OZONE PUZZLES—WILL A HOLE OCCUR OUTSIDE POLAR REGIONS ?

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The importance of the ozone layer in the stratosphere has long been known and is only briefly explained here. During the 1970s theories were developed which implicated man-made organic chlorine chemicals in the progressive destruction of the ozone layer. However, until the last few years these theories were in some difficulty because there were no real measurements of ozone being depleted, let alone any depletion being attributable to anthropogenic chlorine. The recent Ozone Trends Panel report has gone a long way towards clarifying the relationship between chlorine and ozone destruction.

The recognition of the Antarctic ozone hole in 1985 was a surprise. The hole develops very rapidly each spring, and was soon shown to be a lower stratosphere phenomenon. This did not fit the established theories for ozone destruction by chlorine which involve catalytic chlorine action in the upper stratosphere.

Intensive experimental work in and under the ozone holes of 1986 and 1987 established the direct involvement of chlorine and also some new heterogeneous chemistry for ozone destruction depending on the seasonal formation of polar stratospheric clouds.

The question then arises: Could these rapid heterogeneous reactions ever lead to major ozone depletion away from the polar regions? Recent theoretical and experimental work by Hofmann and Solomon indicates that while high concentrations of chlorine remain in the stratosphere, we are vulnerable to severe ozone depletion in the aftermath of a major volcanic eruption, by way of heterogeneous reactions involving sulphuric acid droplets.

Can international treaties such as the Montreal Protocol prevent a catastrophy of this sort? Much broader international acceptance of the Protocol is required and the cutbacks of ozone depleting substances must be much greater than those presently in the agreement, before there can be long term stability for the ozone layer.

THE NATURAL OZONE LAYER

Solar ultraviolet radiation, which is harmful to most animal and plant life, is largely filtered out by the atmosphere. The main ultraviolet absorber is ozone.

Although ozone is found throughout the atmosphere, about 90% resides in the lower part of the stratosphere, a distinct layer of the atmosphere between 15 and 50 kilometres up.

The existence of the ozone layer is the result of a balance between the amounts created and destroyed. Both these processes occur naturally in the upper atmosphere. In the upper stratosphere, at altitudes of about 50 km, oxygen molecules, O_2, are destroyed by high energy ultraviolet radiation and can reform as ozone, O_3. This ozone has an appreciable lifetime in the atmosphere, until it too succumbs to ultraviolet radiation, usually in the lower stratosphere, and reforms the common oxygen gas. The amount of ozone over any one place depends not only on this photochemical balance, but also on the stratospheric climate, the winds that disperse the ozone. These processes cause quite large weekly and seasonal variations. For example there is about 50% more ozone over New Zealand in spring than in autumn. The global distribution is shown in Figure 1, which clearly shows the lower natural ozone concentrations in the tropics and higher values towards the poles.
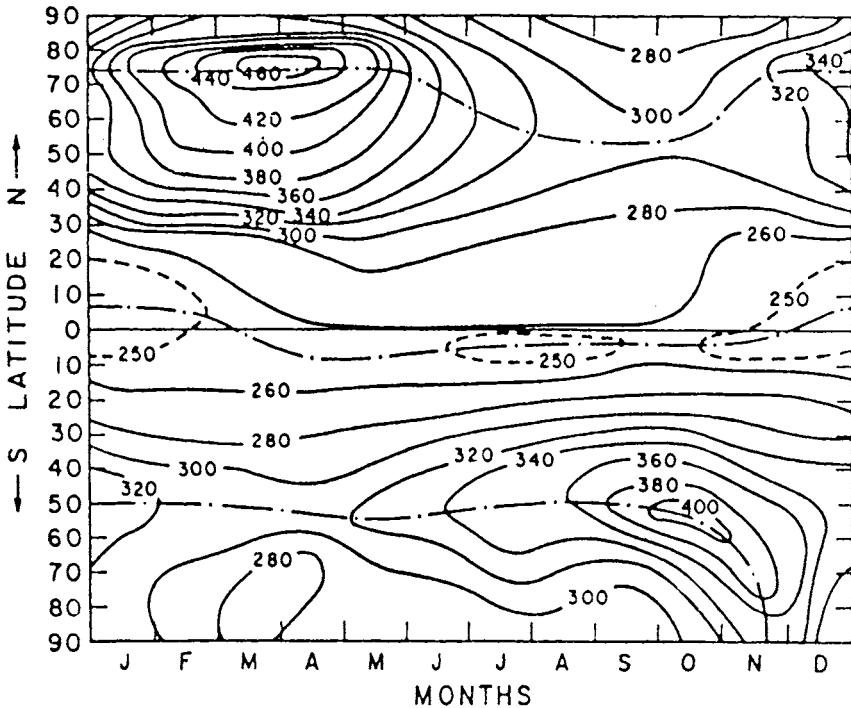

