Reports

Freon Consumption: Implications for Atmospheric Ozone

Abstract. *Freons are a potential source of stratospheric chlorine and may indirectly cause serious reductions in the concentration of ozone. The reduction could be as large as 3 percent by 1980, or 16 percent by 2000, if Freon consumption were to grow at 10 percent per year. Even if Freon use were terminated as early as 1990, it could leave a significant effect which might endure for several hundred years.*

Ozone is an important minor constituent of the atmosphere, formed photochemically in a complex sequence of reactions initiated by dissociation of molecular oxygen (*1*). The gas is removed by reaction with atomic oxygen, and the net rate of this reaction, and consequently the abundance of ozone, may be critically affected by the presence of trace quantities of OH (*2*), NO (*3*), and ClO (*4, 5*).

Nitric oxide plays a major role in the normal stratosphere (*3*). It is formed by reactions involving N_2O

$$O(^1D) + N_2O \rightarrow 2NO$$

where $O(^1D)$ is an excited oxygen atom, and contributes to ozone removal by reaction sequences such as

$$NO + O_3 \rightarrow NO_2 + O_2$$

followed by

$$NO_2 + O \rightarrow NO + O_2$$

The mixing ratios of NO and NO_2 near 30 km are of order 2×10^{-9} (*6*) and 5×10^{-9} (*7*), respectively.

There has been concern in recent years that large fleet operations of supersonic aircraft (SST's) could add significant quantities of NO to the normal stratosphere, with consequent reduction in the abundance of O_3 and an associated rise in the flux of ultraviolet radiation reaching the earth's surface (*3*). According to one estimate (*8*), a fleet of 320 Concordes operating for 7 hours a day at 17 km could reduce O_3 by 1 percent. Larger fleets, such as those projected by Grobecker (*9*) for 1995 to 2025, could reduce ozone by more than 20 percent in the year 2000 (*10*). These projections assume an affluent world in which air travel is a larger percentage of total economic activity than it is currently in the United States, with most of the longer flights in supersonic planes. We shall argue here that chlorine, released into the stratosphere by photolysis of various chlorofluoromethanes (*11–13*) may be comparably serious. The ultimate reduction in O_3, effected by reaction sequences such as

$$Cl + O_3 \rightarrow ClO + O_2$$

followed by

$$ClO + O \rightarrow Cl + O_2$$

could be as large as 13 percent, if production of CF_2Cl_2 and $CFCl_3$ were to continue at its present rate. Allowing for reasonable growth in the Freon industry, ~ 10 percent per year, the reduction in O_3 could be 2 percent by 1980 and, if left unchecked, could grow to the disastrous level of 20 percent by the year 2000.

We shall investigate six conceptual models for future global consumption of Freon. Model A assumes that consumption continues indefinitely at 1972 rates, approximately 2×10^5 metric tons per year for Freon 11 ($CFCl_3$) and 3×10^5 metric tons per year for Freon 12 (CF_2Cl_2). Models B to D consider an initial growth rate of 10 percent per annum. A somewhat larger rate, approximately 21 percent per annum, is adopted for models E and F. The initial growth rate is allowed to continue indefinitely in models D and F, while consumption of Freons is assumed to end abruptly in models B, C, and E after the years 1978, 1995, and 1987, respectively (*14*).

According to Molina and Rowland (*12*), Freons are removed from the atmosphere by photolysis at altitudes in excess of 25 km. The primary reactions are

$$h\nu + CFCl_3 \rightarrow CFCl_2 + Cl$$

and

$$h\nu + CF_2Cl_2 \rightarrow CF_2Cl + Cl$$

where $h\nu$ is a photon. Subsequent chemistry leads to release of additional chlorine, and for present purposes we assume that all of the available chlorine is eventually liberated to form compounds such as HCl, ClO, ClOO, and Cl_2. We shall refer to these compounds collectively as odd chlorine. Odd chlorine, formed in the stratosphere by photolysis of Freon, is transported downward and removed from the atmosphere, mainly by heterogeneous processes in the lower troposphere (*15*).

