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Seasonal Variations of Tropospheric Ozone at Natal, Brazil

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We present an analysis of ozone measurements from Natal, Brazil (6°S, 35°W), with a focus on the seasonal behavior in the troposphere. The amplitude of the seasonal cycle at Natal is much larger than at Panama (9°N), the only other tropical site for which similar data are available. Concentrations of ozone in the middle troposphere in the southern spring are unexpectedly high, 60–70 ppb, similar to values found at northern mid-latitudes in summer, and larger by 20–30 ppb than values found at Panama and at southern mid-latitudes. We suggest that photochemical production of ozone associated with emissions of CO, hydrocarbons, and NO_x from biomass burning may contribute significantly to the high values of ozone, but note that stratospheric intrusions could also play a role. The data available at present do not permit a definitive evaluation of the relative importance of these two sources of ozone. The data from Natal, in combination with recent aircraft and surface data, show that tropical ozone exhibits strong spatial and temporal inhomogeneities. The distribution of tropospheric ozone appears to be considerably more complex than the traditional view, which suggested a northern midlatitude maximum, and north/south hemispheric asymmetry. The seasonal cycle in the total column of ozone at Natal appears to mirror the behavior of the tropospheric contribution to the ozone column rather than the stratospheric contribution, and this may account for differences in the annual cycle of the total column at Natal versus other tropical locations.

1. INTRODUCTION

Ozone plays a fundamental role in controlling the chemical composition and climate of the troposphere. Tropospheric photochemistry is initiated by photolysis of ozone near 300 nm, leading to production of $O(^1D)$, which then reacts with water vapor to form the hydroxyl radical. Absorption by ozone of thermal radiation at 9.6 μm influences the energy budget of the troposphere [*Ramanathan and Dickinson*, 1979; *Fishman et al.*, 1979*a*]. Our knowledge of the distribution of ozone is not commensurate with its importance in the chemistry and physics of the lower atmosphere. Data for ozone in the tropics are particularly lacking. We present in this paper an analysis of the first systematic series of measurements of the vertical distribution of ozone in the southern tropics made with reliable instrumentation. These data not only alter our view of the global distribution of ozone, but they challenge conventional ideas concerning the processes that control its distribution.

The majority of measurements of ozone have been made at midlatitudes of the northern hemisphere. Analysis of the few available measurements from the tropics indicated that ozone is more abundant in the northern tropics than the south and more abundant at midlatitudes than in the tropics [e.g., *Fabian and Pruchniewicz*, 1977; *Fishman et al.* 1979*b*]. These conclusions were based on (1) a series of vertical soundings made at Panama (9°N) by Hering and Borden in the 1960s [*Chatfield and Harrison*, 1977*a*] and a few soundings made in the southern hemisphere with instrumentation that has since been shown to be unreliable [*Chatfield and Harrison*, 1977*b*], (2) 34 aircraft flights over Africa [*Fabian and Pruchniewicz*, 1977], and (3) surface measurements at 4 locations in Africa [*Fabian and Pruchniewicz*, 1977]. Subsequent measurements of ozone on the island of Samoa [*Oltmans*, 1981] and aircraft data from the Pacific Ocean [*Routhier et al.*, 1980] and South America [*Seiler and Fishman*, 1981] were consistent with this simple picture of the global distribution of ozone.

Observational data for ozone have contributed significantly to our understanding of the dynamical and chemical processes that influence the distribution of the gas [e.g., *Junge*, 1962; *Fishman and Crutzen*, 1978]. Ozone enters the troposphere from the stratosphere, and is removed by interactions at the earth's surface. It is formed during the photooxidation of CO, CH_4, and hydrocarbons in the presence of nitrogen oxides, and is removed by reactions involving HO_x radicals. Stratosphere-troposphere exchange of ozone is most effective at middle and high latitudes during late winter and spring [*Danielson*, 1968; *Danielson and Mohnen*, 1977; *Mahlman and Moxim*, 1978]. The photochemical source of ozone associated with emissions of CO, hydrocarbons, and NO_x from fossil fuel combustion should be largest at northern mid-latitudes in summer. Since the lifetime of ozone in the troposphere is only about one month [*Logan et al.*, 1981], it seems reasonable that highest concentrations of ozone should occur at northern midlatitudes in spring and summer, and that concentrations should be larger in the northern hemisphere than the south.

