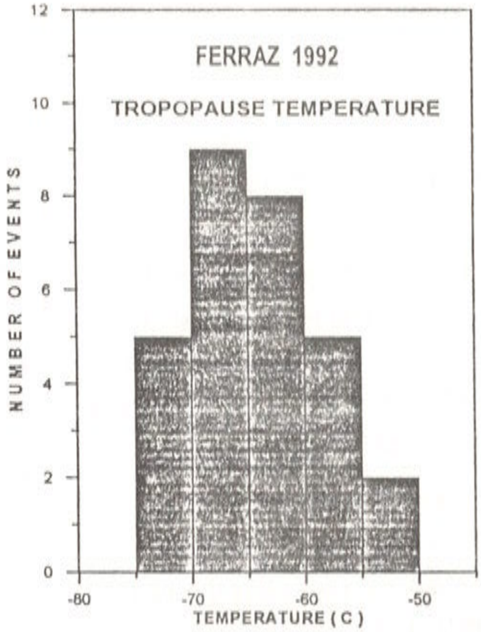

Figure 3. Histogram for the tropopause temperature at Ferraz station.

Histograma para a temperatura da tropopausa na estação Ferraz.

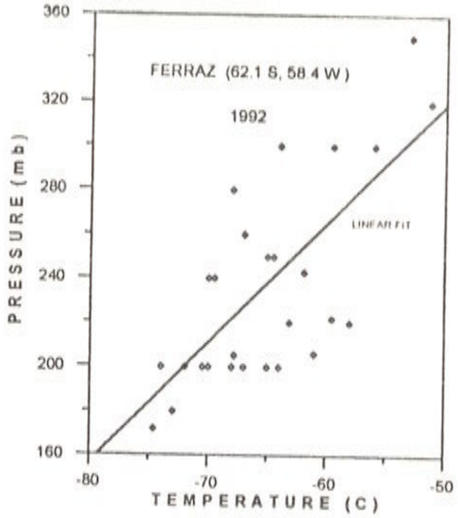

Figure 4. Correlation between tropopause pressure and temperature.

Correlação entre pressão e temperatura da tropopausa.

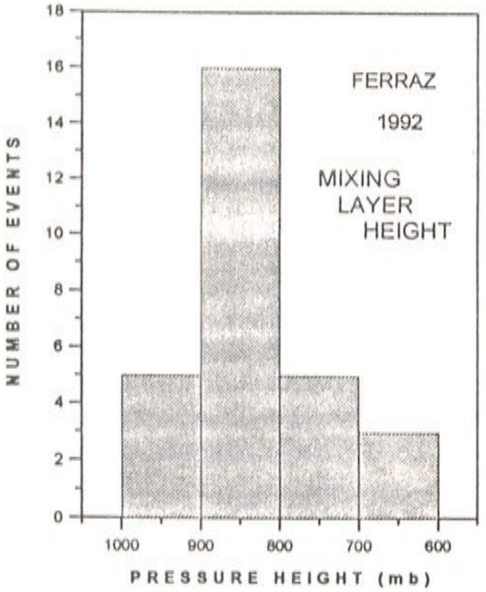

Figure 5. The mixing layer pressure height.

A altura em pressão da camada de mistura.

layer. The interesting feature here is that there is no corresponding change in the mixing ratio of ozone. Since the mixing layer is in direct contact with the surface, it is in this layer that most of the anthropogenic activity occurs. In a perturbed mixing layer, larger ozone concentrations may be expected, but in a very clear troposphere there should be no difference in concentration, as is the case shown in Fig. 6. The ozone concentrations, expressed in mixing ratio, have no change in value above the mixing layer, indicating a well-mixed and clean troposphere.

In contrast to the Antarctic profile, another profile is shown in Fig. 7 for Porto Nacional, (10°S, 48°W) Brazil, for a sounding during the Brazilian dry season period. For this day, September 17, the mixing layer top is much higher at Porto Nacional, roughly 3 km or 650 mb. It is a clear case when the mixing layer shows more ozone than the planetary boundary layer above, in this case a result of nearby biomass burning which produced ozone in the mixing layer. At about the boundary of the mixing layer there is a

