

The Antarctic 'Ozone Hole' and Its Possible Global Consequences

The Antarctic 'ozone hole', first observed at Halley Bay by the British team as reported by Farman *et al.* (1985), and then confirmed by the observational series at the South Pole (Komhyr *et al.*, 1986) as well as by satellite measurements (Nimbus 7, Stolarski *et al.*, 1986), at first provoked a considerable scientific controversy—decreased ozone transport due to changes in stratospheric circulation *versus* direct photochemical causes.

The phenomenon in the Antarctic could not be understood from the current photochemical models; therefore, a number of new photochemical schemes were developed during 1986 (Crutzen & Arnold, 1986; McElroy *et al.*, 1986a, 1986b; Rowland, 1986; Solomon *et al.*, 1986), which attempted to explain this new feature. There are differences between them in some details, but all those theories agree in the main points: very low NO_x content in the Antarctic lower stratosphere at the end of the polar night, and high concentrations of active chlorine or of other chemical species from which active chlorine is easily produced by photodissociation after the return of the Sun.

The new theories assume that N₂O₅, which originates from NO₂ by the action of ozone, is converted to HNO₃ by heterogeneous reactions at the surface of aerosols, and/or by cycles including hydrated ions produced by cosmic rays (Crutzen & Arnold, 1986). A basic feature of the further chemical development which takes place is the very low temperature that occurs in the Antarctic lower stratosphere in the latter part of the polar night, due to weaker meridional exchange processes than in the Northern Hemisphere. These temperatures of below -80°C lead to the formation of ice-crystals of a mixture of H₂O and HNO₃, and thus to an increase of the aerosol mass which can again speed up the catalytic processes at their surface, leading to an almost complete removal of gaseous NO_x.

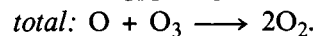
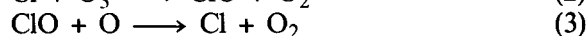
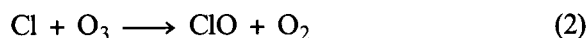
Stratospheric Chemistry

OH-radicals, produced from water vapour through the effect of cosmic rays, and, after the return of the Sun, much more efficiently by excited oxygen atoms stemming from the photodissociation of ozone, are therefore not lost rapidly by reaction with gaseous HNO₃, but are available to produce active chlorine from HCl:

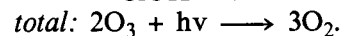
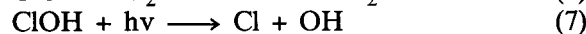
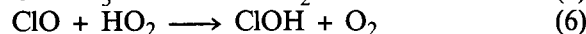
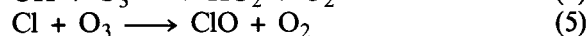
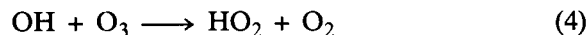


In the absence of NO₂, the active chlorine (as well as bromine) cannot be rapidly deactivated by the formation of ClNO₃ (or BrNO₃, respectively). Somewhat more hypothetical, at least at present, is the formation of additional active chlorine by reaction of ClNO₃ with HCl or H₂O, catalyzed at the surface of the aerosol.

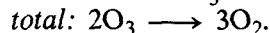
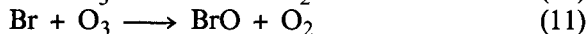
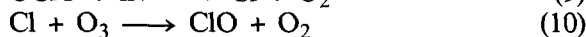
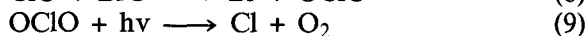
The catalytic cycles destroying ozone in the Antarctic lower stratosphere are different from, and more complicated than, those leading to ozone loss in the middle and upper stratosphere where, according to the conventional models, processes involving atomic oxygen are predominant:



Because atomic oxygen is rather rare in the lower stratosphere where the 'ozone hole' develops, one of such cycles as the following (the list is not complete), or several of them together, leads or lead to the rapid disappearance of ozone early in the Antarctic spring:



The involvement of bromine, which is estimated—with considerable uncertainty—to be represented by about 1% of the chlorine concentration in the stratosphere, and which is also of anthropogenic origin (from CF₃Br and CF₂ClBr used in fire-extinguishers), has also been proposed (McElroy *et al.*, 1986a) through the following cycle:



Whether this contribution is important depends on the unknown (but certainly rising) concentration of HBr in the stratosphere; HBr reacts much more rapidly with OH than does HCl (reaction 1).