Analysis of the first 40 vertical profiles of ozone from Natal, Brazil (6°S) [*Kirchhoff et al.*, 1983] in combination with recent aircraft data from South America [*Gregory et al.*, 1984; *Delany et al.*, 1985] suggested that the global distribution of ozone was more complex than described above. *Kirchhoff* [1984] showed that average concentrations of ozone at Natal are considerably higher than at Panama. Furthermore, there appears to be a significant seasonal variation in ozone at Natal, in contrast to the more uniform behavior found at Panama [*Logan*, 1985]. Recent measurements from surface sites, balloons, and aircraft indicate that the distribution of ozone in the tropics is quite heterogeneous. Latitudinal gradients in ozone appear to vary considerably with season and

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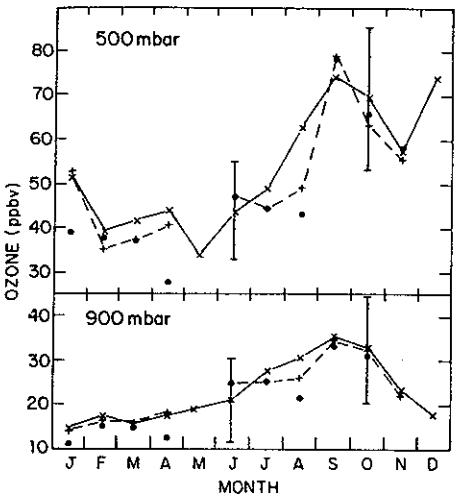

Fig. 1. The effect of scaling to Dobson measurements on values derived for ozone. The crosses show monthly means calculated from measurements which have not been scaled to the ozone column; the vertical lines show one standard deviation. The pluses are obtained if results for each sounding are scaled to a Dobson measurement of the ozone column before forming the monthly mean; the dots show similar results, omitting all soundings for which the ratio Dobson/sonde is outside the range 0.8–1.2.

witn longitude. The data from Natal suggested that, at certain times of year, concentrations of ozone in the southern tropics exceed those in the northern tropics, and are of similar magnitude to those at midlatitudes [*Logan*, 1985].

We present here the results of 84 ozone soundings from Natal, with a focus on the behavior of ozone in the troposphere. These data permit a more definitive analysis of the seasonal behavior of ozone. The larger data set confirms the conclusions based on the preliminary measurements, and allows us to assess the contribution of the seasonal cycle of ozone in the troposphere to the seasonal cycle in the vertical column of ozone. We speculate about the possible causes of the elevated concentrations of ozone found over Natal in the austral spring, and suggest further studies which should help elucidate the alternative mechanisms. The data are described in section 2, results are presented in section 3, and are discussed in section 4. Conclusions are summarized in section 5.

2. Data

The vertical distribution of ozone has been measured at Natal (6°N, 35°W) since November 1978, as part of a collaborative project between the National Aeronautics and Space Administration of the U.S. and the Instituto de Pesquisas Espaciais of Brazil. Results from this program, with a focus on the stratosphere, were described in *Kirchhoff et al.* [1981, 1983]. *Kirchhoff* [1984] discussed results for the troposphere. The measurements are made using an electrochemical concentration cell (ECC) ozonesonde [*Komhyr*, 1969; *Komhyr and Harris*, 1971], which is based on the reaction of ozone with potassium iodide. The instrument is flown with a standard meteorological radiosonde, so that ozone data are obtained in conjunction with measurements of temperature, humidity, wind direction and wind speed. Measurements were made twice a month in 1978–1981, rather infrequently in 1982, and have continued on a weekly basis since September 1983.

Laboratory studies have shown that these sondes tend to overestimate the concentration of tropospheric ozone by 8%–14%. Recent field tests indicate that the precision of the sondes in the troposphere is 6%–10% [*Barnes et al.*, 1985; *Hilsenrath et al.*, 1984]. The sondes used in this program are checked against a Dasibi UV instrument before flight; they are identical to those used for soundings at Wallops Island (Barnes et al, 1985). The average ratio ECC/UV for 51 sondes used at Natal was 1.04 ± 0.07, which is similar to the ratio obtained recently for 75 soundings at Wallops Island, 1.08 ± 0.04 [*Barnes et al.*, 1985].

