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MEASUREMENTS OF ATMOSPHERIC OZONE
AT THE ARGENTINE ISLANDS AND
HALLEY BAY, 1957-72

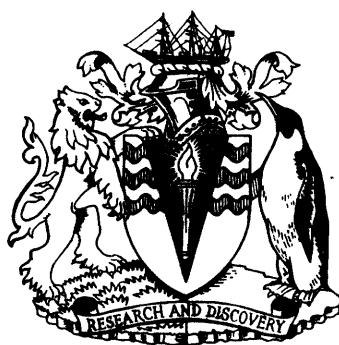
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ABSTRACT

A CRITICAL review of all the ozone observations obtained at Halley Bay and the Argentine Islands shows that extra-terrestrial constants adopted annually were, in general, in error. Corrections have been established and the data recalculated using revised ozone absorption coefficients to provide a reasonably consistent sequence from October 1957 to March 1973. The values adopted, which are mainly based on AD observations, are tabulated, means and standard deviations calculated, and the general variations in the period briefly described. The data show a consistent increase in ozone of 3 m atm-cm. in the afternoon relative to the corresponding morning values. The principles of the technique of ozone measurement using the Dobson spectrophotometer are briefly described and the tests and precautions found necessary to produce accurate data are discussed in detail. The use of focused sun and focused moon data is critically reviewed and the effects of internal scattering and of skylight evaluated. The former is effectively eliminated by using a nickel sulphate filter for values of μ up to about 6.5. The additional correction for focused moon data is most probably zero.

A case of wedge deterioration at the Argentine Islands is discussed and methods devised to reject doubtful data. The reliability of the re-evaluated data is estimated. Short- and long-term variations in the spectrophotometers, shown by the standard lamp tests, are evaluated and discussed. The value of the AD comparison for minimizing effects due to changes in the extra-terrestrial constant is stressed. The more limited CD measurements show that these are not appreciably affected by skylight or internally scattered light when μ is less than 3.5 so that CD measurements may be preferable to AD at these latitudes.

The discussion in the paper is mainly concerned with evaluating the corrections to the extra-terrestrial constant, and developing means of testing whether they were likely to be correct. Adequate intercomparisons could be established between different instruments and, in most cases, the instrumental correction was little changed by overhaul at the manufacturers. Tests before and after final correction showed strong correlations between the adopted error ΔN and ozone amount before correction, but negligible correlation after correction. With the possible exceptions of some data taken with the faulty wedge, the overall reliability of the daily values is believed to be within ± 5 m atm-cm.

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I. INTRODUCTION

MEASUREMENTS of the total amount of ozone, using Dobson ozone spectrophotometers, have been made at the Argentine Islands (lat. $65^{\circ} 15'S.$, long. $64^{\circ} 16'W.$) and at Halley Bay (lat. $75^{\circ} 31'S.$, long. $26^{\circ} 40'W.$) since the beginning of the International Geophysical Year (I.G.Y.) in 1957. The British Antarctic Survey (formerly Falkland Islands Dependencies Survey) has operated the Argentine Islands station since its inception, and took over the Halley Bay station in 1959 from the Royal Society International Geophysical Year Antarctic Expedition which operated the station during the I.G.Y. and the following year. The results obtained at Halley Bay during the I.G.Y. have been published by MacDowall (1962) and are also reviewed in this publication.

The Dobson ozone spectrophotometer, its mode of operation and the methods used to deduce the total amount of ozone from its measurements are fully described by Dobson (1957) in the handbook and are briefly described in section II.

The main difficulty with the Dobson spectrophotometer is its absolute calibration, i.e. the determination of its extra-terrestrial constants. The need to keep under review the original constants of the spectrophotometer, and to revise them when required, is emphasized in the handbook and other official publications, e.g. *W.M.O./I.Q.S.Y. Report No. 5*. Furthermore, the charts used to determine ozone amounts from observation of the zenith sky can be constructed only as a result of a long series of comparisons of such observations with direct sun observations at each station, and to a lesser extent, with each instrument. This need for a long-term review of the constants is inconsistent with the need to submit the results as soon as possible for publication by the Atmospheric Environment Service of Canada in co-operation with the World Meteorological Organization. The procedure has been for each geophysicist, on his return to the geophysics section of the British Antarctic Survey in Edinburgh, to review the results of the previous year's observations, to determine the extra-terrestrial constants of the instrument and the corrections required to all types of observation, and to apply these corrections to the measurements of ozone amount before despatching the results to the World Data Centre. A comprehensive review has now been carried out of all the determinations of the extra-terrestrial constants of the spectrophotometers used at the two stations. This shows that some of the values used in calculating the ozone amounts published by the World Data Centre were incorrect.

This paper is the outcome of the review. In section II is given a brief description of the spectrophotometer and the principles of its use for those not conversant with this method of measuring atmospheric ozone; it is followed in sections III–V by notes on the physical constants used, the observation sites and the spectrophotometers. Sections VI–X are more specialized and describe the methods adopted to determine the ozone amounts from the individual measurements. So far as we know, this is the first occasion on which a full analysis of high-latitude data has been published. The revised daily ozone amounts are given in Table VI in section XI, and some properties of the data are summarized in sections XII–XIV. The vertical distribution of ozone deduced from Umkehr measurements is given in section XV.

II. BRIEF DESCRIPTION OF THEORY OF THE DOBSON SPECTROPHOTOMETER

SOLAR radiation is directed on to the entrance slit of the spectrophotometer, and then passes through a flat quartz plate and, after refraction and reflection, forms a spectrum in the focal plane of the instrument. Two narrow wavebands are isolated by means of two slits in the focal plane, and the light beams which pass through them are further refracted and brought together on to a photomultiplier. The wavebands are identified by their central wavelengths. The spectrum can be moved across the focal plane by rotating the quartz plate and thus different pairs of wavebands can be isolated. The relative intensity of the two wavebands is measured by a null method—by turning a graduated dial which moves a calibrated optical wedge in the path of one of the slits, until the intensity of the two wavebands is equal. The ratio of their

intensities I and I' is given by the reading R of the dial and the calibration, which is of the form $\log I/I' = f(R)$.

The intensity I of the shorter waveband when received by the spectrophotometer is related to the intensity of the waveband outside the Earth's atmosphere by the equation

$$\log I = \log I_0 - a\mu x - \beta m - \delta \sec z,$$

where x is the equivalent thickness of ozone in one vertical thickness of the atmosphere, and a , β and δ are evaluated for $\log I/I_0$ to base 10.

μ is the relative path length of sunlight through the ozone layer ($\mu = 1$ when $z = 0$).

m is the equivalent path length of sunlight through the atmosphere allowing for curvature of the Earth ($m = 1$ when $z = 0$).

a is the absorption coefficient per atm-cm. of ozone for wavelength λ .

β is the scattering coefficient due to air molecules per unit atmosphere for wavelength λ .

δ is the attenuation coefficient for aerosols per unit atmosphere for wavelength λ .

z is the zenith angle of the sun.

For the longer waveband we have a similar equation

$$\log I' = \log I_0' - a'\mu x - \beta' m - \delta' \sec z$$

and thus

$$\log I/I' = \log I_0/I_0' - (a - a')\mu x - (\beta - \beta')m - (\delta - \delta') \sec z.$$

The term $\log I/I'$ is the extra-terrestrial constant of the spectrophotometer; this is a misnomer as it would vary if there was a relative change in the intensity of the solar radiation in these wavebands and it would be affected by changes in the sizes of the slits, relative variations in the spectral sensitivity of the photomultiplier, etc.

The nominal value of the extra-terrestrial constant of each instrument is determined by comparison with a standard spectrophotometer, and it is included in the wedge calibration tables ($R-N$ tables) which are of the form $N = f(R)$, where

$$N = \log I_0/I_0' - \log I/I'.$$

Thus

$$N = (a - a')\mu x + (\beta - \beta')m + (\delta - \delta') \sec z \quad (1)$$

is a measure of the relative attenuation of the atmosphere and becomes zero outside it.

Lack of accurate knowledge of the extra-terrestrial constant is probably the main source of error in the measurements of ozone. The method used in monitoring it is described in section VIII.

Four pairs of wavelengths, referred to as A, B, C and D, have been selected as suitable for ozone measurements, choosing wavelengths where the rate of change of mean absorption coefficient over the whole waveband is small. Of these, A, C and D are used at our stations. The absorption coefficients and molecular scattering coefficients for these wavelength pairs are given in section III.

The error due to aerosol attenuation is generally small in the Antarctic, though not negligible in industrial areas. It is the general practice to eliminate its effect by making observations successively on two pairs of wavelengths, say A and D, and so from Equation (1)

$$N_A - N_D = \{(a - a')_A - (a - a')_D\}\mu x + \{(\beta - \beta')_A - (\beta - \beta')_D\}m + \{(\delta - \delta')_A - (\delta - \delta')_D\} \sec z. \quad (2)$$

δ varies only slowly with wavelength, and it is generally accepted that the last term may be neglected.

We shall show, on p. 8, that there is a further advantage in making observations on two pairs of wavelengths, in that changes in the extra-terrestrial constant are about the same for all pairs; thus changes in their differences are relatively small. Almost invariably, therefore, observations are made on two pairs, normally an AD observation, in which $N_{AD} = N_A - N_D$ is measured. When μ is large and the intensity of the A radiation is low, CD observations are made.

Direct sun observations are the only measurements which provide absolute measurements of ozone amount. Such observations, however, cannot be made when the sun is obscured by cloud, and most routine observations are made by allowing light from the zenith to fall on the entrance slit of the spectrophotometer. The ozone amount is read from a standard chart relating x to N and μ . These values are then modified by a correction evaluated by making successive observations, when possible, on sun and zenith. The presence or absence of cloud in the zenith does not matter when AD observations are made.

When the intensity of an A wavelength is too low, zenith observations are made on C and C' pairs. In the C' observation the intensity of the longer of the C wavelengths is compared with that of a much longer wavelength. Neither of the C' wavelengths is appreciably absorbed by ozone so the C' measurement is a measure of the attenuation by the cloud. Cloud-correction charts for CC' observations are issued with the spectrophotometer, and these too are checked and corrected on the station by the method which will be described in section IX.

III. PHYSICAL CONSTANTS AND UNITS ADOPTED

TABLE I gives the values which have been used for the absorption coefficient differences, $a - a'$, and for the molecular scattering coefficient differences, $\beta - \beta'$, for the wavelength pairs used in the ozone measurements. These have been extracted from the handbook, except for the ozone absorption coefficients for which we have adopted the values measured by Powell (1971) which are almost identical with those measured by Walshaw and others (1971).

TABLE I
WAVELENGTHS, ABSORPTION COEFFICIENTS PER atm-cm.
AND MOLECULAR SCATTERING COEFFICIENTS PER UNIT
ATMOSPHERE OF THE SELECTED WAVELENGTH PAIRS

Designation of wavelength pair	Wavelengths (Å)		$a - a'$	$\beta - \beta'$
A	3055	3254	1.743	0.116
C	3114	3324	0.810	0.110
D	3176	3398	0.355	0.104
C'	3324	4536		
AD	A pair	D pair	1.388	0.012
CD	C pair	D pair	0.455	0.006

The value of μ , the ratio of the length of the path of solar radiation through the ozone layer to the length of the path if the sun were in the zenith, depends only weakly on the height of the ozone layer. The centre of gravity of the ozone layer has been assumed to be 22 km. for both stations for all seasons.

The total amount of ozone is expressed as the equivalent thickness of the ozone layer at S.T.P. in thousandths of a centimetre; the unit is called a milli-atmo-centimetre (m atm-cm.).

IV. THE OBSERVATION SITES

THE station in the Argentine Islands is situated on land near sea-level on one of the islands in the archipelago. The spectrophotometer is housed in a room of the living hut with a hatch in the roof. The instrument is rigidly suspended below the hatch from a circular track attached to the roof which enables it to be orientated in any direction. Zenith observations are made through the hatch; for direct sun observations the sun director protrudes through it. The temperature in the room is maintained near 15° C. When intercomparisons have been made with a second instrument, this has been operated outside the hut.

At Halley Bay the station is near sea-level on the ice shelf about 2 km. from the ice edge. The ice shelf is moving, and the quoted position is that in 1964; the latitude is almost constant but west longitude increases by about 1' per year. The ozone spectrophotometer is housed in a hut which is mounted on skis and which is moved once or twice a year to keep it clear of snowdrifts. The hut is heated and is kept near 15° C by thermostatic control. The mounting of the instrument is similar to that at the Argentine Islands; the sun director is somewhat longer than standard.

V. THE SPECTROPHOTOMETERS

ALL spectrophotometers were calibrated before transport to Antarctica: in the earlier years they were calibrated by comparison with the standard spectrophotometer at Oxford, in latter years the calibration has been carried out by the manufacturers, Messrs R. & J. Beck Ltd., to whom instruments, on being withdrawn from the Antarctic stations, have been sent for cleaning and overhaul.

The instruments in use at the stations have been Nos. 31, 51, 73, 88 and 103. In the text a letter A, B . . . is added, which is changed after any significant change, such as a change of wedges and each time the instrument is re-issued by Messrs Beck Ltd. after renovation.

VI. MONTHLY ROUTINE TESTS OF THE SPECTROPHOTOMETERS

1. Wavelength setting

In addition to the routine mercury lamp test, wavelength-setting test 15.1 of the handbook was normally carried out at least once in each summer season. No serious errors of wavelength setting occurred; smaller errors were corrected before they became significant.

TABLE II
STANDARD LAMP READINGS

Period	Number of tests	Instrument number	Lamp number	A		C		D		A-D	
				Mean	dR	Mean	dR	Mean	dR	Mean	dR
<i>Argentine Islands</i>											
October-December 1957	6	51A	B	86.9	0.8	79.1	0.7	73.3	0.7	13.6	0.2
January-March 1958	3	51A	B	86.8	0.5	78.6	0.4	72.9	0.4	13.9	0.1
October-December 1958	3	51A	B	86.3	0.3	78.3	0.2	72.8	0.3	13.5	0.3
January-March 1959	3	51A	B	87.2	0.4	79.2	0.1	73.5	0.2	13.7	0.2
October-December 1959	8	51A	B	88.7	1.2	80.5	1.0	74.6	0.6	14.1	0.6
January-March 1960	3	51A	B	91.1	0.6	82.6	0.4	75.9	0.6	15.2	0.1
April-May 1960	2	51A	51	53.5	0.0	56.0	0.2	58.3	0.1	-4.8	0.1
October-December 1960	3	51B	51	43.8	0.4	42.8	0.4	40.9	0.2	2.9	0.4
January-March 1961	3	51B	51	43.0	0.3	42.4	0.1	40.4	0.4	2.6	0.4
October-December 1961	3	51B	51	40.6	0.1	40.0	0.2	38.3	0.2	1.3	0.1
February-March 1962	3	73A	73C	45.6	0.4	42.2	0.2	43.0	0.1	2.6	0.4
October-December 1962	3	73A	73C	44.9	1.0	41.6	0.6	42.3	0.1	2.6	0.8
January-March 1963	4	73A	73C	44.9	0.9	41.3	0.2	42.2	0.2	2.7	0.7
October-December 1963	3	73A	73C	45.9	0.4	42.1	0.2	42.6	0.1	3.3	0.4
January-March 1964	4	31B	31A	55.4	0.4	54.3	0.6	53.6	0.6	1.8	0.2
October-December 1964	4	31B	31A	57.4	0.6	56.0	0.4	55.2	0.4	2.2	0.3
January-March 1965	4	31B	31A	58.6	0.3	57.1	0.2	56.0	0.2	2.6	0.1
October-November 1965	2	31B	31A	59.7	0.1	58.0	0.0	56.7	0.0	3.0	0.0
November-December 1965	3	31B	31A	55.2	0.2	53.2	0.1	52.2	0.1	3.0	0.2
January-March 1966	3	31B	31A	55.6	0.3	53.3	0.3	52.1	0.2	3.5	0.2
October-December 1966	3	31B	31A	55.5	0.2	54.2	0.6	52.5	0.0	3.0	0.2
January-February 1967	3	31B	31A	56.1	0.3	53.4	0.3	52.2	0.3	3.9	0.1
October-December 1967	3	103	C2	43.1	0.3	44.6	0.2	46.1	0.2	-3.0	0.1
January-March 1968	3	103	C2	42.7	0.6	44.2	0.6	45.5	0.6	-2.8	0.0
October-December 1968	2	103	C2	41.4	0.1	43.1	0.1	44.5	0.0	-3.1	0.1
January-March 1969	3	103	C2	41.4	0.0	43.1	0.1	44.6	0.0	-3.2	0.0
October-December 1969	3	103	C2	40.9	0.1	42.6	0.1	44.1	0.1	-3.2	0.0
January 1970	2	103	C2	40.5	0.2	42.2	0.1	43.8	0.2	-3.3	0.0
February-March 1970	3	73C	73C	22.6	0.1	25.6	0.1	27.1	0.1	-4.6	0.1
October-December 1970	3	73C	73C	22.3	0.1	25.7	0.0	27.2	0.0	-4.9	0.1
January-February 1971	3	73C	73C	22.7	0.3	26.5	0.6	28.0	0.5	-5.3	0.3
April 1971	2	73C	D28	11.1	0.0	16.9	0.0	20.3	0.0	-9.2	0.0
October-December 1971	3	73C	D28	11.1	0.2	17.0	0.1	20.3	0.1	-9.2	0.1
January-March 1972	3	73C	D28	11.0	0.1	16.6	0.1	19.7	0.3	-8.7	0.3
October-December 1972	4	73C	D28	9.5	0.5	14.7	0.5	17.4	0.5	-7.9	0.1

2. Wedge calibration

The constancy of the wedge calibration is checked by the rhodium plate test. This test showed that the calibration of the wedges remained constant, except in the case of No. 51, whose behaviour is fully described in section VII. This example illustrates well the value of this test. If the test had not been carried out, the deterioration of the wedge would not have been noticed, though inconsistent ozone values would throw suspicion on it.

