

# Role of chlorine in stratospheric chemistry

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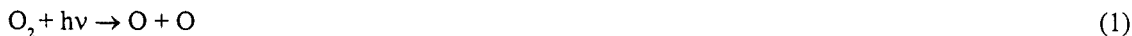
*Abstract:* The chlorofluorocarbons (CFCs) are industrial chemicals used as solvents, refrigerants, plastic foam blowing agents, etc. These compounds are eventually released to the environment; they slowly drift into the stratosphere, where they decompose, initiating a catalytic process involving chlorine free radicals and leading to ozone destruction. The stratospheric ozone layer is important for the earth's energy budget, and it shields the surface of the earth from ultraviolet radiation from the sun. very significant depletion of the ozone layer has been observed in the spring months over Antarctica during the last 10–15 years. Laboratory experiments, model calculations and field measurements, which include several aircraft expeditions, have yielded a wealth of information which clearly points to the CFCs as the main cause of this depletion.

## INTRODUCTION

A variety of industrial organic compounds containing chlorine have applications which result in their release to the atmosphere. Concerns about the environmental consequences of such release were originally focused on local effects, because some of these compounds are toxic and others contribute to urban smog. In contrast, the chlorofluorocarbons (CFCs), which are fully halogenated hydrocarbons, are non-toxic and are too stable to contribute to local air pollution. In fact, it is their chemical stability that creates a global scale problem: they can reach the stratosphere, where they decompose and release halogens that affect the ozone layer.

## STRATOSPHERIC OZONE

The chemistry of the stratosphere is dominated by the presence of ozone ( $O_3$ ). About 90% of the total amount of atmospheric ozone is contained in the stratosphere, where it is present at parts-per-million levels. This species is continuously being made by the action of solar radiation on molecular oxygen ( $O_2$ ), and destroyed by a variety of catalytic processes involving free radicals, including a number of chlorine-containing species. Ozone is generated predominantly in the upper stratosphere at low latitudes; the basic formation mechanism was first suggested by Chapman in the 1930s [1] and consists of the following reactions:



Absorption of solar radiation by molecular oxygen at wavelengths around 200 nm releases oxygen atoms (reaction 1) which rapidly combine with oxygen molecules to form ozone (reaction 2). Absorption of solar radiation destroys ozone (reaction 3), but the oxygen atoms produced by this reaction readily regenerate the ozone molecule by reaction 2. Thus, the net effect of reactions 2 and 3 is the conversion of solar energy (at wavelengths between about 200 and 300 nm) to heat, without ozone destruction. This process leads to an increase of temperature with altitude, which is the feature that gives rise to the stratosphere; the 'inverted' temperature profile in this layer is responsible for its large stability towards vertical

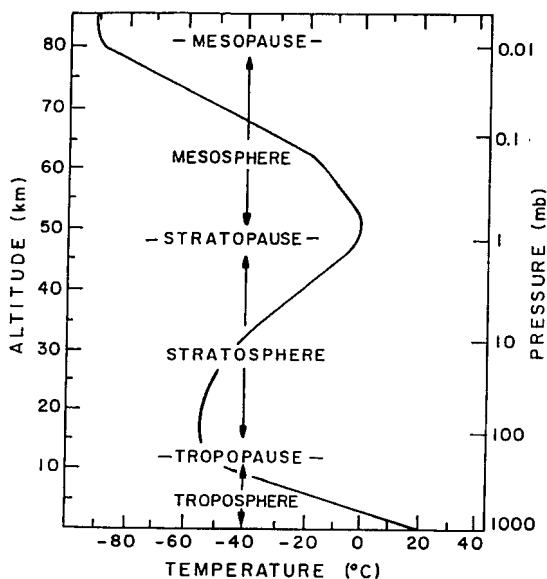
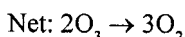
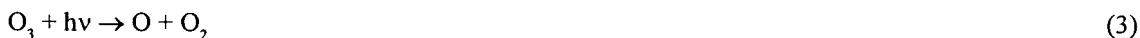