In this study we consider a total of 84 balloon soundings, which took place between November, 1978, and April, 1984. Most of the measurements were taken near 1200 GMT, midmorning local time. Another 10 soundings were excluded from this analysis, three because they showed unacceptably high ozone concentrations, and seven because they were multiple launches on the same day, at times other than 1200. Comparison could be made between the integrated column of ozone obtained by the sonde and the total overburden of ozone obtained with a Dobson spectrophotometer for 57 soundings. The mean ratio Dobson/sonde was 0.96 ± 0.11, which is consistent with the UV comparisons described above. This ratio was outside the range 0.8–1.2 for only 4 soundings, and all were within the range 0.7–1.3, which is considered acceptable according to criteria of the *World Meteorological Organization* [1982].

It has been common practice to normalize ozone concentrations obtained with electrochemical sondes to concurrent Dobson measurements [*Dutsch et al.*, 1970]. This procedure was developed originally because Brewer Mast sondes typically underestimate the column of ozone by as much as 20%. We elected not to normalize our measurements in this manner, since there appears to be no real justification for such a scaling of ECC data, and we would have had to omit over 30% of the soundings from the analysis. We show in Figure 1 monthly mean values for ozone obtained using (1) all 84 soundings, (2) 57 soundings scaled to the Dobson results, and (3) 53 soundings scaled to the Dobson results for which the ratio Dobson/sonde is in the range 0.8–1.2. Evidently the results are not sensitive to the use of the scaling procedure. Monthly mean values are calculated from between 3 and 11 soundings per month for the full data set.

3. Results

3.1. *Ozone at Natal*

The seasonal cycle of ozone in the troposphere at Natal is shown in Figure 2. Concentrations below 250 mbar are highest in September and October, the austral spring, and are lowest in March, April, and May. Typical concentrations are 60–70 ppb from 700 mbar to 200 mbar during the seasonal maximum, and about 25–40 ppb during the minimum. The monthly mean concentrations in Figure 2 are derived from a rather small number of measurements. We wish to emphasize, however, that the seasonal pattern is reproduced in five years of data, and that the difference between averages for spring and autumn is not due to a few extreme values. This is illustrated in Figure 3 which shows individual ozone measurements at 500 mbar for the two seasons, displayed as cumulative probability distributions. Almost 80% of the autumn values are below 50 ppb, while all the spring values are above 50 ppb.

The springtime values are similar to concentrations found at midlatitudes in summer, as shown in Figure 4, which compares averaged vertical profiles for March–May and for

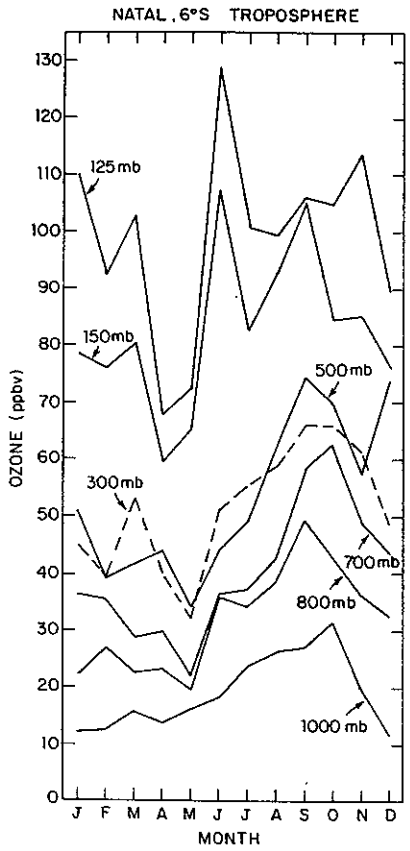

Fig. 2. The seasonal distribution of tropospheric ozone at Natal. Monthly mean values are derived from between 3 and 11 soundings per month.