All proposed photochemical explanations of the 'ozone hole' rely, for the removal of NO_2 , on the catalytic action of aerosols or ions, namely on processes which are somewhat hypothetical or at least not quantitatively known. Therefore, in the special issue of *Geophysics Research Letters* (November 1986) which was consecrated to the ozone 'hole' problem, the circulation hypothesis was still favoured by the majority of authors—on the basis either of reduced meridional transport or of tropospheric air upwelling into the lower stratosphere over Antarctica.

Photochemical Explanation Now Favoured

In the meantime, the results of the American National Ozone Expedition to Antarctica (McMurdo) during the (southern) winter and early spring of 1986, have become at least partly available, and strongly favour the photochemical case. Thus the data from an extended series of ozone soundings (Hofmann *et al.*, 1987) point strongly to an *in situ* photochemical destruction between August and October (Fig. 1), and are hardly compatible either with rising motion from below—the mixing ratio decreases by a factor 2 at altitudes of from 12 to 20 km at the time of the maximum development of the 'ozone hole'—or with reduced meridional transport. Furthermore, spectroscopic and microwave measurements indicate very low NO_x content and relatively high concentrations of ClO and OCIO, i.e. exactly the prerequisites for the new photochemical models for explaining the ozone 'hole'.

Global Aspects

As long as the 'ozone hole' was thought to be confined to the Antarctic early spring, it could be considered as an interesting scientific problem without much practical importance, as the path-length of the solar beam through the ozone layer would still be large. This confinement, however, is hardly the case. Firstly, feedback effects on stratospheric circulation must be expected, as the decreased ozone concentration is—due to reduced radiational warming—coupled with lower temperatures (which are already observed) and thus lead to a reinforcement of the circumpolar vortex. This again may accentuate the 'ozone hole' by reduced transport, and may extend it in time.

Still more important is the additional sink component in the global stratospheric ozone budget resulting from the Antarctic loss-process. Its effect on the stratosphere's ozone content at lower latitudes, due to meridional exchange processes, is already clearly seen in Fig. 2, which shows—based on satellite observations (Storlarski *et al.*, 1986)—not only the rapidly deepening and expanding ozone 'hole', but also a pronounced decrease of total ozone in the surrounding subpolar maximum belt; this reduction is, due to the still comparatively high values, less spectacular than the 'hole', although its absolute magnitude is almost as large as in the region of the 'hole'.

There remains the intriguing question of whether a similar development could also occur over the Arctic, where the polar-night stratosphere is less cold than in the South. It might, nevertheless, locally and for certain periods, become cold enough for the crystallization of HNO_3 , and related processes, while the stronger meridional exchange might also counteract the chemical changes that are taking place in Antarctica. It has already been suggested, on the basis of satellite observations (Borman, 1986), that the March values of total ozone are already considerably decreased in the North-polar region, while an ozone decrease may also have occurred at other latitudes. It is thus quite possible that global ozone depletion due to chlorofluorocarbons (CFCs)* may be considerably stronger than has so far been expected on the bases of prognostic calculations with the conventional photochemical models.

Certainly the photochemical theory concerning the Antarctic 'ozone hole' has not yet reached a mature state. There are still slight inconsistencies or at least hypothetical parts, although the overall correctness of the

* See the Guest Comment by the Deputy Executive Director of UNEP on pp. 290–2 of our Winter issue of last year, the DuPont Position Statement by the Director of their Freon Products Division on pp. 363–4 of the same issue, and other recent items.—Ed.

photochemical cause of the 'hole' can hardly be doubted any more. Laboratory work, but especially more trace-substance measurements during the Antarctic polar-night and early spring, are urgently needed for a further-improved understanding of this important feature.