Fig. 1 Typical atmospheric temperature profile.

molecules of ozone have been destroyed. Although the concentration of NO and NO<sub>2</sub> is small (several parts-per-billion), each radical pair can destroy thousands of ozone molecules before being temporarily removed by reactions such as the following:



Chlorine atoms are also very efficient catalysts for ozone destruction, as suggested originally by Stolarski & Cicerone [4]:



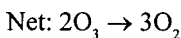
The stratosphere contains, however, only small amounts of chlorine compounds of natural origin: the only important source is methyl chloride, CH<sub>3</sub>Cl, which is present at a level of less than one part per billion. This species is produced at the Earth's surface by biological activity and also to some extent by biomass burning; most of it is destroyed in the troposphere, but a few percent reaches the stratosphere. There are large natural sources of inorganic chlorine compounds at the Earth's surface, i.e. NaCl and HCl from the oceans; these compounds are, however, water soluble and hence are removed from the atmosphere by clouds and rainfall long before they reach the stratosphere.

## THE CHLOROFLUOROCARBONS

In 1974 Molina and Rowland suggested that CFCs could provide an important source of chlorine free radicals to the stratosphere [5], and that these industrial compounds would pose a threat to the ozone layer. The CFCs were invented in the 1930s by Thomas Midgley in order to replace the toxic fluids that were used as coolants in home refrigerators. Subsequently, these compounds found uses as propellants for spray cans, solvents, cleaners, blowing agents for plastic foam, etc. The two most important ones are CFC-11 (CFCl<sub>3</sub>) and CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>). These compounds are practically insoluble in water, and thus are not removed by rainfall. Furthermore, they are inert towards the hydroxyl radical (OH); reaction with this radical to form water is the process that initiates the oxidation of hydrocarbons in the lower atmosphere. That is, the CFCs are not removed by the common atmospheric cleansing mechanisms that operate in the lower atmosphere; instead, they rise into the stratosphere, where they are eventually destroyed by the short wave-

movements (Fig. 1). In contrast, in the lowest layer—the troposphere—temperature decreases with altitude, and winds disperse atmospheric trace components very efficiently on a global scale within the troposphere.

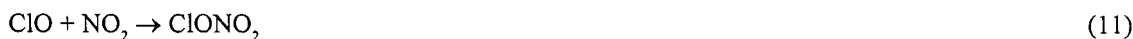
In reaction 4 of the Chapman mechanism oxygen atoms destroy ozone, instead of making it, as in reaction 2; however, reaction 4 is too slow to explain the actual abundance of ozone observed in the stratosphere. In the early 1970s Crutzen [2] and Johnston [3] suggested that trace amounts of nitrogen oxides (NO<sub>x</sub>) which are naturally present in the stratosphere control the ozone abundance through a catalytic cycle consisting of the following reactions:



After these three reactions have occurred, the free radicals NO and NO<sub>2</sub> are still present, but two mol-

length solar ultraviolet radiation (of wavelengths around 200 nm) which is shielded by the ozone layer and by molecular oxygen. Because transport into the stratosphere is very slow, the residence time for the CFCs in the environment is of the order of a century.

The destruction of CFCs by solar radiation leads to the release of chlorine atoms, which participate in ozone destruction cycles: these atoms attack ozone within a few seconds (as in reaction 8) and are regenerated on a time scale of minutes (as in reaction 9). These cycles may be temporarily interrupted, for example, by reaction of chlorine monoxide (ClO) with HO<sub>2</sub> or NO<sub>2</sub> to produce hypochlorous acid (HOCl) or chlorine nitrate (ClONO<sub>2</sub>) respectively; or by reaction of the Cl atom with methane (CH<sub>4</sub>) to produce the relatively stable hydrogen chloride molecule (HCl):



The chlorine-containing product species HCl, ClONO<sub>2</sub> and HOCl function as temporary 'inert reservoirs': they are not directly involved in ozone depletion, but eventually break down by reaction with other free radicals or by absorption of solar radiation, returning chlorine to its catalytically active free radical form (Fig. 2). At low latitudes and in the upper stratosphere, where ozone is formed fastest, a few percent of the chlorine is in this active form; most of the chlorine is in the inert reservoir form.

