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Surface layer ozone above the Weddell Sea during the Antarctic spring

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Abstract: Ozone concentrations in the atmospheric surface layer above the Weddell Sea during the Antarctic spring season of 1989 varied significantly. Lower levels of ozone were associated with colder Antarctic air masses and higher values with warmer mid-latitude air. The lowest ozone concentration (1 to 2 ppbv) was measured in the centre of a low pressure system. A definite diurnal variation of tropospheric ozone observed during clear days with low total ozone amount (177 matm cm) may be interpreted as a consequence of the occurrence of photochemical reactions under conditions of increased ultraviolet solar radiation.

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Key words: ozone, surface layer, Weddell Sea, chemiluminescent analyzer.

Introduction

The experimental study of tropospheric ozone in Antarctica is very important for several reasons. First of all, increased ultraviolet radiation associated with the depleted ozone column during the Antarctic spring could influence the tropospheric ozone concentration through photochemistry. Secondly, active tropospheric synoptic processes above the Weddell Sea result in changes of the ozone concentration. Finally, studies of this type can help solve problems of the sources and sinks of both tropospheric and stratospheric ozone.

Ozone measurements were carried out aboard the West German *R.V. Polarstern* during the expedition WWGS-89 (Winter Weddell Gyre Study) in September and October 1989, when the icebreaker crossed the Weddell Sea from King George Island (Antarctic Peninsula) to Kapp Norvegia. The abundance of total ozone and the turbidity of the whole atmosphere at different visible wavelengths were measured.

An ozone analyzer, produced by the Leningrad Hydrometeorological Institute (LHMI) (Sirota & Chelibanov 1987), which uses the principle of chemiluminescence (CL) of rhodamine reacting with tropospheric ozone, made the measurements. In this paper only a part of the data set is reported and discussed. The rest of the results, both from the Antarctic from the transit to Antarctica and back, are still being processed and analyzed.

Experimental considerations

The air to be analyzed is pumped through a reaction chamber containing a disc made of a synthetic material covered by rhodamine and gallic acid. Ozone is destroyed by these chemicals, and the resulting luminescence is detected by a photomultipler tube (PMT-119). The PMT signal is amplified and run in parallel to a chart recorder and to a frequency converter, a frequency meter and a digital indicator. The temperature inside the chamber is maintained automatically at a constant level of 43±3 °C using a heating element located inside the gas stream close to the sensitive disc. The gas flow rate is 2.5 l min^{-1}.

A typical drawback of a solid state CL detector is the dependence of its sensitivity on the concentration of ozone in the gas mixture being analyzed; the sensitivity increases when the concentration of ozone is high, and vice versa. Therefore regular monitoring of the sensitivity is necessary. This is done using an ozone photolytic generator, also made in the LHMI. According to the instrument calibration, the ozone concentration in the gas mixture is 150 µg m^{-3} corresponding to 78 parts per billion by volume (ppbv) at room temperature and normal atmospheric pressure. This equipment has been compared with Dasibi UV absorption ozone analyzers in Zvenigorod, at the Scientific Station of the Institute of Atmospheric Physics, USSR Academy of Sciences (IAP) and in Toronto, Canada, at the Atmospheric Environment Service (AES). Additionally the instruments were compared with Dasibi instruments belonging to German research groups on board *R.V. Polarstern*. After being transferred to the *R.V. Akademik Fedorov*, the CL analyzer was again compared with the IAP Dasibi and with an electrochemical cell belonging to the Hamburg Meteorological Observatory. The calibration gas mixture supplied by the generator was tested using different analyzers in Zvenigorod, Toronto, *R.V. Polarstern* and *R.V. Akademik Fedorov* (Table I). According to the Table most of the values are in the range from 67 to 87 ppbv; only two sets of measurements, made in Canada, lie significantly outside this range. The causes of the 35% difference are not clear at present; in this paper a reference value of 78 ppbv will be used for the ozone concentration in the standard gas mixture of the generator at room temperature and normal air pressure. The uncertainty of an individual measurement may be estimated as ± 20%;

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Table I. Results using the LHMI ozone generator, obtained by different ozone analyzers. The calibration value was taken to be C_o=78 ppbv, as discussed in the text.