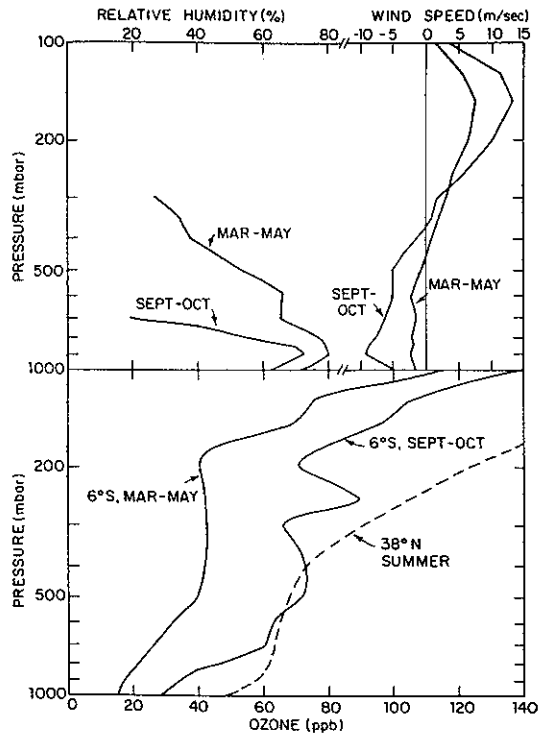

Fig. 4. Vertical profiles for ozone (lower panel), relative humidity and the easterly component of the wind (upper panel) at Natal. Results are shown for March to May, 18 profiles, and for September to October, 20 profiles. The lower panel shows also the average vertical profile for June to August at Wallops Island, 38°N. The ozone measurements were all made with ECC sondes.

September–October from Natal with results from Wallops Island (38°N). These measurements are all made with the same type of ozonesonde prepared in the same manner.

The data in Figures 2 and 4 show that the mixing ratio of ozone generally increases with altitude, with largest gradients below 700 mbar and above 200 mbar. The average mixing ratio is rather uniform in the middle troposphere. There is a suggestion of a local minimum in the upper troposphere. Figure 4 illustrates also that there are significant seasonal differences in relative humidity and in the easterly component of the wind, in addition to those in ozone. Representative individual profiles for the two seasons are shown in Figure 5.

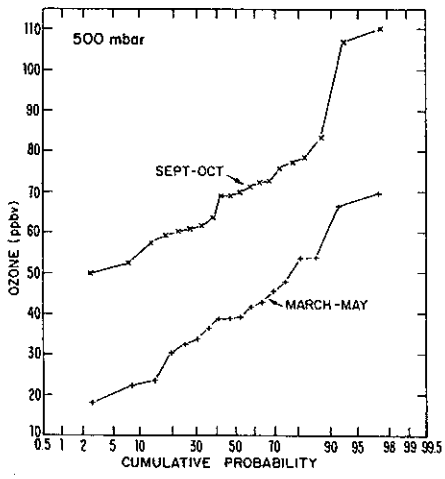

Fig. 3. Cumulative probability distributions for ozone at 500 mbar. Results are shown for September–October (crosses) and March–May (pluses). The concentrations are arranged in order of ascending magnitude. The probability of finding a value less than c_i is approximated by $(i - 1/2)/N$, where i is the rank of c_i in the list and N is the total number of observations. Results are plotted on probability paper such that normally distributed data define a straight line.

The meteorological characteristics of spring and autumn are quite different at Natal. The dry season occurs in September–January [*Ratisbona*, 1976], and this period is characterized by subsidence of dry air, and a boundary layer height of about 800 mbar. In spring Natal is on the northern edge of a subtropical high pressure cell, and the associated anticyclonic winds are easterly up to about 400 mbar [*Sobral*, 1979]. March–July is the wet season, and during this period of frequent convective activity the boundary layer may reach as high as 600 mbar. These differences are reflected in the profiles of relative humidity; in spring the relative humidity exceeds 50% below 800 mbar, while in autumn it exceeds 50% below 500 mbar, as shown in Figure 4. Concentrations of ozone are much lower in the boundary layer than in the middle troposphere in both seasons. The top of the boundary layer in spring is characterized by a temperature inversion, a rapid decrease in humidity and a rapid increase in ozone. There is considerable structure in the ozone profiles above the boundary layer, which we believe to be real, since the magnitude of the excursions is much larger than the precision of the measurements. Furthermore, measurements made on three consecutive days show that these layers in the ozone profile may be relatively long lived [see *Logan*, 1985, Figure 26]. There is often a local maximum in the vertical profile associated with the change from easterly winds below ~400 mbar to westerlies above.

The seasonal behavior of ozone is different above 200 mbar

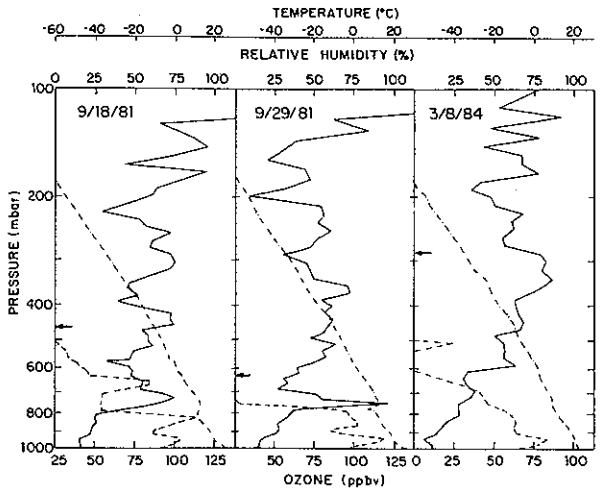

Fig. 5. Representative vertical profiles of ozone (solid lines), temperature (dotted dashed lines) and relative humidity (dashed lines). Note the change of origin for the ozone scale for September versus March. The arrows show where the winds change from easterly to westerly.

