

Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction

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Recent attempts^{1,2} to consolidate assessments of the effect of human activities on stratospheric ozone (O_3) using one-dimensional models for 30°N have suggested that perturbations of total O_3 will remain small for at least the next decade. Results from such models are often accepted by default as global estimates³. The inadequacy of this approach is here made evident by observations that the spring values of total O_3 in Antarctica have now fallen considerably. The circulation in the lower stratosphere is apparently unchanged, and possible chemical causes must be considered. We suggest that the very low temperatures which prevail from midwinter until several weeks after the spring equinox make the Antarctic stratosphere uniquely sensitive to growth of inorganic chlorine, ClX , primarily by the effect of this growth on the NO_2/NO ratio. This, with the height distribution of UV irradiation peculiar to the polar stratosphere, could account for the O_3 losses observed.

Total O_3 has been measured at the British Antarctic Survey stations, Argentine Islands $65^\circ\text{S } 64^\circ\text{W}$ and Halley Bay $76^\circ\text{S } 27^\circ\text{W}$, since 1957. Figure 1a shows data from Halley Bay. The mean and extreme daily values from October 1957 to March 1973 and the supporting calibrations have been discussed elsewhere^{4,5}. The mean daily value for the four latest complete observing seasons (October 1980–March 1984) and the individual daily values for the current observing season are detailed in Fig. 1. The more recent data are provisional values. Very generous bounds for possible corrections would be ± 30 matm cm. There was a changeover of spectrophotometers at the station in January 1982; the replacement instrument had been calibrated against the UK Meteorological Office standard in June 1981. Thus, two spectrophotometers have shown October values of total O_3 to be much lower than March values, a feature entirely lacking in the 1957–73 data set. To interpret this difference as a seasonal instrumental effect would be inconsistent with the results of routine checks using standard lamps. Instrument temperatures (recorded for each observation) show that the March and October operating conditions were practically identical. Whatever the absolute error of the recent values may be, within the bounds quoted, the annual variation of total O_3 at Halley Bay has undergone a dramatic change.

Figure 1b shows data from Argentine Islands in a similar form, except that for clarity the extreme values for 1957–73 have been omitted. The values for 1980 to the present are provisional, the extreme error bounds again being ± 30 matm cm. The changes are similar to those seen at Halley Bay, but are much smaller in magnitude.

Upper-air temperatures and winds are available for these stations from 1956. There are no indications of recent departures from established mean values sufficient to attribute the changes in total O_3 to changes in the circulation. The present-day atmosphere differs most prominently from that of previous decades in the higher concentrations of halocarbons. Figure 2a shows the monthly mean total O_3 in October at Halley Bay, for 1957–84, and Fig. 2b that in February, 1958–84. Tropospheric concentrations of the halocarbons F-11 (CFCl_3) and F-12 (CF_2Cl_2) in the Southern Hemisphere⁶ are also shown, plotted to give greatest emphasis to a possible relationship. Their growth, from which increase of stratospheric ClX is inferred, is not evidently dependent on season. The contrast between spring and autumn O_3 losses and the striking enhancement of spring loss at Halley Bay need to be explained. In Antarctica, the lower stratosphere is $\sim 40\text{ K}$ colder in October than in February. The stratosphere