3. Standard lamp tests

The standard lamp tests monitor changes in the calibration of the spectrophotometer, i.e. errors in the $R-N$ tables. Two lamps were normally used, and these always showed similar patterns of slow variation, indicating that these were variations of the spectrophotometer rather than of the lamps; variations in the meters controlling the electric power supply to the lamps are believed to be negligible.

The types of variations which occur are illustrated in Table II. This table shows mean values of R , for each wavelength, for periods which are normally the first and last 3 month period of each summer season, thus giving the longer-period changes and drifts. The values of dR are the mean deviations of the values of each test from the mean value of R for the period, and thus show the short-period variations. While

TABLE II—continued

Period	Number of tests	Instrument number	Lamp number	A		C		D		A-D	
				Mean	dR	Mean	dR	Mean	dR	Mean	dR
<i>Halley Bay</i>											
October-December 1957	3	31A	31A	55.5	0.1	56.4	0.1	57.6	0.1	-2.1	0.1
January-March 1958	4	31A	31A	56.0	0.3	56.9	0.3	57.9	0.4	-2.0	0.1
October-December 1958	3	31A	31A	59.0	0.0	59.0	0.1	59.8	0.2	0.8	0.2
October-December 1958	3	31A	31C	43.6	0.1	47.9	0.0	51.9	0.0	-8.3	0.0
January-March 1959	3	31A	31C	43.5	0.4	47.8	0.4	52.0	0.3	-8.5	0.1
October-December 1959	3	31A	31C	44.0	0.0	48.2	0.1	52.3	0.1	-8.3	0.1
January-March 1960	4	31A	31C	42.9	0.5	47.4	0.3	51.5	0.3	-8.6	0.3
October-December 1960	4	31A	31C	43.6	0.3	48.0	0.3	52.2	0.3	-8.6	0.3
January-March 1961	3	31A	31C	43.9	0.1	48.1	0.1	52.4	0.4	-8.5	0.3
October-December 1961	3	31A	31C	44.5	0.0	48.8	0.1	53.0	0.1	-8.4	0.0
January-March 1962	3	31A	31C	43.8	0.3	48.5	0.1	52.8	0.3	-9.0	0.6
October-December 1962	3	31A	31C	42.5	0.5	47.2	0.6	52.0	0.7	-9.6	0.2
February-April 1963	3	88	88A	44.6	0.2	44.4	0.4	43.3	0.3	1.3	0.1
October-December 1963	3	88	88A	44.6	0.2	44.4	0.0	43.2	0.1	1.3	0.1
January-March 1964	3	88	88A	45.1	0.3	44.8	0.5	43.8	0.6	1.3	0.3
October-December 1964	3	88	88A	45.0	0.1	44.9	0.1	44.7	0.0	0.3	0.2
March-April 1965	2	73B	73D	50.2	0.1	47.7	0.1	46.1	0.1	4.1	0.0
October-December 1965	3	73B	73D	51.9	0.0	49.2	0.2	47.4	0.1	4.5	0.1
January-March 1966	3	73B	73D	52.2	0.1	49.4	0.1	47.5	0.2	4.6	0.2
October-December 1966	5	73B	73D	52.4	0.4	49.3	0.3	47.6	0.2	4.8	0.2
January-March 1967	4	73B	73D	52.7	0.6	49.4	0.6	47.4	0.2	5.3	0.1
October-December 1967	6	73B	73D	52.5	0.5	49.1	0.4	47.3	0.3	5.2	0.2
February-March 1968	5	31C	31A	50.0	0.4	47.5	0.5	46.2	0.6	3.8	0.2
October-December 1968	4	31C	31A	50.9	0.2	47.5	0.1	46.1	0.1	4.9	0.2
January-March 1969	6	31C	31A	50.3	0.6	47.1	0.5	45.5	0.7	4.8	0.1
October-December 1969	3	31C	31C	46.5	0.2	45.8	0.1	46.2	0.2	0.3	0.1
January-March 1970	3	31C	31C	47.1	0.2	46.3	0.2	46.8	0.2	0.2	0.2
October-December 1970	3	31C	31C	47.5	0.4	46.2	0.2	46.4	0.3	1.0	0.1
January-March 1971	3	31C	31C	49.3	0.4	47.8	0.5	47.9	0.3	1.4	0.0
October-December 1971	3	31C	31C	47.2	0.5	45.8	0.7	45.9	0.6	1.3	0.2
January-March 1972	3	31C	31C	46.9	0.2	45.5	0.2	45.6	0.1	1.3	0.1
October-December 1972	3	31C	31C	47.7	0.1	46.0	0.1	46.0	0.1	1.7	0.0
October-December 1971	2	31C	C10	45.0	0.1	44.1	0.1	44.7	0.1	0.3	0.1
January-March 1972	3	31C	C10	45.1	0.1	44.2	0.2	44.7	0.1	0.4	0.0
October-December 1972	3	31C	C10	45.5	0.0	44.5	0.1	45.0	0.1	0.5	0.0

Table showing period means of standard lamp readings for A, C and D wavelengths for each spectrophotometer. The number of tests carried out in each period of about 3 months is given in column 2, and the number of the lamp in column 4. The difference of the dial readings for A and D wavelengths is also given. dR is the average deviation of the individual readings from the mean of each period.

there are exceptions to the general rule, it appears that generally the short-period variations and the long-period variations are less for AD comparison than for any single pair of wavelengths. This is an important advantage in the use of a pair of wavelengths, which has not been adequately stressed in the literature.

Standard lamps of the original type have been in use for most of the time at both stations, but latterly they have been replaced by quartz-iodine lamps, e.g. C2 and D28 in Table II. These seem to be somewhat steadier but only marginally so, while the accessory equipment is more elaborate and expensive.

VII. THE ABNORMAL BEHAVIOUR OF INSTRUMENT 51

IN October 1959 the rhodium plate test showed significant changes in the wedge for dial readings between about 100° and 150° , the apparent N value of the rhodium plate changing from 0.490 to 0.460, and in December the thicker end of the wedge deteriorated even more drastically, the N value decreasing to about 0.360. This was confirmed in November 1959 by an on-site recalibration, by the two-lamp method, which showed inappreciable changes for dial readings below 100° , but increasingly large changes above 100° . New wedges were fitted in May 1960 and were calibrated both by the two-lamp and by the rhodium plate method. These agreed and new R - N tables were computed. Monthly wedge calibration tests of the new wedge gave a value of N for the rhodium plate markedly different from the values obtained in earlier years, suggesting that the deterioration of the wedge began as early as 1957, and that all observations made with R greater than about 100° must be treated with caution.

The corrections to the extra-terrestrial constant, derived by the method described on p. 8-13 in the period October 1957 to March 1959, were $\Delta N_{AD} = -0.059$ and $\Delta N_{CD} = +0.014$. These values, however, produce mean values of x for December 1957 and 1958 which differ from the mean value for December in the 1960-69 period by about ten standard deviations for AD observations, and by about five standard deviations for CD observations. In addition, values of x_{AD} and x_{CD} obtained from simultaneous direct sun observations, when used with these values of ΔN_{AD} and ΔN_{CD} , give a difference $x_{CD} - x_{AD}$ of near 0.015, significantly different from zero. Furthermore, this increases with μ instead of decreasing as would be found for errors in ΔN_{AD} and ΔN_{CD} . This is further proof that the wedge calibration was in error.

However, the calibration of the wedge in November 1959 agreed with the previous calibrations for all values of R less than about 100° . Thus, all observations with R less than 100° are reliable. For most C-wavelength observations with $\mu \leq 2$, R was less than about 110° , and so most CD observations for low values of μ will be valid, and those made at $\mu = 2$ will be little in error. The residual errors may be too large for the data to be used for the determination of ΔN_{CD} by the normal method. We have, therefore, derived ΔN_{CD} for the 1957-59 period from the value obtained with the new wedges after May 1960, and the change in standard lamp readings, which are made at values of R around 50° . This leads to a value of $\Delta N_{CD} = 0.040$, and to mean December values of x less than one standard deviation from the 1960-69 mean. For the period October 1957 to March 1959 all AD observations have been rejected.

The CC' zenith sky observations for $\mu = 2$ have been calibrated by comparing them with simultaneous CD observations when R is less than 105° ; 50 per cent of these values of $x_{CC'} - x_{CD}$ were within ± 0.005 of the mean value. The CC' zenith sky observations for $\mu = 3$ were calibrated by comparison, on days of little apparent change of ozone, with the CC' ($\mu = 2$) and any valid CD direct sun observations, and again 50 per cent of the values of $x_{CC'}(\mu = 3) - x_{CC'}(\mu = 2)$ lay within ± 0.004 of the mean value.

From October 1957 to October 1959, therefore, only CD and CC' observations have been used in determining the ozone amount, but these values are probably only a little less reliable than in other years. For the period October 1959 to March 1960, when the wedge was deteriorating more rapidly, the standard must be accepted as lower than normal.

VIII. DETERMINATION OF EXTRA-TERRESTRIAL CONSTANTS

1. General considerations and adopted procedure

The method of determining the extra-terrestrial constants of a spectrophotometer has been fully described by Dobson and Normand (1962). The method, briefly summarized, is as follows.

The extra-terrestrial constant of a spectrophotometer for any waveband, or pair of wavebands, is determined by measuring the rate of change of N/μ with $1/\mu$, and assuming that there is no change in the amount of ozone during the period of measurement. At two direct sun observations giving N_1, N_2 in the same half-day

$$\begin{aligned}\mu_1(a-a')x_1 &= N_1 + \Delta N - m_1(\beta - \beta') \\ \mu_2(a-a')x_2 &= N_2 + \Delta N - m_2(\beta - \beta'),\end{aligned}$$

where ΔN is the correction to the extra-terrestrial constant, i.e. the quantity to be added to the values of N in the $R-N$ tables to make them correct.

We can write $m_1/\mu_1 = m_2/\mu_2$ and so

$$(a-a')(x_1 - x_2) = N_1/\mu_1 - N_2/\mu_2 + \Delta N \left(\frac{1}{\mu_1} - \frac{1}{\mu_2} \right).$$

During a period of constant ozone amount $x_1 - x_2 = 0$, and so

$$-\Delta N \left(\frac{1}{\mu_1} - \frac{1}{\mu_2} \right) = \frac{N_1}{\mu_1} - \frac{N_2}{\mu_2}. \quad (3)$$

In accordance with the instructions in the handbook, routine observations were made at noon, and in the forenoon and afternoon when $\mu=2$ and $\mu=3$. Appendix II of the handbook gives instructions for determining ΔN by Equation (3) from these measured values.

In practice, the slope of the N/μ vs $1/\mu$ lines for AD wavelengths is steeper (positively) between $\mu=3$ and $\mu=2$ than between $\mu=2$ and noon. This has been attributed (*W.M.O./I.Q.S.Y. Report No. 5*) to the effect of skylight which is received by the spectrophotometer in addition to the direct solar radiation. Skylight is richer in shortwave radiation with a lower N value than direct solar radiation, an effect which is inappreciable at high solar elevations, but which increases relatively as μ increases. Scattered light within the instrument is also a contributory, perhaps an important, cause of error (Dobson, 1968). The combined effect is shown in Table III where the values of ΔN for AD and CD wavelengths determined for spectrophotometers at the Argentine Islands and at Halley Bay over the range μ at noon to $\mu=2$ are compared with those for the range $\mu=2$ to $\mu=3$.

To avoid these effects, *W.M.O./I.Q.S.Y. Report No. 5* recommends that $\mu=2.6$ should be accepted as the limit of reliability of AD observations, and consequently since 1966 the first and last of the daily observations at the Argentine Islands have been made when $\mu=2.6$ instead of 3, but the corresponding change was not made at Halley Bay until 1972.

For the whole period of observation at Halley Bay, and for about half the period at the Argentine Islands, therefore, only the $\mu=2$ and noon observations are available for the determination of the extra-terrestrial constant, though these are occasionally supplemented by extra observations. For the sake of consistency, this range of μ has also been adopted for determining ΔN in later years at the Argentine Islands, even though the $\mu=2.6$ observations were available.

The standard direct sun observations were made on AD wavelengths, as instructed in the handbook, but in most years CD observations were also made, though not so frequently. Thus ΔN_{AD} and ΔN_{CD} could be determined independently, but there was little advantage in this as the greatest uncertainty in the determination of ΔN is due to changes of ozone, which cause equal errors in $\Delta N_{AD}/(a-a')_{AD}$ and $\Delta N_{CD}/(a-a')_{CD}$. We have, therefore, only used this method to determine ΔN_{AD} , for which there is the largest number of observations available, and which henceforth is denoted by ΔN .

ΔN_{CD} has been determined by taking the mean of a set of ten simultaneous AD and CD direct sun observations at $\mu=2$ approximately for each instrument, and determining the value of ΔN_{CD} required to give the same mean value of x as given by the AD observations.

It appears from the values in Table III that CD wavelengths measurements at $\mu=3$ are not appreciably affected by skylight or internally scattered light, and valid observations for the determination of ΔN_{CD} can be made over a greater range of μ than for AD wavelengths. For these reasons it may be better to adopt CD rather than AD for routine observations at high latitudes.

TABLE III
VALUES OF EXTRA-TERRESTRIAL CONSTANT ΔN
MEASURED OVER DIFFERENT RANGES OF μ

Instrument number	AD wavelengths		CD wavelengths	
	Noon to $\mu=2$	$\mu=2$ to $\mu=3$	Noon to $\mu=2$	$\mu=2$ to $\mu=3$
31A	-0.024	-0.090	0.009	0.012
88	0.014	0.000	0.015	0.012
73B	-0.046	-0.115	0.011	-0.006
51B	0.049	0.000	0.009	0.000
73A	-0.007	-0.049	0.025	0.030
31B	-0.021	-0.071	0.008	0.023
MEAN	-0.006	-0.054	0.013	0.012
	$\mu=2$ to $\mu=2.6$		$\mu=2$ to $\mu=2.6$	
31B	-0.040	-0.045	0.014	0.008
103	-0.012	-0.033	0.004	0.016
73C	-0.037	-0.033	0.008	0.025
31C	0.001	-0.003		
MEAN	0.022	0.029	0.009	0.016

Note. The difference between the values of ΔN in this table and those in Table IV is due to different samplings. In this case all half days are considered when there are measurements available of ΔN over the two ranges, while the values in Table IV are obtained from days when measurements were made from $\mu=2$ in the forenoon to noon, and also from noon to $\mu=2$ in the afternoon.

2. Calibrations and interrelations of the individual spectrophotometers

Altogether five spectrophotometers have been in operation at the Antarctic stations; two of them were used for three periods separated by intervals when they were withdrawn for overhaul by the manufacturers. In most cases, standard lamp tests with the same lamps have monitored changes which have taken place during the periods of overhaul, and thus provide a link between the values of ΔN determined during successive periods of operation. In addition, on three occasions it was possible to carry out intercomparisons between two spectrophotometers during the short overlap when the instrument at the Argentine Islands was being replaced; no such intercomparisons have been carried out at Halley Bay. For some reason, which is not understood, the deduced differences between the values of ΔN of the two instruments for a pair of observations varied through a rather large range. Nevertheless, the intercomparisons enable this difference of ΔN between two instruments to be evaluated to an accuracy of about 0.010.

