

REVIEW

THE EFFECTS OF RELEASES OF CHLOROFLUOROCARBONS ON
STRATOSPHERIC OZONE: THE PRESENT POSITION [1]

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SUMMARY

Current estimates of the depletion of the global content of ozone, due to the release of chlorofluoromethanes at present levels will be about 6% or less, but these are associated with changes in the vertical distributions of ozone. Recent analyses of ozone content show no evidence of depletion, consistent with the small estimates of depletion until about the present time. Relevant information is reviewed briefly.

INTRODUCTION

About ten years ago it was suggested [3] that man-made chlorofluorocarbons might, following their release in various applications, pass into the lower stratosphere and there be photolysed and cause the destruction of ozone, which absorbs UV radiation that could harm animal and plant life if it reached the Earth's surface. In response to anxieties caused by this

suggestion [4], the production of chlorofluoromethanes was, from the year 1975, held constant at about, or a little below, that obtaining in 1973 [5,6]. Estimates of the ultimate depletion of ozone due to these releases, to be attained in about 2010 to 2100, have varied from about 3% to about 20% [7,9]. Authoritative recent estimates [8,10,11,12] are about 3 to 6%. It has usually been held that such depletions would be tolerable. These estimates remain subject to uncertainties despite refinement of underlying assumptions and often involve changes in the vertical distribution of ozone [10,12].

BEHAVIOUR OF CHLOROFLUOROCARBONS IN THE ATMOSPHERE

The concentrations of trichlorofluoromethane and dichlorodifluoromethane in the troposphere continue to increase [13]. World-wide observations [14], using refined procedures, have verified, that, as commonly asserted [2,3,15], these substances have long lifetimes (60-70 y) [16] in the troposphere, consistent with their being removed mainly by passage into the stratosphere. Carbon tetrachloride, whose current rate of release [6,13] probably about 20% of that of the chlorofluoromethanes, is similarly long-lived, [15,17] and a potential contributor to the destruction of ozone, 1,1,1-trichloroethane is released in large and probably increasing amounts [6,13] has a lifetime in the troposphere of about 10 y, since much of it is destroyed by reaction hydroxyl radicals [6,13,18]. Some, however, passes into the stratosphere and may destroy ozone. Other chlorocarbons, such as chloroform, methylene chloride, trichloroethene and 1,2-dichloroethane, are destroyed so readily in the troposphere that their potential to destroy ozone in the stratosphere is negligible.

The concentrations of the chlorofluoromethanes, carbon tetrachloride, and 1,1,1-trichloroethane, fall rapidly with increasing altitude above the tropopause, consistent with the substances's passing into the stratosphere and their being photolysed rapidly [2,6,19]. Chlorine atoms, produced by these photolyses are able to destroy ozone in long chain free radical reactions, which also involve chloroxy-radicals (ClO \cdot). Chlorine atoms and chloroxy-radicals have been observed in the stratosphere [20]. Chlorine atoms react with hydrogen-containing substances (such as methane) to form hydrogen chloride, whose concentration increases with altitude above the tropopause. The substance flows towards the troposphere, where it is 'rained out' [2]. More measurements of reactive species in the stratosphere are in hand (e.g. of hydrogen chloride, hydrogen fluoride, nitrogen oxides and ozone by the Solar Mesosphere Explorer (SME)) [21]. It will be difficult because of the averaging procedures involved in most models, to interpret comparisons between observed and calculated values of concentrations at any latitude or altitude. Overall patterns of behaviour must be compared. The time-dependences of concentrations be characterised.

Nitrogen oxides (NO and NO $_2$) also catalyse the destruction of ozone. The reaction



couple the cycles of reactions involved in the destruction of ozone induced by nitrogen oxides and chlorine atoms. The formation of chlorine nitrate (ClONO $_2$), has the effect of

holding reactive species (ClO and NO_2) and reducing the rate of removal of ozone. It has been detected in the stratosphere [22]. More observations are needed (not only to dispel a doubt about the first observation [9]).

OZONE: PREDICTIONS AND OBSERVATIONS

To calculate the behaviour of chemicals in the atmosphere it is necessary to model their transport (commonly but not invariably on a one-dimensional, vertical, eddy-diffusion basis), and to specify releases or concentrations of substances of interest. Data for kinetics of reactions have been evaluated by panels of experts set up by CODATA and NASA [23], and generally, are not likely to be improved [24].

We consider models in which outputs of chlorofluoromethanes continue at levels for the years 1975-80 [26]. The last major report of the World Meteorological Organisation on ozone [7] gives estimates of the ultimate depletion of ozone in the range 5-9%. Another study, using the less recent kinetic data [23a] predicts a depletion of 5.8% [10]. One investigation, [27], which, whilst using essentially the earlier kinetic data, considers the effects of varying some rate coefficients. The predicted ultimate depletions lie in the range 6-9%. The effect of using more recent kinetic data [23b] may reduce this estimate. For example [12] a WMO estimate [7] is reduced in this way to 3.2%. The latest view of UNEP CCOL [8] is that depletions will be 3-6%. The ultimate depletions will be attained well into the next Century.

Many calculations ignore other factors, such as increasing atmospheric burdens of nitrous oxide (N_2O) [27] or of nitrogen oxides, including those from aircraft emissions [11], or of increasing burdens of carbon dioxide (associated with the 'greenhouse' effect [30]). Plausible models for such future changes predict smaller depletions of ozone, in the range 0-5% [11].

Most recent calculations [10,11,12,27,28] (except when certain factors are taken into account [11]) predict a substantial depletion of ozone at altitudes of about 40 km, which are partly compensated for by increases in the ozone layer (at about 20 km). The depletion at higher altitudes increases the transmission of UV radiation and enhances of production of ozone at lower altitudes. The ozone concentration at about 40 km must [9,28] (taking account of exceptions mentioned above), be regarded as an indicator of future changes. No such depletion has been detected [28,29,31], suggesting [12] weaknesses in some models. It is essential to understand the possible consequences of the accompanying redistribution of ozone [9], (noting that under some circumstances there may be an increase in the tropospheric burden of ozone from these effects, e.g. [11]).

Observations on the atmospheric content of ozone are numerous. Until close to the present time, expected losses of ozone should have been small [2,10,11,27,28]: indeed according to one calculation [27] (see also [28]), the ozone content should have increased very slightly. Concentrations of ozone vary greatly with time and region, making more difficult [29,31] than is sometimes admitted the detection of trends.

Statistical analyses have shown that for similar periods in the years 1970-81, the global ozone content has increased by 1.5% [32] and 0.28% [33]. The difference between these estimates, which have large standard errors, shows how difficult detection of small changes may be. A sophisticated analysis [34], which attempts to take account of factors that might affect ozone, suggests that the global content of ozone may have been increased, by about 0.1%, over the period 1970-80, but within 95% confidence limits the (small) expected depletion of ozone could be accommodated. Other factors that regulate concentrations of ozone are not adequately understood. Until they are, it will be difficult to identify the effects of chlorofluoromethanes, or to be certain whether these will lead to a dangerous fall in ozone content.

CONCLUSIONS

The more pessimistic views of the effects of chlorofluoromethanes no longer obtain, but the situation must be watched closely, and more complete understanding of some effects sought. Had the growth in output in chlorofluorocarbons been sustained [4], the predicted depletions would be greater than they are. Early precautionary steps were well justified.

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