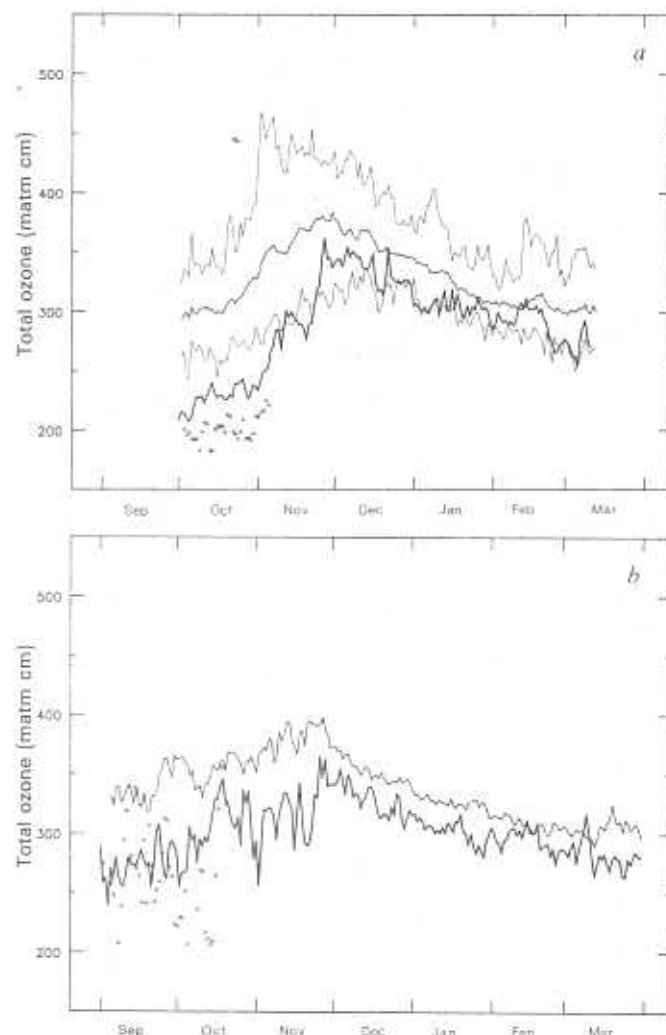


Fig. 1 Daily values of total O_3 . a, Halley Bay: thin lines, mean and extreme values for 16 seasons, 1957–73; thick line, mean values for four seasons, 1980–84; +, values for October 1984. Observing season: 1 October to 13 March. b, Argentine Islands: as for Halley Bay, but extreme values for 1957–73 omitted. Observing season: 1 September to 31 March.

over Halley Bay experiences a polar night and a polar day (many weeks of darkness, and of continuous photolysis, respectively); that over Argentine Islands does not. Figure 3 shows calculated amounts of NO_x in the polar night and the partitioning between the species⁶. Of these, only NO_3 and NO_2 are dissociated rapidly by visible light. The major reservoir, N_2O_5 , which only absorbs strongly below 280 nm, should be relatively long-lived. Daytime levels of NO and NO_2 should be much less in early spring, following the polar night, than in autumn, following the polar day. Recent measurements⁷ support these inferences. The effect of these seasonal variations on the strongly interdependent ClO_x and NO_x cycles is examined below.

The O_3 loss rate resulting from NO_x and ClO_x may be written⁸

$$L = N + C = 2 k_2[\text{O}][\text{NO}_2] + 2 k_3[\text{O}][\text{ClO}] \quad (1)$$

L accounts for over 85% of O_3 destruction in the altitude range 20–40 km. At 40 km, N and C are roughly equal. Lower down, C decreases rapidly to 10% of L at 30 km, 3% at 20 km (refs 6, 8). Equation (1) is based on two steady-state approximations, (see Table 1a for the reactions involved)

$$\psi = \frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_1[\text{O}_3] + k_4[\text{ClO}]}{k_2[\text{O}] + j_3} \quad (2)$$

and

$$\chi = \frac{[\text{Cl}]}{[\text{ClO}]} \sim \frac{k_6[\text{O}] + k_4[\text{NO}]}{k_3[\text{O}_3]} \quad (3)$$

valid in daytime, with $[\text{O}]$ in steady state with $[\text{O}_3]$. Reaction (4) has a negative temperature coefficient, whereas reaction (1) has large positive activation energy⁹, with the result that ψ is strongly dependent on $[\text{ClO}]$ at low temperature, as shown in Fig. 4. $[\text{ClO}]$ is not simply proportional to total CIX, because ClONO_2 formation (reaction (10)) intervenes. Throughout the stratosphere, $\chi \ll 1$, so that $[\text{ClO}] \sim [\text{Cl} + \text{ClO}]$. From a steady-state analysis of the reactions given in Table 1b,

$$[\text{Cl} + \text{ClO}] \sim \frac{k_7[\text{HCl}][\text{OH}] + j_8[\text{ClONO}_2] + j_9[\text{HOCl}]}{k_{10}[\text{NO}_2] + k_{11}[\text{HO}_2] + \chi(k_{12}[\text{CH}_4] + k_{13}[\text{HO}_2])} \quad (4)$$