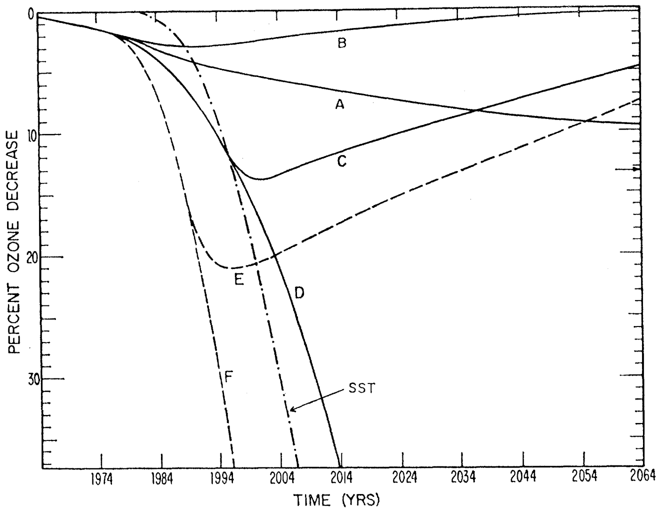

Fig. 1. Reductions in global ozone computed for six models of Freon use. Emissions of CF_2Cl_2 and $CFCl_3$ were assumed to be 3.5×10^5 and 2.2×10^5 metric tons, respectively, in 1972. The growth rates for each of the Freons are taken as 10 percent per year (7-year doubling) for models B, C, and D; 22 percent per year (3.5-year doubling) for E and F; and production held constant for A. In models D and F growth continues indefinitely, but in models B, C, and E Freon emissions are assumed to cease abruptly in 1978, 1995, and 1987, respectively. For comparison, we show ozone reductions due to SST operations calculated with our earlier model (*8*) and Grobecker's (*9*) estimate for the upper bound on NO injection by future fleets. The arrow indicates steady-state conditions approached by model A at long times.

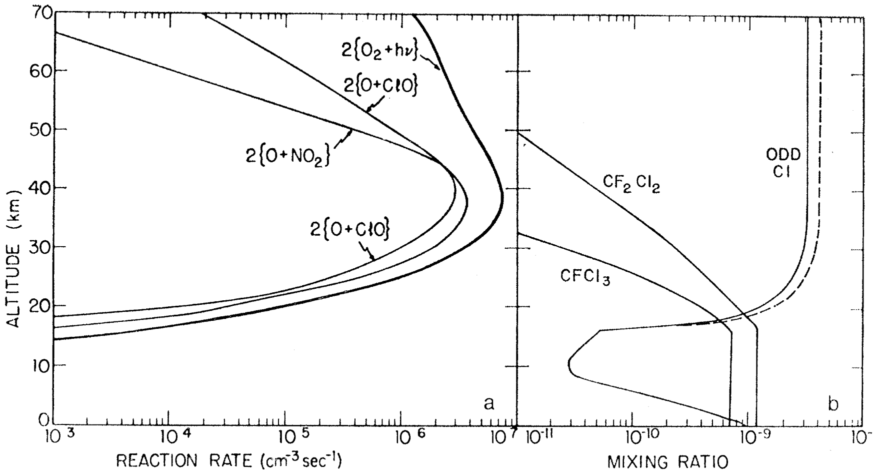

Fig. 2. (a) Production rates for odd oxygen from photolysis of O_2 (bold line) together with loss rates due to reactions of O with ClO and NO_2 (model C, 1995). Above 45 km, removal of odd oxygen is dominated by reactions of O with O_3, OH, and HO_2. (b) Vertical profiles of $CFCl_3$ (Freon 11), CF_2Cl_2 (Freon 12), and odd chlorine are given for model C in 1995. In that year Freon production is assumed to end, and the dashed curve shows odd chlorine concentrations calculated for 2001. Model C predicts a stratospheric concentration of HCl consistent with Farmer's (*20*) upper limit in 1973.