Besides chlorine, bromine also plays an important role in stratospheric chemistry. There are industrial sources of brominated hydrocarbons, as well as natural ones. The 'halons' are fully halogenated hydrocarbons, produced industrially as fire extinguishers; examples are CF<sub>3</sub>Br and CF<sub>2</sub>ClBr. Methyl bromide, CH<sub>3</sub>Br, is both natural and human-made: it is used as an agricultural fumigant. These sources provide bromine to the stratosphere at parts per trillion level, compared with parts per billion for chlorine. On the other hand, bromine is about 50 times more efficient than chlorine for ozone destruction on an atom per atom basis [6]: a large fraction of the bromine compounds are present as free radicals, because the temporary reservoirs are less stable, and are formed at considerable slower rates than the corresponding chlorine reservoirs. In contrast, fluorine very rapidly abstracts hydrogen atoms from methane and from water vapor, forming the very stable HF molecule, which functions as a permanent inert fluorine reservoir. Hence, fluorine free radicals are extremely scarce and the effect of fluorine on stratospheric ozone is negligible.

Our understanding of the effects of chlorine and bromine on stratospheric ozone can be investigated by comparing predictions of computer models of the atmosphere with actual observations. The models typically incorporate information on the rates of over a hundred chemical and photochemical reactions, as well as information on atmospheric motions and on natural levels of a variety of compounds. Because of the complexity of the system, calculations were carried out initially with one-dimensional models, averaging the motions and concentrations of species over latitude and longitude and leaving only their dependency on altitude and time. Two-dimensional models, in which the averaging is over longitude only, are now being used extensively; more recently, three-dimensional models have been developed. The models can be further tested with measurements of atmospheric trace species conducted as a function of time of day, season, latitude, etc.

Various fundamental aspects of the CFC-ozone depletion hypothesis were verified in the late 1970s and early 1980s, following the initial publication of this hypothesis. Measurements of the concentrations of the CFCs indicated that they accumulate in the lower atmosphere and that they reach the stratosphere in the predicted amounts. Chlorine atoms and ClO radicals were found in the stratosphere, together with other species such as HCl, ClONO<sub>2</sub>, HOCl, O, NO, NO<sub>2</sub>, etc., with observed concentrations in reasonable agree-

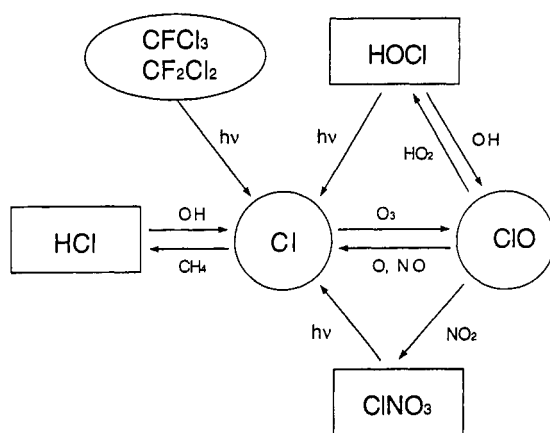


Fig. 2 Schematic representation of the stratospheric chemistry of chlorine at low and mid-latitudes.

ment with the model predictions. On the other hand, a decrease in stratospheric ozone levels was not observable at that time because of the large natural variability of this species. However, as first pointed out by Farman and coworkers in 1985 [7], the ozone levels in the Antarctic stratosphere dropped dramatically in the spring months starting in the early 1980s. Ozone is being depleted in the northern hemisphere as well, particularly at high latitudes and in the winter and spring months. More recently, it has been possible to show by examination of the ozone records that significant changes have also taken place in the lower stratosphere at mid latitudes [6].