Number	Institute name	Site of observation	Date 1989	Duration minutes	Mean concentration, C, ppbv	C/C_o
1	Institute of Atmospheric Physics Moscow, M Pustygin	Zvenigorod	19 June	50	67±2	0.86
2	"	"	20 June	140	76±2	0.97
3	AES of Canada Toronto, N Trivett	Toronto	28 June	70	105±1	1.35
4	"	"	28 June	35	105±0.6	1.35
5	Institute of Atmosperic Chemistry Jülich, FRG C Place	*R.V. Polarstern*	2 Sept	50	87±2	1.10
6	Ruhr University Bochum, FRG, T Papenbrock	"	3 Sept	140	86±2	1.12
7	Institute of Atmospheric Physics Moscow, M Pustygin	*Akademik Fedorov*	19 Nov	190	68±2	0.87
8	"	"	1 Dec	30	70±2	0.90
9	Meteorological Observatory Hamburg, FRG, P Winkler	"	1 Dec	120	73±5	0.94

it is determined mostly by variations of analyzer sensitivity between calibrations and the instability of the generator itself. The analyzer's internal noise is significantly less; it does not generally exceed ± 2%.

The calibration of the CL analyzer was verified in Toronto, Canada, using a Dasibi generator (Fig. 1). Simultaneous monitoring of the ambient air using CL and Dasibi generators carried out at the same site (Fig. 2) demonstrated a good agreement between the two types of instruments, although the CL analyzer had a lower level of noise than some examples of the Dasibi instrument, and a shorter response time.

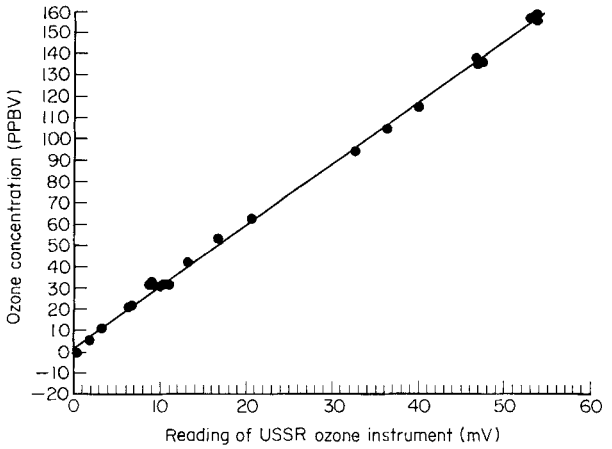


Fig. 1. A test of calibration of the Soviet LHMI analyzer. The vertical axis shows the ozone concentrations in the standard mixture of Dasibi, AES, Canada, and the horizontal axis gives the corresponding output signal of the LHMI chemiluminescent analyzer, in millivolts.

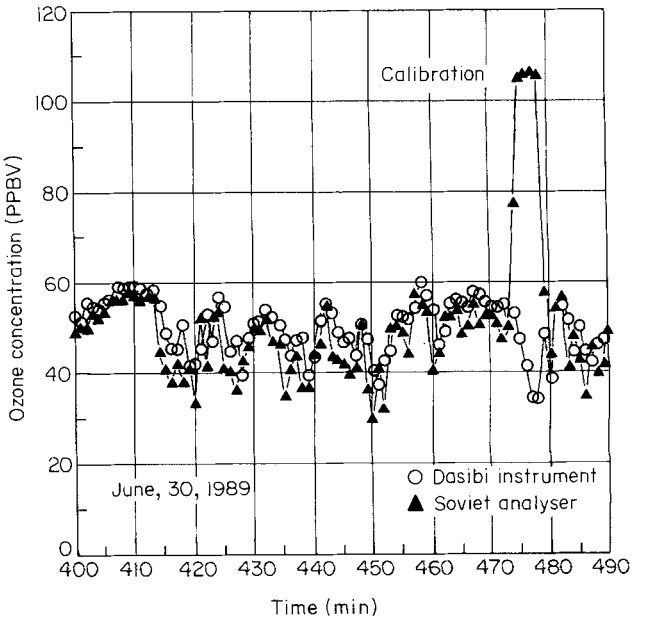


Fig. 2. An example of simultaneous ozone monitoring of ambient urban air in Toronto by two ozone analyzers, the Dasibi, AES (circles) and LHMI (triangles)