The height distribution and time variability of O_3 was obtained by numerical solution of a set of time-dependent, one-dimensional, diffusion equations (*16*). The approach was shown elsewhere (*8*) to give a good representation of the undisturbed atmosphere, with predicted profiles for O_3 showing excellent agreement with the available observational data. The results in the present instance are summarized by Figs. 1 and 2. Figure 1 shows reductions in global ozone predicted to take place as a function of time if Freon usage follows the patterns assumed in models A to F. Figure 2 shows some details of the results obtained with model C. Figure 2a shows volume production and loss rates for odd oxygen and indicates that the catalytic effects of odd chlorine could be comparable to those of NO_x by 1995. Concentrations of $CFCl_3$, CF_2Cl_2, and odd chlorine, computed for the year 1995, are shown in Fig. 2b, which also illustrates the continued growth in the concentration of stratospheric odd chlorine which is expected to take place even after termination of Freon usage. The continued growth is a consequence of the relatively long lifetimes, 45 and 68 years, of atmospheric $CFCl_3$ and CF_2Cl_2, respectively (*17*).

The results in Figs. 1 and 2 raise serious questions which must be addressed as a matter of urgent priority by those responsible for public health and environmental policy. On the basis of best current models for the stratosphere and contemporary knowledge of Freon chemistry, there are reasons to believe that present consumption levels of Freon may pose serious problems for atmospheric ozone. There may be significant reductions in ozone, accompanied by important increases in the intensity of ultraviolet radiation, with a variety of associated biological impacts (*18*). We note particularly the long time constants which appear to be associated with the disturbance. A decision reached as early as 1978 (model B) to eliminate Freon use could still allow for a reduction in ozone which might grow to a value as large as 3 percent by 1990. If the decision to eliminate Freon were postponed until 1995 (model C), the reduction in ozone could exceed 10 percent, and would be significant for as long as 200 years after termination of Freon use.

Note added in proof: Since this report was written, we have learned of measurements by Lovelock (*19*) of atmospheric CCl_4 and also measurements by Lazrus (private communication) which may be interpreted in terms of stratospheric HCl. The HCl data are larger by about a factor of 2 than values predicted by the present model. The model would give good agreement with Lazrus's data if one allowed for the additional chlorine contribution due to photocomposition of CCL_4.

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→ A. J. Grobecker [*Acta Astronaut.* **1**, 179 (1974)] assumes optimistic (larger) demand for air travel and does not allow for possible reduction of NO emissions in future engine designs.
10. J. M. English (private communication) estimates "most probable" air travel demand as one-half to one-quarter of that presented by Grobecker (*9*).
11. The role of Freons as a source of stratospheric chlorine and their possible effect on ozone were first noted in an important paper by Molina and Rowland (*12*). More recent contributions by P. J. Crutzen [*Geophys. Res. Lett.* **1**, 205 (1974)] and Cicerone *et al.* (*13*) confirm the potential hazard to ozone.
→ M. Molina and F. S. Rowland, *Nature (Lond.)* **249**, 810 (1974).
13. R. J. Cicerone, R. S. Stolarski, S. Walters, *Science* **185**, 1165 (1974).
14. R. L. McCarthy, technical manager of the Freon Products Laboratory of Dupont, suggested that a value of 10 percent per year would be a reasonable projection for the growth of world Freon production and thought that this value could be maintained for the indefinite future. The 10 percent figure is somewhat less than the growth rate experienced between 1960 and 1972. In that period the growth rate for Freon 11, used primarily as an aerosol propellant, averaged roughly 22 percent per annum, a value adopted by Cicerone *et al.* (*13*) for total Freon and used also in models E and F of the study reported here. The expansion of Freon production is currently inhibited by a temporary shortage of chlorine, but ongoing construction of new plants is expected to soon alleviate the problem.
15. The relative abundance of various forms of odd chlorine is determined mainly by chemical processes, treated here by using the model described by Wofsy and McElroy (*4*), with one important modification. The rate constant for the reaction $OH + HCl \rightarrow H_2O + Cl$ is assumed here to have the value 2.0×10^{-12} exp$(-313/T)$ cm^3 sec^{-1} determined by M. S. Zahniser, F. Kaufman, J. G. Anderson [*Chem. Phys. Lett.* **27**, 507 (1974)], which is larger by a factor of 2 at stratospheric temperatures than the rate constant adopted in the earlier work. The present model therefore gives a relatively larger abundance of ClO for a given concentration of odd chlorine. The efficiency of chlorine as a catalyst in ozone recombination is increased accordingly, and the present calculations give somewhat larger reductions in ozone than might be derived using the results presented in the earlier study (*4*). Heterogeneous removal of odd chlorine in the troposphere was described by a first-order rate constant, set equal to 3×10^{-6} sec^{-1} between 0 and 9 km and taken equal to zero elsewhere. Dissociation of $CFCl_3$ and CF_2Cl_2 was treated by using cross sections measured by M. J. Molina and F. S. Rowland (private communication). Dissociation rates were computed in a manner which allowed properly for the diurnal variation of solar illumination.
16. The computations allowed for time-dependent vertical flow of N_2O, NO_x, CH_4, CO, O_3,