3. Accuracy of determination of ΔN

The accuracy in determining ΔN from the slope of the N/μ vs $1/\mu$ line from $\mu=2$ to noon will clearly depend on the number of measurements, and when this number is small, on luck! The changes of ozone during a half-day can be so large as to make it inadvisable to use only half-days, and in general only days when both forenoon and afternoon observations were made and the sun was clear of all cloud have been accepted. Even then, changes in the rate of change of ozone amount, or random errors at one of the observations, particularly that at noon, cause very large errors in ΔN , e.g. 0.100 or more. If not balanced by large values of opposite sign, such samples would cause large errors in the average of a rather small number of determinations. For this reason, the median value of a series of values of ΔN has been adopted rather than the mean value. The final accuracy, therefore, depends on the total number of observations,

on how small was the real change of ozone on the median day, and on whether the number of days of unbalanced increases of ozone was equal to the number of unbalanced decreases.

There is also the effect of random errors. Dobson and Normand (1962) estimated the standard error of an observation of N/μ as about 0.004, so the standard error of a measurement of the difference between noon and $\mu=2$ is about 0.0055; for a forenoon and afternoon pair over a range of $1/\mu$ of about 0.25, this leads to a random standard error of about 0.016 in ΔN , and to about 0.004 for a set of about 16 days.

The weather at these Antarctic stations, however, is only infrequently suitable for ΔN measurements; in some years there is almost continuous cloud during the summer, with only broken periods of clear sun. During the three bad summers of operation of No. 103 at the Argentine Islands, whole-day observations were possible on only five, two and two occasions. In this case considerable errors in ΔN must be expected; fortunately No. 103 was intercompared with the previous and following spectrophotometers.

Table IV gives, for each period of operation of each instrument, the measured value of ΔN , i.e. the median of the individual values, the number of days of observation on which it is based, and the range of ΔN within which half the individual observations are contained. It will be seen that Nos. 31 and 73 were both in operation on three occasions, and that their values of ΔN are linked by standard lamp tests and by three intercomparisons, details of which are also given in the table. The last columns of Table IV give in (b) and (c) the accepted differences in ΔN indicated by standard lamp measurements and by intercomparisons, and in (a) the final accepted values of ΔN , all so chosen that they form a consistent set, with only small differences between the accepted and the measured values.

The r.m.s. value of the difference between the measured and accepted values of ΔN of instrument Nos. 31, 73 and 103 is about 0.006. If this is regarded as the magnitude of the error in the accepted value of ΔN , it gives rise to an error in the general level of x of about 3 m atm-cm.

It should be noted that the value of $\Delta N = -0.017$ for No. 31A is somewhat greater than the value of -0.032 determined for the instrument during the I.G.Y. at Halley Bay by MacDowall (1962), but he used $\mu=3$ observations and this would lead to too low a value of ΔN .

TABLE IV
RESULTS OF THE DETERMINATIONS OF EXTRA-TERRESTRIAL CONSTANT
OF EACH SPECTROPHOTOMETER, AND OF SOME DIFFERENCES
BETWEEN PAIRS

	<i>Instrument number</i>	<i>Number of observations</i>	<i>50 per cent range</i>	<i>Measured ΔN</i>	<i>Accepted ΔN</i>
a. <i>Argentine Islands</i>	51B	9	0.005 to 0.040	0.023	0.023
	73A	10	-0.036 to 0.044	0.015	0.010
	31B	19	-0.050 to -0.010	-0.027	-0.035
	103	8	-0.037 to -0.002	-0.019	-0.010
	73C	16	-0.061 to -0.030	-0.040	-0.040
<i>Halley Bay</i>	31A	14	-0.043 to 0.035	-0.017	-0.013
	88	13	-0.013 to 0.050	0.008	0.008
	73B	26	-0.071 to -0.029	-0.040	-0.035
	31C	21	-0.049 to 0.004	-0.036	-0.043
b. <i>Changes in ΔN indicated by standard lamp measurements</i>				<i>Measured ΔN</i>	<i>Accepted ΔN</i>
	From 31A to 31C			-0.030	-0.030
	From 31B to 31C			-0.010	-0.008
	From 73A to 73B			-0.040	-0.045
				0.000	-0.005
c. <i>Differences in ΔN indicated by intercomparisons</i>				<i>Measured difference</i>	<i>Accepted difference</i>
	73A to 31B			-0.048	-0.045
	31B to 103			0.030	0.025
	103 to 73C			-0.030	-0.030

4. Correlation between ΔN and mean ozone amounts

As the corrections found above are so large, it is worth testing whether there is any internal evidence that they are correct. In fact, appreciably different values of x are given on AD and CD wavelengths when the uncorrected $R-N$ tables are used which implies that there are significant errors in the calibration.

If the values of ΔN used in calculating ozone amounts are appreciably incorrect, then there will be a significant correlation between the mean ozone amounts and the value of ΔN used to calculate them. We can, therefore, obtain some idea of the relative accuracy of our values of ΔN by correlating them with the calculated year-to-year variation of ozone amount. The best period to select will be a period of minimum variation. It will be seen in Fig. 5 that the standard deviation is a minimum around the summer solstice at the Argentine Islands, and about a month later at Halley Bay, and thus the last 15 days of December and of January have been chosen for correlation with the values of ΔN at the Argentine Islands and Halley Bay, respectively. We have considered the period 1960 to 1972 so as to avoid use of the less reliable Argentine Islands data before May 1960, and the I.G.Y. period at Halley Bay for which the basic data are not available.

The correlation coefficient between our values of ΔN and the annual ozone amounts obtained by using the original $R-N$ tables ($\Delta N=0$) is -0.72 for the Argentine Islands and -0.62 for Halley Bay. These very significant negative correlations indicate that the original $R-N$ tables are appreciably incorrect and require corrections of the same sign as ΔN .

The correlation coefficients between the ozone amounts for the Argentine Islands and Halley Bay published by the World Data Centre, and the values $\Delta N'$ used in calculating them (see Table V) were 0.17 and 0.76 , indicating that the correction terms $\Delta N'$ had been seriously overestimated at Halley Bay.

Finally, the correlations between our values of ΔN and the revised ozone amounts in Table VI are -0.08 and 0.08 , suggesting an almost complete correction of the error.

TABLE V
ORIGINAL ($\Delta N'$) AND REVISED (ΔN) CORRECTIONS TO THE
AD EXTRA-TERRESTRIAL CONSTANTS FOR THE SPECTROPHOTOMETERS
AT HALLEY BAY AND THE ARGENTINE ISLANDS AND THE APPROXIMATE
CORRECTION REQUIRED TO THE PUBLISHED OZONE AMOUNTS

Period	Instrument number	$\Delta N'$	ΔN	Approximate correction to x (m atm-cm.)
<i>Argentine Islands</i>				
October 1957–May 1960	51A	See text		
May 1960–December 1960	51B	0.036	0.023	– 5
January 1961–January 1962	51B	0.018	0.023	2
January 1962–December 1962	73A	–0.052	0.010	22
January 1963–January 1964	73A	–0.028	0.010	14
January 1964–December 1964	31B	–0.045	–0.035	4
January 1965–December 1965	31B	–0.051	–0.035	6
January 1966–February 1967	31B	–0.043	–0.035	3
February 1967–February 1968	103	–0.050	–0.010	14
February 1968–January 1970	103	–0.015	–0.010	2
January 1970–December 1970	73C	–0.030	–0.040	– 4
January 1971–March 1973	73C	–0.045	–0.040	2
<i>Halley Bay</i>				
January 1959–December 1960	31A	–0.062	–0.013	18
January 1961–January 1963	31A	–0.065	–0.013	19
February 1963–December 1963	88	0.009	0.008	0
January 1964–January 1965	88	0.014	0.008	– 2
February 1965–December 1966	73B	–0.106	–0.035	26
January 1967–January 1968	73B	–0.086	–0.035	18
February 1968–December 1969	31C	0.000	–0.043	–16
January 1970–December 1970	31C	–0.036	–0.043	– 3
January 1971–March 1973	31C	–0.040	–0.043	– 1

While these low correlation values are satisfactory and indicate that the ozone values do not appear to reflect the instrumental corrections, it must be admitted that the periods selected, though chosen on logical grounds, give lower correlations than some other periods.

Our analysis gives a constant ΔN for each period of operation of a given instrument. There is no indication of any systematic changes across these periods though, of course, small changes might have been present which could perturb the year-to-year variations slightly, particularly when the number of calibration measurements was small. Of course, most instrumental changes are automatically monitored and corrected by the standard lamp tests. We feel that any residual errors in the year-to-year changes in ozone due to such causes are likely to be less than the sampling errors.

In Table V are given, for various periods, the spectrophotometer number in operation at the two stations, the value of $\Delta N'$ of the correction to the $R-N$ tables which was used in calculating the daily values of ozone amount and published by the World Data Centre, the revised value of ΔN (except in the case of No. 51A when ΔN_{CD} was used), and the approximate correction to be applied to the published values.

IX. ZENITH OBSERVATIONS

WHILE direct sun observations are the only ones producing absolute measurements, most of the data is given by zenith observations in cloudy conditions, mainly AD at noon and at $\mu=2$ and CC' at $\mu=2.6$ or 3.

The method of calculating ozone amounts from the AD zenith measurements at $\mu=2$ has been as follows. We have examined all cases when zenith and direct sun observations have been made simultaneously in the range $\mu=1.8$ to 2.2, and have determined the difference, $x-x'$, between the direct sun measurement, x , using the corrected $R-N$ tables, and the zenith measurement, x' , using the charts supplied by the manufacturers. Normally, the values of $x-x'$ were grouped fairly closely to a median value of $\overline{x-x'}$, with half the values in the range of about $\overline{x-x'} \pm 4$ m atm-cm., and no significant difference was found between blue sky and cloudy zenith conditions. The correction $x-x'$ was then added to all the AD zenith observations in the range $\mu=1.8$ to 2.2. No use has been made of AD zenith observations outside this range.

The method of determining x from the CC' observations at $\mu=2.6$ or 3 was somewhat similar. We have measured x'' , the CC' zenith value determined from the original charts, when μ was in the range 2.4 to 2.8 or 2.8 to 3.2. On those days for which (a) the forenoon and afternoon values of x'' and (b) the two corrected AD zenith measurements at $\mu=2$ differed by less than 10 m atm-cm. we have taken the difference, $x-x''$, between the means of the two AD and the two CC' observations as the CC' correction. Again, the values clustered fairly closely to a median value, $\overline{x-x''}$, half the values lying in the range $\overline{x-x''} \pm 4$ m atm-cm., and with no significant difference between the blue sky and cloudy zenith conditions. The correction, $x-x''$, was then added to all CC' observations.

X. FOCUSED IMAGE OBSERVATIONS

1. Focused sun observations

When a direct sun observation is being made, the ground quartz plate is illuminated partly by sunlight and partly by light from a considerable area of sky around the sun, which, as mentioned on p. 9, is richer in short-wave light and causes too low a value of N to be measured. At higher values of μ this skylight effect becomes appreciable, and the light from the sun may become too weak to be measured accurately. It is necessary, then, to remove the ground quartz plate and to focus an image of the sun on to the entrance slit of the spectrophotometer, thereby increasing the amount of sunlight and greatly decreasing the amount of skylight entering the spectrophotometer. This is a more demanding technique than the standard as the image must be positioned very accurately on the slit.

Even when the focused image method is used, the measured ozone amounts still begin to decrease rapidly when μ exceeds a certain value. This is due to two causes (Dobson, 1968):

- i. The contribution from the bright aureole round the sun increases with μ .
- ii. The presence of visible light which is internally scattered within the instrument.

Internal scattering may be expected to vary from one instrument to another, and is much reduced by the addition of a nickel sulphate filter; this is mounted on a shaft which can be rotated from outside the instrument so that the filter can be put in or out of the path of the radiation between the isolating slits and the photomultiplier. Fig. 1 shows the results of measurements of ozone amount on CD wavelengths by the focused sun method, with and without filter, at the Argentine Islands on 25 March 1964 ($x=346$ m atm-cm.) and 21 August 1964 ($x=325$ m atm-cm.) and at Halley Bay on 25 October 1967 ($x=331$ m atm-cm.; no filter measurements); the measurements are normalized by expressing them as a percentage of the low μ values. It can be seen that errors become appreciable when μ exceeds about 5 without the filter, and when μ exceeds about 6.5 with the filter.

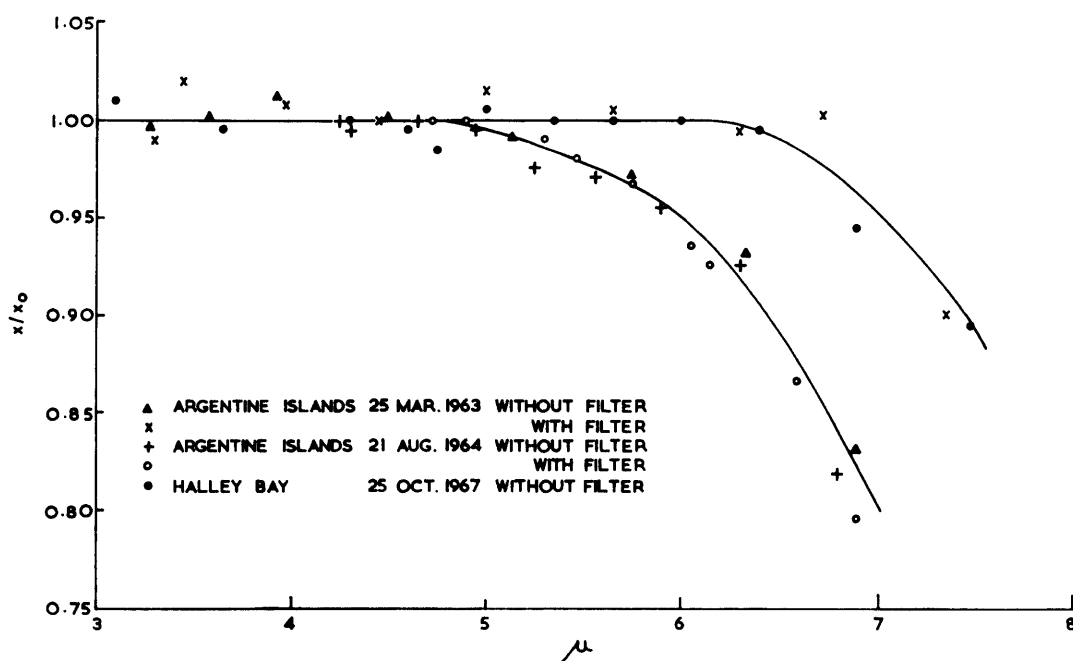


FIGURE 1

Variation with μ of the ratio of the apparent amount of ozone as measured by the focused sun method to the true amount.

a. *Measurement of skylight.* During 1972 a number of observations were made at Halley Bay to measure the effect of skylight; they were similar to those described by Dobson (1968) but in different conditions of albedo and atmospheric turbidity.

To measure the ratio of the intensities of skylight and sunlight, the longer wavelength slit is closed and the photomultiplier current is measured when the sun is focused on the entrance slit; the sun director prism is then moved slightly so that the sun's image is just off the slit and the current measured again. The ratio M of the currents is equal to the ratio of the intensity of the skylight to the sum of the intensities of skylight and sunlight.

The longer wavelength slit is now opened and the N value of the sky, N_k , and that of the focused sun (+ sky), N_m , are measured.

When an observation is made with the sun focused on the entrance slit, let t_s and t_l be the intensities of the shorter and longer wavebands, and k_s and k_l the corresponding intensities of skylight.