Fig. 1. Latitude-season characteristics for total ozone, 1958-1977 (London, 1980).

The stratosphere itself is dependent on ozone for its existence. The energy absorbed by the ozone in the course of the creation and destruction of its layer warms the surrounding atmosphere, so that as one passes upwards through it the temperature

actually increases, it is a temperature inversion. This inverted layer, which is the stratosphere, is very resistant to vertical movements of air, and so acts as a cap on the turbulent weather processes in the troposphere below. Thus the balance established by these natural stratospheric chemistry processes is of critical importance to our climate at the surface.

OZONE DESTRUCTION BY CHLOROFLUOROCARBONS

It was not appreciated until the 1970s that the ozone layer might be vulnerable to anthropogenic emissions of gases, even from the surface. A particular gas emitted may be chemically very inert in the troposphere, but any molecule can be decomposed by solar ultraviolet radiation if it survives long enough to be transported high enough into the stratosphere to encounter ultraviolet radiation of sufficiently short wavelength. Molecular fragments resulting can take part in reaction chains involving ozone, so interfering with the natural processes of ozone creation and destruction.

Many of these reaction sequences are now well known (e.g. WMO, 1986) and one of the most important is that from the breakdown of stable organic chlorine compounds, mainly chlorofluorocarbons (CFCs), where an active chlorine atom can catalytically destroy ozone:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

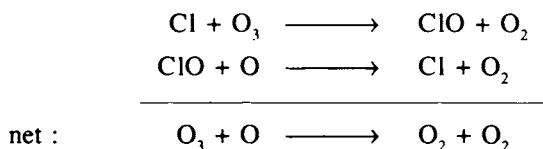$$\text{net :} \quad O_3 + O \longrightarrow O_2 + O_2$$

Figure 2 shows this interference with the natural ozone cycle in a simplified format. First we have the natural ozone cycle converting oxygen between its two forms(I). When a CFC molecule encounters the high energy ultraviolet radiation in the upper stratosphere, a chlorine atom is split off (II). The chlorine interacts with ozone to form chlorine monoxide (III) which subsequently reacts with an oxygen atom to regenerate the free chlorine atom (IV). The net effect of this reaction sequence is the loss of ozone. The chlorine atom is then available to initiate ozone destruction once more.

Laboratory work indicates that one chlorine atom can destroy about 100,000 ozone molecules by this process before it is itself destroyed, usually by encountering a molecule such as methane with which it reacts. We also note that this chlorine catalysed destruction of ozone is dependent on the presence of sufficient single oxygen atoms. This limits this reaction to occurring in the upper stratosphere.

