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Surface Ozone in Antarctica

SAMUEL J. OLTMANS AND WALTER D. KOMHYR

Air Resources Laboratory, NOAA, Boulder, Colorado 80302

Surface ozone measurements made in Antarctica during the 1960's show a pronounced annual variation with a summer minimum and winter to late winter maximum. Furthermore, the maximum in surface ozone precedes that in total ozone by from 3 to 5 months, the indication being a loose coupling between the Antarctic stratosphere and troposphere. The annual cycle in surface ozone, instead of reflecting changes in the Antarctic stratosphere, may be a consequence of the variation in low-level meridional transport of ozone from higher latitudes into the Antarctic continent by synoptic scale disturbances. As might be expected from a consideration of Antarctic geography and meteorology, no significant diurnal variations occur in surface ozone. The nonperiodic surface ozone fluctuations observed during the late spring and summer months at South Pole station are most likely caused by sporadic breakdowns of the low-level inversion layer. At the lower latitude stations the day-to-day variations in surface ozone are in all likelihood associated with changes in weather systems.

INTRODUCTION

Surface ozone measurements have been made by the NOAA Environmental Research Laboratories, and their predecessors, for a number of years at several locations in Antarctica. Only a small portion of this data has been published in the past [*Aldaz*, 1965]. Several other authors have published data with shorter periods of record from other stations in Antarctica [*Wexler et al.*, 1960; *MacDowall*, 1962; *Wisse and Meerburg*, 1969]. A variety of instruments was used in making the observations, and a brief description of each is given here. Information on the location of the observing stations, the types of instruments used, and the periods of observation is included in Table 1. The data presented here are primarily in graphical form. The complete body of surface ozone data, including hourly mean values, daily means and maxima, and monthly means will be available in a NOAA technical report.

In presenting the data, emphasis is placed on the secular and spatial variations of near-surface ozone in Antarctica. The data are, furthermore, examined with reference to total ozone measurements and observations of the vertical distribution of ozone made in Antarctica.

INSTRUMENTATION

The Regener automatic ozone recorder [*Bowen and Regener*, 1951] was one of the first instruments designed to sample surface ozone automatically and continuously. It is an elaborate device which is somewhat difficult to maintain in operation. Observations were made with this instrument for a little over 2 years during the period 1961–1963 at South Pole station. The same instrument was used at Little America in 1957 and 1958 [*Wexler et al.*, 1960].

Like almost all ozone instruments using wet chemical methods to determine the ozone amount, operation of the Regener automatic ozone recorder is based on the oxidation of iodide to iodine by atmospheric ozone. The technique is, in principle, an absolute one which yields ozone amounts directly. The instrument is specific to ozone under the assumption that oxidants other than ozone are not destroyed during heating in an oven at 300°C.

The Regener chemiluminescent surface ozone recorder [*Regener*, 1960] was used extensively to measure ozone on the Antarctic continent during the period 1962–1967. Observations with this instrument were made at South Pole, Byrd, Eights, and Hallett stations.

The heart of the chemiluminescent ozone recorder is a small disc consisting of an organic dye, Rhodamine B, absorbed on silica gel that fluoresces when ozone comes in contact with it. The faint light produced, proportional to the ozone concentration, falls on a sensitive photomultiplier tube which converts the light into a current that is amplified and recorded. In order to translate the recorded information into ozone amounts, the instrument must be made to sample periodically a known concentration of ozone. The reaction of ozone with Rhodamine B is rather specific to ozone.

The Mast ozone meter [*Brewer and Milford*, 1960; *Mast and Saunders*, 1962] was also widely employed in Antarctica to measure surface ozone. At several locations it was used concurrently with the Regener chemiluminescent ozone instrument, providing an opportunity for cross-checking the results.

This instrument is of the coulometric type. Sensing of ozone in an air sample is accomplished by the oxidation-reduction of potassium iodide, which is contained in the sensing solution. Like the Regener automatic surface ozone recorder the Mast ozone meter is, in theory, an absolute ozone measuring device.