We measure $M = \frac{k_s}{t_s}$,

$$N_k = \log \frac{k_1}{k_s} + \text{const.},$$

$$N_m = \log \frac{t_1}{t_s} + \text{const.}$$

Let N be the true value for direct sun,

$$\text{then } N = \log \frac{(t_1 - k_1)}{t_s - k_s} + \text{const.},$$

$$\text{whence } N = N_m + \log \left(1 - \frac{M}{J}\right) - \log(1 - M),$$

$$\text{where } J = \frac{t_1}{t_s} \cdot \frac{k_s}{k_1},$$

$$\begin{aligned} \text{i.e. } \log J &= \log \frac{t_1}{t_s} - \log \frac{k_1}{k_s} \\ &= N_m - N_k. \end{aligned}$$

For small values of M and $N_m - N_k$ this reduces to

$$N - N_m = 2.3M(N_m - N_k).$$

Fig. 2 shows the variation of M with μ for typical values of x (there is some x -dependence) and Fig. 3 shows the variation of $N_m - N_k$ with μ , while Fig. 4 shows how the correction to x , i.e. $\Delta x = \frac{N - N_m}{\mu(a - a')}$ increases with μ for CD wavelengths.

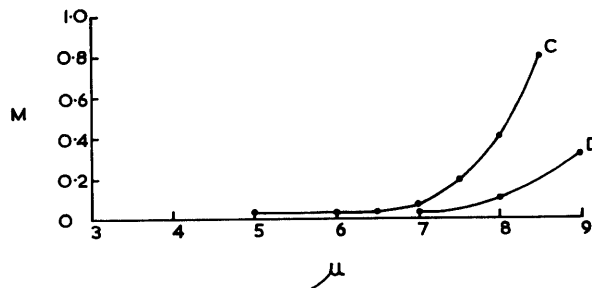


FIGURE 2
Variation of the function M with μ for C and D wavelengths.

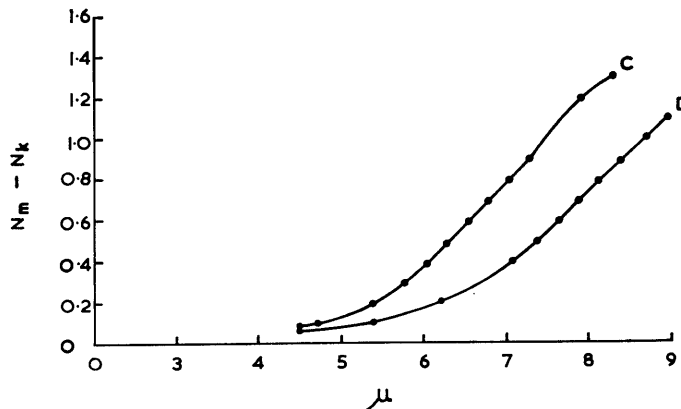


FIGURE 3
Variation of $N_m - N_k$ with μ for C and D wavelengths.

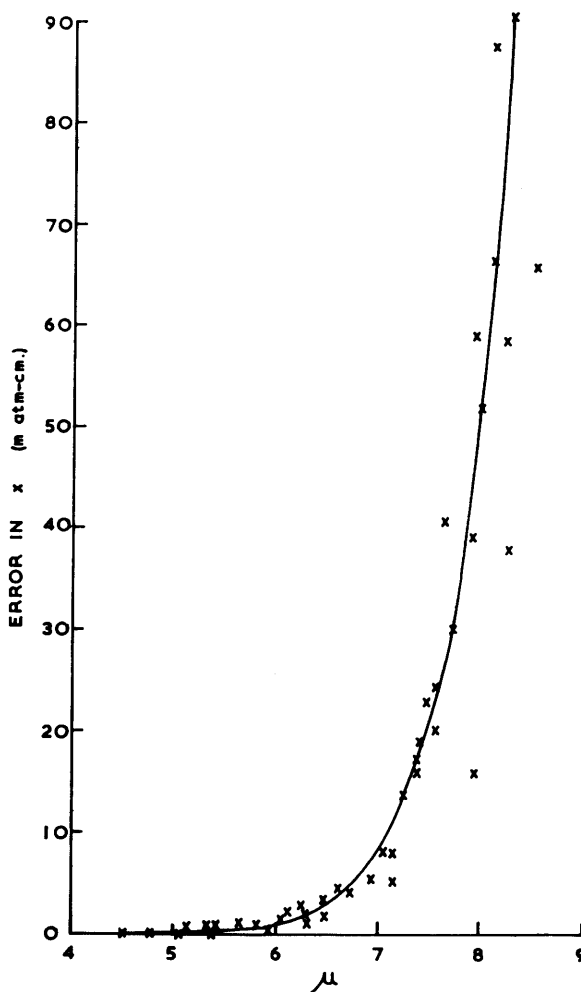


FIGURE 4

Variation with μ of the error in ozone amount due to skylight.

b. *Measurement of internal scattering.* The error due to the internal scattering is measured by closing the long-wave slit and measuring the photomultiplier current, a , when only the short-wave radiation reaches it. The second Q lever is now offset so that none of the correct radiation passes through the final slit; the photomultiplier current, b , is due to internally scattered radiation.

Let d_s and d_l be the intensities of the shorter and longer wavebands in the incident radiation. Then

$$N_m = \log \frac{d_l}{d_s} + \text{const.}$$

$$\text{but } N = \log \frac{d_l}{d_s} \cdot \frac{a}{a-b} + \text{const.}$$

$$\text{so } N - N_m = -\log \left(1 - \frac{b}{a}\right)$$

$$= 0.43b/a \text{ approx.}$$

Measurements with the filter gave values for $0.43b/a$ of 0.006 which, rather surprisingly, showed little variation with μ . It is apparent from this experiment that the nickel sulphate filter is effective in almost eliminating the error arising from internally scattered light.

c. *Corrections to focused sun observations.* A small correction to N is necessary when focused sun observations are made, since the ground quartz plate is removed and there is a change in the optical paths when

the sun is focused on the entrance slit. The correction $\Delta N(\text{focus})$ is determined by making alternate standard CD and focused sun measurements at times when both overloading is unlikely and the skylight and internal scattering effects are negligible—when μ is around 3 or less. The values of $\Delta N_{\text{CD}}(\text{focus})$ determined for the various instruments were:

<i>Argentine Islands</i>		<i>Halley Bay</i>	
<i>Instrument number</i>	$\Delta N_{\text{CD}}(\text{focus})$	<i>Instrument number</i>	$\Delta N_{\text{CD}}(\text{focus})$
51B	0.008	31A	0.005
73A	-0.007	88	-0.012
31B	0.016	73B	-0.007
103	-0.010	31C	0.006
73C	0		

In addition, the filter correction $\Delta N(\text{filter})$ must be evaluated by alternate observations with and without the filter.

All focused sun observations made at the two stations have been recalculated using the revised values of ΔN_{CD} and the measured values of $\Delta N(\text{focus})$ and $\Delta N(\text{filter})$. These are all CD observations, and only those made with μ less than 6.5 with filter and 5 without filter have been entered in Table VI.

2. Focused moon observations

A number of focused moon CD observations have been made during the winter months, with a few AD observations. The ozone amounts have been calculated using the same values of ΔN_{CD} and $\Delta N(\text{focus})$ as with the focused sun observations.

We then tested whether a further correction of $\Delta N(\text{moon})$ is needed, due to differences between the spectral distribution of moonlight and sunlight.

First, we examined the data for 14 nights during which these observations covered a fair range of μ . The random error of measurement is much larger than in the case of sun observations, and we were content to estimate the sign of $\Delta N(\text{moon})$ from the sign of the change of x with μ . We estimated the sign to be positive on five occasions, negative on three, and indeterminate in the remaining six. Thus, there was no evidence that the magnitude of $\Delta N_{\text{CD}}(\text{moon})$ is appreciable.

Secondly, we examined the occasions when moon observations at the Argentine Islands were sandwiched between focused sun observations on the previous and subsequent day, and vice versa, and a few pairs of a moon observation and a sun observation made within about 12 hr. of one another. On eight occasions the difference (moon minus sun) was positive, on seven occasions negative, and once zero. The median value was 0.003 and the mean value 0.

Thus, there is no clear indication that $\Delta N_{\text{CD}}(\text{moon})$ is appreciably different from zero, and no additional correction for moon observations has been made. This is in agreement with the results of Larsen (1959) at Tromsø (lat. 70°N.) and at Spitzbergen (lat. 78°N.).

XI. DAILY VALUES OF OZONE AMOUNT

ON most days during the season of normal observations, at least five measurements have been made, AD zenith at noon, two AD zenith at $\mu=2$ and two CC' zenith at $\mu=2.6$ or 3, and in addition, on many days there are some direct sun measurements. Owing to the rapid changes which take place, particularly during the spring, the range of values during the period of observation on one day may be considerable, occasionally about 40 m atm.-cm., and it is difficult to choose a single representative value for the day; our procedure has been to estimate a value centred at local noon.

Early in the spring and late in the autumn, when μ at noon exceeds 2.2, only the two CC' observations are available, and when μ at noon exceeds 2.8 (or 3.2), only focused sun or focused moon observations can be used.

All the moon observations during one night have been attributed to the following Greenwich day. On these days the median of all measurements, after rejecting discordant values, has been accepted as the daily ozone amount.

Table VI gives the daily values of ozone amount for each year and each day of the month for both stations for all days on which at least one acceptable observation was made.

TABLE VI
DAILY VALUES OF TOTAL AMOUNT OF OZONE IN m atm-cm.

JANUARY																	ARGENTINE ISLANDS	
DAY	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	MEAN	SD
1	357	367	365	338	348	360	316	327	341	341	311	344	361	318	278	329	338	23
2	355	353	365	331	324	362	318	307	346	362	304	340	326	327	261	351	333	26
3	355	320	368	332	306	390	335	323	339	364	326	329	300	336	267	354	334	28
4	347	306	360	329	306	385	330	332	331	346	324	351	284	340	275	340	330	27
5	349	330	341	313	303	373	332	334	337	324	340	336	305	344	282	335	330	21
6	347	343	368	311	287	364	327	331	325	329	334	339	310	344	313	351	333	20
7	347	356	369	320	300	335	338	329	333	330	339	340	311	337	332	340	335	16
8	346	350	363	313	292	330	319	327	321	323	335	348	311	330	316	324	328	17
9	347	350	373	326	311	325	322	341	294	319	349	338	310	325	309	333	330	19
10	357	342	368	337	314	305	313	333	279	327	331	325	321	316	326	319	326	20
11	357	381	338	315	344	334	296	329	305	328	331	318	321	320	313	325	328	20
12	388	370	327	329	338	308	307	320	306	324	331	325	303	333	320	331	329	22
13	375	338	338	328	311	320	305	310	307	324	345	323	305	339	314	338	326	18
14	364	357	339	324	319	315	296	309	309	329	337	314	299	336	323	347	326	19
15	359	357	328	324	295	322	299	328	298	316	324	325	308	344	330	329	324	18
16	368	370	323	329	307	318	303	334	313	304	340	327	310	355	339	348	331	21
17	362	365	335	317	296	308	301	309	303	308	341	313	297	355	328	348	324	23
18	343	364	324	316	310	306	274	340	309	304	346	317	302	340	326	344	303	22
19	340	369	336	319	326	307	305	333	313	309	344	310	303	343	325	337	326	18
20	327	363	333	341	289	307	308	343	312	301	361	313	295	331	324	357	325	23
21	325	350	336	319	297	313	296	335	311	296	355	333	298	334	327	365	324	21
22	336	363	361	329	285	305	290	326	308	296	335	303	283	332	319	375	322	27
23	331	372	342	343	307	340	293	304	305	321	351	325	293	323	329	353	327	22
24	327	356	347	342	296	334	304	303	304	342	348	333	306	318	336	365	329	21
25	351	363	356	312	300	338	306	315	308	345	350	351	313	300	326	343	330	21
26	349	379	340	340	290	335	317	315	311	329	367	325	302	298	332	343	330	23
27	342	350	348	324	306	312	314	316	291	325	365	330	282	305	322	344	324	22
28	295	339	357	330	316	309	318	307	318	326	363	327	320	336	323	348	327	18
29	325	330	369	330	318	301	313	314	319	304	341	346	319	338	314	338	326	17
30	318	313	358	317	312	314	335	317	305	309	341	333	320	318	303	324	321	14
31	325	302	349	326	302	306	290	322	310	315	333	302	320	332	294	302	314	16
MEAN	346	351	349	326	308	328	310	323	313	323	340	328	308	331	314	341	327	14

FEBRUARY																	ARGENTINE ISLANDS	
DAY	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	MEAN	SD
1	310	334	364	314	301	288	308	306	303	324	325	327	318	325	295	297	315	18
2	307	331	365	315	303	290	320	311	301	318	323	306	331	330	299	310	316	17
3	304	323	351	307	318	283	309	322	289	323	327	326	313	337	315	305	316	16
4	330	325	353	326	319	280	300	320	285	303	313	302	297	342	331	302	314	19
5	322	315	355	316	299	303	303	323	286	308	311	311	295	340	326	302	313	17
6	304	341	358	335	327	310	314	322	311	317	307	315	281	327	333	292	318	18
7	297	351	370	350	317	306	313	338	287	294	311	314	300	317	318	295	317	23
8	305	331	368	358	323	321	323	305	274	289	307	316	304	315	330	289	316	23
9	297	310	353	301	323	307	332	296	295	291	319	310	299	315	331	313	312	16
10	283	304	346	301	338	291	327	308	286	305	313	308	276	327	325	297	308	19
11	308	292	369	315	357	288	335	305	271	310	335	313	267	324	325	287	313	27
12	310	323	365	316	337	300	332	297	290	306	312	317	273	330	324	297	314	21
13	292	311	340	321	302	318	315	291	315	288	297	300	304	322	302	313	308	13
14	295	327	343	331	294	302	324	296	306	286	305	296	341	310	305	295	316	17
15	307	322	351	349	292	290	339	298	309	275	289	294	305	287	298	321	308	22
16	268	333	337	349	291	284	330	311	313	290	306	300	300	293	287	310	306	21
17	300	310	335	333	267	292	323	278	311	288	311	288	285	317	263	300	300	21
18	328	311	324	352	269	285	349	281	295	283	313	305	299	324	261	296	305	25
19	332	317	317	356	283	276	331	296	312	291	317	303	315	329	262	308	309	23
20	320	324	313	354	309	263	335	305	303	310	317	317	323	309	240	302	309	25
21	286	310	288	364	276	278	354	292	296	319	319	325	316	302	289	314	308	24
22	275	307	288	350	255	275	291	312	308	323	313	325	311	304	287	317	303	22
23	293	317	308	331	299	287	297	308	301	282	288	317	307	307	283	271	300	15
24	319	313	327	305	258	297	306	300	310	284	300	309	316	315	263	333	303	20
25	324	325	306	307	293	306	324	315	290	282	324	329	335	311	261	328	310	19
26	312	321	291	327	295	298	327	309	282	303	335	326	284	320	269	376	311	25
27	293	325	276	331	301	301	357	292	307	299	297	326	293	313	263	312	305	22
28	292	333	321	320	317	282	350	295	303	290	277	308	301	301	265	309	304	21
29			337				318				311				278		311	
MEAN	304	321	335	330	302	293	324	305	298	299	311	312	303	318	294	307	310	12

ATMOSPHERIC OZONE AT THE ARGENTINE ISLANDS AND HALLEY BAY 19

TABLE VI—continued

MARCH

ARGENTINE ISLANDS

DAY	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	MEAN	SD
1	288	319	325	313	317	288	332	288	305	311	289	331	323	307	276	361	311	21
2	276	331	329	316	274	291	315	296	285	281	303	335	328	296	300	354	307	23
3	267	334	291	328	266	301	294	297	281	295	297	318	317	280	306	317	299	19
4	278	306	308	305	270	290	294	289	296	311	316	297	312	296	302	280	297	13
5	274	320	320	324	270	298	298	276	298	289	323	291	302	304	286	297	298	17
6	293	333	350	319	273	291	294	270	303	318	311	300	299	305	281	265	300	22
7	297	328	338	335	302	317	336	262	335	301	297	320	276	270	285	267	304	26
8	273	306	343	312	305	277	331	274	351	283	305	291	291	320	276	277	301	24
9	280	280	330	297	305	288	316	327	282	289	320	293	320	328	285	292	302	18
10	301	305	303	313	300	275	297	300	277	315	329	273	270	276	271	275	293	18
11	317	294	295	300	288	272	308	297	305	271	333	300	278	280*	306	288	296	16
12	283	301	287	323	298	267	305	295	305	281	311	309	269	285	279	290	293	15
13	280	301	338	319	284	299	323	295	333	300	323	329	275	248	292	312	302	25
14	287	322	342	322	298	322	280	306	338	290	333	318	268	290	273	358	307	28
15	272	340	346	353	309	329	257	261	313	313	341	336	252	330	294	327	311	33
16	297	330	307	303	295	317	314	269	322	293	335	325	277	361	307	327	314	25
17	347	292	349	280	316	275	342	264	329	295	387	375	291	311*	271	344	317	37
18	335	329	347	325	299	263	333	293	337	304	344	326	281	262	295	316	312	27
19	312	334	380	326	301	297	315	313	330	315	325	270	293	277	306	295	312	25
20	290	341	338	358	330	312	308	321	341	305	327	300	281	289	276	297	313	23
21	289	325	363	351	330	288	328	321	308	321	306	277	268	272	274	343	308	31
22	278	297	343	352	339	290	322	312	292	319	327	317	299	272	276	293	308	24
23	283	308	357	361	321	311	333	298	312	326	301	305	323	275	276	305	312	24
24	266	288	359	369	322	305	343	295	339	322	307	272	302	300*	234	332	310	34
25	254	287	338	366	305	326	337	313	315	348	276	285	317	325*	254*	322	311	31
26	264	293	342	286	299	285	348	305	312	301	277	271	287	350	281	357	304	29
27	285	289	346	304	291	299	354	343	309	375	264	264	256	305*	274	307	304	34
28	313	309	330	308	295	256	316	376	287	277	297	277	295	261	273	309	299	28
29	315	308	371	320	300	276	292	329	302	283	301	303	279	301		293	305	23
30	303	329	312	303	312	311	324	342		265	325	305	298	315*		312	311	17
31	284	337	323	297	267	323	285	354		330		312	304	330		352	314	27
MEAN	287	313	335	322	299	295	315	303	312	304	314	304	291	297	282	312	305	13

APRIL

ARGENTINE ISLANDS

DAY	1957	1968	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1		313	344	361	311	232	292	319	299								300	
2		308	344	389	358	235	288	327	319								320	
3		328	341	375	341	278	324	355	332		323						333	
4		355	318	359	334	275	312	363	349		346						335	
5		390	316	361	296	268	315	353	366								333	
6		325			297	321	337	307	339								321	
7					286	287	311	352	321								311	
8							314										314	
9							333										333	
10							247		353								300	
11					292		222	266	358								285	
12					301			293									297	
13					326		265	258									283	
14					287												287	
15										330							330	
16																		
17							291			333							312	
18										287					275		281	
19														286			286	
20									320				329				325	
21																		
22																		
23							260										260	
24																		
25																		
26								309									309	
27																		
28																		
29																		
30																		
MEAN		335	333	369	312	271	295	319	336	317	335		329	286	275		316	27

*Estimated values.