In spite of this theory being well established in the chemical literature since 1974, there has always been doubt about it, as there remain possibilities of interfering reactions or feedbacks which are not yet appreciated. Thus the report of the Ozone Trends Panel (WMO, 1989) is of particular significance. This is the first broadly-based scientific consensus to identify a depletion of ozone over much of the globe that is beyond what is attributable to the natural variations such as the solar cycle,
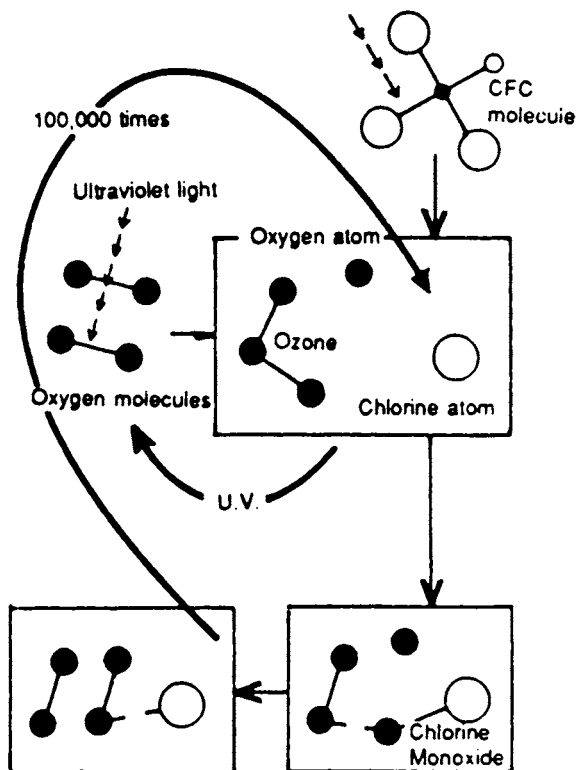
Fig. 2. A simplified representation of the interference of chlorine in the natural reactions of stratospheric ozone.

TABLE 1: Percent Total Ozone Change for 1969-1986, from the International Dobson Instrument Network [Ozone Trends Panel, WMO (1989)]

	Latitude band		
	53-64 deg N	40-52 deg N	30-39 deg N
Winter average	−6.2±1.5	−4.7±1.5	−2.3±1.3
Summer average	+0.4±0.8	−2.1±0.7	−1.9±0.8
Annual average	−2.3±0.7	−3.0±0.8	−1.7±0.7
(Uncertainties represent one standard error)			

the quasi-biennial oscillation, and volcanic activity. The depletions identified for the period 1969-1986 by the Panel are summarised in Table 1.

The Ozone Trends Panel has reported only for latitudes between 30 and 64 degrees North, on account of the lack of confidence in data for other regions. The

Panel noted that it appeared that Southern Hemisphere depletion was at least as great through the same period, and that the depletions determined for high latitudes and in winter were generally greater than predicted by the best regarded theoretical models.

THE OZONE HOLE

The first reports of severe depletion of ozone from the Antarctic (Farman *et al.*, 1985) took the scientific community by surprise. The knowledge of stratospheric catalytic cycles at that time did not allow for the rapid disappearance of ozone in spring over such a wide region, and for a time it seemed that there may have been other mechanisms for this "hole" formation, not involving chlorine chemistry in a major way.

However, the first season of intensive study on this phenomenon, in the austral spring of 1986, revealed that although only about a third of the total ozone column was vanishing from over the Antarctic continent, in a layer between 12 and 20 km up (the very lowest parts of the stratosphere), virtually all ozone was being destroyed during September (Hofmann, 1987). This could not possibly have been by the established mechanisms for ozone destruction by chlorine, as outlined above which are known to require upper stratospheric conditions of short wavelength solar ultraviolet radiation and relatively high concentrations of unattached oxygen atoms. This mechanism does not destroy ozone very rapidly, particularly because there are important interferences from other species, e.g. NO_x, which constrain it.

The ozone hole is now a well established annual phenomenon (e.g. UNEP/WMO, 1989), and many of its characteristics are understood as the result of the intense efforts to study it, especially with the Airborne Antarctic Expedition of spring 1987. The 1987 work coincided with the deepest hole so far, with virtually all ozone between 12 and 20 km up disappearing from mid-September until well into November.

HETEROGENEOUS CHEMISTRY

In order to understand the processes that lead to gas phase chlorine compounds destroying gas phase ozone over Antarctica in spring, we must introduce some heterogeneous chemistry, with solid or liquid particles involved. The airborne experiments in Antarctica in spring 1987 established the importance of some very unusual chemistry.

