

# THE CHANGING ATMOSPHERE

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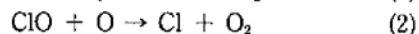
The observation in 1971 that the man-made inert gas trichlorofluoromethane ( $\text{CCl}_3\text{F}$ , commercially known as CFC-11) was widespread throughout the Earth's atmosphere presented an unusual challenge to atmospheric scientists: Was it possible to determine from the known laboratory properties what the ultimate fate of CFC-11 would be in the atmosphere? In 1973, I proposed such a study to the U.S. Atomic Energy Commission, and later that year my colleague Dr. Mario J. Molina and I began seeking the answer to this question. Several different CFC molecules have found technological success as refrigerants, expanders of polymer foams, propellants for aerosol sprays, and in cleaning electronic components, and most of these uses eventually involve release of the CFC to the atmosphere. World-wide CFC production doubled every 5 to 7 years for two decades, and reached about one million tons per year by 1974.

Atmospheric removal or destruction of chemicals in the atmosphere usually occurs by one of three processes. Colored gases such as green chlorine gas ( $\text{Cl}_2$ ) absorb visible solar radiation and are broken into fragments, and similar destruction can also occur following the absorption of invisible ultraviolet radiation. Other gases such as hydrogen chloride ( $\text{HCl}$ ) can dissolve in water droplets, and are removed from the atmosphere in rainwater. Still other gases such as methane ( $\text{CH}_4$ ) can react with oxidizing species such as hydroxyl ( $\text{HO}$ ). The CFCs, however, are transparent, insoluble in water, and completely inert toward the oxidants. Because none of the major removal processes is effective toward the CFCs, they can wander unchanged through the atmosphere for many decades. If nothing destructive happens quickly, then what slower process controls the atmospheric fate of the CFCs?

The solar ultraviolet radiation which reaches the top of the Earth's atmosphere can be considered in terms of three energy bands :

UV-A, UV-B and UV-C, with UV-C the most energetic. The CFC molecules are transparent to UV-A and UV-B, but will absorb UV-C radiation and be destroyed in the process. However, the abundant oxygen ( $\text{O}_2$ ) in the atmosphere can also absorb UV-C radiation 30 to 50 kilometers (km) above the Earth's surface, splitting into two oxygen atoms. These O atoms then combine with other  $\text{O}_2$  molecules to create the three atom molecule, ozone ( $\text{O}_3$ ). Because ozone can absorb both UV-C or UV-B, no solar UV-C penetrates below an altitude of about 25 km, and only a small fraction of UV-B reaches the surface. The CFCs are thus protected from UV-C radiation by this "ozone shield", and are not exposed to it until they drift randomly above most of the atmospheric  $\text{O}_3$  and  $\text{O}_2$ , at altitudes of 30 km or higher. Here, CFC molecules such as  $\text{CCl}_2\text{F}$  do absorb UV-C radiation, and are cracked into the highly reactive free chlorine atom ( $\text{Cl}$ ) and a reactive  $\text{CCl}_2\text{F}$  fragment. The average CFC molecule survives for 75 to 150 years before its eventual mid-stratospheric destruction by solar UV-C radiation above the ozone shield.

Unlike the inert CFC molecules, the newly released Cl atom immediately attacks ozone and takes one of its oxygen atoms to form chlorine oxide ( $\text{ClO}$ ) by reaction (1). The  $\text{ClO}$  then quickly collides with a free oxygen



atom, again releasing Cl. The combination of reaction (1) plus (2) has two important aspects : (a) the *net* change is the conversion of ozone back into ordinary oxygen ; and (b) the chlorine atom is free to begin the sequence again. These continuing series of reactions are called *catalytic chain reactions* and can repeat themselves thousands of times before being interrupted by some alternative process. In the stratosphere, the average Cl atom eventually destroys about 100,000 molecules of ozone before it strays downward and is caught in rainfall. The emission to the atmosphere of

many millions of tons of CFC molecules, multiplied by chain lengths of 100,000, is the key for producing ozone loss significant on a global scale. In 1974, Molina and I predicted that continued release of CFCs to the atmosphere would eventually lead to ozone depletion of 7% to 13% averaged world-wide.