Ozone amounts were calculated on the assumption that the meter is a perfect detector. Since any substance which produces or consumes iodine in the sensor affects the measured current, this instrument is not specific to ozone. In particular, other oxidizing agents such as nitrogen oxides or reducing agents such as sulfur dioxide may interfere with ozone measurements. Such interferents, however, exist at such low levels in the unpolluted atmosphere of Antarctica that they do not appreciably affect ozone measurments there.

Electrochemical concentration cell oxident meters [*Komhyr*, 1969], including the carbon-iodine meter, also depend on the oxidation-reduction of potassium iodide to measure ozone. Unlike other instruments of this type, however, the driving electromotive force for the sensor is not applied externally but is derived from different electrolyte concentrations in the halves of the sensing cell. As in the case of the Mast ozone meter these instruments are presumed to measure ozone on an absolute scale.

DATA HANDLING

Data obtained with obviously malfunctioning instruments were not included in final tabulations. Instrument malfunc-

TABLE 1. Observing Stations, Types of Instruments Used, and Periods of Observations for Surface Ozone Data from Antarctica

Instrument Type	Period of Observation	Missing Data
	Amundsen Scott Station 90.0°S 680 mbar	
Regener automatic	Feb. 1961 to July 1963	Sept. and Dec. 1962
Regener chemiluminescent	Jan. 1962 to Oct. 1966	Nov. 1965
Mast	Dec. 1963 to Oct. 1966	Feb. 1964 and Nov. 1965
Carbon-iodine	May 1967 to Oct. 1969	Nov. and Dec. 1968
Electrochemical concentration cell	Dec. 1971 to July 1972 March 1973 to Dec. 1973	Jan. 1972 July and Oct. 1973
	Byrd Station 80.0°S, 119.5°W 805 mbar	
Regener chemiluminescent	Nov. 1963 to Nov. 1965	Sept. 1964
Mast	March 1963 to Oct. 1965	
	Eights Station 75.2°S, 77.2°W 938 mbar	
Regener chemiluminescent	Oct. 1963 April 1964 to Oct. 1965	
	Hallett Station 77.3°S, 170.2°E 984 mbar	
Regener chemiluminescent	Jan. 1962 to Oct. 1963	
Mast	March 1962 to Oct. 1963	
	Wilkes Station 66.2°S, 110.5°E 984 mbar	
Mast	March 1963 to Nov. 1963 (daily average values only)	April and June 1963

tions can often be identified by sudden shifts in the chart recorder traces. Elimination of such data was, however, kept to a minimum. At several of the locations two different instruments were often used simultaneously. This dual measuring system helped to confirm the validity of elimination of portions of records that looked suspicious.

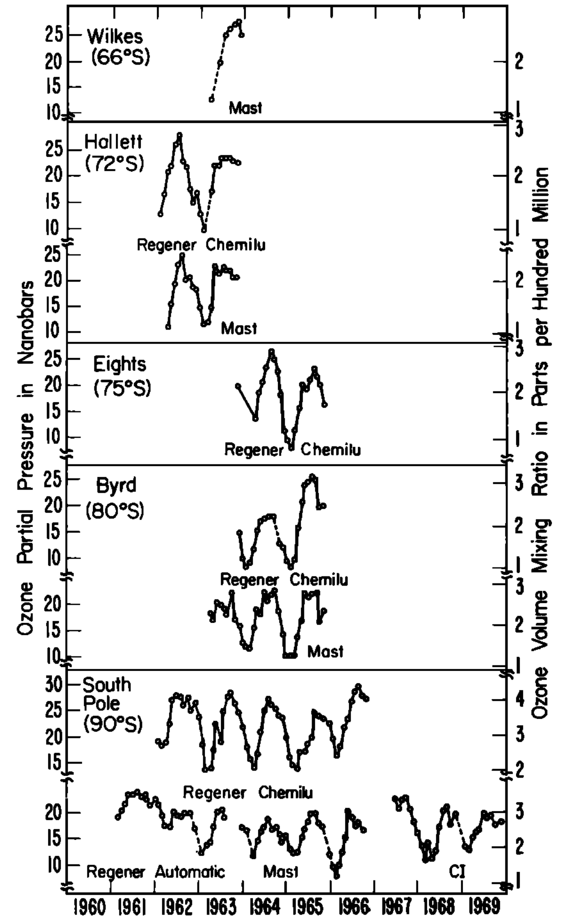

Fig. 1. Mean monthly surface ozone concentrations in Antarctica.