In the polar stratosphere, the important solid surface is provided by ice crystals, in the form of "polar stratospheric clouds". Such clouds will only condense in an exceptionally cold stratosphere, colder than –80 degrees C. This condition is reached only within the polar stratospheric vortex, an Antarctic circulation feature which confines Antarctic stratospheric air to high latitudes right through winter and spring, where the air can cool in the polar night without mixing back to warmer regions.

Throughout the stratosphere, much of the chlorine is in the form of HCl and $ClONO_2$, relatively inactive compounds, which are referred to as "reservoir" species.

In order for a reaction to occur, the chlorine must be released to take up a more reactive form, and active nitrogen oxides must be suppressed to reduce the occurrence of
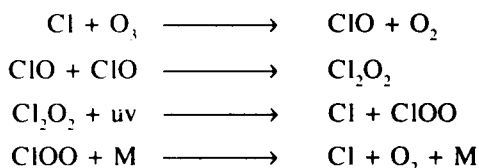
$$Cl + NO_2 \longrightarrow ClO + NO$$
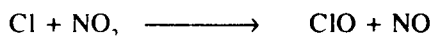
which does not involve ozone depletion. The presence of an ice surface on which HCl is absorbed allows:

$$ClONO_2(g) + HCl(s) \longrightarrow Cl_2(g) + HNO_3(s)$$
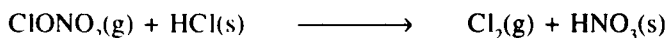
which can serve the dual purpose of releasing the chlorine in an active form, and tying up active nitrogen oxides as the reservoir species HNO_3.

Experiments in 1987, and recent laboratory work (e.g. Molina *et al.*, 1987) have confirmed the enhanced activity of HCl when absorbed on ice crystals, and also the existence of nitric acid trihydrate as part of polar stratospheric clouds.

Thus in the Antarctic spring, in the presence of polar stratospheric clouds and the returning sunlight, active chlorine is available to take part in chemical and photochemical reaction chains. The catalytic cycle outlined above for lower latitudes cannot account for the huge ozone loss in the lower stratosphere and several other cycles seem to be implicated. For example

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + ClO \longrightarrow Cl_2O_2$$
$$Cl_2O_2 + uv \longrightarrow Cl + ClOO$$
$$ClOO + M \longrightarrow Cl + O_2 + M$$

There are other similar cycles which also appear to be active, some of which involve bromine, but the idea is the same. Chlorine destroys ozone catalytically, ClO is an intermediate, and single oxygen atoms are not required.

The 1987 airborne work in Antarctica confirmed a very strong anticorrelation between ozone and ClO amounts, and also confirmed the exceptionally low concentrations of active nitrogen. Chlorine chemistry is definitely the leading contributor to the formation of the annual Antarctic ozone hole.

Thus as a result of the Ozone Trends Panel and our understanding of the ozone hole mechanisms, we can see that stratospheric chlorine is the main culprit, and we know that most of this comes from anthropogenic emissions of CFCs.

A recent evaluation of the 1987 ozone hole experimental studies seems to indicate that there may yet be other mechanisms involved to account for observations of some rapid ozone destruction outside the ozone hole and also earlier in the season (Proffitt *et al.*, 1989).

