

GLOBAL CHANGE AND THE ANTARCTIC OZONE HOLE

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It was only in the second half of the twentieth century that it became clear that human activities may have impacts on the environment truly on a planetary scale. Human beings started altering the surface of the planet a long time ago, at least since they began to develop an agriculture that required plowing, irrigation and the clearing of forests. However, until recently those changes were mostly local, and possibly regional.

The potential impact of human activities on the atmosphere can be appreciated by considering its size: about 95% of its mass resides in the first 20 km above the Earth's surface, whereas the distance between the two poles is 20,000 km. The atmosphere makes life on Earth possible, and yet from a cosmic perspective it is a very thin, very fragile layer. For this reason its chemical composition can be inadvertently changed as a consequence of human activities.

The clearest example of a global environmental problem is the one involving the depletion of the ozone layer of the stratosphere by industrial chlorofluorocarbons (CFCs). These compounds were developed in the 1930's as replacements of the refrigerant fluids that were in use at that time, namely ammonia and sulfur dioxide. These two compounds are rather toxic, and a number of accidents took place when they were accidentally released in small rooms where people were sleeping. The CFCs have two important properties: they are non-toxic and non-flammable, and they can be readily converted under mild pressures from a liquid to a vapor and vice versa, which is what makes them so valuable as refrigerants. The CFCs became very successful in other applications as well, such as propellants for aerosol spray cans. For this reason their industrial production increased rapidly during the 1960's and 70's.

The CFCs are so stable that practically the entire industrial production ends up in the atmosphere. In the early 1970's it became possible to moni-

tor their presence throughout the globe, their atmospheric concentration at that time being at the parts per trillion level. In 1973, together with my colleague Sherwood Rowland, we set out to investigate the fate of the CFCs in the environment; we also wanted to find out if the presence of these industrial compounds in our atmosphere had any significant consequences. We were not aware at that time that another group of scientists had asked the same question, concluding that there was no cause for concern: they reasoned that the CFCs are not only extremely stable, but their concentration appeared so small that no significant effects appeared plausible.

In 1974 we published a very different conclusion, namely that the release of CFCs could lead to a serious environmental problem. To understand how we arrived at such a conclusion, let us examine some important properties of our atmosphere. In the lowest layer, called the troposphere, temperature decreases with altitude; in the next layer, the stratosphere, temperature increases with altitude, giving rise to an "inverted" temperature profile that leads to stability: mixing in the vertical direction is very slow (Figure 1). The troposphere has very efficient cleansing mechanisms: first of all, it has clouds and rain, which remove particles and pollutants that are soluble in water on a time scale of at most a few weeks. Some compounds such as hydrocarbons that are emitted naturally as well as by human activities are not directly removed by rain; instead, they are first oxidized and subsequently transformed into water-soluble species. The stratosphere, however, has no rain, because most water condenses before reaching that layer. Thus, if pollutants are somehow introduced into the stratosphere, they may remain there for periods of several years before being removed by finding their way into the troposphere.

The atmosphere is heated mostly from below, at the Earth's surface, which explains why it is that temperature decreases with altitude. The reason that temperature increases with altitude in the stratosphere is that there is a component of the atmosphere at higher altitudes that absorbs solar radiation: this is ozone, a form of oxygen with three atoms per molecule. Ozone is extremely efficient in absorbing ultraviolet radiation at wavelengths shorter than about 290 nm, radiation that is damaging to biological systems. In fact, life as we know it could only evolve after the ozone layer was formed. Ozone is a rather unstable chemical species: it is continuously being formed by the action of short wavelength solar radiation (around 200 nm) on molecular oxygen, and it is continuously being destroyed by various chemical processes. Its maximum concentration reaches only several parts per million. In the natural stratosphere the