CF_2Cl_2, $CFCl_3$, and odd chlorine. Transport was treated by using the expedient concept of eddy diffusion. Diffusion coefficients were taken from (*8*) but were adjusted upward by a factor of 2 between 16 and 20 km in order to improve the agreement with observational data for NO. The chemical model combined lists of reactions given in (*4*) and (*8*).

17. The lifetime is obtained by dividing the total quantity of atmospheric Freon by its corresponding production or destruction rate under steady-state conditions.
18. A discussion of possible biological effects is given in K. Smith *et al.*, *Biological Impacts of Increased Intensities of Solar Ultraviolet Radiation* (National Academy of Sciences, Washington, D.C., 1973). We should caution that the papers which have appeared to date discussing Freon and its effects on ozone, including the present contribution, are preliminary in nature. They do not establish that the effects discussed here will necessarily ensue from continued Freon usage. They develop a case, however, for serious concern and emphasize the need for intensive further investigation. We have not explicitly allowed for possible removal of stratospheric chlorine by heterogeneous reactions, and we have assumed that the Freon lifetime is set by photolysis. If additional removal processes could be identified for Freon, or if additional sinks could be identified for stratospheric odd chlorine, the atmospheric and biological impacts of Freon would be reduced accordingly.

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21. We acknowledge valuable discussions with M. Molina, F. S. Rowland, and R. L. McCarthy during preparation of this manuscript. Supported by NSF grant GA-33990X and NASA grant NG 2031.

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Earthquake Prediction: Modeling the Anomalous V_P/V_S Source Region

Abstract. *Soviet observations of anomalously low values of the ratio of the compressional wave velocity to the shear wave velocity* (V_P/V_S) *in a restricted volume around the locus of a future earthquake are duplicated by models based on the dilatancy hypothesis. In nature the cracks that cause the dilation may be oriented, leading to anisotropic seismic wave propagation in the anomalous region. The models show that vertical cracks are most effective in producing the observed effects, but that a slightly higher density of randomly oriented cracks will yield similar effects. The premonitory observations at Blue Mountain Lake, New York, are also duplicated by the models. These models demonstrate that* V_P/V_S *measured at the surface is not that of the anomalous zone, but is related to it by a transfer function, involving the shape and velocity gradient of the zone boundary.*

Soviet seismologists (*1, 2*) found significant delays in P-wave arrival times relative to S-wave arrival times for foreshocks that preceded large earthquakes in the Garm region of the Soviet Union (*3*). These observations were confirmed in upstate New York and in southern and central California (*4*). They have been explained by dilatancy (*5*), and many related phenomena have been correlated as a basis for earthquake prediction (*6*). One aspect of the Soviet observations has not yet been dealt with quantitatively—the fact that the anomalous region is small compared to the dimensions of the seismic array. In this report we deal only with this problem of how a localized anomalous region can produce the distant effect.