The unit of ozone amount used is the partial pressure of ozone in nanobars (10^{-6} mbar). The relationship between the ozone partial pressure (p_3) in nanobars, volume mixing ratio (r_3) in parts per million, and density (ρ_3) in micrograms per cubic meter is

$$p_3 = r_3 \cdot p = 1.73 \times 10^{-3} \rho_3 \cdot T$$

where p is the atmospheric pressure in millibars and T the atmospheric temperature in degrees Kelvin.

ANNUAL OZONE VARIATION

The most striking feature of the near-surface ozone record at all of the stations in Antarctica is the annual cycle with a range equal to about 50% of the average annual concentration. Figure 1 summarizes the surface ozone data gathered during the 1960's in Antarctica. Plotted are mean monthly surface ozone partial pressures based on hourly means measured with various instruments at five locations. In general, the Regener chemiluminescent instruments gave higher overall readings than did the wet chemical instruments (Regener automatic, Mast, and carbon-iodine). This is most likely a result of the different calibration methods associated with the two classes of instruments. The wet chemical instruments are, in principle, absolute measuring devices; ozone values are computed from the basic instrument equations. The chemiluminescent instruments were calibrated independently by the manufacturer, and these calibrations were used throughout the observing program.

Other discrepancies between instruments are less easily explained and are probably the result of variations in instrument performance rather than real differences in the ozone being measured.

Although the annual ozone variation is very strong, it is by no means completely regular from one year to the next. At Hallett, for example, the maximum was very definitely peaked in 1962, while in 1963 it was much broader in character with no monthly mean achieving the high value recorded in 1962. No obvious pattern emerges in this year-to-year variability, but it is clear that continuous measurements are required to provide information on the true character of the annual cycle.

The average behavior of the annual cycle in surface ozone for four stations in Antarctica with at least 2 years of data is plotted in Figure 2. At all stations there is a summer minimum and a winter to late winter maximum. On the average at each station the maximum is quite broad, while the minimum is of considerably shorter duration. Except at Byrd the average values in Figure 2 are based on the Regener chemiluminescent instrument. At Byrd the Mast data were used because they represented almost a year longer of record than that available from the chemiluminescent instrument. It is for this reason that the overall average value at Byrd is somewhat less than at the other stations.

The minimum ozone value appears to occur slightly earlier in the year at lower latitudes (January at Hallett and Eights) than at South Pole (between February and March). The maximum also occurs at South Pole somewhat later than at the other stations. Because of the variations from year to year in the annual cycle and because the periods of record are short, the patterns depicted in Figure 2 for Hallett, Eights, and Byrd are probably only suggestive of the true behavior of the annual cycle in surface ozone at these stations.

Measurements of the integrated amount of ozone in a column of the atmosphere (total ozone) show a maximum for Antarctic latitudes that occurs in November and December after a gradual rise during the months of June through October. A rapid drop-off in total ozone to a minimum occurs from February to May. This annual cycle in total ozone is shown averaged in Figure 3 for the latitude belt 60°-90°S, as well as for the latitudes 30°-60°S and 0°-30°S. The data are taken from monthly analyses of total ozone for the southern hemisphere during the period 1960-1969 [see *London et al.*, 1976]. Since the total ozone data plots encompass the entire 10-year period, they do not correspond exactly to any one of the shorter periods of record from which the surface ozone average behavior shown in Figure 2 has been derived.

Whereas the Antarctica surface ozone annual cycle shows a broad maximum and a narrow minimum, the opposite effect is observed in the high-latitude total ozone plot of Figure 3. This difference in characteristics of the surface and total ozone maxima and minima suggests little coupling between the tropospheric and stratospheric ozone distributions. The maxima in surface ozone at Hallett, Eights, Byrd, and South Pole stations, furthermore, precede the total ozone maximum over Antarctica by from 5 to 3 months.