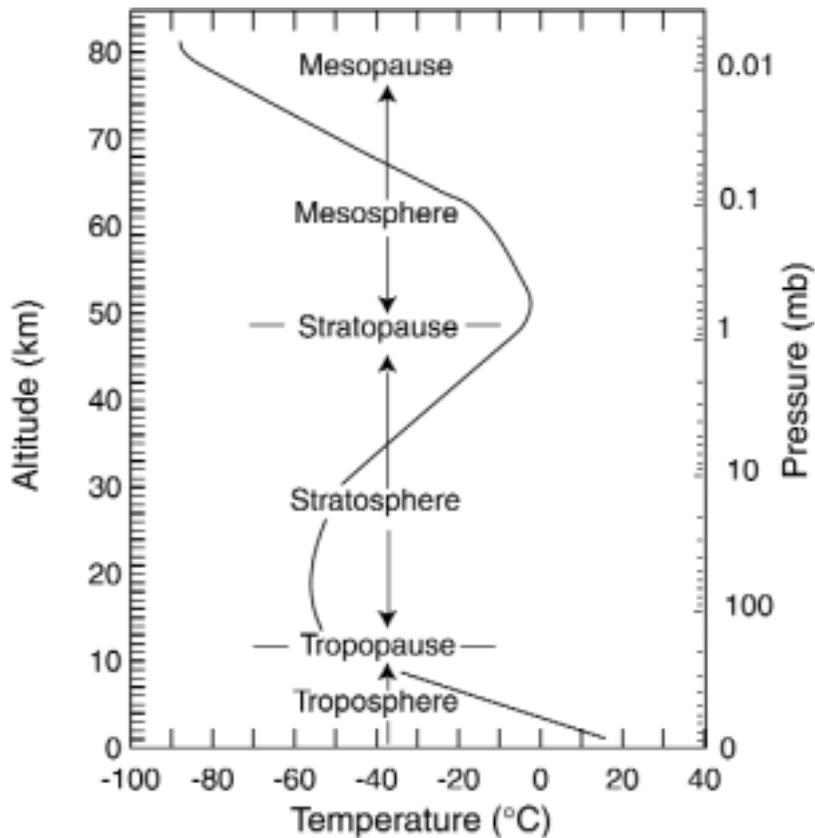


Figure 1. Typical atmospheric temperature and pressure as a function of altitude.

ozone abundance is controlled mainly by nitrogen oxides. These compounds function as catalysts: they are present at only parts per billion levels, and yet they destroy much larger amounts of ozone through a recycling mechanism.

With these ideas in mind we can explain how is it that the CFCs can affect the ozone layer (Figure 2). After their release at the Earth's surface, the CFCs mix rapidly in the troposphere, unaffected by the cleansing mechanisms that operate in this layer. Eventually these compounds reach the stratosphere, and are transported above the ozone layer, where they are

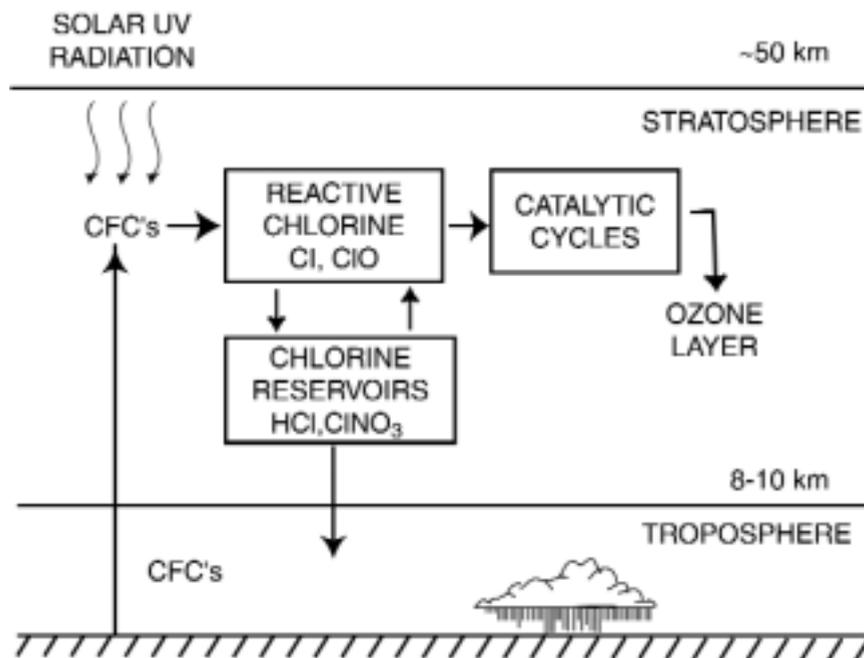


Figure 2. Schematic representation of the CFC-ozone loss hypothesis.

destroyed by short wavelength radiation. The decomposition products from the CFCs are chemically very active, and through catalytic cycles accelerate the destruction of ozone. These cycles provide a very efficient amplification factor: a single chlorine atom may destroy tens of thousands of ozone molecules before returning to the troposphere.