Global ozone depletion on a large scale has two important consequences: (1) the absorption of all solar UV-C and part of the UV-B in the upper atmosphere furnishes a major energy input at high altitudes, actually creating the *stratosphere* (higher temperature with higher altitude); and (2) the loss of stratospheric  $O_3$  allows more solar UV-B radiation to reach the Earth's surface.

The stratospheric ozone "shield" protects all biological species at the Earth's surface, and increased amounts of UV-B can cause damage to many living systems. Solar UV-B radiation is the major cause of human skin cancer. Ozone depletion will therefore result in an increased incidence of skin cancer, an illness which already produces 400,000 new cases *every year* just in the United States and a much larger number globally. Effects can also be anticipated on plankton, agricultural crops, and various other biological systems. Finally, alteration of the stratospheric temperature structure carries with it the possibility of changes in wind patterns and eventually of climate.

The atmospheric concentrations of the major CFCs have increased steadily over the past 15 years, confirming the original estimate that their atmospheric lifetimes are in the 75-150 year range. The atmospheric concentrations of other trace gases are also rising rapidly; carbon dioxide ( $CO_2$ ) is up about 10% since 1958; methane, 12% since 1978; nitrous oxide ( $N_2O$ ) is increasing 0.2% per year; and ozone near the Earth's surface is steadily rising as well. All of these gases retain infrared radiation outgoing from the Earth, leading to a warmer atmosphere (the "greenhouse effect"),

with the major contribution from the release of  $CO_2$  during the burning of coal, gas, oil and tropical forests.

As the concentrations of these trace gases continue to increase, the average temperature of the Earth will rise, perhaps by as much as  $3^\circ C$  by the middle of the 21st century. Such temperature increases can be accompanied by a variety of other geophysical consequences: rising sea-level, more hurricanes of greater intensity, shifting wet and dry regions, partial melting of polar ice-caps, etc.

During the 1980s a new atmospheric phenomenon has appeared: a major depletion of ozone now happens over Antarctica every spring, with ozone losses as great as 98% at some altitudes, and 60% in total throughout the atmosphere. The causes for this ozone depletion involve a mixture of chemistry and meteorology. The stratosphere becomes very cold during the darkness of the Antarctic winter, allowing the formation of *polar stratospheric clouds* (PSCs). The PSCs perturb stratospheric chlorine and nitrogen chemistry, and catalytic reactions of ClO proceed without interruption for a few weeks until the PSCs disappear with the springtime warming of the stratosphere. Experiments from ground stations and from aircraft flying over Antarctica have definitely established that the primary cause of this Antarctic "ozone hole" is the large amount of chlorine now present in the atmosphere, especially from the CFCs.

Ozone measurements have been made for as long as 50 years from many ground stations, most of them located between  $30^\circ N$  and  $65^\circ N$  latitudes. Statistical analyses of these ozone data have also shown an average ozone depletion of several percent in the northern hemisphere, with larger losses in the winter months and smaller in the summer. Arctic expeditions in 1989 have shown the presence of PSCs and also very high stratospheric concentrations of ClO radicals, findings quite similar to those for the Antarctic.

Concern about chlorine-initiated depletion of stratospheric ozone led during the late 1970s to prohibition of CFC use as propellant gases in aerosols in the United States, Canada, Sweden and Norway. Despite these aerosol bans, the development of extensive new uses—especially the cleaning of electronic components with CFC-113—has maintained CFC release at about one million tons yearly since 1974. The very long lifetimes of the CFCs will keep the atmospheric chlorine concentrations at elevated levels for the next one or two centuries, independent of any future regulatory actions. Furthermore, atmospheric transport of CFCs to the stratosphere requires a few years and the maximum depletion of stratospheric ozone will be delayed for a decade or more after substantial CFC release to the atmosphere has been stopped.

Global control of CFC releases was first agreed upon through the Montreal Protocol of the United Nations Environment Programme in September 1987. The initial goal of this Protocol was a cutback in 1998 to 50% of the current atmospheric release of CFCs, but this partial ban would still permit the total amount of atmospheric chlorine to increase for many decades. Many major CFC-producing companies and countries have now agreed to eliminate CFC production completely within the next decade, and vigorous searches for alternatives are under way. Controls for other gases will be more difficult, but may be necessary if the concentrations of other trace gases continue to increase steadily.