

The small concentration of stratospheric ozone represents a balance between photochemical processes which produce it and others which destroy it. More than 50% of the destructive processes are controlled by catalytic chains involving compounds containing nitrogen (NO_x), hydrogen (HO_x) and chlorine (ClO_x). The recognition that these compounds are present in concentrations thousands of times smaller than ozone itself, is the basis for the concern that human activities might increase their concentrations and thereby lower the steady-state concentration of ozone. The first of these potential activities to be identified was the operation of fleets of supersonic aircraft, which could add considerable quantities of NO_x to the stratosphere. When such fleets failed to materialize, the focus of attention shifted to chlorofluorocarbons (CFCs) as a more imminent threat.

Computer models were used to describe the current atmosphere and to predict the effects of various scenarios of future emissions of CFCs. These models use rate coefficients, measured in the laboratory, of the chemical reactions believed to occur in the atmosphere, and highly parameterized descriptions of air motions. The validity of the models can be checked by measurements of the current concentrations of a number of atmospheric constituents.

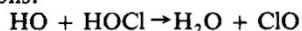
The predictions of these models for ozone depletion as a result of continuing emissions of CFCs have appeared in a number of reviews²⁻⁶ and have vacillated widely over the past 10 years. For example, take the US Academy of Sciences prediction in response to Congress's requirement for a biennial report on the health of the ozone layer. Assuming continual emissions of CFCs at their present rates, the Academy predicted in 1976 that the most probable reduction in the ozone level would eventually (in about 100 years) reach 6-7.5%. The figure was raised to 16.5% in 1979, lowered to 5% in 1982 and this year is 2-4%. Moreover, if emissions of other atmospheric gases, such as CH_4 , CO_2 and tropospheric NO also continue to increase, ozone depletion could be vanishingly small.

The main reason for these vacillations is that the stratosphere is a very promiscuous place — a great deal of coupling occurs between the NO_x , HO_x and ClO_x families. Current models incorporate about 200 chemical reactions between some 50 members of these families. Over the past 10 years a number of new reactions have been identified and new laboratory measurements have led to significant changes in the rate coefficients of many of the important reactions.

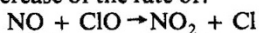
Prather *et al.*¹ claim that this system of reactions could become dramatically non-linear if the amount of Cl compounds in the stratosphere were to exceed the amount of nitrogen compounds. This could occur if the emission rates of CFCs were not

constant, but were allowed to increase exponentially. Under those conditions a 10% ozone depletion could occur within 50 years for a 5% per year increase in CFC emissions, or within 75 years for a 3% per year increase. This prediction is similar to those made by Wuebbles⁷ and in the latest Academy report⁵.

The reasons for non-linearity have been analysed by Prather *et al.* Where CFC emission is constant, the ClO_x compounds are most effective in destroying ozone above 30 km, whereas the NO_x and HO_x chains dominate in the lower stratosphere. But, with higher Cl content, the ClO_x catalytic chains can be active at much lower altitudes. The increased chlorine ties up most of the NO_x in the form of non-reactive ClNO_3 . This, in turn, increases the amount of HO because NO_x reactions are the major sinks for HO radicals. The decrease in NO_x and increase in HO produce a more than linear increase in ClO, mainly because of increased rate of the reactions:



and a decrease of the rate of:



When chlorine compounds exceed the nitrogen compounds, ClO increases three times faster than total chlorine and becomes the most effective ozone destroyer down to altitudes of 20 km.

The current chlorine content of the stratosphere is 3 parts per 10^9 by volume (mixing ratio 3×10^{-9}) and would reach the NO_x concentration of 13 parts per 10^9 in 50 years if CFC emissions were to increase at a rate of 5 per cent per year.