Values of ψ , χ and $[\text{Cl} + \text{ClO}]$ obtained from equations (2), (3) and (4) are in good accord with full one-dimensional model results for late summer in Antarctica⁶. Neglecting seasonal effects other than those resulting from temperature and from variation of $[\text{NO} + \text{NO}_2]$, it is possible to solve simultaneously for $[\text{NO}_2]$ and $[\text{ClO}]$, and to derive L . Results are shown in Table 2 as relaxation times⁸, $[\text{O}_3]/L$, for various conditions. The spring values (lines 2, 3 and 4) are highly dependent on CIX

Table 1 Reaction list

<i>a</i> Governing ψ and χ (see text)	
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	(1)
$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	(2)
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	(3)
$\text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}$	(4)
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	(5)
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	(6)
<i>b</i> Governing $[\text{Cl} + \text{ClO}]$	
$\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$	(7)
$\text{ClONO}_2 + h\nu \rightarrow \text{ClO} + \text{NO}_2$	(8)
$\text{HOCl} + h\nu \rightarrow \text{Cl} + \text{OH}$	(9)
$\text{ClO} + \text{NO}_2 \rightarrow \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	(10)
$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	(11)
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	(12)
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	(13)
<i>c</i> $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$	(14)

amount (compare columns *a* and *b*), the autumn values (line 1) much less so. At Argentine Islands, the sensitivity to CIX growth should resemble that seen in line 2, attributable solely to low temperature. Lines 3 and 4 show the enhanced sensitivity possible at stations within the Antarctic Circle, such as Halley Bay, arising from slow release of $[\text{NO} + \text{NO}_2]$ following the polar night. It remains to be shown how stable O_3 budgets were achieved with the relaxation times for the lower chlorine level (Table 2, *a*).

Much O_3 destruction is driven by visible light, but production requires radiation below 242 nm. On the dates shown (Table 2), destruction persists for some 11 h, while, because of the long UV paths, production is weak (except around noon) at 29 km, and is virtually absent below that altitude. Line 1 of Table 2 then demands O_3 transport in autumn from the upper to the lower stratosphere, which is consistent with inferred thermally-driven lagrangian-mean circulations¹⁰. A mean vertical velocity of 45 m per day is in good accord with calculations of net diabatic cooling¹¹ and gives a realistic total O_3 decay rate in an otherwise conventional one-dimensional model⁶. The short relaxation times in the lower stratosphere in autumn are tolerable, with adequate transport compensating for lack of O_3 production.

In early spring, on the other hand, wave activity scarcely penetrates the cold dense core of the Antarctic polar vortex and with very low temperatures the net diabatic cooling is very weak¹¹. Lagrangian transport in the vortex should then be almost negligible. (The virtual exclusion of Agung dust from the vortex supports this view⁵.) The final warming signals the end of this period of inactivity and is accompanied by large dynamically induced changes in O_3 distribution. However, before the warming, with low chlorine, total O_3 was in a state of near-neutral equilibrium, sustained primarily by the long relaxation times. With higher chlorine, relaxation times of the order seen in line 4, Table 2, entail more rapid O_3 losses. With negligible production below 29 km and only weak transport, large total O_3 perturbation is possible. The extreme effects could be highly localized, restricted to the period with diurnal photolysis between polar night and the earlier of either the onset of polar day or the final spring warming. At the pole $[\text{NO} + \text{NO}_2]$ rises continuously after the polar night, with the Sun. The final warming always begins over east Antarctica and spreads westwards across the pole. At Halley Bay the warming is typically some 14 days later than at the pole. Maximum O_3 depletion could be confined to the Atlantic half of the zone bordered roughly by latitudes 70° and 80° S.

Comparable effects should not be expected in the Northern Hemisphere, where the winter polar stratospheric vortex is less cold and less stable than its southern counterpart. The vortex is broken down, usually well before the end of the polar night,