TABLE VI—continued

MAY		ARGENTINE ISLANDS																
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1					297	309				323							310	
2					300												300	
3						299											299	
4						300											319	
5									339								339	
6									314			327					321	
7									321			323					322	
8												296					296	
9																		
10								286									286	
11									293								293	
12									301			307					304	
13									320								320	
14									320			294					307	
15									251								251	
16																		
17																		
18																		
19																		
20																		
21																		
22																		
23																		
24																		
25								333									333	
26																		
27																		
28					359												359	
29																		
30																		
31																		
MEAN					319	303		310	307	331		309					313	

JUNE		ARGENTINE ISLANDS																
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1										331							331	
2																		
3																		
4																		
5																		
6																		
7					327		294										311	
8					299												299	
9					316												316	
10					305												305	
11																		
12																		
13					221				330								276	
14																		
15																		
16																		
17																		
18																		
19																		
20																		
21																		
22									316								316	
23									299								299	
24									299								299	
25																		
26									330								330	
27																		
28																		
29																		
30					347												347	
MEAN					294	347		294	313	330	331						318	

ATMOSPHERIC OZONE AT THE ARGENTINE ISLANDS AND HALLEY BAY 21

TABLE VI—continued

JULY

ARGENTINE ISLANDS

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																		
2																		
3																		
4																		
5																		
6																		
7				339								303					321	
8							313										313	
9																		
10																		
11									294								294	
12									317								317	
13																		
14																		
15									327								327	
16																		
17																		
18																		
19																		
20																		
21																		
22									369								369	
23									336								336	
24					374												374	
25									305								305	
26																		
27					342												342	
28																		
29																		
30																		
31																		
MEAN				339	358		313	337	313			303					327	

AUGUST

ARGENTINE ISLANDS

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																		
2																		
3									325								325	
4									316								316	
5									325								325	
6											319						319	
7									317	346							332	
8										297							297	
9																		
10										332							332	
11										353							353	
12										340							340	
13					401						313						307	
14					399							320					360	
15					377	288											333	
16												342					342	
17						300				338							319	
18						257					334						296	
19						269					324	343					312	
20						354						351					353	
21												325					306	
22												317					299	
23																		
24																	328	
25																287	293	
26																	347	
27												359					360	
28												371					337	
29																	295	
30																	298	
31																	308	
MEAN				371	294	286	323	323	328	369	262	356				287	319	34

TABLE VI—continued

SEPTEMBER																	ARGENTINE ISLANDS	
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1					299				344								322	
2				283	261		336	318	331	394						274	314	
3				317	282		307	351									314	
4				291	320			315	334								315	
5			361	291	361	356		316	296		348						333	
6			348	327	314	308	273		363		334						324	
7	391	357	359	336	344	339	266	320	337								339	
8	345	387	344	299	352	303	317	340	346		321					386	340	28
9	313	373	339	300	343	275	290	302	369	361							327	33
10	320	357	334	321	331	284	300		386								329	
11	287	369	325	336	321	313	284	347	446								336	
12	287	327	322	383	310	293	319	335	376	302	360	378	418	286			341	40
13	291	368	305	315	311	315	326	316	372	397	347	386	397	299	279		335	38
14	309	325	331	336	293	296	302	334	344	379	311	324	352	306	285	300	325	27
15	317	335	332	426	323	410	336	354	366	294	292	329	349	296	305	368	348	38
16	314	356	368	322	372	340	301	336	341	299	315	299	325	282	301	321	325	25
17	351	345	343	349	343	336	281	332	331	267	277	305	323	296	354	324	322	27
18	355	358	355	324	302	354	295	316	334	320	310	355	335	323	344	309	334	20
19	329	296	360	302	312	324	282	332	319	291	299	312	304	314	329	333	320	25
20	317	370	335	340	323	319	296	330	376	294	285	305	314	278	299	306	318	27
21	341	430	358	386	318	311	285	361	358	356	272	339	294	296	311	311	333	40
22	329	346	375	399	304	333	285	407	319	312	343	297	322	317	295	315	331	35
23	309	415	462	336	318	328	296	347	322	291	335	303	362	328	295	321	336	44
24	292	470	435	361	343	329	315	344	335	319	399	323	341	363	279	364	351	48
25	304	505	387	366	352	371	318	344	331	336	336	359	336	384	280	376	355	48
26	342	494	414	341	355	393	285	362	343	365	349	374	319	326	297	461	364	53
27	339	533	400	358	336	424	347	304	341	378	321	316	345	371	293	414	364	57
28	313	365	364	356	369	418	361	354	330	341	310	331	334	341	299	469	353	41
29	369	320	332	385	399	318	335	318	307	307	323	345	363	325	357	463	348	40
30	359	381	353	386	396	393	307	305	312	331	330	379	410	352	395	476	367	44
MEAN	326	383	359	343	332	338	305	335	345	334	324	335	344	320	311	367	338	19

OCTOBER																	ARGENTINE ISLANDS	
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1	339	303	337	350	381	404	311	354	327	332	368	333	455	363	418	428	363	42
2	355	307	357	340	393	369	335	337	386	338	424	374	415	298	415	367	363	36
3	343	311	345	328	399	374	345	365	406	342	407	375	472	343	375	317	365	40
4	357	367	340	305	357	414	355	392	328	392	371	341	479	357	305	304	360	44
5	369	387	373	311	402	405	365	357	334	341	321	331	437	383	339	288	359	38
6	353	379	356	346	409	330	347	345	333	375	319	331	369	358	351	271	348	29
7	330	414	353	318	412	390	359	394	325	383	327	355	381	354	265	295	353	41
8	317	340	375	298	400	338	367	394	314	368	336	327	369	314	250	293	338	39
9	344	370	333	320	403	367	360	362	336	365	298	331	332	284	285	332	338	31
10	330	353	301	294	412	321	347	329	332	380	443	361	359	272	323	287	340	44
11	311	336	285	312	393	325	290	403	328	388	369	321	371	270	308	270	330	42
12	298	309	305	353	412	343	335	357	302	412	441	350	321	298	340	289	342	44
13	340	343	317	368	379	339	334	343	324	356	411	329	393	291	307	305	342	32
14	350	333	380	349	357	314	365	329	359	350	399	352	351	360	343	287	349	25
15	314	314	350	332	400	339	404	446	352	325	609	323	366	332	343	293	359	54
16	311	314	350	408	410	373	336	387	328	333	404	333	355	388	323	311	354	35
17	310	317	373	378	420	373	353	381	375	365	351	335	336	348	314	332	354	29
18	317	316	363	391	379	436	326	448	355	319	417	339	317	347	337	376	361	42
19	343	353	380	355	371	389	328	393	384	343	431	341	331	316	327	399	362	31
20	335	327	350	303	393	378	282	427	374	319	465	361	365	286	314	379	354	48
21	328	312	429	328	390	413	298	464	338	323	536	368	419	311	309	340	369	65
22	357	310	450	345	356	411	292	468	329	340	484	356	431	291	357	297	367	61
23	347	319	379	365	388	475	304	460	314	351	452	329	441	327	369	275	368	59
24	343	372	389	356	375	362	310	509	300	446	390	329	417	296	384	282	366	57
25	350	366	390	332	330	355	317	439	312	416	453	335	388	315	409	287	362	47
26	327	370	373	286	309	367	331	489	365	351	438	327	335	362	338	364	358	47
27	329	367	370	299	319	357	315	457	337	304	389	317	326	357	325	427	350	43
28	333	402	487	321	332	316	303	437	339	306	449	301	299	355	330	468	361	63
29	345	423	487	302	338	301	306	404	340	328	397	320	286	394	317	476	360	61
30	339	415	409	288	365	372	273	391	401	379	392	337	294	422	300	466	365	54
31	325	372	419	308	357	351	291	395	378	338	366	329	282	455	327	422	357	47
MEAN	335	349	371	332	379	368	329	401	344	355	405	338	371	337	334	340	355	24

ATMOSPHERIC OZONE AT THE ARGENTINE ISLANDS AND HALLEY BAY 23

TABLE VI—continued

NOVEMBER																	ARGENTINE ISLANDS	
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1	333	353	373	292	336	360	297	388	353	329	411	341	285	436	306	437	352	46
2	345	400	388	361	319	350	305	427	322	315	425	388	291	452	348	450	368	51
3	355	387	373	341	315	331	311	398	313	355	433	386	320	458	381	457	370	47
4	347	363	391	383	341	339	267	388	356	336	452	365	318	469	375	481	373	54
5	341	344	350	390	309	360	297	363	367	334	465	369	307	483	367	475	370	56
6	361	383	370	335	315	396	311	421	422	314	455	367	298	469	401	466	380	55
7	365	354	375	326	301	401	317	386	402	333	437	368	290	503	440	465	379	58
8	355	339	363	329	323	354	320	413	378	327	415	375	293	433	385	350	360	37
9	359	363	349	390	361	326	317	393	381	332	425	367	311	438	405	365	368	36
10	379	440	340	413	380	369	320	431	334	324	469	401	341	427	424	384	386	44
11	368	468	349	420	405	365	290	451	297	314	417	411	323	387	407	385	379	51
12	305	481	363	422	344	385	266	437	370	341	392	452	342	426	407	414	384	55
13	332	481	381	443	360	369	285	451	348	330	475	433	342	444	415	422	394	57
14	379	451	386	462	385	346	320	469	331	330	436	425	329	415	408	431	394	49
15	355	421	349	480	364	363	302	442	312	323	412	405	365	384	368	397	378	46
16	320	408	337	440	397	346	305	441	360	307	379	403	397	410	370	369	374	42
17	343	383	352*	438	398	351	329	399	344	300	366	406	377	365	339	394	368	33
18	390	394	367*	422	411	383	346	370	401	312	354	401	412	433	347	432	386	33
19	433	356	381	380	440	425	403	366	364	311	330	408	409	384	426	389	388	35
20	415	367	322	320	425	401	427	350	364	345	316	422	395	385	403	337	375	38
21	465	427	316	370	422	412	420	408	383	387	389	420	400	372	351	363	394	34
22	377	412	372	417	385	443	426	399	433	403	399	421	409	343	294	388	395	36
23	364	441	419	391	401	432	410	387	416	356	385	379	415	392	283	406	392	36
24	407	439	403	368	401	444	394	386	401	365	394	363	427	406	312	371	393	31
25	385	436	321	414	397	444	385	397	380	403	404	401	383	402	344	368	392	29
26	367	416	321	446	389	421	361	394	369	399	427	417	419	337	404	385	392	33
27	341	383	446	437	375	401	400	404	402	406	422	427	382	373	417	353	398	28
28	350	362	427	416	359	414	412	364	391	387	424	428	340	372	410	351	388	30
29	337	387	385	411	354	407	396	372	350	375	407	423	399	360	409	363	383	25
30	337	375	349	403	329	372	386	382	333	366	392	423	385	371	396	389	372	25
MEAN	364	400	367	395	368	384	344	403	366	345	410	400	357	411	378	400	381	22

DECEMBER																	ARGENTINE ISLANDS	
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1	356	400	369	403	358	359	363	390	328	366	397	400	350	395	385	367	374	21
2	380	416	355	405	330	356	351	373	332	388	396	385	363	373	381	403	374	24
3	385	393	359	407	331	344	364	385	329	393	397	367	366	348	356	406	371	25
4	362	395	344	409	346	345	363	398	333	365	391	366	368	366	356	420	370	24
5	385	347	363	418	397	357	336	368	340	361	396	348	400	316	361	330	364	28
6	379	367	384	418	390	359	341	352	394	354	404	346	383	316	334	363	368	26
7	383	364	392	415	361	362	382	374	355	364	395	354	357	322	339	379	369	22
8	341	375	386	400	320	345	364	371	346	361	384	359	340	346	334	386	360	22
9	323	387	351	394	306	361	365	371	348	353	375	356	378	341	342	375	358	22
10	329	371	360	396	326	352	377	364	370	358	361	372	350	336	343	347	357	18
11	324	364	395	374	353	346	355	366	370	340	370	335	320	337	334	365	353	20
12	310	367	386	353	365	357	375	341	348	348	355	353	322	331	336	343	349	19
13	322	329	398	350	369	372	363	327	396	350	373	344	332	351	344	364	355	22
14	361	353	406	332	352	395	345	318	366	347	345	353	342	364	358	381	357	21
15	359	341	395	335	352	376	345	353	372	342	355	353	348	365	353	335	355	15
16	359	327	386	327	363	363	358	332	366	345	319	335	335	363	355	311	347	20
17	370	369	379	323	347	358	351	329	374	333	319	351	369	358	339	318	349	20
18	354	362	367	328	352	350	361	299	371	338	343	363	359	346	347	356	350	17
19	366	351	356	337	326	348	331	307	369	320	349	365	372	360	351	350	347	18
20	367	356	350	346	360	353	341	366	341	336	338	364	354	366	348	356	353	10
21	371	336	340	350	372	340	379	330	344	320	359	363	318	350	325	357	347	18
22	372	330	338	346	348	349	384	335	340	302	330	340	336	366	305	375	344	22
23	371	377	365	344	310	345	363	319	357	329	328	329	316	353	308	371	343	23
24	363	347	359	360	324	363	347	329	348	331	342	336	313	363	338	353	345	15
25	362	327	377	360	336	359	355	326	335	329	320	341	334	370	346	333	344	17
26	357	344	379	342	317	369	353	335	334	325	322	345	324	339	342	365	343	17
27	349	353	384	310	320	364	373	361	321	342	326	346	342	354	349	373	348	20
28	338	316	376	305	321	365	362	350	329	343	319	349	350	353	359	356	343	19
29	363	355	368	309	324	357	349	350	299	365	313	350	380	349	340	361	346	22
30	347	359	374	347	316	354	329	352	330	371	334	339	368	329	352	358	347	16
31	352	358	375	334	326	363	311	346	366	342	332	349	355	321	317	348	343	18
MEAN	357	389	371	361	343	358	356	349	350	347	354	353	350	350	344	361	354	7

*Estimated values.