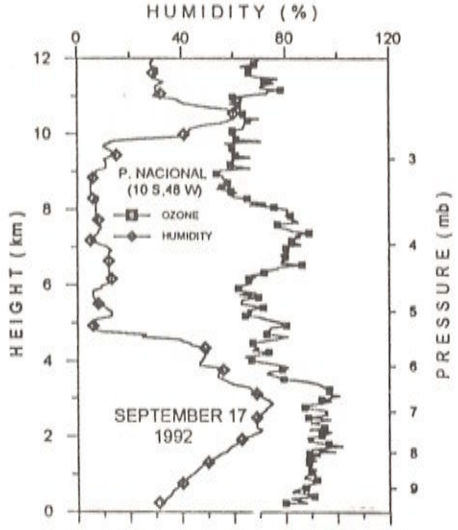

Figure 6. Ozone and humidity at Ferraz station (62°S, 58°W) as a function of height (and pressure) for June 20, 1992.

Ozônio e umidade na estação Ferraz em função de altura (e pressão) para 20 de junho de 1992.

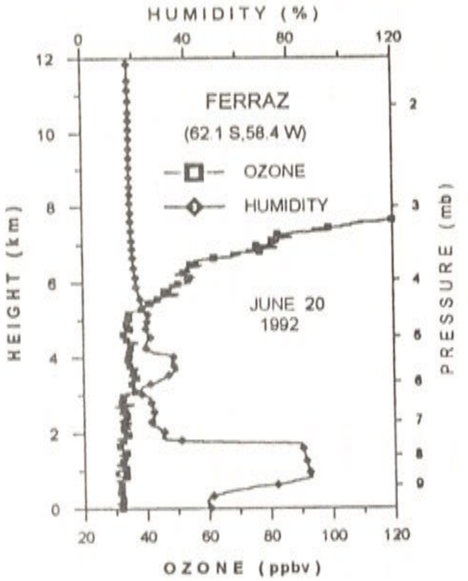

Figure 7. Ozone and humidity at Porto Nacional (10°S, 48°W) as a function of height (and pressure) for September 17, 1992.

Ozônio e umidade observados em Porto Nacional (10°S, 48°W) em função de altura (e pressão) para 17 de setembro de 1992.

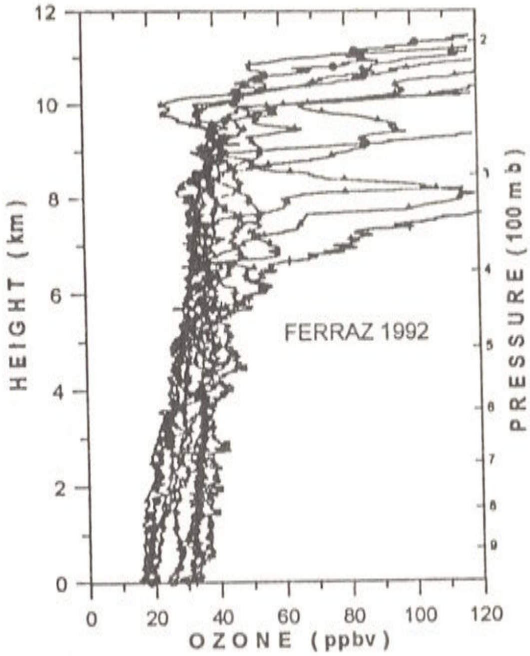

Figure 8. Mass plot of the first 10 tropospheric ozone profiles.

Superposição dos 10 primeiros perfis de ozônio na troposfera.

drop of the ozone mixing ratio from about 90 to 75 ppbv.

Fig. 8 shows a mass plot of the first 10 ozone profiles obtained at Ferraz station in 1992 (from 27 March to 07 July, see Table 1), showing the general behavior in the troposphere and lower stratosphere. In the troposphere, the ozone mixing ratio shows a small continuous vertical gradient of about 2.5 ppbv/km, with no apparent difference in the mixing layer and the layer above. This vertical mixing ratio gradient is about one half of the gradient observed in the tropics, about 5.5 ppbv/km (Kirchhoff et al., 1991). The large variability above about 8 km is the result of the vertical displacement of the Antarctic tropopause.

SURFACE OZONE

Surface ozone has been measured at about 1.5m above surface level using the UV absorption technique, which has been used extensively at other sites (Kirchhoff, 1988a; Kirchhoff and Rasmussen, 1990).

Surface ozone mixing ratios are obtained at every 15 seconds and are recorded on a strip chart. Since most of the time the variations are rather smooth, it is usually sufficient to register the values at the full hours. For every day, there are then 24 hourly ozone values. The average daily ozone is the mean of these 24 values. From these, the monthly mean is obtained, which is useful to display the seasonal variation (Fig. 9).