Figure 3 shows how chlorine has been building up over the past few decades. From a pre-industrial level of about 0.6 ppb (parts per billion) we have steadily increased the concentration to over 3 ppb, with a continuing increase of about 5% per year.
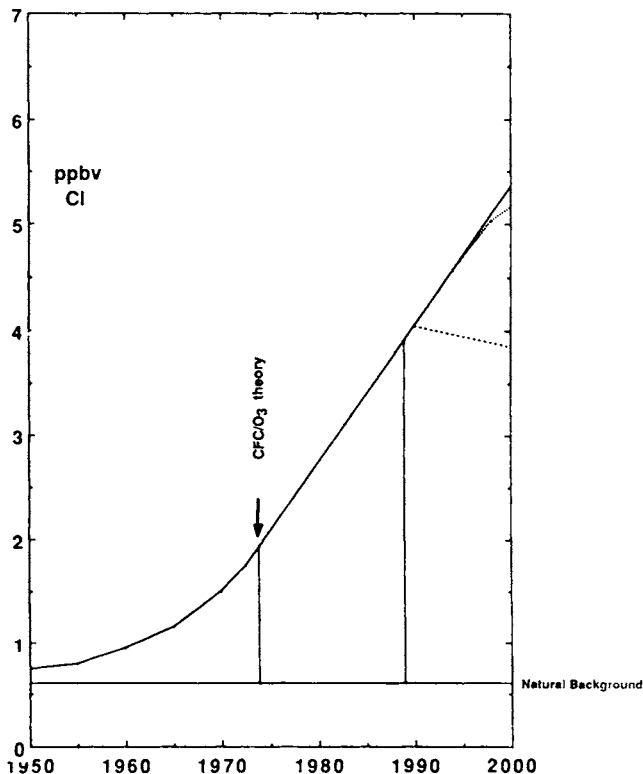
Stratospheric Chlorine

Fig. 3.   The solid line shows estimated stratospheric chlorine concentration with no controls over CFC emissions, with the dotted line showing the projected influence of the present Montreal Protocol. The dashed line is an approximation of the effect of an immediate halt to all chlorine emissions.

OZONE HOLES ELSEWHERE ?

In the paragraphs above we have seen that there are two distinct sets of mechanisms for destruction of ozone by CFCs.

First there is the "standard" mechanism, outlined first, occurring mainly in the upper stratosphere, destroying ozone quite slowly, and giving rise to the trends reported on by the Ozone Trends Panel. Then there is the "ozone hole" mechanism, occurring low in the stratosphere, requiring polar statospheric clouds and acting very fast.

Under what conditions could the rapid "ozone hole" reaction occur away from poles? The main requirement appears to be a suitable reaction surface in the lower stratosphere to tie up the active forms of nitrogen and to release chlorine from its inactive reservoirs.

As a result of the work on the Antarctic ozone hole, it is now widely accepted that reactions on the surfaces of particles can have a major influence on stratospheric trace gas composition. In particular heterogeneous reactions can affect the partitioning of chlorine and nitrogen species between active and less active species. As explained above, this can happen in the extreme cold of the polar winter and spring stratosphere where the formation of water or nitric acid clouds can occur.

Although sufficiently cold temperatures can occur in the equatorial stratosphere, it appears that insufficient active chlorine can become available there because the air resides there for too short a time. In mid-latitudes, however, there is another possibility. Throughout the lower stratosphere there is an aerosol layer, the "Junge" layer, composed mainly of sulphuric acid droplets that have arisen from tropospheric SO_2 and COS rising into the stratosphere, oxidising and hydrating. This aerosol layer may be vastly increased in concentration after a large volcano injecting sulphur gases into the lower stratosphere. The droplets added through volcanic action are postulated to provide the reaction surface to enable the release of active chlorine, the suppression of nitrogen dioxide and the consequent rapid destruction of ozone, that is, an ozone hole phenomenon at mid-latitudes. The interactions between these particles have been modelled and supporting laboratory studies have recently been put forward by Hofmann and Solomon (1989).

Since the build-up of chlorine in the stratosphere there have been no very large volcanic eruptions. The largest eruption of the past decade, El Chichon in 1982, was not large enough to cause a major drop in ozone levels globally. However, there was a significant reduction in total ozone in mid-latitudes of both hemispheres during the year following El Chichon which is consistent with the Hofmann and Solomon models and which has not been explained by any other mechanism. Larger volcanoes, such as Krakatoa (1883) and Tamboura (1815) put much more material into the stratosphere and we could expect a volcano of such a size perhaps about once a century. A Krakatoa-sized volcano could possibly lead to the destruction of much of the ozone layer over the mid-latitudes, for months or even years.