In the years subsequent to the publication of our CFC-ozone depletion hypothesis many experiments were carried out to test various aspects of the hypothesis. Laboratory investigations were conducted to determine the rates of the chemical reactions thought to be important for ozone depletion. Field measurements indicated that the CFCs were indeed reaching the stratosphere, and that their decomposition products were present at the expected concentrations. It took, however, more than a decade to establish that the amount of stratospheric ozone was being affected. The reason is that ozone concentrations have large natural fluctuations, so that a

decreasing trend has to be rather large before it can be attributed to human activities.

In 1985 it became apparent that something unusual was happening to the ozone layer over Antarctica: in the spring months – September and October in the Southern Hemisphere – ozone was reaching extremely low values. Nobody had predicted that ozone would first begin to disappear over Antarctica; in fact, a number of scientists first thought that such a disappearance had nothing to do with the CFCs, postulating that natural meteorological cycles were responsible for the ozone changes. Several important expeditions were then organized to probe the stratosphere over Antarctica, using ground observations as well as measurements from aircraft flying through the cold polar stratosphere. The results showed that meteorology alone could not explain the observations. Instead, it became very clear that the drastic depletion of polar ozone was caused by chlorine coming from the decomposition of CFCs at lower latitudes. The depletion became known as the “Antarctic ozone hole”.

It soon became clear that the reason ozone depletion was taking place specifically over Antarctica was related to the presence of thin ice clouds. As mentioned above, the stratosphere is very dry, and hence mostly cloudless. However, the temperature drops so much over Antarctica – down to $-80\text{ }^{\circ}\text{C}$ – that even the parts per million of water vapor that are present there condense to form ice crystals, making polar stratospheric clouds (PSCs). We were able to show with laboratory experiments that those ice crystals “activate” chlorine by transforming relatively stable species such as hydrogen chloride (HCl) and chlorine nitrate (ClONO_2) to molecular chlorine (Cl_2). This last compound is a green gas, and hence it decomposes readily by absorbing even the faint amount of light that from the sun that reaches the Antarctic stratosphere in the spring, after the long polar night. Molecular chlorine decomposes to yield free chlorine atoms, which then destroy ozone very efficiently through catalytic cycles. This destruction process is particularly efficient in the presence of PSCs because the cloud particles scavenge nitrogen oxides, which normally interfere with the chlorine catalytic cycles.

Several expeditions were launched in the years following the initial discovery of the ozone hole to measure trace species in the stratosphere over Antarctica. The ground-based National Ozone Expedition (NOZE) to McMurdo, Antarctica, provided the first evidence for the crucial role played by industrial chlorine in the depletion of ozone in 1986 and 1987. A subsequent expedition based on aircraft flights over Antarctica from a base in

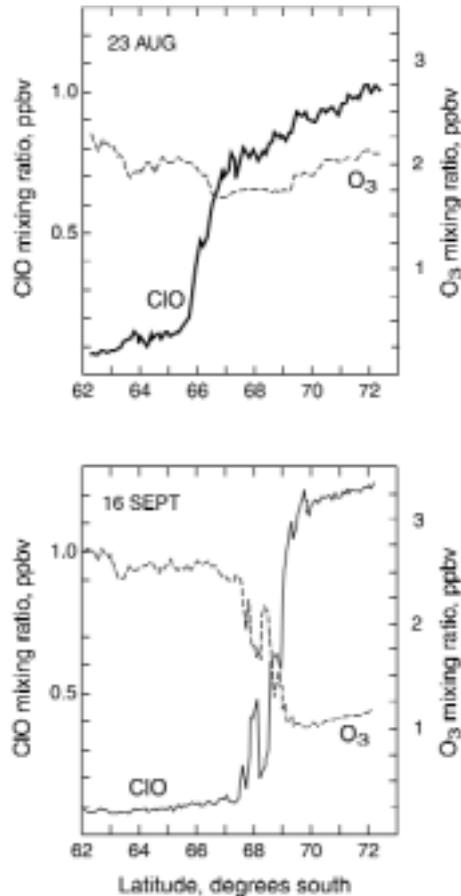


Figure 3. Aircraft measurements of chlorine monoxide by James Anderson and coworkers, and of ozone by Michael Proffitt and coworkers, conducted on August 23 and September 16, 1987.

southern Chile provided some of the most convincing pieces of evidence in 1987. At the time that ozone is strongly depleted in the Polar stratosphere (during the spring), a large fraction of the chlorine is present as a free radical: parts per billion levels of chlorine monoxide is strongly anti-correlated with ozone loss (Figure 3). These results were further confirmed by satellite measurements.