There is no diurnal variation of surface ozone at Ferraz station, contrary to what occurs at mid and low latitudes, where a distinct daytime maximum is observed (Kirchhoff, 1988a, b; Kirchhoff and Rasmussen, 1990). This behavior has been described previously at Ferraz station (Kirchhoff and Pereira, 1986) and also for other Antarctic stations (Oltmans and Komhyr, 1976; Robinson et al., 1983, 1984). It is interesting to note that the absolute values of mixing ratios observed at Ferraz station and Natal (6°S, 35°W), for example, are similar, of the order of 20 ppbv, although the air masses have completely different origins.

Surface ozone could change its concentration by either ozone loss/production by chemical reactions, or ozone losses by contact (loss reactions) on surfaces. It has been shown (Wesely et al., 1981) that the ozone flux to the ground is larger than that to wet (water, snow, ice) surfaces. The largest downward flux of ozone occurs in forest areas where the numerous leaves present a very large effective contact area, which makes the ozone concentrations small, as in the Amazon forest, for example (Kirchhoff, 1988a; Kirchhoff et al., 1988). At Ferraz station the air masses near surface lack the necessary chemical ingredients to produce ozone. On the other hand, the rather smooth contact surfaces of snow, water, and ice destroy ozone at a relatively small rate. In addition, the surface is often isolated from the troposphere above, by temperature inversion a few meters above surface. All these factors contribute for an almost constant ozone mixing ratio near the surface during the diurnal period.

Fig. 9 shows the seasonal variation of surface ozone at Ferraz station using all available data from 1985 to 1992. The vertical bars represent ± one standard deviation from the average. The seasonal variation is quite large, almost a factor of 3 between minima and maxima. The maximum is centered around July (winter) with 29.6 ppbv and the minimum is observed in January-February with about 11.7 ppbv. Also shown in this figure are the maxima observed each month. These maxima are not much above the averages plus standard deviations.

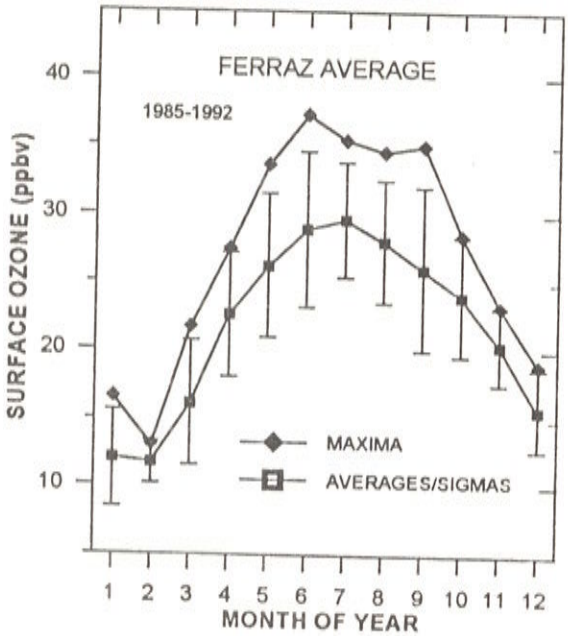

Figure 9. Overall surface ozone mixing ratio monthly averages for all available data, between 1985 and 1992. Standard deviations from the mean are shown as vertical bars.

Médias mensais da razão de mistura do ozônio de superfície para todos os dados já obtidos entre 1985 e 1992. Barras verticais são os desvios-padrão da média.

The seasonal variation is believed to be a consequence of tropospheric large scale air circulation. The whole Antartic troposphere is influenced by cell motions that include vertical and horizontal branches which, besides influencing ozone, also have a strong effect on other atmospheric parameters, such as temperature, for example. One of these early models of circulation affecting Antarctic stations, has motions towards the pole from subantarctic latitudes, with subsidence to the surface, and equatorward outflows (Wexler et al., 1960). Another candidate process for contributing winter maximum ozone concentrations near the surface is downward transport of ozone from stratospheric heights, as for example, in tropopause fold events (Browell et al., 1987).

Fig. 10 a and b show strong perturbations of the ozone record during abrupt frontal passages. The air masses, having different origins and different meteorological histories, also have different chemical composition as clearly shown by the examples of Fig. 10 a and b. For the period in August 1990 there is excellent correlation between atmospheric pressure variations at the surface and the surface concentration of ozone. This is also seen in the October 1990 event shown in Fig. 10 b.