The depletion of ozone at high latitudes was not predicted by the earlier models. However, its cause became very clear in recent years when laboratory experiments, field measurements over Antarctica and model calculations provided very strong indications that the ozone loss can indeed be traced to the human-made CFCs.

## HIGH LATITUDE OZONE CHEMISTRY

The high latitude stratosphere is unique in several ways. First of all, ozone is not generated there, because high energy solar radiation is scarce as a consequence of the large solar zenith angles. Furthermore, the total ozone column abundance at high latitudes is large because ozone is transported towards the poles from higher altitudes and lower latitudes. In addition, the prevailing temperatures over the poles in the winter and spring months are the lowest throughout the stratosphere, particularly over Antarctica. Thus, ozone should be rather stable over the poles if one considers only gas phase chemical and photochemical processes, because regeneration of ozone-destroying free radicals from the reservoir species would occur only very slowly at high latitudes.

Clouds do not form in the low latitude stratosphere because it is very dry: a large fraction of the water vapor condenses on its way to the stratosphere. Over the poles, a somewhat larger amount of water is present, coming from the oxidation of methane. The temperature can drop to below 185 K over Antarctica in the winter and spring months, leading to the formation of ice clouds. The presence of nitric and sulfuric acids enables the formation of polar stratospheric clouds (PSCs) a few degrees above the frost point (the temperature at which ice can condense).

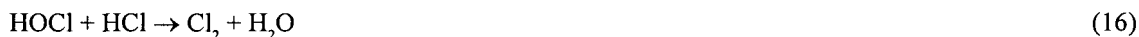
Solomon *et al.* [8] first suggested that PSCs could play a major role in the depletion of ozone over Antarctica by promoting the release of photolytically active chlorine from its reservoir species. This occurs mainly by the following reaction:



Laboratory experiments showed that in the gas phase this reaction occurs very slowly, if at all [9,10]. However, in the presence of ice surfaces this reaction proceeds with remarkable efficiency [10]. The product  $\text{Cl}_2$  is immediately released to the gas phase, and decomposes readily even with the faint amount of sunlight present over Antarctica in the early spring:



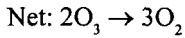
The following are also chlorine activation reactions promoted by PSCs:



The net effect of these two reactions is reaction 13. The catalytic effect of ice to promote reactions 13 and 16 was unexpected, because HCl is only sparingly soluble in the ice matrix; however, experimental observations [11,12], as well as recent theoretical work [13], indicates that HCl solvates readily on the ice surface, thus explaining its high affinity for this molecule. It appears, then, that the chlorine activation reactions proceed through ionic mechanisms analogous to those in aqueous solutions.

The presence of PSCs also leads to the removal of nitrogen oxides ( $\text{NO}_x$ ) from the gas phase; the source for these free radicals is nitric acid, which condenses in the cloud particles. Furthermore, some of the particles consist of large enough ice crystals to fall out of the stratosphere, permanently removing the nitric acid, a process referred to as 'denitrification'. This process turns out to have important consequences: the nitrogen oxides normally interfere with the catalytic ozone loss reactions involving chlorine oxides, mainly by forming chlorine nitrate. In the absence of nitrogen oxides, chlorine is capable of destroying ozone much more rapidly.

The catalytic cycles such as those involving reactions 8 and 9 are efficient only in regions where ozone is being produced, because they require the presence of free oxygen atoms which are scarce at high latitudes. Several different cycles have been suggested as being at work over Antarctica, such as the following one involving chlorine peroxide [14]:



No free oxygen atoms are involved in this cycle. The species ClOOCl, chlorine peroxide, had not been characterized previously; its geometry is now well established from submillimeter wave spectroscopy [15]. This species is thermally unstable at room temperature, but it is stable around 200 K and in the polar stratosphere it is mainly decomposed by photolysis to yield chlorine atoms, as indicated in reaction 18. Laboratory experiments [16,17] have shown that the photolysis products are indeed chlorine atoms, rather than ClO radicals, which are the products of the thermal decomposition reaction. Figure 3 summarizes the chlorine reactions of importance in the high-latitude stratosphere.