ATMOSPHERIC OZONE AT THE ARGENTINE ISLANDS AND HALLEY BAY 25

TABLE VI—continued

MARCH

HALLEY BAY

DAY	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	MEAN	SD
1	289	299	285	311	321	296	330	319	290	274	288	295	267	294	343	344	303	22
2	292	309	307	307	320	304	345	327	284	277*	277	295	250	287	286	354	301	26
3	295	311	292	291	333	287	336	319	284	280	289	313	254	266	287	325	298	23
4	281	309	292	299	347	279	317	316	289	290	291	307	286	259	295*	312	298	19
5	263	312	292	333	345	306	292	317	297	289	294	305	272	272	304		300	21
6	268	325	306	329	353	319	302	322	322	279	301	287	302	289	306*		307	21
7	302	307	321	311	352	303	328	310	296	277	309	270	302	290	308		306	19
8	299	293	323	311	355	339	328	287	280	268	305	301	293	291	322*		306	23
9	292	298	300	305	329	347	337	265	291	279	320	286	308	285	336		305	23
10	295	294	272	292	331	335	340	269	299	282	334	282	291	296	333		303	24
11	294			292	340	342	321		287	268	322	267	302	294	321		304	24
12	295												297		301		298	
13										262					299		281	
14										255				303			279	
15				322													322	
16				310						264		291					288	
17												283			287		285	
18				283													283	
19																		
20			315														315	
21			342										228				285	
22													231	267			249	
23																		
24												274					274	
25							361			289		286	270				302	
26				397			376						269				347	
27													280		300		290	
28							337				284		269	280	302		294	
29													277	274	316		289	
30							357		287		263			271			295	
31							350										350	
MEAN	289	306	304	313	339	314	335	305	292	276	298	289	276	282	309	334	304	19

APRIL

HALLEY BAY

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1							292							282		340	305	
2							286			281						304	290	
3							302			309				261	222	242	267	
4							301							281		284	289	
5							300	312						285		268	291	
6														292			292	
7																		
8																		
9																		
10																		
11												287					287	
12												310				294	302	
13																295	295	
14																		
15												303					303	
16																		
17																		
18																	286	
19																		
20																		
21																260	260	
22																259	259	
23																251	251	
24																		
25																274	274	
26																		
27																270	270	
28																		
29																		
30																		
MEAN							296	312		295		288	252	266	286	322	290	

*Estimated values.

TABLE VI—continued

MAY																	HALLEY BAY	
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																		
2					284								283				284	
3													307				307	
4																		
5																275	275	
6																		
7									322								322	
8							273										273	
9				311			278										295	
10																		
11															286		286	
12															287		287	
13												265			298		282	
14							250					251			269		257	
15																		
16												269					269	
17																		
18																		
19															305		305	
20																		
21						321											321	
22															266		266	
23															245		245	
24															261	237	249	
25																		
26															228	258	243	
27																		
28																240	240	
29																		
30					344												344	
31					252											254	253	
MEAN				311	293	321	267			322		262	295	261	285	253	287	24

JUNE																	HALLEY BAY	
DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																		
2										272			345				345	
3																	272	
4																		
5							271								276		274	
6																		
7				287			315								286		301	
8															295		291	
9															318		318	
10				322													322	
11				334			293										329	
12																		
13				290													315	
14				300													300	
15																		
16																		
17															323		323	
18															347		347	
19															311		311	
20																		
21																		
22															330		330	
23																		
24															285		285	
25																269	299	
26																		
27						269										315	292	
28																323	323	
29																308	308	
30							262									304	304	
MEAN				307	287		293			272			345	319	313	304	305	

ATMOSPHERIC OZONE AT THE ARGENTINE ISLANDS AND HALLEY BAY 27

TABLE VI—continued

JULY

HALLEY BAY

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																		
2																		
3							258										258	
4																		
5							262								300		281	
6																306	306	
7																266	266	
8							292					263				275	277	
9							306									260	283	
10							291					264					278	
11												299					299	
12																		
13												285					285	
14															313		313	
15															288		288	
16																309	309	
17																297	297	
18																		
19																322	322	
20																		
21																		
22																		
23																		
24																		
25																		
26						314											314	
27						299							329				314	
28																		
29																		
30																		
31																		
MEAN						307	282					278	329	306	281		297	

AUGUST

HALLEY BAY

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																		
2																		
3																		
4																		
5																		
6							323										323	
7																		
8																		
9												293					293	
10																		
11																		
12																		
13																		
14															313		313	
15															329		329	
16																326	326	
17								249								304	277	
18								270								313	292	
19								279									279	
20																319	319	
21								294									312	
22																		
23								304								295	300	
24																295	295	
25																326	326	
26																		
27																		
28																		
29																		
30																		
31																		
MEAN							323	279				293		317	313		305	

TABLE VI—continued

SEPTEMBER

HALLEY BAY

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1									234							281	258	
2												338					338	
3												317			287	329	311	
4												300				300	300	
5																260	260	
6																	275	275
7													254				264	
8													283				277	
9				270													280	
10				280										276	283		296	
				328														
11				299								242	287		319		287	
12				283				357	298			270	301		312	298	303	
13								348					329			298	325	
14								357					309		304		323	
15								375	311			274			261		305	
16				297				403				269		254		277	300	
17								381				290			263	252	297	
18					281			376				266			264	256	289	
19				310				393	337			280				252	314	
20				291	295							292					293	
21				303													285	
22								339								250	339	
23					291			330	326			294				236	297	
24								331				301				252	295	
25								348	281								315	
26					301			354									328	
27					249			359	306								305	
28					261			351	293								302	
29					263			351	295							282	298	
30					260		284	343	287			291					293	
MEAN				296	275		284	359		297		288	294	254	287	273	291	26

OCTOBER

HALLEY BAY

DAY	1957	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972	MEAN	SD
1																	293	
2		291	321	278	323		299	317	270			277		282			298	20
3	299	311	323	270	300	336	308	306	269	309		304	288	267	285		300	22
4	305	315	322	272	297	335	309	312	294	295		313	303	245	280		294	19
5	305	290	306	273	305	329	305	297	291	305		293	304	242	289	282		
6	303	310	297	291	319	367	307	310	290	327	276	311	308	279	290	279	304	22
7	316	316	282	281	306	339	300	315	283	327	269	288	296	290	286	278	298	19
8	341	289	256	300	321	329	298	324	291	328	273	296	291*	267	281	275	298	23
9	323	315	272	297	307	339	314	321	296	326	272	299	287*	281	299	289	302	19
10	319	305	310	304	319	331	319	317	287	325	285	287	282	268	308	297	304	17
11	335	337	295	313	291	333	313	313	289	334	287	291	290	260	313	259	303	24
12	331	328	302	318	319	331	319	293	291	341	284	275	290	283	316	258	305	23
13	330	297	297	308	330	337	310	305	270	317	295	272	293	286	287	284	301	19
14	329	304	296	309	354	331	324	308	278	303*	311	279	289	293	275	264	303	23
15	309	306	288	312	338	325	325	312	266	290	341	298	261	263	279	265	299	26
16	309	302	295	317	337	323	320	310	275	306	325*	292	243	275	304	270	300	24
17	307	311	289	319	331	337	308	310	281	331	309	277	259	276	286	273	300	23
18	299	317	295	303	306	329	303	297	283*	331	306	282*	256	274	278	309	298	19
19	305	309	291	307	307	331	315	314	285	323	340	288	259	281	300	306	304	19
20	330	315	295	325	310	322	315	310	285	315	370	280	259	290	302	320	309	24
21	343	303	287	314	309	323	300	319	309	319*	382	291	273	277	292	327	311	26
22	355	305	320	296	321	321	300	308	285	323	372	305	283	279	290	298	310	24
23	350	322	340	294	295	321	289	318	275	317	310	337	285	277	294	292	307	22
24	336	322	351	305	303	353	295	335	273	319	321	317	278	271	313	291	311	25
25	334	311	375	287	315	330	299	331	272	313	328	317	290	285	303	302	312	24
26	344	331	363	306	325	314	289	314	275	299	356	321	286	283	326	315	315	25
27	352	343	335	308	306	331	295	311	275	310	379	322	280	291	335	337	319	27
28	344	330	303	299	335	329	322	341	267	323	348	325	285	320	331	378	324	25
29	339	319	336	294	331	333	319	342	268	325	350*	335	275	343	316	377	325	27
30	375	327	340	305	331	331	321	372	274	299	353*	339	282	328	306	389	330	31
31	390	326	325	320	319	325	318	365	287	291	356*	325	292	315	296	391	328	31
MEAN	330	314	311	301	317	332	309	318	281	316	323	301	282	282	299	304	307	18

*Estimated values.

The day-to-day changes at the Argentine Islands are sometimes so large as to throw doubt on the validity of the ozone measurement. We have carefully examined the ozone measurements and the meteorological charts on all occasions when the difference in the tabulated amounts between successive days is 100 m atm-cm. or more, viz. 27/28 September 1958, 14/15 September 1962, 28/29 September 1962, 23/24 October 1962, 14/15 October 1964, and 9/10 and 14/15 October 1967. On no occasion is there any reason to doubt the abnormal value; at least two and usually more measurements had been made on each day, and the change in ozone amount was accompanied by a marked meteorological change. Normally, these large changes were associated with the passage of frontal systems as a deep depression passed to the south of the station, and the 100 mbar temperatures showed that marked changes were occurring in the stratosphere, though the changes in ozone amount did not always occur simultaneously with the temperature changes.

No such marked day-to-day variations in ozone have occurred at Halley Bay.

XII. ANNUAL VARIATION OF TOTAL OZONE AMOUNT

1. Daily values of ozone amount: October 1957–March 1973

The daily values of ozone amount at the two stations are set out in Table VI. Estimates of the daily values have also been made on those few days during the observing season with no observed value; these are marked by an asterisk. Normally, these estimates have been linear interpolations from preceding and succeeding values, but for the longer periods in January and February 1963 and 1965, when there was no spectrophotometer at Halley Bay, the estimate is based on a correlation between ozone amount and 100 mbar temperature. No estimates of daily values have been made outside the main observing season, i.e. when the noon value of μ exceeds 2.8.

2. Means and standard deviations: September 1960–March 1973

For the purpose of calculating mean values and studying year-to-year variations, it seems prudent to omit the less reliable data, i.e. the Argentine Islands data before May 1960 and the Halley Bay data before January 1959. It is convenient to compare the same period at the two stations, thus giving the period September 1960 to March 1973.

We consider first the seasonal change in the variability of ozone; this is illustrated by the standard deviations given in Table VI, which are calculated only when more than nine daily values are available. Standard deviations (S.D.) for the data from five successive days are averaged and plotted in Fig. 5 in

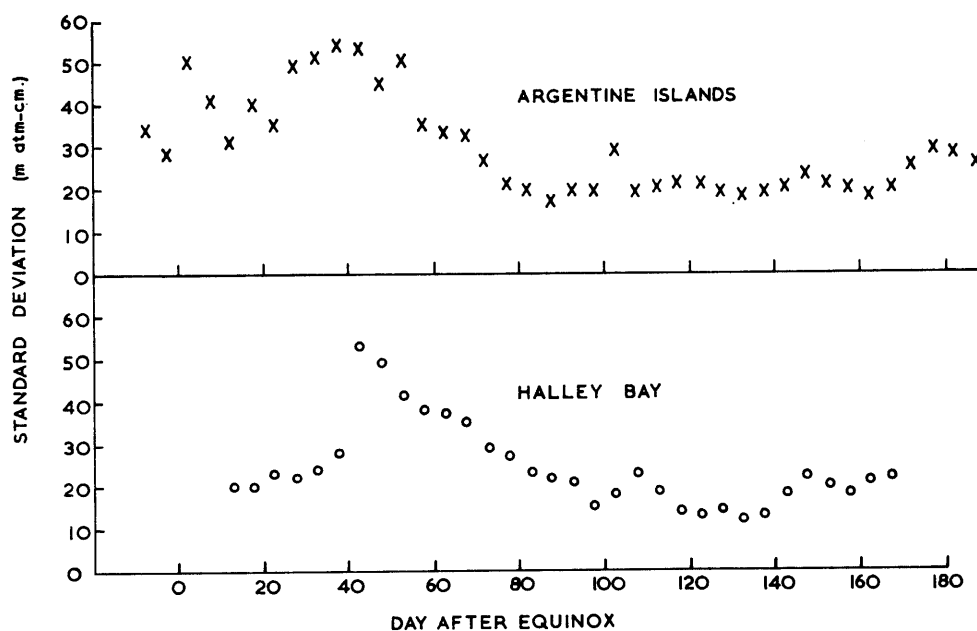


FIGURE 5
Change of variability of ozone concentration with season.

which the abscissa is time measured in days after 22 September (day 1 is the spring equinox). At the Argentine Islands the S.D.'s are generally high from day 0 to day 55. After day 55 the S.D. falls quickly to a minimum at the summer solstice, after which it remains fairly steady until it begins to rise towards the autumnal equinox.

At Halley Bay the S.D. remains low up to day 40 when a sudden rise occurs; by day 70 the S.D. is again fairly low and falls to a minimum value around day 130, the end of January.

Table VI also gives the average of the means for each month for the 1960-73 period and the S.D. of the annual means from this monthly average.

3. Annual variation of ozone

The annual trend of the total ozone amount at the two stations is shown in Fig. 6. The 13 yr. means of the average ozone over 5 days are plotted for the summer period and the average monthly values in winter. Corresponding 5 day means of the 100 mbar temperature are also shown throughout the year.

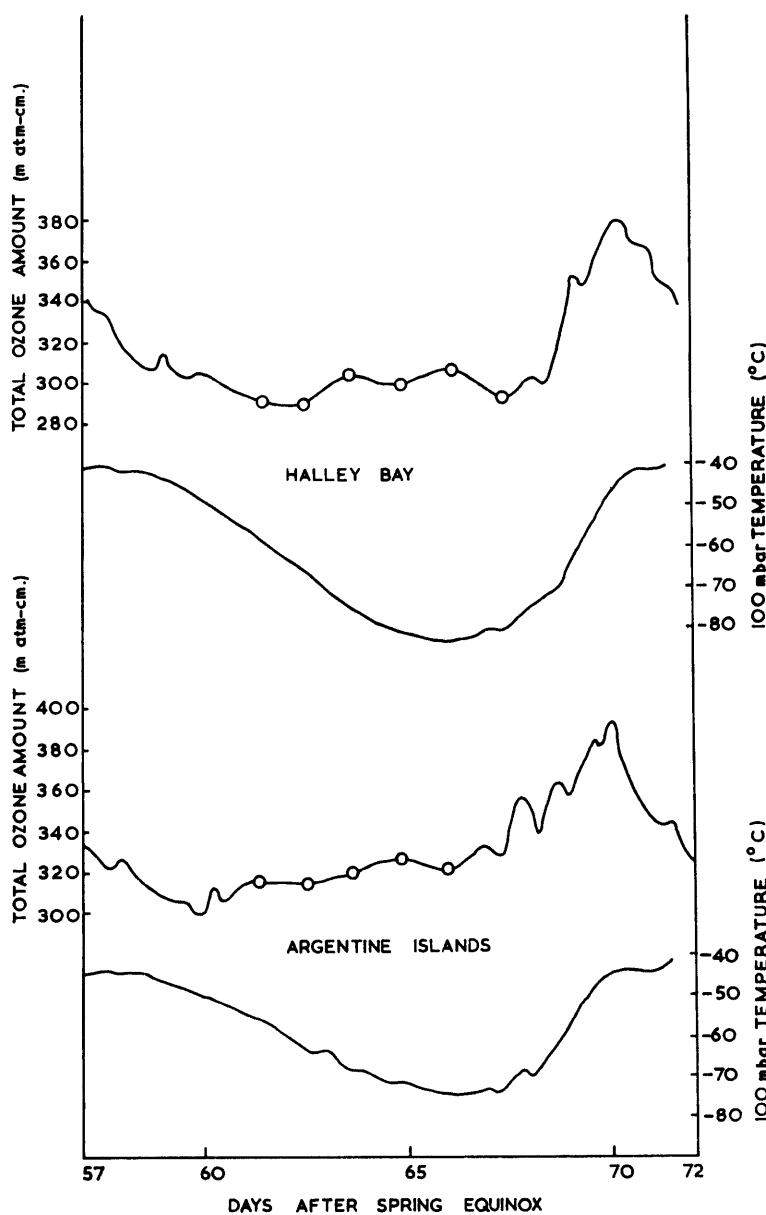


FIGURE 6

Variation of total ozone and 100 mbar temperature, 1957-72.