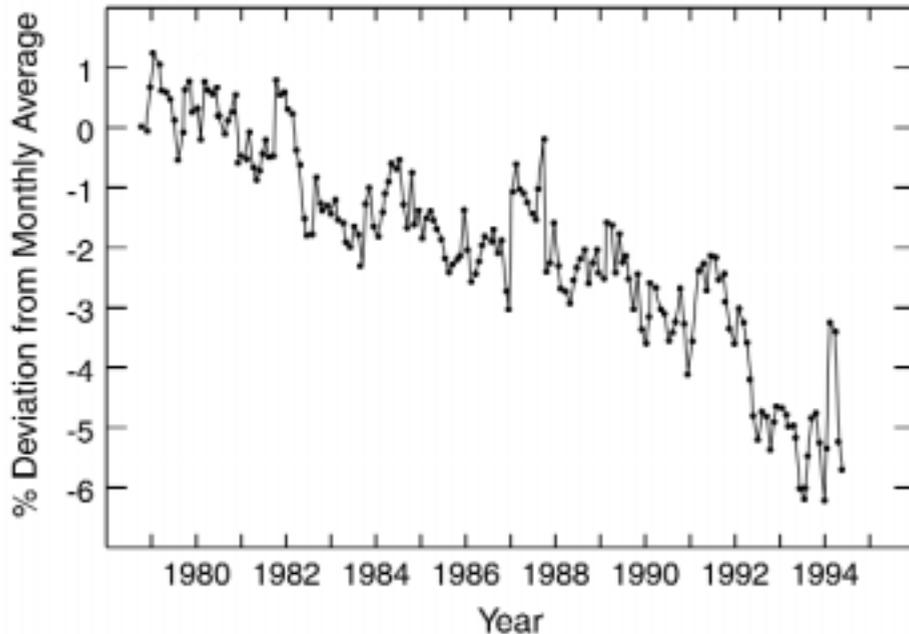


Figure 4. Trend in global ozone values averaged between 60° North and 60° South.

The Antarctic ozone hole is a very striking phenomenon: in recent years measurements show that more than 99% of the ozone disappears every spring over a 5 km altitude range in the middle stratosphere, where it is normally most abundant. Ozone produced at low latitudes replenishes the polar stratosphere in subsequent months, so that its level returns to near-normal values in the summer. Significant depletion also takes place over the Arctic, but it is less localized and less severe, because the northern polar stratosphere does not get as cold. In fact, over the past decade there has been a measurable downtrend in ozone levels even at mid-latitudes: the concentrations averaged over latitudes between 60° North and 60° South were about 6% lower in 1994 than in 1980 (Figure 4).

How has society responded to the stratospheric ozone depletion issue? In 1978 the use of CFCs as propellants for spray cans was banned in the United States, in Canada, and in the Scandinavian countries. In 1987 many nations negotiated an international agreement, coordinated by the United Nations