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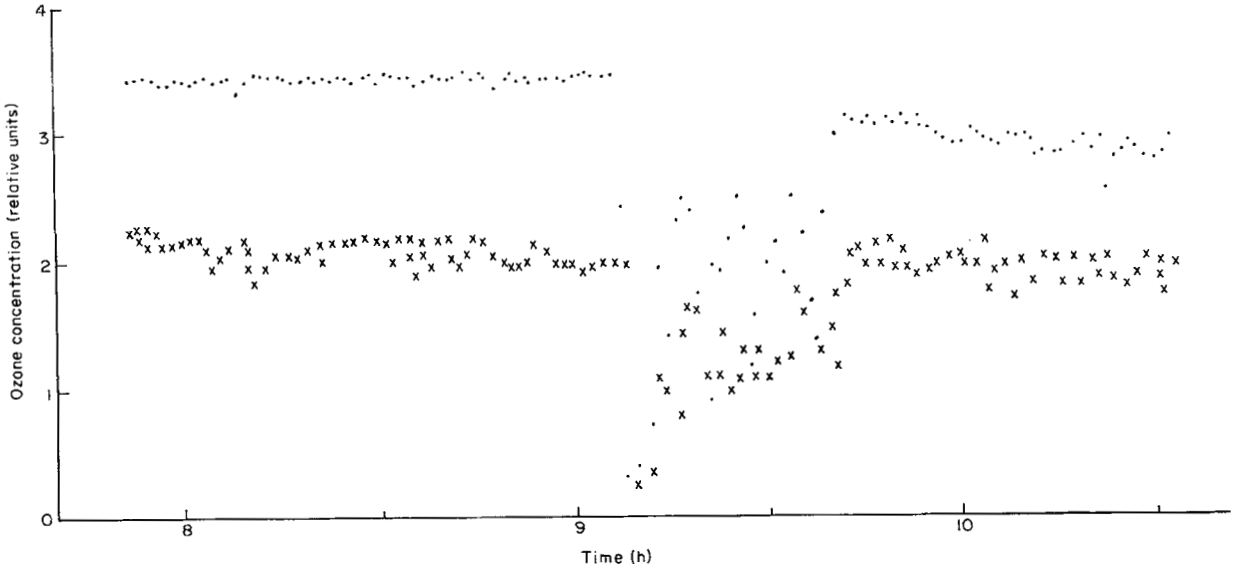


Fig. 3. An example of simultaneous ozone monitoring of background Antarctic air aboard *R.V. Akademik Fedorov*, by LHMI (points) and Dasibi (crosses) ozone analyzers. From 0910 to 0940, the influence of the ship's exhaust is evident.