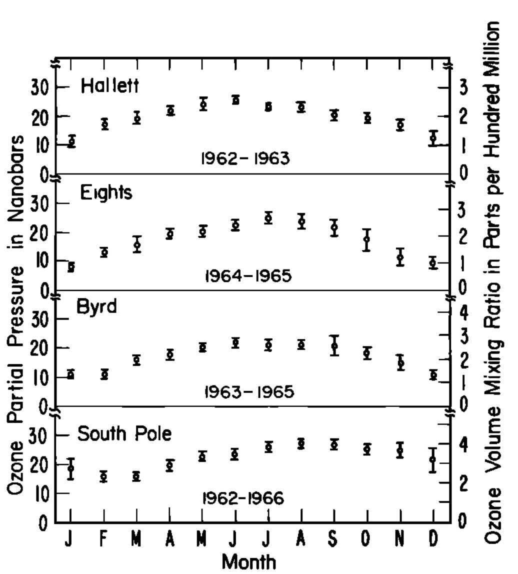

Fig. 2. Averaged monthly Antarctica surface ozone amounts.

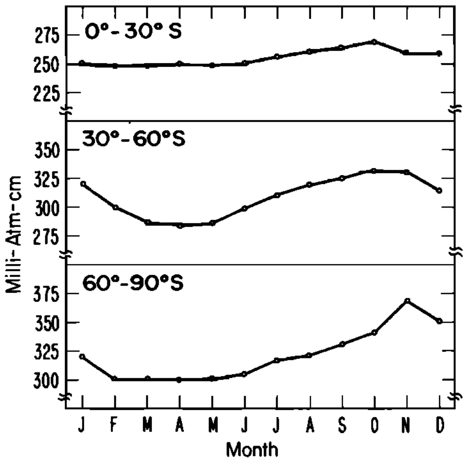

Fig. 3. Average annual total ozone for 30°-latitude belts in the southern hemisphere (1960-1969).

A possible candidate as a forcing mechanism for the annual surface ozone variations is the intensity and frequency of synoptic scale disturbances moving from subpolar latitudes in Antarctica. Increased southward meridional transport of air by these disturbances during the winter months is believed to be one process that causes tropospheric temperatures during the Antarctica winter to be considerably higher than might be expected from a consideration of the radiation budget alone [*Schwerdtfeger,* 1970]. A climatological parameter which reflects such cyclonic activity is the average magnitude of the interdiurnal pressure variations. Table 2 (extracted from the article by *Schwerdtfeger* [1970]) gives the pressure variation index values for several Antarctic stations located in the 60°-90° latitude belt. The results, based on 2 years of available data at each station, are directly comparable irrespective of the widely different station elevations, since they are expressed as ratios of the interdiurnal pressure variations P and the average station pressures P_s. Clearly, there is a maximum in this index during the winter months and a minimum during the summer paralleling the variation in surface ozone. The spring and fall seasons also show relatively strong cyclonic activity in comparison with the summer minimum. In surface ozone this corresponds to a rather broad maximum and a narrow minimum.

A mechanism that contributes to keeping the annual temperature range in the Antarctica troposphere relatively small is vertical advection which varies with the seasons. More downward motion is present in winter than in summer. This downward motion transports air from the high and middle troposphere to lower levels. This model of poleward transport of tropospheric air, subsidence to near the surface, and northward outflow at low levels corresponds to an earlier model of Antarctic circulation [*Wexler et al.,* 1960].

Downward transport of ozone from the stratosphere to the troposphere probably also occurs, as has been borne out by numerous ozone soundings made in Antarctica during 1962-1966 [*Komhyr and Grass,* 1968]. The main transport mechanism, however, appears to be slower small-scale diffu-