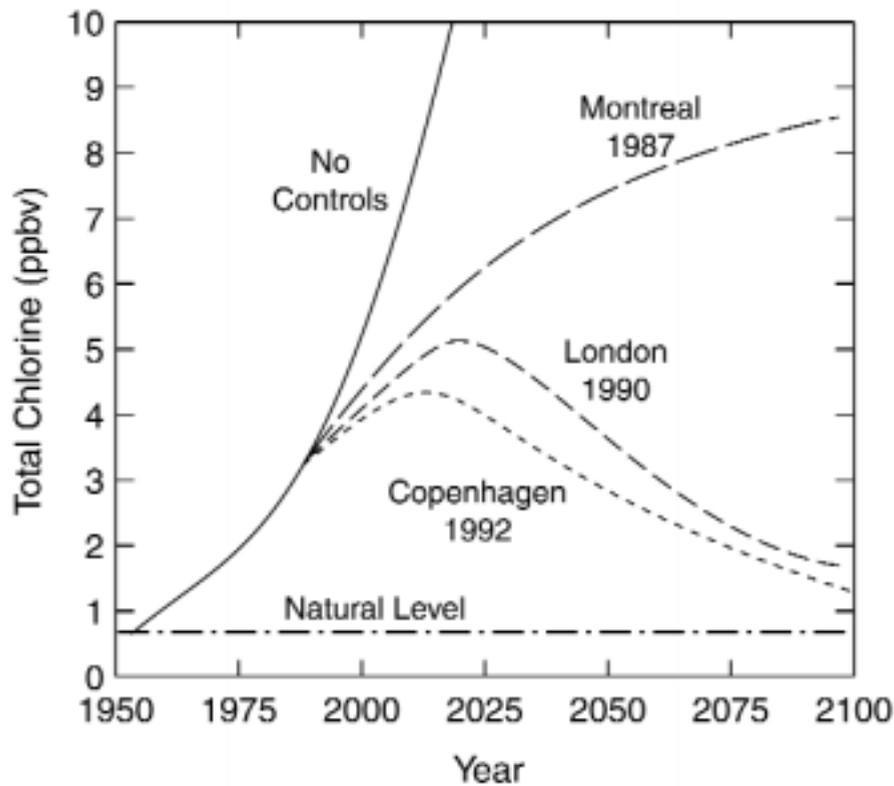


Figure 5. Measured and projected organic chlorine concentrations in the atmosphere according to the provisions of the Montreal Protocol and subsequent amendments.

Environment Program, calling for restrictions in the manufacture of CFCs. The agreement – called the “Montreal Protocol on Substances that Deplete the Ozone Layer” – has provisions for periodic revisions in response to scientific and technological developments. The strong scientific evidence linking ozone depletion to the release of CFCs led to important changes in the Protocol. It was first strengthened in London, in 1990, and later in Copenhagen, in 1992, where the various nations participating in the negotiations agreed to a complete phase out in the production of CFCs by the end of 1995. This phase out is restricted to the developed countries; developing countries have a grace period to facilitate a smooth transition to CFC-free technologies.

Measurements have shown very clearly that chlorine levels in the stratosphere have been increasing rapidly since the 1970's, as a consequence of the increase in the concentrations of CFCs. There is one compound of natural origin, methyl chloride (CH_3Cl), which provides a background source of chlorine to the stratosphere and whose concentration has not changed with time. At present, however, the amount of chlorine reaching the stratosphere from the industrial CFCs is several times larger than the amount of natural origin. Thanks to the Montreal Protocol the atmospheric concentrations of the CFCs are no longer increasing. Nevertheless, because of their long residence times in the environment – of the order of a century – the chlorine concentration in the stratosphere is expected to decrease only very slowly (Figure 5), so that the Antarctic ozone hole will not disappear for several decades.

The formulation of the Montreal Protocol sets a very important precedent for addressing global environmental problems. The Protocol demonstrates how the different sectors of society – industrialists, scientists, environmentalists and policy makers – can be very productive by working together, rather than functioning in an adversary mode. Another important precedent of the Montreal Protocol was the establishment of a funding mechanism – financed by the industrialized countries – to help the developing countries meet the costs of complying with the Protocol.

The development of new technologies also played an important role in the solution to the problem. A significant fraction of the former CFC usage is being dealt with by conservation and recycling. Furthermore, roughly 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 their molecules contain hydrogen atoms and hence are less stable in the atmosphere. A large fraction of the HCFCs released industrially is oxidized in the lower atmosphere before reaching the stratosphere. 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 employing new, different technologies. For example, CFC-113 – used extensively in the past as a solvent to clean electronic components – is being phased out by using other cleaning methods such as soap-and-water or terpene-based solvents. But the most elegant new technology involves the manufacture of electronic boards that no longer need to be cleaned.

The CFC-ozone issue has shown us that human activities can lead to serious environmental problems not just on a local, but also on a global

scale. Society faces many other environmental challenges in this coming century. For example, pollution in many large cities is already a very serious local problem; when coupled to pollution resulting from the burning of forests, the problem is beginning to reach global proportions. One of the key elements needed in addressing global environmental issues is to realize that practically all the large problems that society is facing are interconnected. International cooperation will be essential to the solution of these problems.