SUMMARY

Tropospheric ozone measurements are described at the Brazilian Antarctic station Ferraz. At the surface, UV photometers have been used to study ozone variations, and above the surface ozonesondes have been used. Important results of this research are summarized below:

1 - Average ozone concentrations at the surface vary between 12 and 30 ppbv, in February and July, respectively.

2 - There are no systematic diurnal variations.

3 - During distinct frontal passages of air masses there may occur an abrupt change of the surface ozone concentration.

4 - The average mixing layer height is observed between 900 and 800 mb.

5 - There is no ozone concentration change at the boundary of the mixing layer.

6 - The tropopause height is observed between 200 and 250 mb.

7 - The tropopause temperature is between -65 and - 70°C.

8 - There seems to be a correlation between the tropopause height and tropopause temperature, but with large dispersion.

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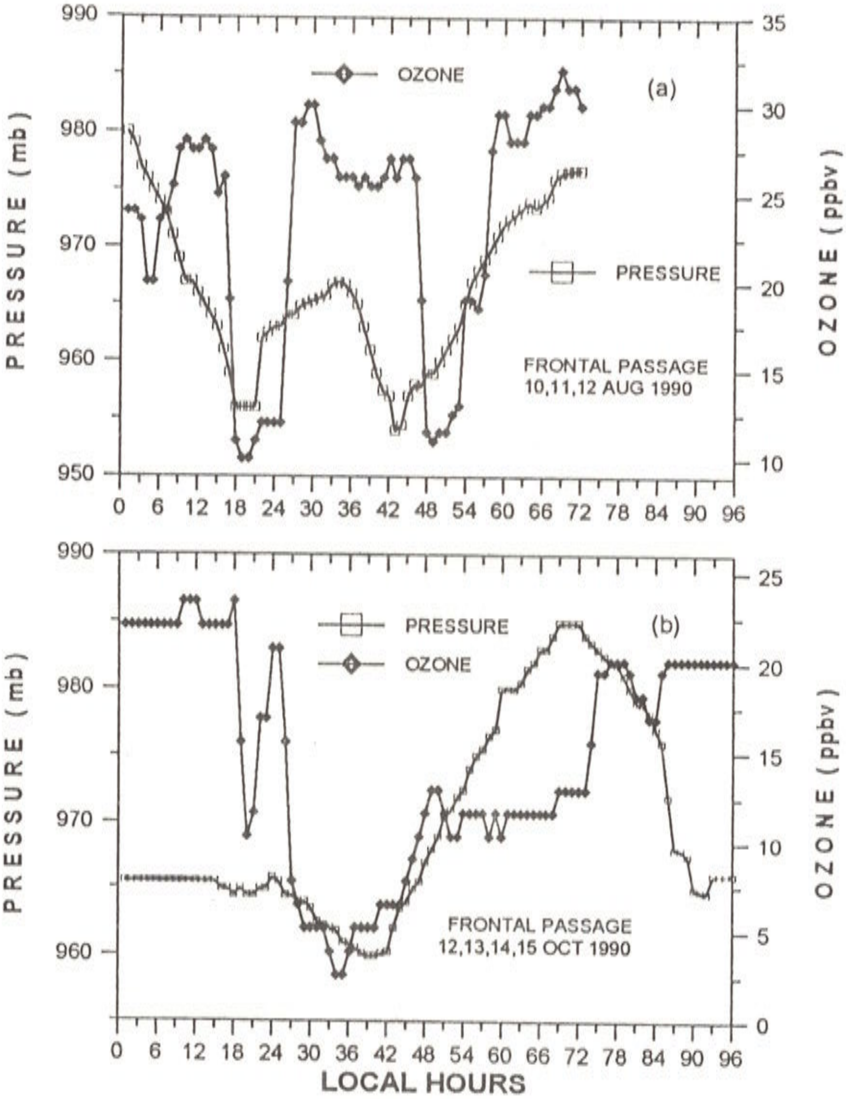

Figure 10. Decreases in atmospheric pressure and surface ozone mixing ratios during frontal passage in (a) August 1990 and (b) October 1990.

Decréscimos da pressão atmosférica e da razão de mistura do ozônio de superfície durante passagem de frentes em agosto (caso a) e outubro de 1990 (caso b).

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