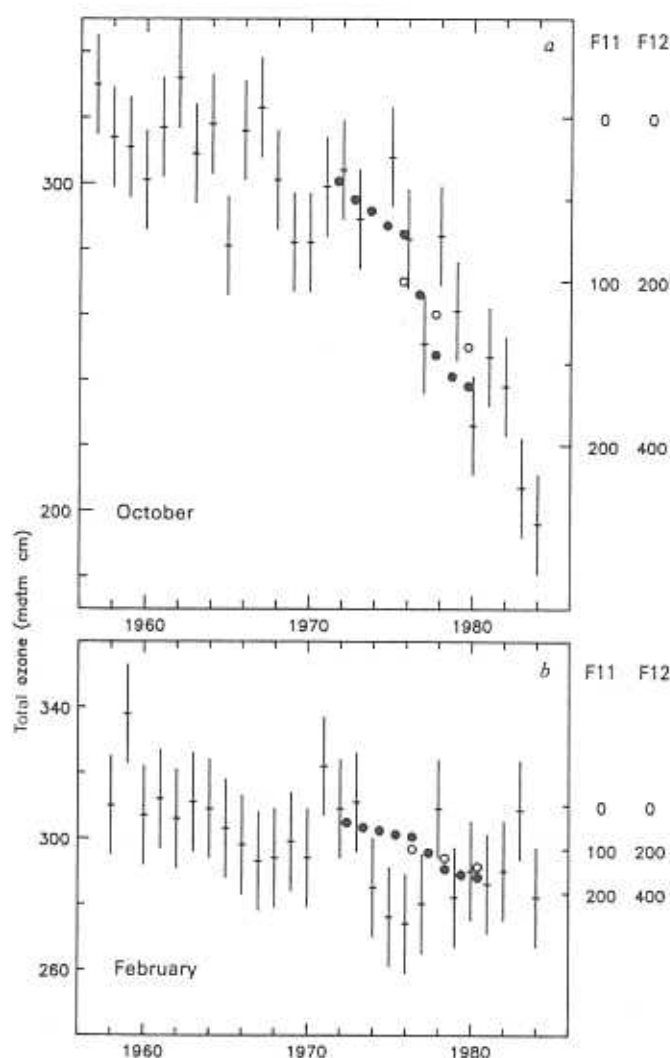


Fig. 2 Monthly means of total O_3 at Halley Bay, and Southern Hemisphere measurements of F-11 (●, p.p.t.v. CFCl_3) and F-12 (○, p.p.t.v. CF_2Cl_2). *a*, October, 1957–84. *b*, February, 1958–84. Note that F-11 and F-12 amounts increase down the figure.

Table 2 Relaxation times in days, $[O_3]/L$, for maximum chlorine levels 1.5 p.p.b.v. (a) and 2.7 p.p.b.v. (b) (1980)

Date	Altitude (km)	22		25.5		29		32.5		36		39.5		43	
		Relative NO + NO ₂													
25 March	1	a	b	a	b	a	b	a	b	a	b	a	b	a	b
17 September	1	105	103	38	37	16	15	6.9	5.7	2.6	2.0	1.2	0.9	0.83	0.57
17 September	0.75	224	210	86	77	32	27	12.2	9.2	4.9	3.4	2.6	1.7	1.90	1.22
17 September	0.5	288	265	107	93	39	31	14.2	10.4	5.7	3.9	3.0	1.9	2.13	1.33
17 September	0.5	398	353	141	118	47	36	17.0	12.0	6.9	4.5	3.5	2.2	2.41	1.46

Noon values at 75.5°S, solar elevation 12.5°. Lower stratosphere at 230 K on 25 March; 190 K on 17 September. The altitudes shown apply to the summer temperature profile used in the model⁶.