compared with that below. Concentrations in the upper troposphere and lower stratosphere tend to be highest in June, July and August, the austral winter, as shown in Figures 2 and 6. There is essentially no variation with season at 15 mbar, just above the maximum in the vertical profile of ozone. The relative amplitude of the seasonal cycle is clearly much larger in the troposphere than in the stratosphere, with implications discussed below.

Measurements of the total column of ozone made with a Dobson spectrophotometer are shown in Figure 7. The ozone column is largest in August–October. The integrated column

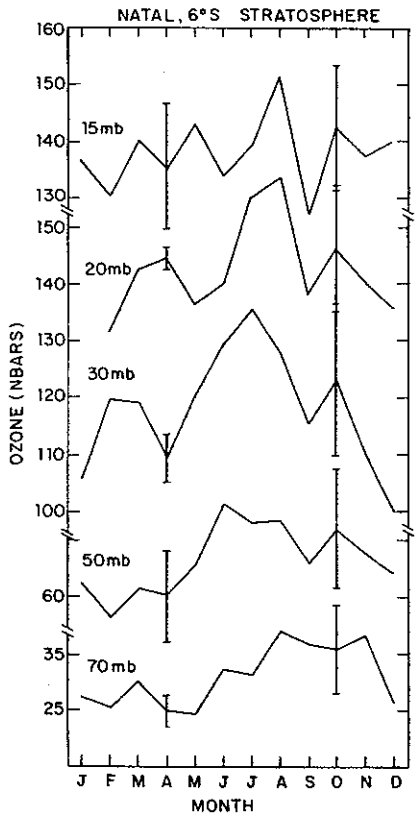

Fig. 6. The seasonal distribution of stratospheric ozone at Natal.

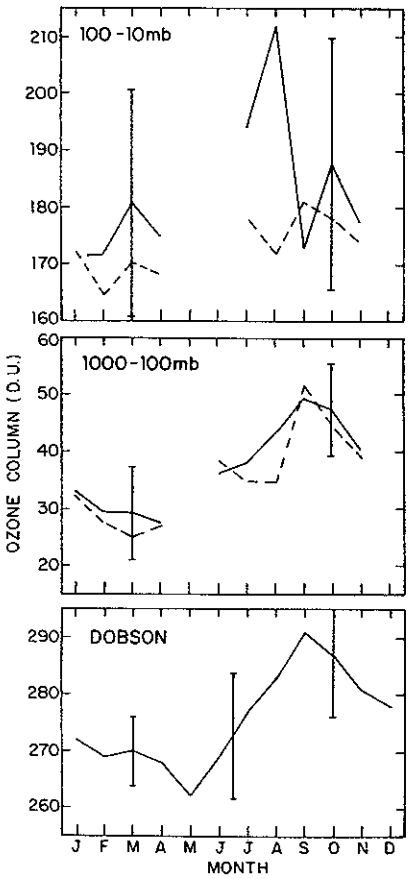

Fig. 7. The seasonal distribution of the vertical column of ozone at Natal. The lower panel shows the overhead column of ozone derived from 3 years of daily Dobson measurements [e.g., *Sahai et al.*, 1982]. The middle panel shows sonde results for the column from 1000 mbar to 100 mbar and the upper panel the column from 100 mbar to 10 mbar. The solid lines show results for soundings which have not been scaled to the Dobson measurement of the column, and the dashed lines show results which have been so scaled, for which the ratio Dobson/sonde was in the range 0.8–1.2. The vertical lines show one standard deviation.

of tropospheric ozone is shown in the middle panel of the figure; the amplitude and phase of its annual cycle is almost identical to that of the total column. The integrated column of stratospheric ozone is shown in the upper panel; there does not appear to be a significant difference between the column amount in spring and autumn. Unfortunately, the standard deviation of the measurement of the stratospheric column is as large as the amplitude of the cycle in the total column. The measurements suggest, however, that the seasonal cycle of the total column at Natal reflects the seasonal cycle of tropospheric ozone, rather than that of stratospheric ozone. The fraction of the total column below 100 mbar is 10% in autumn and 17% in spring.