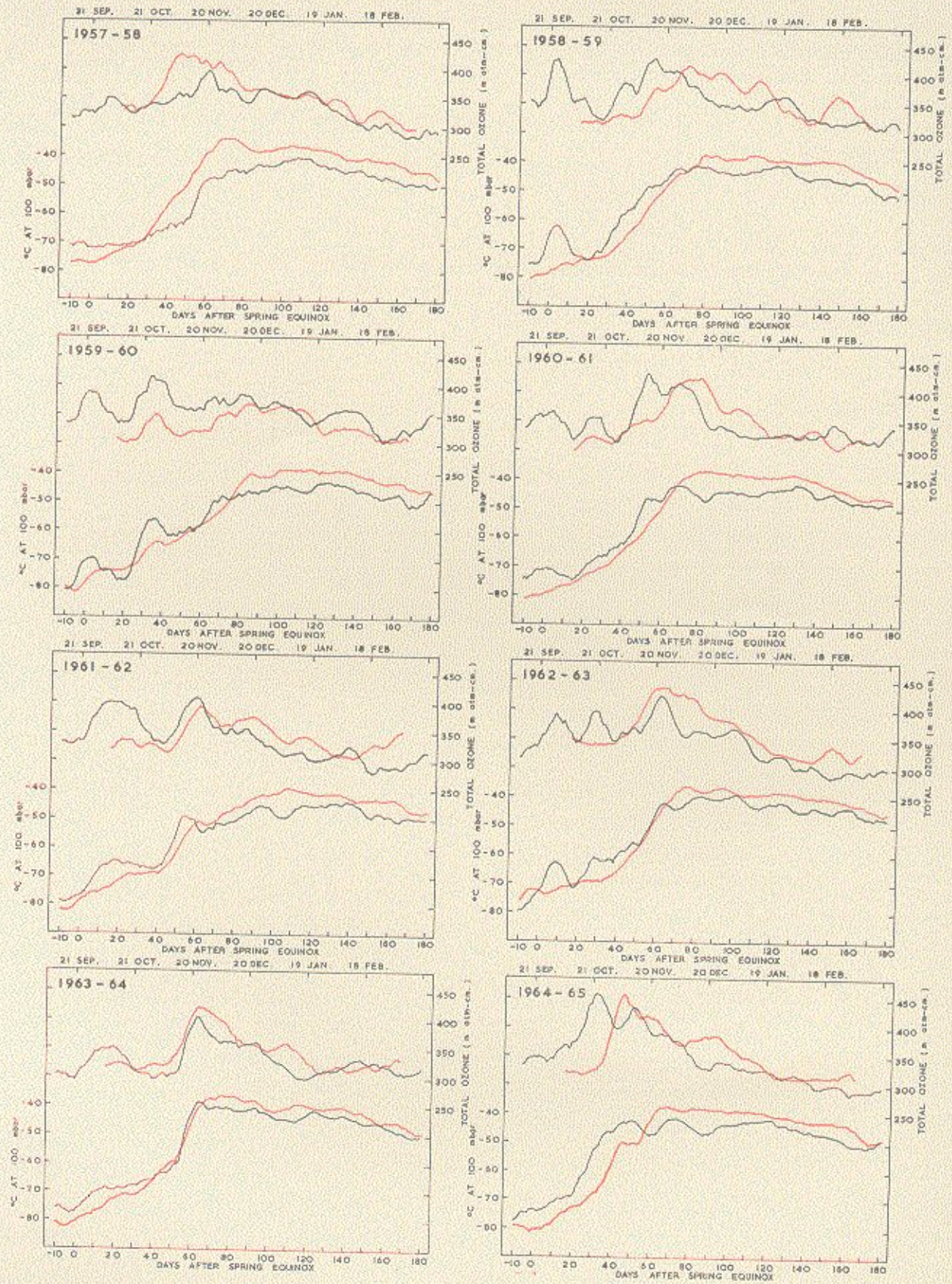


FIGURE 7

Seasonal variations of total ozone and temperature at 100 mbar at the Argentine Islands (black) and Halley Bay (red).

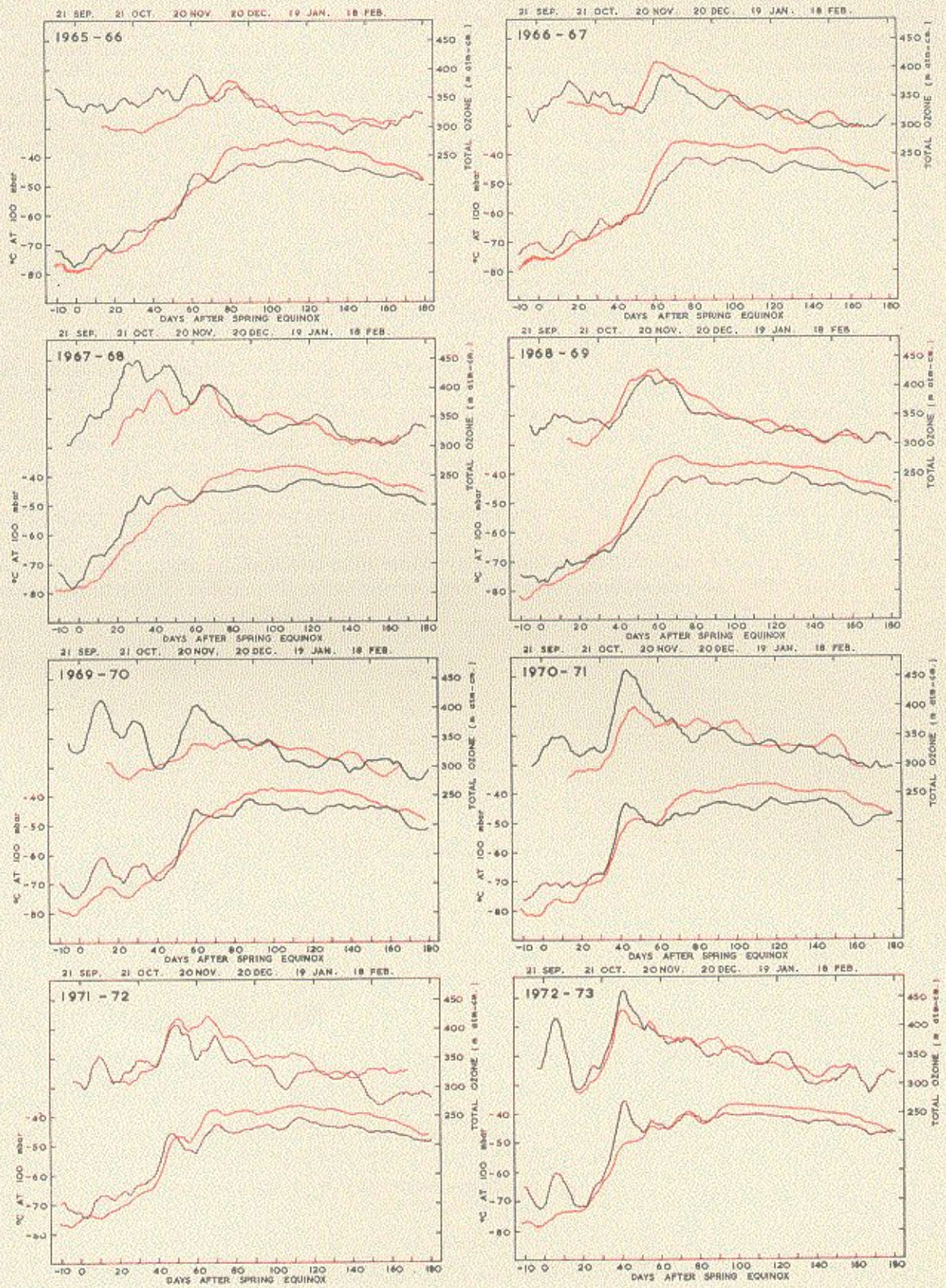


Fig. 6 shows a more or less synchronous rise in ozone content and 100 mbar temperature in the spring, but the ozone amount falls relatively rapidly to its winter level by the autumnal equinox. There are significant differences between the changes at the Argentine Islands and Halley Bay, both in the date of the spring increase and in the variability during the rise which is much larger at the Argentine Islands.

The general correspondence between stratospheric temperature and ozone is clear, and will be discussed later, but it is not a one-to-one correspondence; the ozone maximum occurs nearly 2 months before the temperature maximum, and the ozone reaches its low winter value several months before the temperature minimum. During the winter period, when little photochemical action can take place, the general ozone level remains constant or increases slightly.

XIII. 10 day RUNNING MEANS OF OZONE AND 100 mbar TEMPERATURES

IN Fig. 7 are plotted the 10 day running means of the ozone amounts at the Argentine Islands and Halley Bay, and also the 10 day running means of the 100 mbar temperature at the two stations; in calculating these running means, missing values have been interpolated from previous and following days.

It is noticeable that the seasonal variations for individual years all differ considerably from the mean seasonal variations shown in Fig. 6. There are usually two maxima at the Argentine Islands and only one at Halley Bay.

Table VII and Fig. 8 give for each year and each station the date (day after the spring equinox) of the main ozone maximum, and the maximum 10 day running mean value, and similar data for the early maxima, though these rarely occurred at Halley Bay. More than two maxima are seen in some years at the Argentine Islands. At both stations there is a tendency for late main maxima to be relatively small.

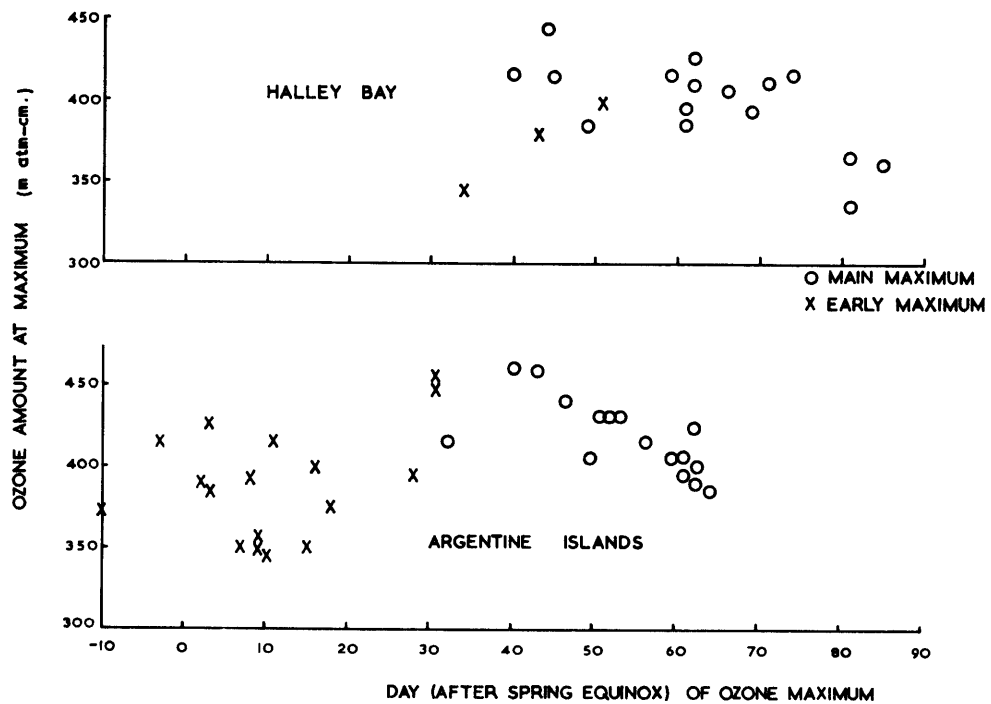


FIGURE 8

Variation of total ozone amount at maximum with date of maximum.

TABLE VII
 DAY (AFTER SPRING EQUINOX) AND MAGNITUDE OF THE OZONE MAXIMA
 IN EACH YEAR AT THE ARGENTINE ISLANDS AND HALLEY BAY

Year	Argentine Islands				Halley Bay			
	Main maximum x Day (m atm-cm.)		Early maximum x Day (m atm-cm.)		Main maximum x Day (m atm-cm.)		Early maximum x Day (m atm-cm.)	
1957	61	395	9	350	45	415		
1958	52	430	3	425	71	410		
1959	32	415	2	388	85	360	34	340
1960	52	430	3	365	74	415		
1961	60	405	16	400	61	385		
1962	62	425	28	395	62	425		
			(8	390)				
1963	62	400	15	350	62	410		
1964	51	430	31	455	44	445		
1965	62	390	-12	370	81	365		
1966	64	385	18	375	61	390		
1967	46	440	31	450	69	390	43	380
1968	56	415	7	350	59	415		
1969	61	405	11	415	81	335		
1970	43	460	10	345	49	385		
1971	49	405	9	355	66	405	51	400
1972	40	460	7	415	40	415		

XIV. DIURNAL VARIATIONS OF AMOUNT OF OZONE

THE method of calibrating the Dobson ozone spectrophotometer is based on the assumption that there is no diurnal variation of ozone in phase with the solar zenith distance. If there is such a variation, it cannot be detected by observations with the spectrophotometer, but measurements made at the same solar zenith distance in the forenoon and afternoon can indicate real changes of ozone amount during the day.

TABLE VIII
 EXCESS OF AFTERNOON AMOUNT OF OZONE OVER THE
 AMOUNT IN FORENOON AT THE SAME SOLAR ZENITH DISTANCE
 (in m atm-cm.)

		Number of observations	50 per cent range	Median	
<i>Argentine Islands</i>					
$\mu=2$	Before midsummer	ADDS	63	-4 to 9	2
		ADZ	209	-5 to 13	4
		Both sets	272	-5 to 13	3
After midsummer	ADDS	82	-2 to 8	3	
		ADZ	178	-2 to 12	4
		Both sets	260	-2 to 10	4
All observations ($\mu=2$)		532	-4 to 11	3	
$\mu=2.6$	Before midsummer	96	-7 to 13	5	
	After midsummer	91	-6 to 9	2	
	All observations ($\mu=2.6$)	187	-6 to 11	4	
$\mu=3$	Before midsummer	122	-6 to 16	6	
	After midsummer	147	-2 to 10	5	
	All observations ($\mu=3$)	269	-4 to 13	5	

TABLE VIII—continued

		<i>Number of observations</i>	<i>50 per cent range</i>	<i>Median</i>	
<i>Halley Bay</i>					
$\mu=2$	Before midsummer	ADDS	93	0 to 8	4
		ADZ	128	-3 to 7	2
		Both sets	221	-2 to 8	3
	After midsummer	ADDS	78	0 to 6	3
		ADZ	138	-1 to 9	4
		Both sets	216	-1 to 7	3
All observations ($\mu=2$)		437	-1 to 7	3	
$\mu=3$	Before midsummer	ADDS	43	-5 to 9	3
		ADZ	118	-4 to 9	3
		Both sets	161	-5 to 8	3
	After midsummer	ADDS	16	-4 to 9	4
		ADZ	127	-3 to 9	3
		Both sets	143	-3 to 9	3
All observations ($\mu=3$)		304	-4 to 9	3	

From the routine measurements made at $\mu=2$, $\mu=2.6$ or $\mu=3$, the difference Δx between the afternoon and forenoon ozone amounts has been evaluated on all occasions when the two observations of each pair were made by the same method of observation and, in the case of zenith cloud observations, on the same type of cloud. All cases when fog or precipitation occurred have been excluded. The results of the AD direct sun, ADDS, AD zenith, ADZ, and CC' zenith observations at $\mu=2.6$ and $\mu=3$ have been analysed separately. The analysis for the Argentine Islands data uses the period starting 50 days before the summer solstice and a similar 50 day period after it. In these periods the interval between the forenoon and afternoon observations varies from about 6 to about 9 hr. for $\mu=2$, and from about 8 to about 12 hr. for $\mu=3$; for Halley Bay only 30 days before and after the summer solstice have been analysed, during which the time intervals between forenoon and afternoon are again about 6-9 hr. for $\mu=2$ and 12-14 hr. for $\mu=3$.

The results of the analysis are given in Table VIII, which shows for each set of observations the median value, the range of values for Δx covered by half the measurements, and the number of measurements of Δx . The consistency with which the median value of Δx is about +3 m atm-cm. is striking. There can be little doubt that there is a daily increase of ozone amount from the time $\mu=2$ in the forenoon to $\mu=2$ in the afternoon of about 3 m atm-cm., on which is superimposed much larger changes due to changes in the general circulation of the atmosphere. There is an indication that Δx increases from 3 m atm-cm. at $\mu=2$ to 5 m atm-cm. at $\mu=3$ at the Argentine Islands, which is statistically significant.