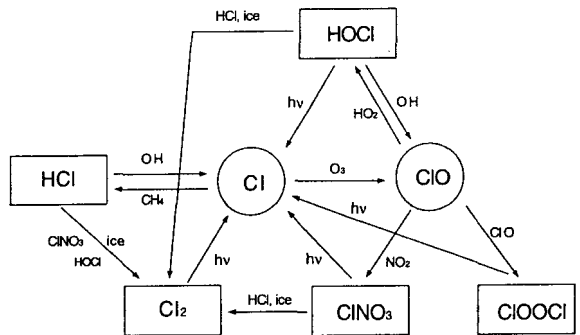
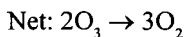
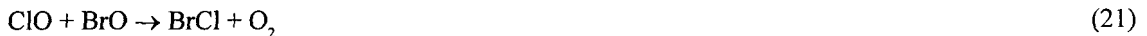


Fig. 3 Schematic representation of chlorine chemistry in the polar stratosphere.

Another important cycle operating in the polar stratosphere involves bromine compounds [18]:



As is the case with the chlorine peroxide cycle, this cycle does not require the presence of free oxygen atoms; furthermore, it can in principle operate in the dark, as there is no photolytic step. However, reaction 19 has other channels which prevent the continuous production of the free halogen atoms in the absence of light [10]:



On the other hand, both products BrCl and OCIO decompose readily in sunlight. In fact, the presence of OCIO at night has been used as an indication of the occurrence of the ClO + BrO reaction, as this appears to be the main source for OCIO [19].

## STRATOSPHERIC OBSERVATIONS

The measurements by Farman and coworkers of rapid ozone loss in the spring months in the stratosphere over Antarctica were conducted from the ground using a Dobson spectrophotometer. This is an instrument which measures solar irradiances at two wavelengths, one strongly absorbed by ozone and the other one not absorbed. Their findings were published in 1985 [7] and were subsequently confirmed by satellite data from the Total Ozone Mapping Spectrometer (TOMS) [20], which measures ozone by a similar principle, namely by monitoring at two such wavelengths the attenuation of solar radiation that has been back scattered from the atmosphere below the ozone layer (Fig. 4).

Several key expeditions to measure trace species in the stratosphere over Antarctica were launched in the years following these findings [see, e.g., Ref. 21]. The results provided strong evidence for the occur-

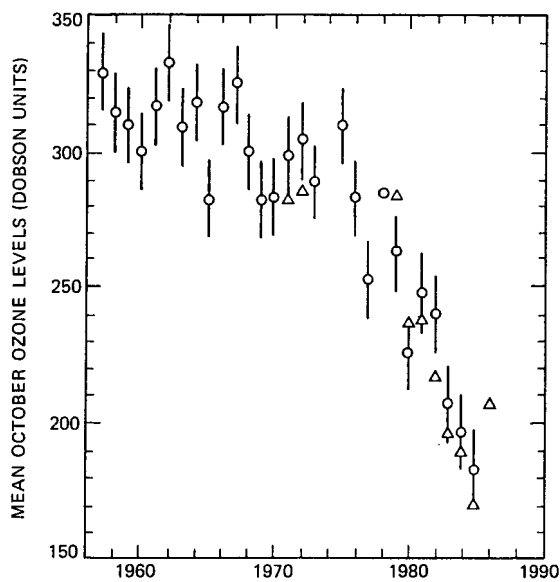


Fig. 4 Average total amount of ozone measured in October over Halley Bay, Antarctica, by Farman *et al.* [7] (circles), and by the TOMS instrument on the NASA satellite [20] (triangles).