3.2. *Comparison With Other Data for Ozone*

Concentrations of ozone at Natal between August and October are considerably higher than values available for the northern tropics, and exceed the majority of values reported for the southern hemisphere. Figure 8 compares ozone at 500 mbar at Natal with results from Panama (9°N) and Aspendale (38°S), the only two other stations between 20°N and 60°S for which such data are available. Concentrations at the seasonal maximum at Natal are 20–30 ppb higher than those at

Panama, while values at the minimum are similar to those observed all year at Panama, allowing for a possible 15% positive bias between the ECC measurements at Natal and the Brewer-Mast measurements at Panama (see discussion in *Logan* [1985]). The majority of aircraft measurements of ozone in the middle troposphere have shown low values in the tropics (typically 20–40 ppb; see *Logan* [1985]), with two important exceptions. *Crutzen et al.* [1985] reported values of 40–50 ppb over central Brazil in August, and *Gregory et al.* [1984] found values from 35 to 80 ppb over the west coast of South America (5°S–20°S) in October. These values are similar to concentrations observed during these months at Natal. Comparison of results for Natal and Aspendale shows that concentrations are similar from January to July, but are much higher at Natal from August to December.

Surface measurements of ozone in the tropics and at southern midlatitudes are shown in Figure 9. Concentrations of ozone at the remote marine locations of Samoa (14°S) [*Oltmans*, 1981] and Cape Grim, Australia (41°S) (I. E. Galbally et al., unpublished manuscript, 1986) are highest in July and August, the southern winter, 2–3 months earlier than the springtime maximum at Natal. The seasonal cycle of ozone at four continental stations in Africa (15°S–34°S) is similar to that at Natal, with highest concentrations between August and October [*Schmidt*, 1980]. Measurements from Venezuela (9°N) show a winter maximum in ozone [*Sanhueza et al.*, 1985], and a much less prominent annual cycle than is evident at the southern hemisphere locations shown in Figure 9. Maximum values of ozone at Natal appear to exceed those at the other tropical locations, allowing for the fact that the sonde measurements are made in mid-morning, while the other surface measurements are daily average values.

We noted above that the seasonal behavior of tropospheric ozone at Natal may be responsible for the annual cycle in the vertical column of ozone. The amplitude of the seasonal cycle

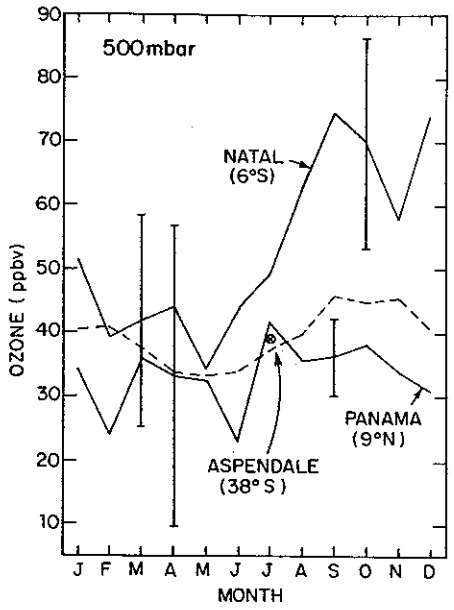

Fig. 8. Ozone at 500 mbar at Natal (6°S), Panama (9°N), and Aspendale (38°S). Results for Panama (43 soundings) are from *Chatfield and Harrison* [1977*b*], while results for Aspendale (752 soundings) are from *Logan* [1985]; these measurements were made with Brewer Mast ozonesondes. Also shown is the average value at Panama in July 1977 derived from 57 ECC soundings. The vertical lines show one standard deviation.