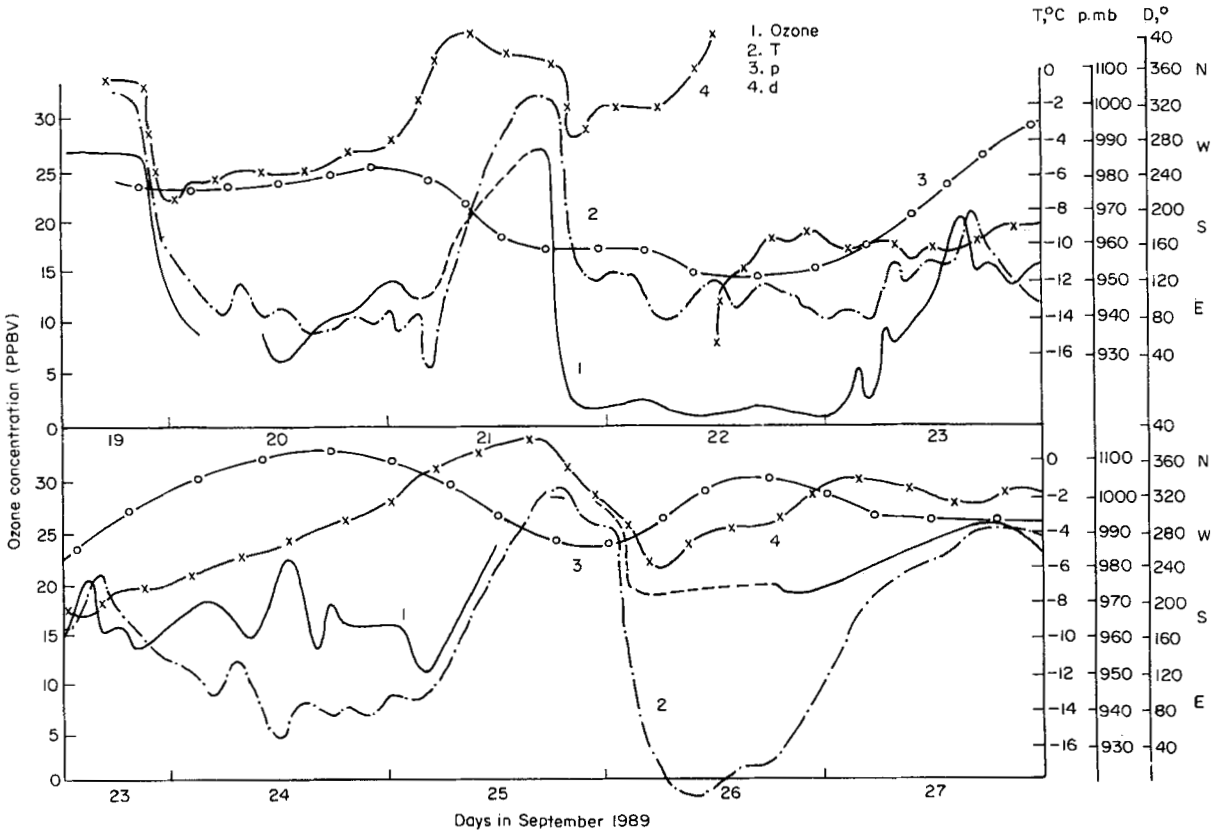


Fig. 4. Temporal variations of the surface layer ozone concentrations (1) and meteorological parameters of the atmospheric surface layer: air temperature T (2), pressure p (3), and wind direction D (4), from 19 to 27 September, 1989 in the Weddell Sea.

The equipment was installed in a laboratory on the port side of the ship. The ambient air was sampled constantly from a height of 17 m above sea level. The length of teflon tube was about 6 m, and the air was cleaned by a nucleopore teflon filter with pore diameter of 5 μm; during the expedition the filters were changed twice. The ozone loss on the tube