Prather *et al.* do not discuss the likelihood of such CFC increases. The production rates of the two major CFCs, CFCl_3 and CF_2Cl_2 , have not changed significantly over the past six years⁸. During that period, the production of these compounds for use as aerosol propellants has been reduced by controls in several countries from 56% to 34% of the total propellant production (at least by those companies that have reported figures). On the other hand, the non-aerosol use of these compounds has increased by 4.0% per year over the period 1976-1982 in the same companies, and by as much as 6.5% per year worldwide⁹. Other chlorine containing compounds such as CCl_4 and CH_3CF_3 make smaller but significant contributions to stratospheric chlorine. Projections for the future emissions of all the human-produced chlorocarbons is extremely speculative and will depend on both economic and social factors. An increase of 3-5% per year into the next century is unlikely but not beyond the realm of possibility.

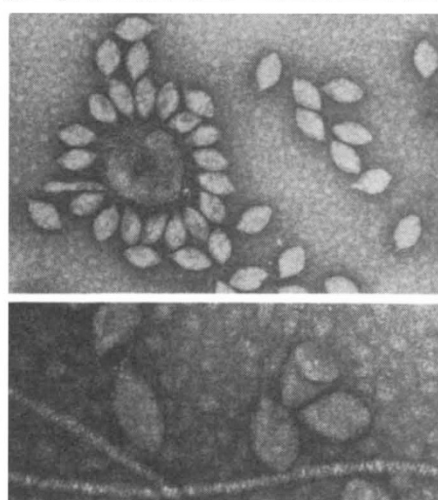
The authors have also considered the effects of increases in emissions of some other gases. Atmospheric concentrations of both CH_4 and N_2O have been observed to be increasing. Continuation of these trends would delay the time when the dramatic effect of CFCs would occur. On

the other hand, increased releases of bromine compounds, used largely as fire extinguishers and fumigants, would lead to additional ozone depletion. However, increased CO_2 emissions, not considered by the authors, which raise the tropospheric temperature but lower the stratospheric temperature, would increase the rate of ozone production and decrease the rate of its destruction.

For their calculations the authors have used a one-dimensional model which treats air motions only in the vertical direction, and not in latitudinal or longitudinal directions. Horizontal motions are particularly important in the lower stratosphere where the effects discussed by these authors occur. Nevertheless the potential effects are sufficiently serious to warrant careful consideration. Fortunately there is still time to monitor the increase in stratospheric chlorine and bromine before effects occur. □

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2. National Research Council *Halocarbons: Effects on Stratospheric Ozone* (National Academy of Sciences, Washington, D.C. 1976).
3. National Research Council, *Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport* (National Academy of Sciences, Washington, D.C. 1979).
4. National Research Council, *Causes and Effects of Stratospheric Ozone Reductions: An Update* (National Academy of Sciences, Washington, D.C., 1982).
5. National Research Council, *Causes and Effects of Changes in Stratospheric Ozone: An Update* (National Academy of Sciences, Washington, D.C., 1984).
6. *WMO Global Ozone Research and Monitoring Project Rep. No. 11: The Stratosphere 1981: Theory and Measurements* (eds. Hudson, R.D. *et al.*) (World Meteorological Organization, Geneva, 1982).
7. Wuebbles, D.J. *J. geophys. Res.* 88, 1433 (1983).
8. *World Production and Release of Chlorofluorocarbons 11 and 12 through 1981*, Report FFP 83-F (Chemical Manufacturers Assoc., Washington, D.C., 1982).
9. Wuebbles, D.J., MacCracken, M.C. & Luther F.M., *A Proposed Reference Set of Scenarios for Radiatively Active Constituents*, Report No. DOE/NBB-0066, (Department of Energy, Washington, D.C. 1984).

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Viral particles produced by the archaebacterium, *Sulfolobus acidocaldarius*. The 100×60 nm particles, many of which can be seen attached to bacterial remains (above), are generally lemon-shaped but, perhaps when halved, occasionally appear bullet-shaped (below). (From Martin, A. *et al.* *EMBO J.* 3, 2165; 1984.)