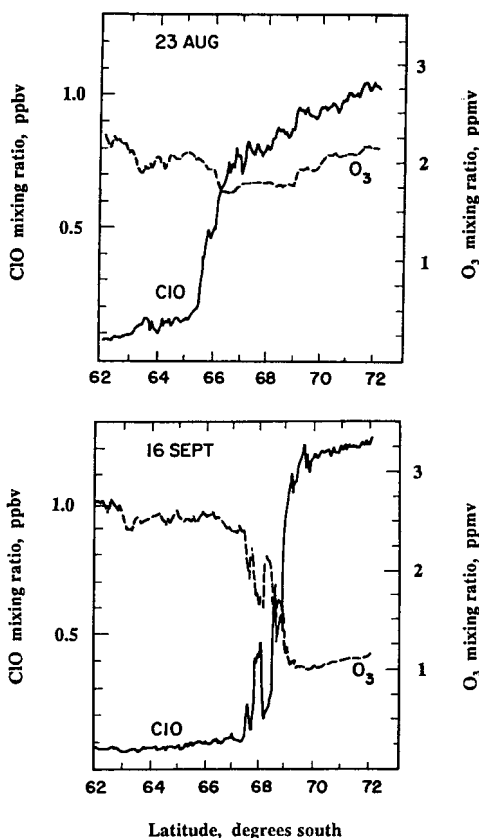


Fig. 5 Results of measurements conducted during the Airborne Antarctic Ozone Experiment on 23 August and 16 September 1987, of chlorine monoxide by Anderson *et al.* [22], and of ozone by Proffit *et al.* [24].

rence of the chemical reactions described above, and hence for the crucial role played by industrial chlorine in the formation of the 'Antarctic ozone hole'. Inside the polar vortex, where ozone is being depleted in the spring months over Antarctica, a large fraction of the chlorine is present as a free radical (Fig. 4). Furthermore,  $\text{NO}_x$  levels are very low; the cloud particles contain nitrate; etc. An analysis of the results of the field measurements by Anderson *et al.* [22] indicates that the chlorine peroxide cycle (reactions 8, 17, 18) accounts for about 75% of the observed ozone depletion, with the bromine cycle (reactions 8, 19, 20) accounting for the rest.

Measurements have also been conducted over the Arctic [23], indicating that a large fraction of the chlorine is also activated there, but ozone depletion is less severe and not as localized because the temperatures are not as low as over Antarctica: the active chlorine does not remain in contact with ozone long enough to destroy it before the Arctic stratosphere air mixes with warmer air from lower latitudes. This warmer air also contains  $\text{NO}_2$ , which passivates the chlorine.

On the other hand, cold winters lead, as expected, to significant ozone depletion over large areas, as was the case over northern Europe in 1995/96. Furthermore, as mentioned above, ozone is also being depleted to some extent at mid-latitudes (Fig. 6).

Much has been learned about the chemistry of the polar stratosphere through laboratory studies, field measurements and modeling calculations; however questions remain such as the chemical identity and the formation mechanism of the various cloud particles which are present in the polar stratosphere. Also, the observed mid-latitude ozone loss is larger than predicted from the models. Hence, additional research should be carried out to improve the reliability of the predictions of ozone depletion in the next few decades.

## THE MONTREAL PROTOCOL

The first international agreement limiting the production of CFCs was approved in September 1987 under the auspices of the United Nations Environment Programme, at a time when the expeditions to the Antarctic stratosphere were just beginning to gather the data that would firmly link the CFCs to the depletion of polar ozone. This agreement, the Montreal Protocol, initially called for a reduction of only 50% in the manufacture of CFCs by the end of the century. In view of the strength of the scientific evidence that emerged in the following years, the initial provisions were strengthened through the London and the Copenhagen amendments to the protocol, in 1990 and 1992 respectively. The production of CFCs in industrialized countries was phased out at the end of 1995, and