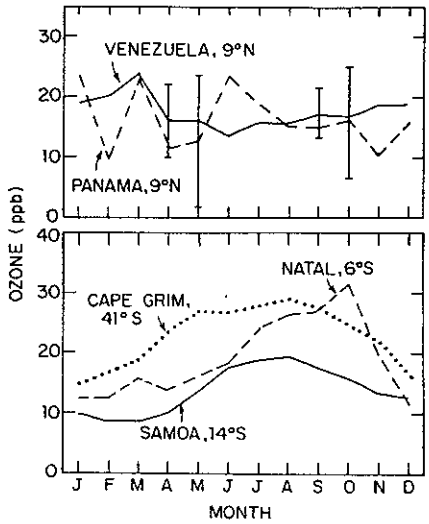

Fig. 9. The seasonal distribution of surface ozone. The upper panel shows monthly mean values for three sites in Venezuela (solid) from *Sanhueza et al.* [1985], and results for 1000 mbar for Panama, from sonde data (see Figure 8). The lower panel shows results from surface sites at Samao (14 S) [*Oltmans*, 1981], and Cape Grim (41°S) (I. Galbally, private communication, 1986), and sonde results for 1000 mbar for Natal. The surface data are daily average values.

in the column is larger at Natal than at other tropical stations in Peru, Samoa, and the Indian Ocean [*Sahai et al.*, 1982], and this may result from differences in concentrations of tropospheric ozone rather than from differences in stratospheric ozone at these sites.

4. Discussion

The observations from Natal challenge conventional wisdom concerning the global distribution of tropospheric ozone. Previous observations had indicated that concentrations were highest at midlatitudes of the northern hemisphere in spring and summer. The location and timing of the global maximum in tropospheric ozone could be explained by a combination of a stratospheric source which is most effective during late winter and spring at these latitudes, and a predominantly summertime photochemical source associated with emissions of NO_x, CO, and hydrocarbons from fossil fuel combustion [e.g., *Fabian and Pruchniewicz*, 1977; *Fishman* and *Crutzen*, 1978; *Levy et al.*, 1985; *Logan*, 1985]. Concentrations of ozone at Natal in the austral spring are as high as summertime values found at midlatitudes. We discuss here the possible roles of photochemistry and stratospheric exchange processes as mechanisms responsible for these unexpectedly high values.

Recent measurements from central Brazil suggest that photochemical oxidation of CO, hydrocarbons, and NO_x from combustion of vegetation provides a significant source of ozone in the tropics [*Delany et al.*, 1985; *Crutzen et al.*, 1985]. In the cerrado region, which is burned annually during the dry season, ozone values were 40–50 ppb above the boundary layer, and maxima of ~60 ppb were found in the polluted boundary layer. Values of 40–50 ppb were also found above the tropical forest, where there was little burning, but concentrations were much lower in the boundary layer. The investigators noted that the residence time of air in the cerrado boundary layer is less than a week; air is either mixed into the free troposphere during the passage of large scale synoptic disturbances, or advected northwesterly toward the Amazon

forest by the prevailing winds. They suggested that significant production of ozone may take in the free troposphere, in addition to production in the vicinity of biomass fires [*Crutzen et al.*, 1985].

We consider here the possibility that ozone produced photochemically could contribute to the high concentrations observed in September and October. Extensive burning takes place during the dry season which lasts from May to September to the south and west of Natal [*Ratisbona*, 1976], and it seems likely that the high values of ozone found in the exploratory studies of *Delany et al.* [1985] (which took place in August) may occur over much of that region. The winds are easterly on the coast of Brazil below ~400 mbar. However, the presence of a large subtropical high pressure cell over central Brazil may result in recirculation of continental air out over the Atlantic. Furthurmore, the winds are westerly above ~400 mbar, so that ozone rich air which is mixed into the free troposphere from the boundary layer during the passage of large scale disturbances may be transported over the coast. It is possible, therefore, that the high ozone values at Natal result in part from transport of ozone produced photochemically over continental Brazil, with the possibility also of transport from the African continent.

The strongest evidence in support of a photochemical source for ozone over Natal comes from measurements of aerosol composition off the coast of Brazil. *Andreae* [1983] showed that the ratio of soot carbon to excess potassium from 0° to 10°S was typical of values in aerosols dominated by emissions from biomass burning. His measurements were made in late October. Trajectory analyses indicated that the air sampled was from tropical Brazil near 2°S, but that a transition to marine air of the southeast tradewinds took place by 6°S; both these sampling locations, however, showed evidence of a combustion influence.