XV. VERTICAL DISTRIBUTION OF OZONE

THE vertical distribution of ozone has been determined by the Umkehr method at both stations on a number of occasions. These Umkehr observations cannot be made during the midsummer period when the sun never sets, nor during the winter period when the solar elevation is less than 30° at noon. In the intervening periods the number of observations is much restricted by cloud.

The method used to estimate the vertical distribution of ozone from the Umkehr observations is that developed by Mateer and Dutsch (1964). The observations have been processed by the Atmospheric

TABLE IX
VERTICAL DISTRIBUTION OF OZONE

Date	a.m. or p.m.	Partial pressure of ozone (in nbar) in layers									Total ozone (m atm-cm.)		
		1	2	3	4	5	6	7	8	9	Solution	Observed	Residual
a. Argentine Islands													
7 October 1957	p	30	88	97	122	103	66	32	14.3	4.6	325	323	0.50
21 October 1957	p	23	88	108	135	115	68	30	14.9	5.4	337	335	0.45
17 December 1957	p	9	145	141	142	109	66	33	13.5	3.7	370	365	1.11
18 December 1957	a	23	106	118	137	116	75	38	15.8	5.1	362	360	0.71
18 December 1957	p	8	125	138	146	114	66	33	16.2	5.7	364	360	0.78
28 December 1957	p	14	106	125	140	112	65	32	16.5	6.0	348	345	0.65
9 February 1958	a	10	83	112	111	106	63	32	17.2	6.2	304	300	1.08
26 February 1958	p	37	77	90	101	97	58	29	16.6	6.3	305	305	0.60
14 October 1958	p	18	106	112	128	103	62	27	14.3	5.2	328	325	0.70
21 October 1958	a	18	95	106	127	104	62	28	13.8	4.7	318	315	0.57
21 October 1958	p	35	83	101	111	97	56	25	13.3	4.4	312	311	0.58
21 December 1958	a	18	104	118	136	110	65	33	15.0	4.6	343	340	0.69
24 December 1958	p	30	102	107	128	108	65	30	13.8	4.6	342	340	0.40
25 December 1958	a	37	87	93	122	109	69	30	13.8	4.7	334	333	0.42
27 January 1959	a	46	106	107	128	109	63	24	14.0	5.7	360	360	0.80
29 January 1959	p	12	111	131	142	105	51	17	11.5	4.2	329	325	2.47
8 February 1959	p	34	99	93	114	96	64	33	13.9	4.0	325	323	0.56
9 February 1959	a	19	101	107	124	99	61	30	15.3	5.5	320	317	0.80
10 February 1959	a	27	81	101	108	99	60	31	15.8	5.3	308	306	0.80
16 February 1959	p	29	79	96	123	105	65	32	16.2	6.0	321	320	0.53
7 March 1959	p	34	92	96	117	97	59	28	15.7	6.2	321	320	0.58
8 March 1959	a	22	98	105	121	96	58	29	16.6	6.5	318	315	0.72
3 October 1959	p	37	130	113	122	95	55	21	11.1	3.6	345	343	1.07
18 October 1959	a	38	130	122	132	103	59	26	12.4	3.8	368	366	0.71
5 November 1959	p	29	136	123	128	99	59	28	14.9	5.4	361	358	0.80
9 October 1960	a	20	86	98	121	102	65	36	17.5	6.2	317	315	0.63
9 October 1960	p	39	80	84	113	98	63	32	15.8	5.4	316	315	0.48
10 October 1960	a	37	73	88	106	99	63	33	16.7	6.1	310	310	0.57
28 October 1960	a	22	104	107	123	97	58	26	13.1	4.2	318	315	0.65
2 February 1961	p	11	75	112	126	110	69	36	16.8	5.9	316	312	0.80
9 February 1961	a	22	79	103	114	102	66	35	16.0	5.3	313	310	0.90
13 October 1961	a	39	96	111	139	126	83	44	19.8	7.6	390	390	0.27
27 October 1961	p	21	88	97	122	107	74	41	15.7	4.6	326	324	0.67
6 November 1961	p	12	81	116	125	107	66	33	15.5	5.5	316	312	0.98
11 November 1961	p	12	115	135	158	137	85	41	14.7	4.2	393	390	0.78
22 December 1961	p	12	99	115	135	112	71	37	15.5	4.9	338	335	0.68
17 January 1962	a	30	75	90	102	103	61	29	15.3	5.0	301	300	0.66
15 February 1962	p	20	65	87	104	117	67	29	16.0	5.5	294	292	0.54
21 October 1962	p	33	113	136	152	131	89	47	16.5	4.9	415	413	0.59
30 November 1962	p	8	105	135	154	126	74	36	17.6	6.7	370	367	0.61
8 January 1963	a	10	84	114	140	121	73	32	16.1	6.5	335	332	0.62
30 September 1963	a	26	79	90	119	104	70	38	16.1	5.1	317	315	0.54
1 October 1963	a	24	77	107	117	103	57	26	16.9	7.3	311	309	0.69
6 October 1963	p	53	69	79	117	112	77	41	18.8	7.1	349	351	0.54
20 October 1963	a	42	64	69	95	107	67	32	15.6	5.0	299	300	0.40
3 March 1964	p	22	69	88	100	111	66	32	17.2	5.9	296	294	0.66
4 November 1964	p	18	110	134	154	129	76	35	15.3	5.2	383	380	0.52
1 December 1964	p	27	134	135	144	114	68	33	14.9	4.9	387	385	0.60
4 December 1964	p	44	134	120	131	109	67	32	13.4	4.0	386	385	0.54
22 January 1965	p	22	97	101	122	103	65	31	13.9	4.5	321	318	0.63
29 September 1965	p	46	71	78	98	96	60	31	18.3	7.6	308	309	0.65
25 October 1965	a	29	79	98	108	100	62	32	16.3	5.8	310	308	0.68
28 October 1965	a	30	82	98	128	113	72	36	17.1	6.3	339	338	0.48
10 December 1965	p	21	95	118	147	129	81	39	15.9	5.2	372	370	0.34
11 December 1965	a	15	105	127	149	128	79	37	15.4	5.2	373	370	0.54
8 October 1966	p	14	91	120	146	127	82	45	20.9	8.1	369	367	0.49
6 November 1966	a	29	80	97	125	106	64	30	14.9	5.3	321	320	0.59
18 November 1966	p	38	59	73	111	110	76	38	15.0	4.5	312	312	0.35
5 October 1972	a	34	67	79	98	112	63	24	14.0	4.6	294	294	0.57
10 October 1972	a	14	73	103	114	113	64	30	17.6	6.9	303	300	0.99
26 October 1972	a	35	85	102	134	119	73	32	13.9	4.5	351	350	0.44
6 November 1972	p	18	123	197	197	155	86	37	18.5	7.5	470	466	0.73
24 November 1972	p	21	110	129	148	122	72	32	15.2	5.4	372	370	0.50

TABLE IX—continued

Date	a.m. or p.m.	Partial pressure of ozone (in nbar) in layers									Total ozone (m atm-cm.)		
		1	2	3	4	5	6	7	8	9	Solution	Observed	Residual
b. Halley Bay													
20 February 1959	p	24	108	115	133	111	68	34	15.9	5.5	352	350	0.52
9 October 1959	p	24	77	92	95	109	57	21	14.1	4.4	287	285	0.77
15 October 1959	a	25	90	104	96	99	51	21	14.0	4.5	293	291	1.00
20 October 1959	p	25	88	105	99	99	50	21	14.6	4.9	295	293	0.94
10 October 1960	a	31	71	88	105	106	64	31	15.5	5.1	303	302	0.56
11 October 1960	p	18	88	100	124	106	67	32	14.5	4.8	317	314	0.49
17 February 1961	p	27	91	105	93	94	47	21	16.9	6.6	294	292	0.94
27 February 1961	a	28	99	96	113	94	61	32	16.3	6.1	318	316	0.57
27 February 1961	p	38	104	87	104	88	59	31	15.2	5.2	317	315	0.64
28 February 1961	p	25	95	98	117	97	61	33	16.7	6.1	317	315	0.63
13 February 1962	p	26	83	97	93	100	53	24	17.9	7.1	292	291	0.76
20 October 1962	a	28	90	95	121	106	68	32	14.2	4.8	324	322	0.48
7 October 1963	p	35	71	82	100	107	64	28	14.6	4.8	301	300	0.43
11 February 1964	a	43	95	87	77	90	47	17	12.9	4.0	287	287	2.57
21 October 1964	a	28	78	98	107	106	58	23	13.2	4.3	301	299	0.64
23 October 1964	a	51	69	80	106	102	56	19	11.8	4.3	307	308	1.03
12 October 1965	p	27	84	95	92	102	54	22	14.2	4.5	289	288	0.76
25 February 1966	p	33	84	87	83	97	51	20	15.5	5.6	284	283	0.69
10 October 1966	p	14	82	106	131	113	72	38	18.8	7.4	330	328	0.66
2 March 1967	a	29	82	91	84	96	46	18	17.2	7.1	278	277	1.03
21 October 1970	p	25	61	73	91	113	65	27	15.0	4.5	278	277	0.56
22 October 1970	p	18	68	87	96	113	61	25	15.6	5.2	281	279	0.65
23 October 1970	a	29	68	77	88	108	59	22	14.4	4.6	278	277	0.47
23 October 1970	p	22	64	79	93	112	62	26	14.9	4.5	276	275	0.61
22 October 1971	p	16	72	98	103	112	60	27	16.9	6.1	292	290	0.75
19 October 1972	p	19	75	108	123	108	63	30	15.4	5.7	314	311	0.65

Environment Service of Canada, the result being expressed in terms of the partial pressure of ozone in nine standard layers defined by the given pressure ranges as follows:

Layer number	Pressure range (mbar)	Approximate height range (km.)
9	1.96– 0.98	44–49
8	3.9 – 1.96	39–44
7	7.8 – 3.9	33–39
6	15.6 – 7.8	28–33
5	31.2 –15.6	23–28
4	62.5 –31.2	19–23
3	125 –62.5	14–19
2	250 –125	10–14
1	500 –250	5–10

The approximate height range is applicable to the Antarctic summer. The method assumes that the partial pressure below 500 mbar is the same as in layer 1, and that the amount of ozone above 0.98 mbar is 54 per cent of the amount in layer 9.

The solution of the Umkehr observations is heavily weighted so that the resultant total ozone very nearly agrees with the observed total ozone. As an indication of the reliability of the computation, the values of $100N$ at the various zenith angles are recomputed from the derived vertical distribution, and the r.m.s. of the differences between the computed and the measured values of $100N$ is termed the residual. Solutions for which the residual exceeds unity are normally rejected.

The results of all the Umkehr observations for which a solution could be computed are collected in Table IX, which gives the partial pressure in each layer, the solution and observed total ozone amount, and the residual.

Table IX shows several cases when two Umkehr observations were made on the same or successive days, and when the total ozone amount was nearly constant, from which the following points can be made:

- i. Consistency between the results of the analysis can be very good, the partial pressures generally agreeing to about 5 per cent, except in the case of layer 1.
- ii. The consistency is very poor in layer 1.
- iii. The mean of the values for layers 1, 2 and 3 is very consistent.

All these points could be a consequence of the method of computation. Point (iii) implies a high negative correlation between the values in layer 1 and in layers 2 and 3 which is, in fact, found. The source factors given by Mateer (1965) are broad for the lower zenith angles which mainly determine the partial pressures in layers 1, 2 and 3. Thus the computed distribution over these layers is fundamentally unstable for small changes in the data at these zenith angles.

Analysis of the results shows that there is generally a high correlation between the total ozone amount x and the partial pressure p_n in the n^{th} layer. The values of the correlation coefficient between x and p_n and the regression equations relating p_n to x are given in Table X. Observations with residuals greater than 1 were not used in this analysis. The high correlation for layer 4 and the low negative correlation for layer 5 at Halley Bay appear to be accidental—in this sample there is little variation in the partial pressure.

TABLE X
CORRELATION COEFFICIENTS AND REGRESSION EQUATIONS
BETWEEN LAYER PARTIAL PRESSURES AND TOTAL OZONE AMOUNT

Layer	Argentine Islands		Halley Bay	
	Correlation coefficient (p and x)	Regression equations (p in nbar, x in m atm-cm.)	Correlation coefficient (p and x)	Regression equations (p in nbar, x in m atm-cm.)
9	0.08	$p_9 = 5.5$	0.33	$p_9 = 5.3 + 0.02(x - 300)$
8	0.18	$p_8 = 16 + 0.01(x - 337)$	0.66	$p_8 = 15 + 0.02(x - 300)$
7	0.46	$p_7 = 33 + 0.07(x - 337)$	0.79	$p_7 = 27 + 0.21(x - 300)$
6	0.67	$p_6 = 67 + 0.15(x - 337)$	0.56	$p_6 = 60 + 0.19(x - 300)$
5	0.78	$p_5 = 110 + 0.28(x - 337)$	-0.11	$p_5 = 104 - 0.04(x - 300)$
4	0.87	$p_4 = 127 + 0.48(x - 337)$	0.97	$p_4 = 104 + 0.73(x - 300)$
3	0.81	$p_3 = 107 + 0.51(x - 337)$	0.65	$p_3 = 94 + 0.36(x - 300)$
2	0.74	$p_2 = 93 + 0.41(x - 337)$	0.72	$p_2 = 82 + 0.48(x - 300)$
1	-0.14	$p_1 = 26 - 0.04(x - 337)$	-0.10	$p_1 = 25 - 0.03(x - 300)$

This method of computing the vertical distribution of ozone is based on modifying one of three standard vertical distributions of ozone with total ozone amounts of 254, 341 and 423 m atm-cm., SII, SI and SIII, so as to fit the observed data. The vertical distributions for the Argentine Islands and Halley Bay for the standard ozone amounts have been calculated from the regression coefficients in Table X, and are given in Table XI, together with the standard distribution. (No vertical distribution is computed for 423 m atm-cm. for Halley Bay as no Umkehr observations were made on days of high ozone amount.)

TABLE XI
COMPUTED VERTICAL DISTRIBUTION OF OZONE AT THE
ARGENTINE ISLANDS AND HALLEY BAY FOR STANDARD OZONE AMOUNTS,
AND THE STANDARD DISTRIBUTIONS SII, SI AND SIII

Layer	$x = 254$ m atm-cm.			$x = 341$ m atm-cm.			$x = 423$ m atm-cm.	
	A.I.	H.B.	SII	A.I.	H.B.	SI	A.I.	SIII
	(nbar)			(nbar)			(nbar)	
9	5	4	7	5	6	7	5	7
8	15	12	20	16	16	20	17	20
7	27	17	46	33	36	53	39	53
6	55	51	87	68	68	95	80	95
5	87	106	129	111	102	134	134	134
4	87	70	90	129	134	133	168	143
3	65	77	38	109	109	84	151	125
2	59	60	17	95	102	42	128	87
1	29	26	12	26	24	23	23	52

It will be seen that the ozone amounts in layers 1, 2 and 3 are larger at the Antarctic stations than in the standard distributions.

MacDowall (1962) made some soundings in 1958 at Halley Bay with an early version of the electrochemical ozonesonde and obtained ozone profiles in the summer which differed considerably from our Umkehr profiles. The ozonesondes indicated low partial pressures, generally less than 10 nbar up to tropopause level, whereas the mean value of p_1 on days on which the tropopause was above 250 mbar (*italics* in Table IX) was 26 nbar at Halley Bay and 33 nbar at the Argentine Islands. The ozonesondes showed a rapid increase of partial pressure above the tropopause to a maximum of about 180 nbar in layer 3, while the average Umkehr maximum is some 30 per cent less and in layer 4. It must be emphasized that the Umkehr observations are made only under special and infrequent meteorological conditions, viz. a cloudless zenith sky, while the ozonesonde measurements require no such stringent conditions. The flattening of the maximum is a well-known feature of the Umkehr profiles, but it appears from MacDowall's measurements that the Umkehr computation puts too much ozone in layer 1 (and below 500 mbar) and, if some of this was put into layers 2 and 3, a better fit with the ozonesonde profiles would be obtained. Mateer's (1965) results suggest that we have no real evidence for the calculated partitioning of ozone between layers 1, 2 and 3 but only information for the total in these layers.

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