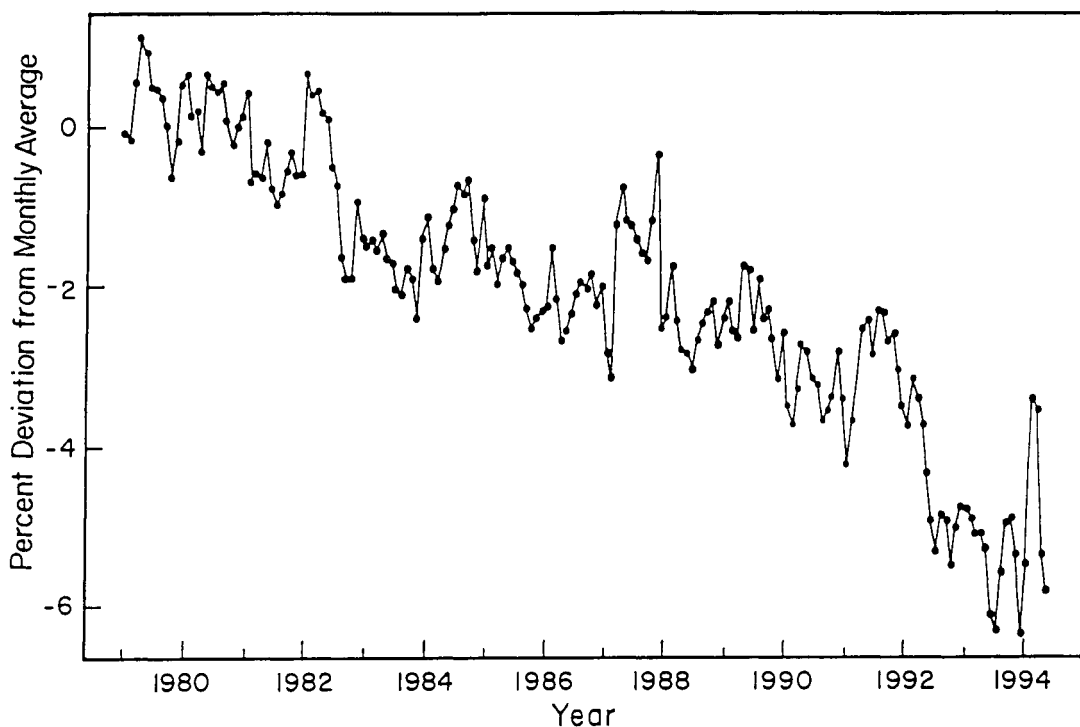


Fig. 6 Trend in global ozone values averaged between 60° North and 60° South. From Ref. 6.

other compounds such as the halons, methyl bromide, carbon tetrachloride and methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ) were also regulated.

If the provisions of the Montreal Protocol are fully enforced—as appears to be the case so far—chlorine levels will peak before the year 2000. On the other hand, because of the long residence times of the CFCs in the atmosphere, ozone depletion is expected to continue well into the next century. Roughly a third to a fourth of the former use of CFCs is being temporarily replaced by hydrochlorofluorocarbons (HCFCs); these are compounds that have similar physical properties to the CFCs, but are less stable in the atmosphere: their molecules contain hydrogen atoms, and hence a large fraction of the surface release reacts with the hydroxyl radical before reaching the stratosphere, forming water and an organic free radical that rapidly photo-oxidizes to yield water-soluble products which are removed from the atmosphere mainly by rainfall. Some hydrofluorocarbons (HFCs)—which do not contain chlorine atoms—are also being used as CFC replacements, e.g., HFC-134a ( $\text{CF}_3\text{-CH}_2\text{F}$ ), for automobile air conditioning. About half of the CFC usage is being replaced by ‘not-in-kind’ compounds; for example, CFC-113 ( $\text{CCl}_2\text{F-CClF}_2$ ) was used extensively as a solvent to clean electronic boards, but there are now CFC-free technologies such as soap-and-water, or terpene-based solvents. Finally, a significant fraction of the former CFC usage is being dealt with by conservation and recycling.

It is important that society continues to learn about the environment to prevent its further deterioration by human activities. The CFC-ozone depletion problem has demonstrated that humankind is capable of seriously modifying the atmosphere on a global scale; it has also shown us that in principle society can solve these global problems by means of international agreements.

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