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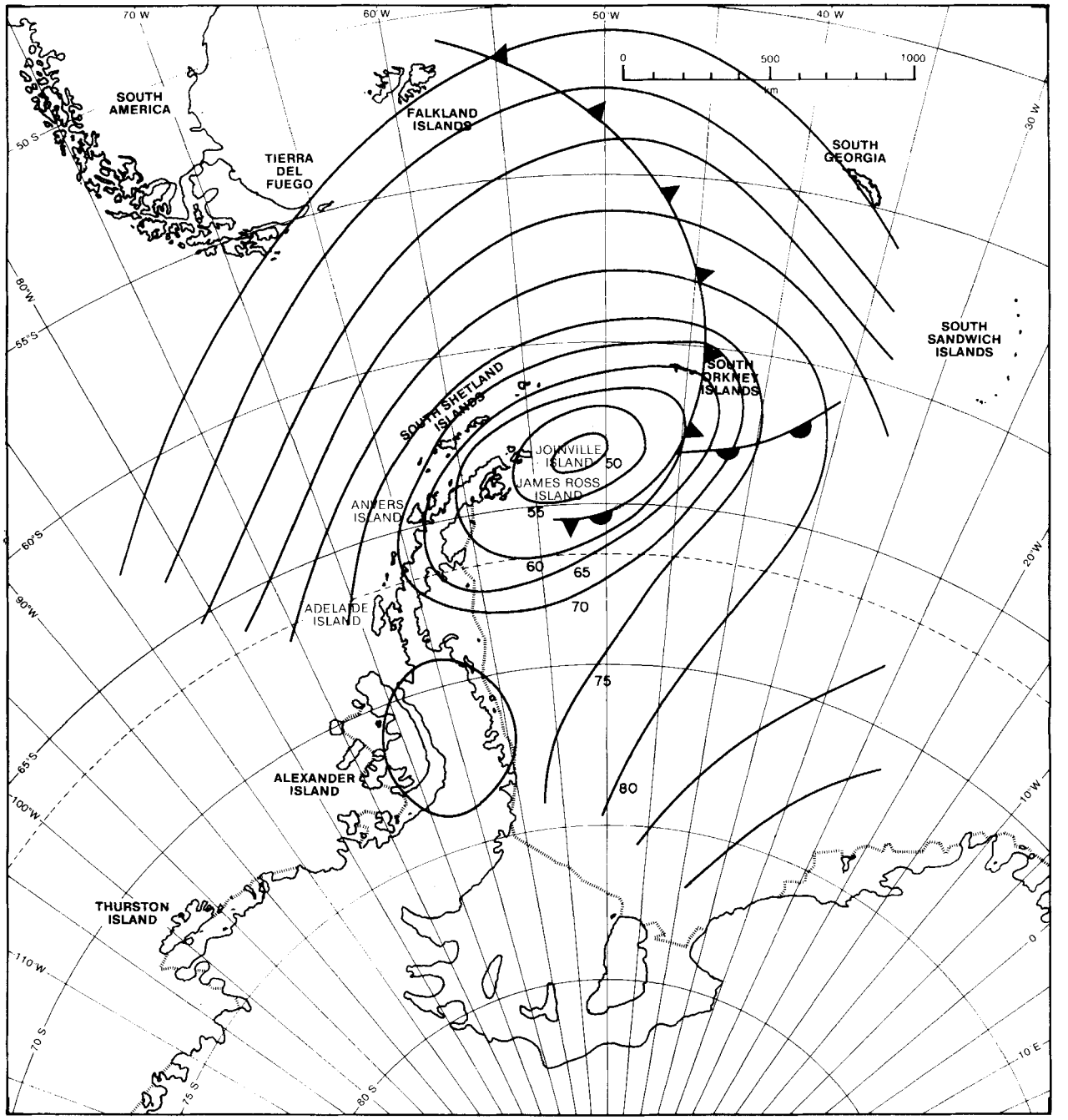


Fig. 5a. Example of synoptic chart for the Weddell Sea region: 21 September, 1200 UTC

and the filter does not exceed 10%. The influence of the ship's air conditioning system and funnel exhaust on the ozone measurements was visible only during calm weather or fair wind; all these cases (eg., Fig.3) were excluded from the following discussion.

Results and discussion

R.V. Polarstern entered the ice-covered Weddell Sea on 15 September 1989. From 17 until 21 September there was a long ice station near 65°S. During the next few days the ship moved SE and, on 27 September, reached 67°S, 29° W. *R.V. Polarstern* approached the German *Georg Von Neumayer* (70° S, 8° W) polar station on 11 October. A rendezvous with *R.V. Akademik Fedorov* took place on 17 October at 65°S, 4°W.