If the Hofmann and Solomon scenario is reinforced by further laboratory and field experiments, it appears that while sufficient chlorine remains in the stratosphere for an "ozone hole" type of reaction to occur we are vulnerable to catastrophic ozone destruction in mid-latitudes by a large volcano. Whatever we do, stratospheric chlorine is unlikely to sink below 2ppb in the next century, and will probably last longer because of continuing use of CFCs. A stronger Montreal Protocol may be all that can save us.

CAN THE MONTREAL PROTOCOL SAVE US ?

The Montreal Protocol on Substances which Deplete the Ozone Layer had been ratified by about 50 countries up to the end of 1989.

This agreement coordinated by the United Nations Environment Programme requires the Parties to progressively phase down their use of five CFCs (11, 12, 113, 114 and 115) to half the 1986 use, by 1999. Three halon compounds are also required to be controlled to their 1986 consumption levels by 1992. These are all widely used

industrial and consumer chemicals with high ozone depletion potentials (ODP). The ODP of CFC-12 is defined as 1.00. Low ODP compounds such as the hydrochloro-fluorocarbons e.g. HCFC-22 (ODP = 0.05), are not controlled and may be suitable alternatives to the controlled substances.

As chlorine is at present accumulating in the stratosphere at about 5% per year, the best the Protocol can hope to do is slow this rate of growth, perhaps to 2% per year. That is, the Protocol still allows a build-up of chlorine to continue into next century. Even a slowing of this build-up can only happen if use of other ozone depleting compounds is not markedly increased, and if there is a high rate of compliance with the requirements of the 1987 Protocol.

Recent scientific opinion (UNEP/WMO, 1989) is that the existing ozone layer is not sustainable while chlorine levels remain above 2 ppb and the hole in the Antarctic ozone layer will be an annual phenomenon also while chlorine levels remain above 2 ppb.

Since the Protocol was drafted in 1987, scientific evidence on ozone depletion has strengthened. As a result of the airborne work of 1987 mentioned above, the role of chlorine has been established far more confidently. The report of the Ozone Trends Panel of 1988 has determined how much global ozone loss appears to be attributable to human chemical influences. The ozone holes of 1987 and 1989 were striking in their completeness of ozone loss through the lower stratosphere of Antarctica and their persistence right to the end of November. The hole of 1989 was notable for the rapidity and completeness of its development during September, in spite of a possible moderation of the effect by the coincidence of the 11-year solar maximum in late 1989.

Thus there is strong scientific justification for a substantial strengthening of the Protocol. A major review is scheduled for 1990, and by late 1989 a series of comprehensive international assessments had been completed and subjected to preliminary negotiations directed towards a stronger Protocol. These assessments take into account the scientific, environmental, technological and economic issues.

At the time of writing, January 1990, all the assessment groups have acknowledged the inadequacy of the present Protocol for protecting the ozone layer. However, the Protocol is recognised as an established framework for taking stronger action.

The present Protocol is most strongly directed towards the elimination of the most widely used CFC compounds, CFC-11 and CFC-12. However, these compounds contribute only about 60% of the anthropogenic chlorine presently burdening the stratosphere. Other major contributions are about 15% from methyl chloroform (also known as 1,1,1-trichloroethane) and about 15% from carbon tetrachloride. Methyl chloroform is manufactured in large amounts as a cleaning solvent, and in spite of its relatively short atmospheric lifetime, the large emission rate and the large chlorine content (three atoms per molecule) enhance its effect. Because the atmospheric lifetime of methyl chloroform is only about seven years, compared to times of about a century for the principal CFCs, a phasing out of methyl chloroform will have a much greater benefit in the short term when compared to a similar action for the CFCs.

Because the longer lived CFCs already produced will continue to contribute active chlorine to the stratosphere through the next century, action taken in controlling them will have little benefit until several decades have passed. The elimination of methyl chloroform thus becomes important for near-term protection of the ozone layer.