The Russians discovered that travel times were anomalous only for small earthquakes occurring within a radius of 5 to 10 km of the focus of a subsequent large earthquake. This was revealed in "Wadati" diagrams (*7*) of these precursor shocks constructed by Semenov (*1*). We attacked the problem of whether a suitably small dilatant region can produce similar Wadati diagrams.

Dilatancy is believed to be due to microfractures created or enlarged as the stress increases in a rock before fracture (*8*). These cracks may be expected to have a preferred orientation, in which case V_P would vary with the direction of propagation. We use Garbin and Knopoff's analysis (*9*) of elastic wave propagation through a medium permeated by circular cracks which are small compared to the seismic wavelength. For cracks of random orientation

$$\left(\frac{V_P{}^0}{V_P}\right)^2 = 1 + \frac{Na^3}{v}\left(\frac{262}{105}\right) \qquad (1)$$

where $V_P{}^0$ and V_P are the P-wave velocities in the uncracked and cracked regions, respectively, and N is the number of cracks of radius a in the volume v. For parallel cracks

$$\left(\frac{V_P{}^0}{V_P}\right)^2 = 1 + \frac{Na^3}{v}\left(\frac{2}{3} + \frac{40}{7}\cos^2\theta - \frac{8}{21}\cos^4\theta\right) \qquad (2)$$

where θ is the angle between the geometric ray and the crack normal. For cracks with normals randomly distributed in a plane

$$\left(\frac{V_P{}^0}{V_P}\right)^2 = 1 + \frac{Na^3}{v}\left(\frac{2}{3} + \frac{20}{7}\cos^2\theta - \frac{1}{7}\cos^4\theta\right) \qquad (3)$$

where θ is the angle from the ray to the plane normal. In a thrust fault region like Garm, one might expect the greatest (compressive) principal stress to be horizontal and the least to be vertical, leading to horizontal extension fractures. Hence, Eq. 2 would be appropriate, with θ measured from the horizontal (that is, V_P least in the vertical direction). In many thrust regions, however, the observed joints and microcracks are predominantly vertical, because of warping of the thrust near the surface (*10*). In this case Eq. 3 applies, with θ measured from the vertical (V_P least in the horizontal direction). All three cases are explored in our model. We assume that V_S remains unchanged; the propagation of S waves, which depends on polarization, is beyond the scope of the present study. In real materials V_S is also reduced by dilatancy, but much less than V_P. We believe that a particular V_P reduction in our model corresponds to a somewhat greater V_P reduction in nature.

The total volume of cracks is $v_c \simeq 3Na^3/A$, where A is the crack aspect ratio. In all cases, we assumed $Na^3/v =$

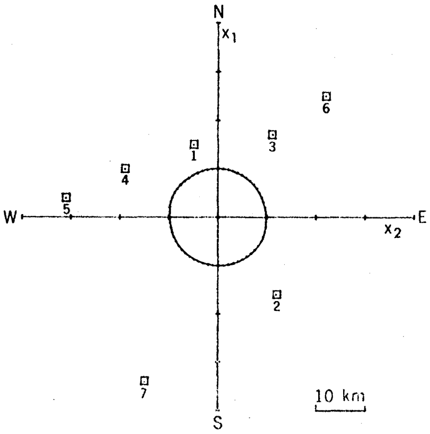

Fig. 1. Map of the seven seismic stations used by Semenov (*1*) in obtaining anomalous V_P/V_S values before large earthquakes near the center of the coordinate system. These stations are used in the models in this report, with an anomalous region centered on the origin. The circle of radius 10 km is the projection of models B and E (Fig. 2), and is approximately the size ascribed to the anomalous region by the Soviet scientists (*1, 2*).