HANS U. DÜTSCH, *Professor Emeritus
Laboratory for Atmospheric Physics
Federal Institute of Technology
8093 Zürich, Switzerland; also
Lightclimatic Observatory
Arosa, Switzerland.*

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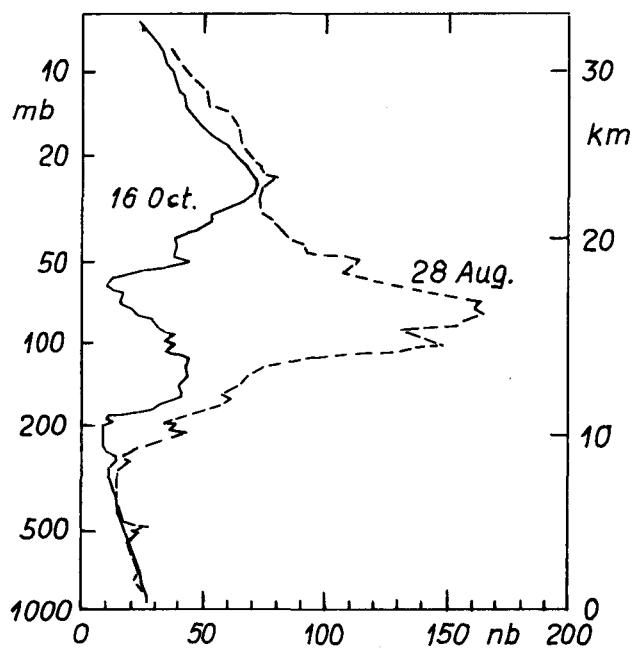


FIG. 1. Loss of ozone between 10 and 22 km altitude over Antarctica from late-August to mid-October 1986, from soundings at McMurdo (after Hofmann et al., 1987). mb = millibars; nb = nanobars.

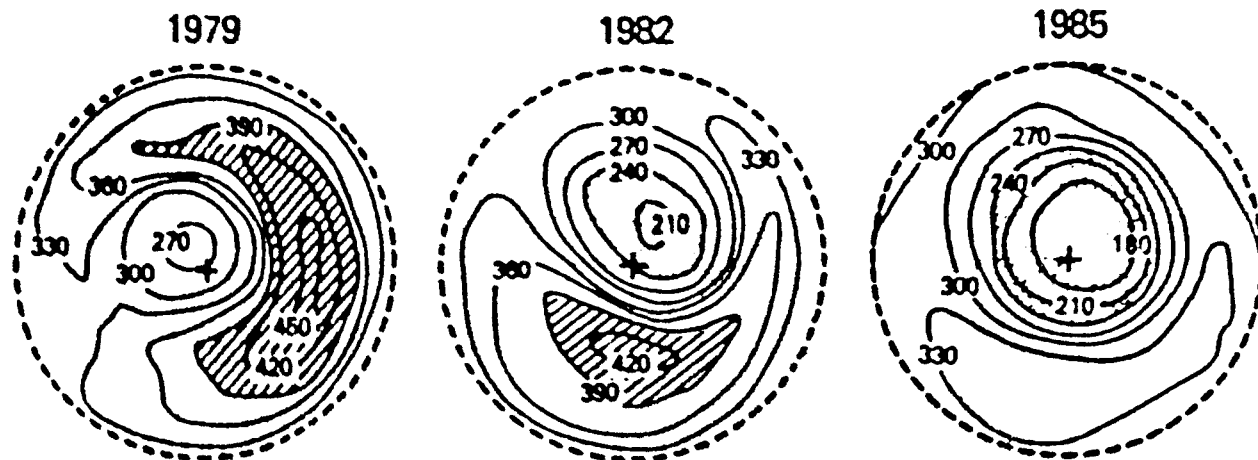


FIG. 2. October mean values of total ozone (in Dobson units [D] = 10⁻³ cm ozone at NTP) from Nimbus 7 satellite observations between the South Pole (+) and 30°S (dashed circle), after Stolarksi et al. (1986).