TABLE 2. Relative Interdiurnal Pressure Variations

				Variations, %			
Station	Location, °S	Elevation, m	Period of Observation	Summer Dec. to Feb.	Fall March to May	Winter June to Aug.	Spring Sept. to Nov.
Orcadas	60.7	4	1941–1942	0.50	0.65	0.78	0.64
Syowa	69.0	15	1960–1961	0.38	0.56	0.66	0.63
South Pole	90.0	2800	1964–1965	0.30	0.51	0.61	0.49
Plateau	79.3	3625	1967–1968	0.31	0.46	0.48	0.41

sion processes, since the majority of the soundings for all seasons of the year exhibit generally constant ozone partial pressures in the troposphere, which imply increasing ozone mixing ratios with altitude. Large-scale mixing processes, on the other hand, should lead to constant mixing ratios with height. This feature of Antarctica ozone vertical distributions is illustrated in Figure 4, which shows plots of ozone soundings obtained at South Pole station at times of the year when surface ozone is a minimum and a maximum (February and August, respectively). Another characteristic readily discernible from the plots of Figure 4 is that the base of the atmospheric ozone layer occurs considerably lower in the atmosphere in late summer, when surface ozone amounts are lowest, than it does in late winter, when surface ozone amounts are highest. This relationship is opposite to that which might be reasonably expected if the major source of Antarctica surface ozone was the high-latitude stratosphere.

It appears, therefore, that the prédominate mechanism responsible for variations in surface ozone in Antarctica is synoptic scale disturbances in the troposphere rather than direct downward mixing of stratospheric air. These disturbances, migrating into Antarctica from the subpolar latitude belt, transport not only large amounts of real and latent heat but also ozone. Variations with the seasons of the strength of meridional transport by weather systems most likely bring about the prominent annual cycle in Antarctica surface ozone.

DIURNAL VARIATION

The absence of nearby materials (vegetation, soil, and bare rock) that can destroy ozone, the cleanliness of the atmosphere which precludes the production of ozone near ground level by photochemical processes, and the high stability of the air generally characterized by strong surface inversions that retard mixing from above suggest that diurnal effects in surface ozone at the Antarctica stations should be small. That this is indeed the case may be seen from the plots of Figure 5.