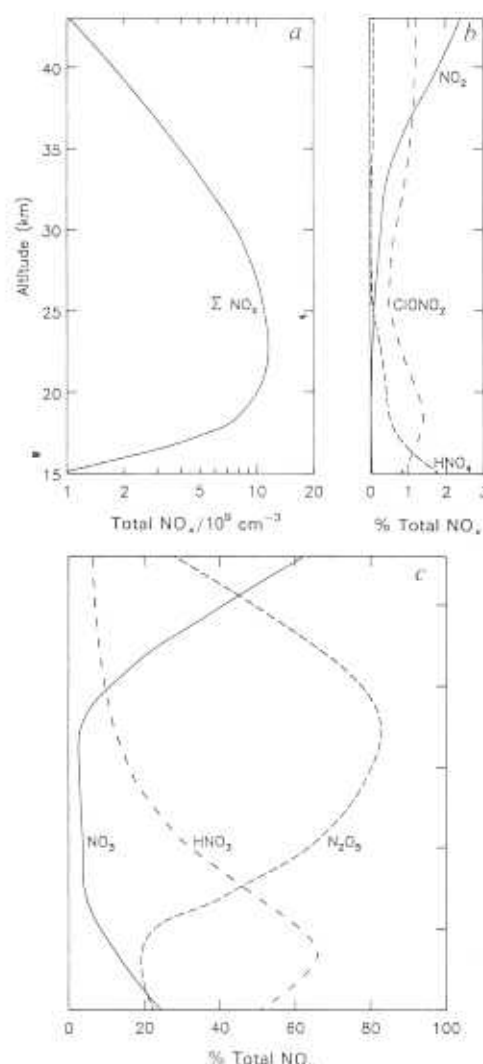


Fig. 3 NO_x during the polar night. a, Total NO_x cm⁻³, from 15 to 43 km. b, NO₂, ClONO₂ and HNO₃ as percentages of total NO_x. c, NO₂, HNO₃ and N₂O₅ as percentages of total NO_x.

by major warmings. These are accompanied by large-scale subsidence and strong mixing, in the course of which peak O₃ values for the year are attained. Hence, sensitivity to ClX growth should be minimal if, as suggested above, this primarily results from O₃ destruction at low temperatures in regions where O₃ transport is weak.

We have shown how additional chlorine might enhance O₃ destruction in the cold spring Antarctic stratosphere. At this time of the year, the long slant paths for sunlight make reservoir species absorbing strongly only below 280 nm, such as N₂O₅, ClONO₂ and HO₂NO₂, relatively long-lived. The role of these reservoir species should be more readily demonstrated in

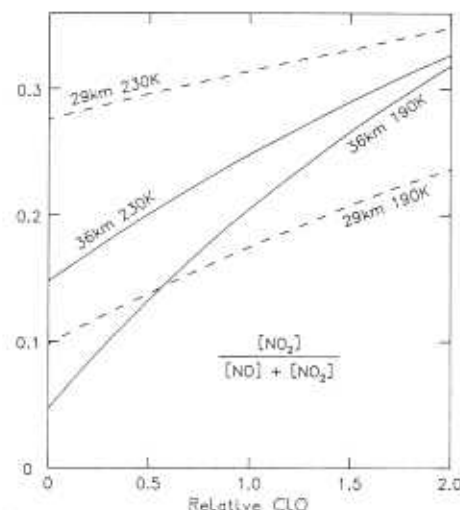


Fig. 4 $[NO_2]/[NO + NO_2]$ has the status of an efficiency factor for O₃ destruction by the NO_x cycle. In terms of the ratio ψ in the text, it is $\psi/(1 + \psi)$. The figure shows how this factor varies with [ClO] at 190 K and at 230 K, at altitudes of 29 and 36 km. Values of $[O_3]$, $[O]$, $[ClO]$ and f_3 were taken from one-dimensional model results⁶ (maximum chlorine 2.7 p.p.b.v.) for noon, 25 March at 75.5°S, solar elevation 12.5°. The abscissa is $[ClO]$ relative to the model value. The rate-limiting reaction, (2) in Table 1, for the NO_x cycle has zero activation energy. Note how, nevertheless, O₃ was protected against destruction by NO_x at low temperatures in a stratosphere with small amounts of ClX, but is losing this protection as ClX grows.

Antarctica, particularly the way in which they hold the balance between the NO_x and ClO_x cycles. An intriguing feature could be the homogeneous reaction (Table 1c) between HCl and ClONO₂. If this process has a rate constant as large as 10^{-16} cm³ s⁻¹ (ref. 2) and a negligible temperature coefficient, the reaction would go almost to completion in the polar night, leaving inorganic chlorine partitioned between HCl and Cl₂, almost equally at 22 km for example. Photolysis of Cl₂ at near-visible wavelengths would provide a rapid source of $[Cl + ClO]$ at sunrise, not treated in equation (4). The polar-night boundary is, therefore, the natural testing ground for the theory of nonlinear response to chlorine^{1,2}. It might be asked whether a nonlinear response is already evident (Fig. 2a). An intensive programme of trace-species measurements on the polar-night boundary could add greatly to our understanding of stratospheric chemistry, and thereby improve considerably the prediction of effects on the ozone layer of future halocarbon releases.

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