From 15 to 19 September, the ozone concentration near the sea surface varied little, being about 30 ppbv. The ozone concentration variations for the next 8 days are plotted in Fig. 4. Values of some meteorological parameters for the

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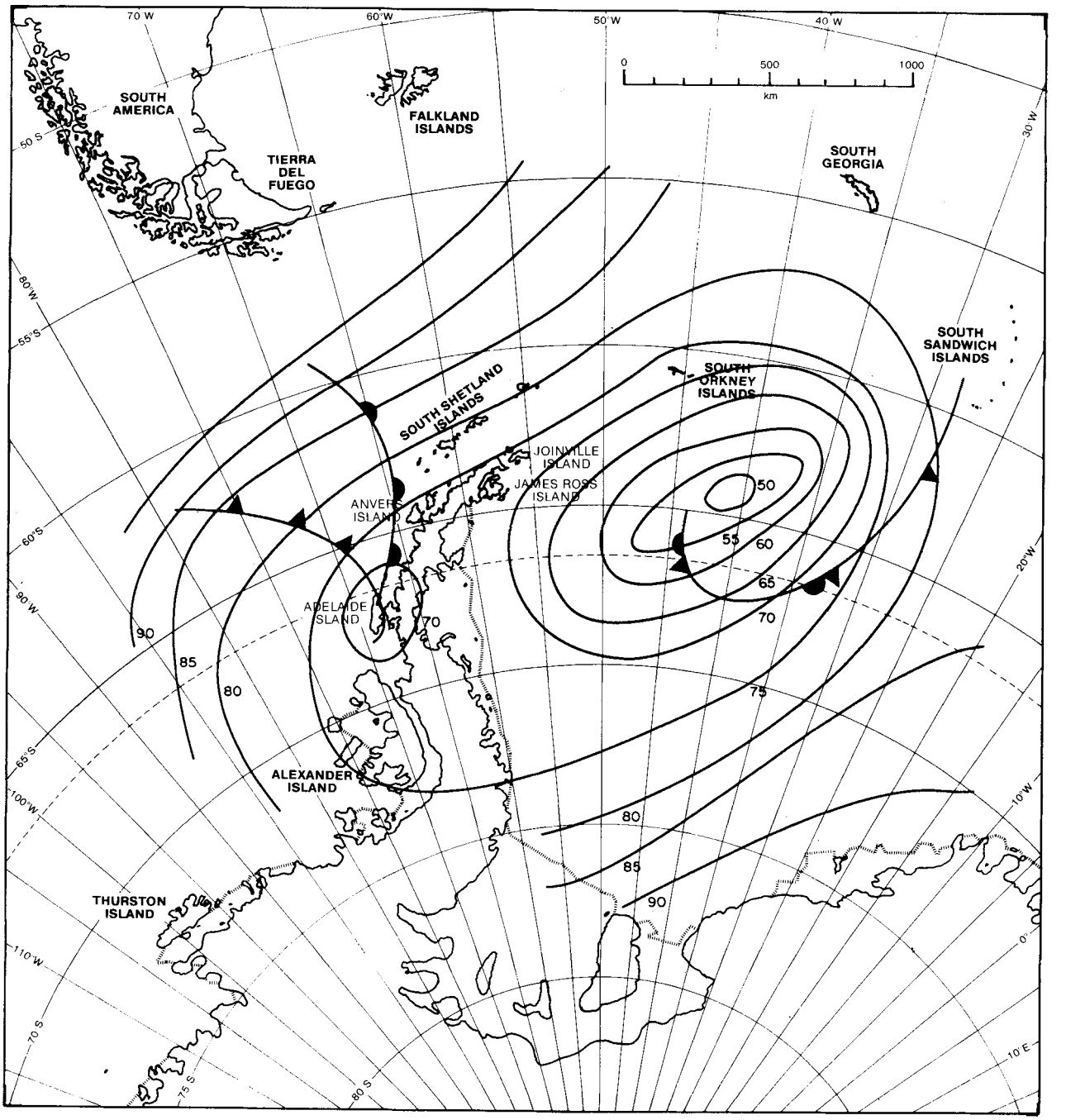


Fig. 5b. Example of synoptic chart for the Weddell Sea region: 22 September, 0900 UTC

atmospheric surface layer are shown on the same plot. The measured concentration varied rapidly; for example, in the evening of 19 September it dropped from 26 ppbv to 18 ppbv in 5 minutes, and then in the next 2 hours it decreased to 9 ppbv. The greatest decrease (from 26 to 2 ppbv) took place on the evening of 21 September. There is a clear link between ozone variations and variations of temperature and wind direction. Low ozone (and cold air) as a rule (20, 24, 26 September as well as on other days not shown) corresponded to a S or W wind. A different picture was observed on 22 September when a very low concentration existed during the day, while the wind turned from W to N, then to E and finally to S in the same period.