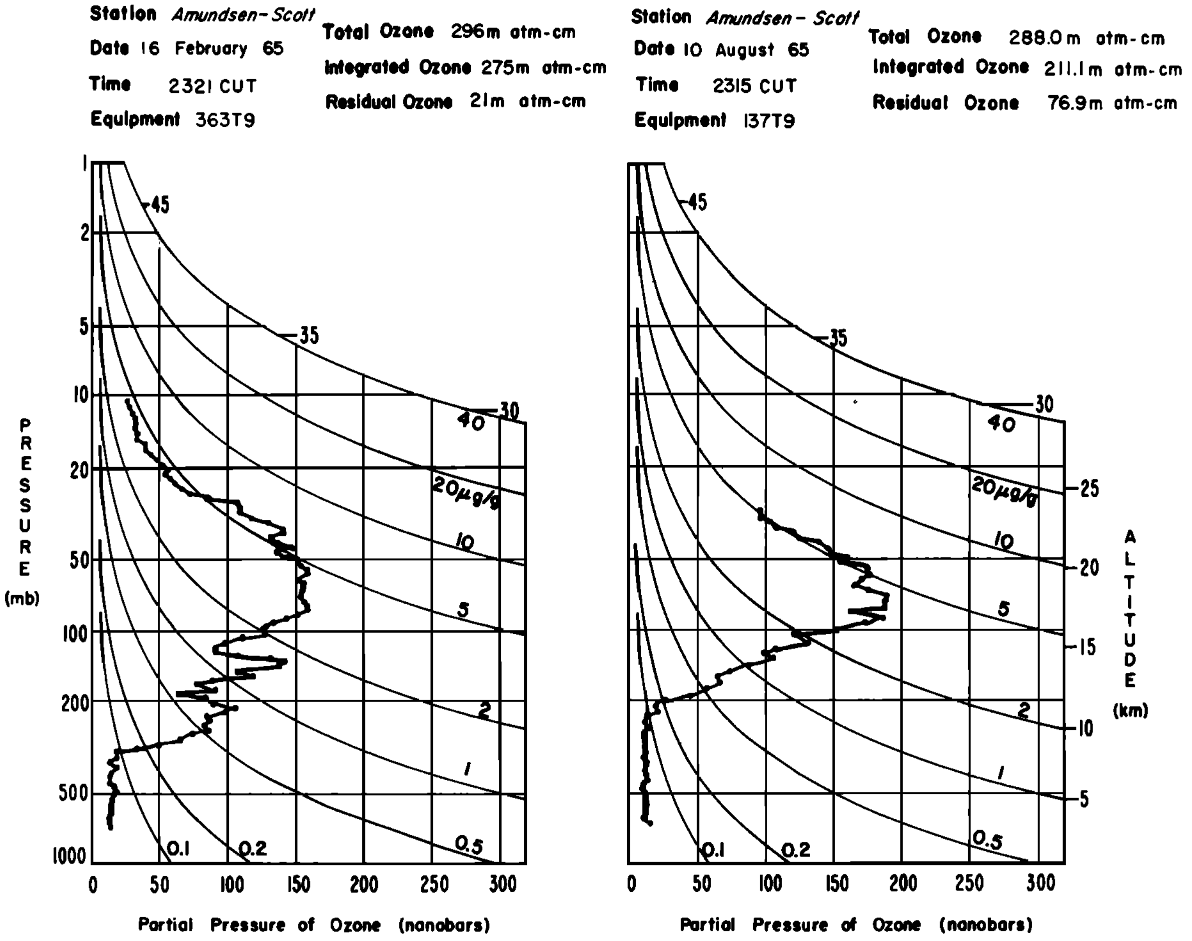

Fig. 4. Sample plots of ozone vertical distribution at South Pole, Antarctica.

In the figure are plotted diurnal surface ozone amounts, averaged over the period of record, for Hallett, Eights, and Byrd stations for times of the year when sunset and sunrise occur. Only at Hallett during the spring season is there any indication of a diurnal variation in surface ozone. Its statistical significance is, however, doubtful in view of the small peak-to-peak amplitude of 1 nbar of partial pressure. With the maximum occurring early in the morning and the minimum in the afternoon this apparent variation is, furthermore, quite different from typical mid-latitude daily variations where enhanced mixing and photochemical production of ozone in polluted air cause peak values to occur in the afternoon and minima in early mornings.

Annual averages of diurnal ozone amounts measured at the Antarctica stations are also plotted in Figure 5. The constancy of these results suggests that the data are not influenced daily by local pollution, instrument temperature variations, and other adverse effects that might potentially be related to 24-hour activity schedules at the Antarctica stations.

DAY-TO-DAY VARIATIONS

Superimposed on the pronounced Antarctic surface ozone annual cycle are large irregularly occurring ozone fluctuations which are particularly pronounced at South Pole in late spring and summer. At the lower latitude stations, similar fluctuations in ozone are observed in the spring and to a lesser extent during autumn. Data variability for the Antarctic stations may be inferred from the plots of Figure 2, where the error bars associated with the data points represent standard deviations primarily resulting from day-to-day variations in ozone.

Examples of irregularly occurring variations in surface ozone at South Pole are reproduced in Figure 6, where data are presented for October and January 1965. While the October trace is relatively smooth, the January trace exhibits large fluctuations. That these fluctuations are real is attested to by the observation that both the Regener chemiluminescent and Mast instrument data agree closely.

At South Pole the period of large day-to-day variations in surface ozone is also the period in which the near-surface temperature inversion is weakest. Increases in surface ozone are observed when periodic breakdowns of the inversion permit ozone rich air from above the layer to penetrate to ground level. At Byrd, on the other hand, the inversion is weakest from November to February, while surface ozone is most variable from September through November. Thus it is likely that a different mechanism is primarily responsible for the observed day-to-day variability in surface ozone at Byrd.

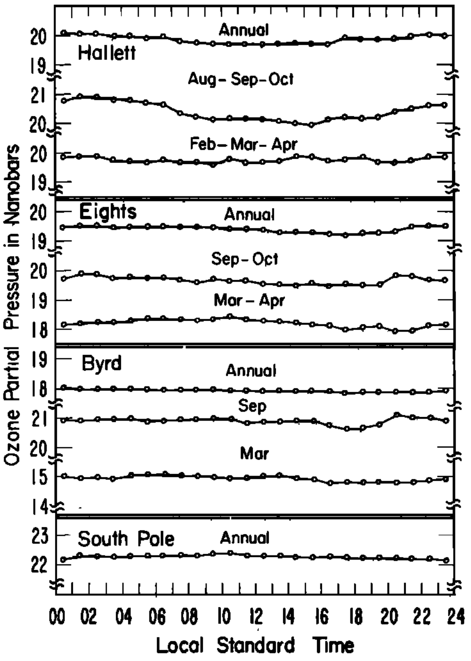

Fig. 5. Averaged diurnal plots of surface ozone in Antarctica.