Within the constraint of no-one wishing to upset the economic and technological infrastructures associated with present CFC use, it appears that much stronger measures are possible. Some of the options now being considered by the Parties as control measures are shown in Figure 4. Continuing with the existing Protocol would

TOTAL Clx CONCENTRATIONS
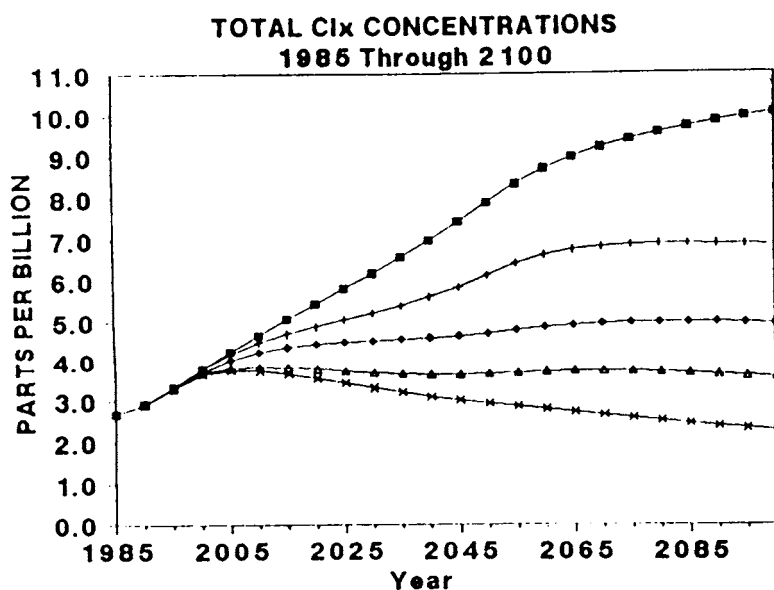**1985 Through 2100**

Fig. 4.   Five possible futures for the Montreal Protocol and their effects on global stratospheric chlorine (being discussed by the Protocol nations, 1989-1990): 1. Existing Montreal Protocol; 2. CFC phaseout; 3. Methyl chloroform freeze; 4. Carbon tetrachloride and methyl chloroform phaseout; and 5. Maximum of 20% HCFC (av. 0.02 ODP) substitution for CFCs.

lead to the highest chlorine option with a trebling of the atmospheric burden during the next century. Even a 100% phaseout of the presently controlled substances (including halons) would leave the atmosphere with more than double its present amount of chlorine. The only prospects for stabilising the chlorine at levels not much above present levels require stringent controls on methyl chloroform. The only option in Figure 4 for which the chlorine loading of the stratosphere is actually reduced during the next century requires not only phaseouts of CFCs, halons, methyl chloroform and carbon tetrachloride, but also strict controls on the use of HCFC substitutes, such that not more than 20% of the phased out uses of existing CFCs, etc.,

are replaced by HCFCs, and even then only an average ODP value of 0.02 is allowed. This in effect cuts out the use of HCFC-22 which has an ODP value of 0.05 and has so far been seen as a part of the technological solution in the short term, to reduce dependence on CFCs 11 and 12.

These predictions of chlorine increase still have a certain amount of optimism associated with them, because they assume 100% global participation in an improved Protocol. So far some of the world's most populous developing countries have not signed or ratified the Protocol and their compliance will be essential if the ozone layer is to be protected. The major problems are of a political or economic type, because of the association of the use of CFCs with advanced industrial development. There is a well-founded perception by the low consuming countries that the problem has been caused by the developed nations, who have already reaped the benefits and so it is appropriate for the developed nations to make the major contribution to a solution.

What the nations of the world must decide is what level of chlorine in the stratosphere is acceptable—should we be allowing indefinite springtime occurrences of the Antarctic ozone hole and continuing our vulnerability to a large volcano as discussed above. The final sentence of the paper by Hofmann and Solomon (1989) should make us think. "A larger eruption than El Chichon occurring in the next half-century or so would therefore provide an important test .... and perhaps determine whether contemporary biological systems may also go the way of the dinosaurs."

The existing Montreal Protocol is inadequate on scientific and environmental grounds for protecting stratospheric ozone, and the technological and economic information now available indicates that a stronger Protocol is both necessary and feasible, and offers the possibility of maintaining the ozone layer as a sustainable resource for mankind and the biosphere.

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