We consider now the possibility that stratospheric input could contribute to the high ozone values observed in September and October. Concentrations of ozone in the stratosphere are highest in June to November at southern midlatitudes [*Pittock*, 1977], and a recent study with a general circulation model suggests that stratospheric input should give rise to a September maximum in tropospheric ozone in the southern hemisphere [*Levy et al.*, 1985]. Transport of air from the stratosphere to the troposphere occurs in large part in association with extratropical cyclogenesis events in the upper troposphere, as discussed for example by *Danielson and Mohnen* [1977] and *Mahlman and Moxim* [1978]. *Fishman and Crutzen* [1978] argued that the average flux of ozone from the stratosphere should be similar in the northern and southern hemispheres, based on a simple analysis of meteorological indicators of large scale cyclonic activity. We note that while the number of cyclones per unit area is similar at midlatitudes of the two hemispheres in winter, there are significantly more cyclones equatorward of 30° in the south than in the north [*Taljaard*, 1972]. In the south, the frequency of cyclogenesis is highest between 35° and 55°S, with important exceptions; about half of the cyclogenesis occurs equatorward of 35°S over S. America and the Atlantic Ocean as far west as 30°W, and a similar pattern is found over the Pacific Ocean from 120° to 180°W [*Taljaard*, 1972]. It might therefore be reasonable to expect a larger source of ozone from the stratosphere at lower latitudes of the southern hemisphere than in the north, although the major region for stratospheric intrusions should be mid latitudes in both hemispheres.

If stratospheric input was the major contributor to the high springtime ozone concentrations at Natal, then one might expect also high values in midlatitudes of the southern hemisphere. This is not however the case. Ozone at 500 mbar at Natal is significantly higher than values at 500 mbar over Aspendale, but is similar to values at 350 mbar (Figure 8). Aspendale should be typical of southern midlatitude, since the streamlines at 500 mbar and 300 mbar indicate primarily zonal flow at ~40°S [*Oort*, 1983]. We conclude that while stratospheric input may contribute to the springtime maximum at Natal, it seems unlikely that it is the dominant mechanism.

Measurements of strontium 90 are sometimes used as an indicator of stratospheric influence on tropospheric composition. Concentrations of Sr-90 are highest in August to October in tropical South America. The seasonal behavior of Sr-90 in the tropics is influenced strongly by the seasonality of the removal process, precipitation scavenging [*Staley*, 1982], thus confounding the utility of these data as an indicator of stratospheric input.

The data available at present do not permit a definitive evaluation of the relative importance of photochemical and stratospheric sources of ozone in the southern tropics. Aircraft measurements of CO and ozone in spring would be extremely useful in this regard. Carbon monoxide is produced in large quantities during combustion of vegetation [e.g., *Crutzen et al.*, 1985], and has a lifetime of a few weeks; it is therefore a suitable tracer of combustion. It is also present at much lower concentrations in the stratosphere and the midlatitude troposphere than at low latitudes of the southern hemisphere. Clearly it would be useful also to make measurements of other tracers of combustion, such as particulate composition [*Andreae*, 1983], and of other tracers of stratospheric air, such as high quality water vapor measurements. Measurement of an appropriate suite of trace species, in combination with careful meteorological analysis, would provide considerable insight into the source of the high concentrations of ozone found over Natal in the southern spring, and could improve significantly understanding of stratosphere-troposphere exchange in the southern hemisphere.

The surface measurements of ozone discussed above suggest that, in the southern hemisphere at least, ozone may be highest in spring over the continents and in winter over the remote oceans. Such inhomogeneities in concentrations are perhaps not unexpected, given the short lifetime of ozone towards photochemical loss, about two weeks at low latitudes [*Liu et al.*, 1983; *Logan et al.*, 1981], and the spatial patchiness that might be expected for the sources of ozone.

5. Conclusions

There is a significant seasonal cycle in ozone at Natal throughout the troposphere, with unexpectedly high values in spring. Concentrations in September and October are as high as values at midlatitudes of the northern hemisphere in summer, and exceed concentrations reported for the northern tropics and for southern midlatitudes. The amplitude of the seasonal cycle in the troposphere is sufficiently large to influence the seasonal behaviour of the total column of ozone at Natal. While it seems likely that photochemical production of ozone associated with emissions of CO, hydrocarbons and NO_x from biomass burning contributes significantly towards the high values of ozone, it is quite possible that stratospheric intrusions also could influence the concentrations of ozone in

springtime. Resolution of this puzzle must await further measurements of ozone and of tracers of combustion in the region.

The data from Natal in combination with aircraft and surface data suggest that there are large inhomogeneities in the distribution of ozone in the tropics. The results presented here have shown that the behavior of ozone in the tropics is more complex than had been thought previously, and point to the need for regular measurements of the vertical distribution of ozone over the tropical oceans and continents. To be most useful, these should be complemented by measurements of the profiles of other trace species.

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