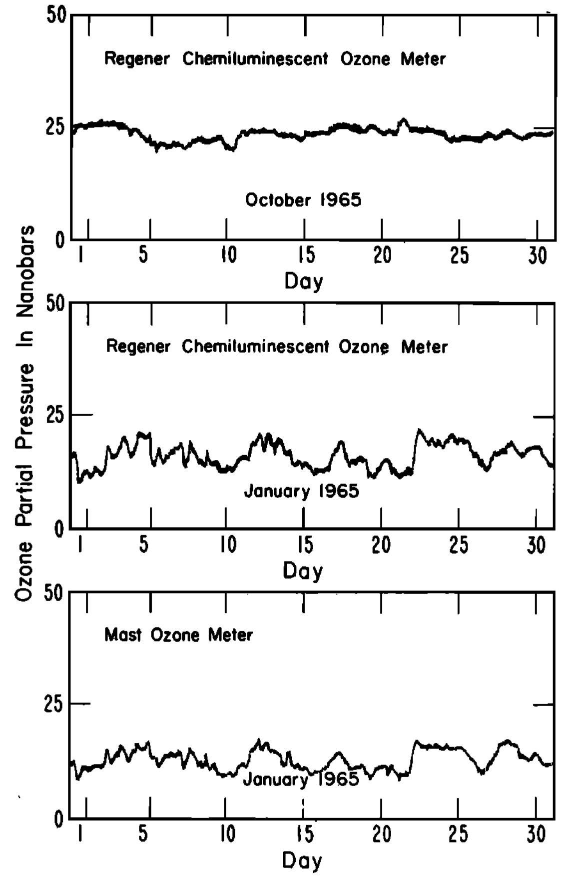

Fig. 6. Plots of hourly South Pole surface ozone amounts illustrating nonperiodic fluctuations that occur in the data.

At Byrd, as well as at Eights and Hallett stations, for which information about the near-surface thermal layers is unavailable, it is likely that increased day-to-day variations in surface ozone are related to the more frequent occurrence of synoptic weather systems associated with the transition from winter to summer temperature regimes and vice versa. During the transitional months, times of enhanced meridional circulation typical of the winter months alternate with periods of relatively weak transport from lower latitudes typical of the summer months.

SPATIAL VARIATIONS

There do not appear to be any large differences in the average surface ozone partial pressures at the stations in Antarctica. Annual maximum values at all stations are about 25 nbar, while the annual minima are around 10 nbar. These results imply that Antarctic surface ozone amounts, when expressed in mixing ratios, vary with station elevation. Thus values of annual ozone maxima approach 4 parts per hundred million (pphm) by volume at the high-altitude South Pole station but only 3 pphm by volume at Hallett station, which is located at sea level. Corresponding annual minimum values at

South Pole and Hallett are about 1.5 and 1.0 pphm by volume, respectively.

As was stated previously, the results expressed above have been borne out by numerous ozone soundings made in Antarctica during 1962–1966, which indicate that tropospheric ozone partial pressures remain, in general, constant with height.

SUMMARY

The most striking feature of the surface ozone record in Antarctica is the annual cycle, which is observed at all stations. This cycle is most likely a consequence of the variation in low-level meridional transport of ozone from higher latitudes into the Antarctic continent by synoptic scale disturbances. As might be expected from a consideration of Antarctic geography and meteorology, no significant diurnal variations occur in surface ozone. The nonperiodic surface ozone fluctuations observed during the late spring and summer months at South Pole station are most likely caused by sporadic breakdowns of the low-level inversion layer. At the lower latitude stations the day-to-day variations in surface ozone are in all likelihood associated with changes in weather systems.

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