This picture becomes clearer when synoptic charts made by the ship's meteorologist, K Dittmer, are examined (two examples of such a chart are presented in Fig. 5). During the period three low pressure systems passed above the *R.V. Polarstern*. Any crossing of a cold front (on 19, 21 and 26 September) was associated with a drop in air temperature and a turning of the wind from N or NE to W or SW. For all

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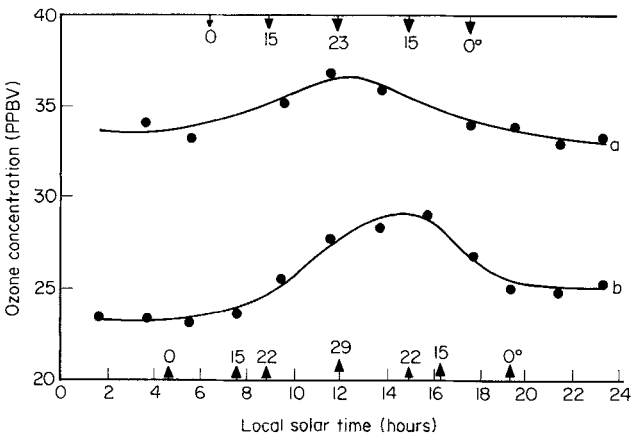


Fig. 6. Averaged diurnal variations of ozone concentration in the Weddell Sea surface atmospheric layer:
a) 12,13,14 September, near 51°S, mean total ozone 276 matm cm;
b) 11,14,15 October, near 69°S, mean total ozone 177 matm cm.
The figures near the arrows show values of the solar elevation above the horizon.

three cases the ozone concentration was high (26 to 28 ppbv) before the passage of the cold front and did not differ significantly from that observed a few days earlier inside air masses at moderate latitudes. Warm sectors of cyclones may be considered as regions of influx of warm, ozone-rich air from lower latitudes. Lower ozone concentrations (12 to 16 ppbv) were usually observed in the cold regions of cyclones. The case of an extremely low ozone concentration and a 240° change of wind direction during 22 September should be studied alongside the synoptic situation for that day (Fig. 5b). During all this period the *R.V. Polarstern* was in the centre of the cyclone, in a region with locally closed isobars. It is not clear, however, what is the detailed mechanism for such a dramatic decrease of ozone in an isolated air mass.

As a rule there was no regular diurnal variation of ozone concentration during the period of the expedition. However, during a few clear days an increase of ozone concentration was observed near noon. Fig. 6 illustrates two rather different diurnal variations, for the beginning (case 'a') and the end (case 'b') of the *R.V. Polarstern's* stay in the Weddell Sea. The figures near the arrows give the solar elevations above the horizon, in degrees. One can see that for case 'b' the ozone increase is greater, but the 'background' level is lower than in case 'a'. It is reasonable to propose that the larger ozone increase in case 'b' is associated with a larger intensity and a longer duration of solar radiation during a day, as well as with a lower total ozone abundance (177 matm cm, instead of 276 matm cm.) Another feature, a shift of 2½ hours in the ozone maximum relative to solar noon, is distinct but this should be analyzed separately.

In this preliminary report it is too early to draw definite conclusions about the causes of the surface layer ozone variations. Nevertheless, it should be noted that there is a similarity in the patterns of ozone variations in the surface and in the stratospheric layers of the atmosphere. It is well-known (see, for example, Voskresensky *et al.*, 1989) that the stratospheric amount of ozone correlates positively with the air temperature, and decreases inside the vortex in association with the stratospheric low pressure system during the Antarctic spring.

Acknowledgements

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