

## STRATOSPHERIC OZONE DEPLETION

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**Keywords:** Stratospheric Ozone, Antarctic Ozone Hole, Ozone Depletion, Biological Effects of Ultraviolet Radiation, Ultraviolet Radiation

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### Summary

There is now strong evidence that a consequence of human activities is the inadvertent accumulation of a variety of trace gases in the earth's atmosphere. In the past decade, these global-scale changes in the chemical composition of the atmosphere have led to a very significant depletion of the stratospheric ozone layer over Antarctica in the southern spring months and also at northern latitudes. The ozone layer is important for the earth's energy budget; also, it shields the earth's surface from the sun's ultraviolet radiation, which is damaging to biological systems. Ozone is continuously being generated in the stratosphere by the action of solar radiation on atmospheric oxygen, and it is destroyed by catalytic processes involving trace amounts of free radical species. In 1974 the release of chlorofluorocarbons (CFCs) of industrial origin was predicted to lead to the production of chlorine free radicals in the stratosphere, with the consequent catalytic destruction of ozone. Atmospheric observations, laboratory measurements, and modeling calculations have clearly established that this rapid decline in ozone is indeed caused by CFCs. There is now an international agreement in place, the Montreal Protocol, which led to the almost complete phase-out of these compounds in industrialized countries by the end of 1995.

### 1. Introduction

While it has been known for centuries that human society is capable of affecting the environment, only in the past couple of decades has it become clear that human activities may have impacts truly on a planetary scale. The atmosphere, which makes life on Earth possible, is a particularly vulnerable component of our environment: it is massive from the human perspective, and yet from a cosmic perspective it is a very thin

and fragile layer. We can appreciate the potential impact of human activities on the atmosphere 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. In fact, its chemical composition can be inadvertently changed as a consequence of human activities not only locally but globally.

Perhaps the clearest example of a global environmental problem is the one involving the depletion of the ozone layer in the stratosphere by industrial chlorofluorocarbons (CFCs). These compounds were developed in the 1930s as replacements of the toxic refrigerant fluids that were used at that time, namely ammonia and sulfur dioxide; a number of accidents occurred when these chemicals were inadvertently released from home refrigerators located in small rooms where people were sleeping. In contrast, the CFCs are nontoxic and nonflammable, 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, blowing agents for plastic foam, and cleansers for electronic components. For this reason their industrial production increased rapidly during the 1960s, reaching about 700 000 t ( $7 \times 10^8$  kg) per year by the early 1970s. The three most common CFCs are listed in Table 1, together with some of their physical properties.

Compound	Formula	Vapor pressure (atm)		Boiling point
		-13°C	27 °C	
CFC-11	CFCl <sub>3</sub>	0.22	1.12	23.8°C
CFC-12	CF <sub>2</sub> Cl <sub>2</sub>	1.93	6.75	-29.8°C
CFC-113	CFCl <sub>2</sub> CClF <sub>2</sub>	0.08	0.47	47.4°C

Table 1: Physical properties of some common CFCs

The CFCs are so stable that practically the entire industrial production ends up eventually in the atmosphere—most are released within a year or two after being manufactured. In the early 1970s it became possible to monitor their presence in the global atmosphere. British scientists James Lovelock and co-workers were able to detect measurable levels in the atmosphere over the North and South Atlantic, using their newly developed electron capture gas chromatography detector. In the fall of 1973, Mario Molina and F. Sherwood Rowland set out to investigate the fate of the CFCs in the environment; they also wanted to find out if the presence of these industrial compounds in our atmosphere had any significant consequence. Unknown to Molina and Rowland, at that time another group of scientists had pondered 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 to be so small—tens of parts per trillion in the early 1970s—that no serious effects seemed plausible.

After carefully examining the various possible chemical and physical processes for the removal of CFCs in the troposphere, Molina and Rowland reached an entirely different conclusion. In an article published in *Nature* in 1974, they predicted that the release of

CFCs could lead to a serious global environmental problem. To understand how Molina and Rowland arrived at such a conclusion, it is necessary first to consider some important properties of our atmosphere. In the lowest layer—the troposphere—temperature decreases with altitude; in the next layer—the stratosphere—temperature increases with altitude, giving rise to an “inverted” temperature profile that makes vertical movements very slow (Figure 1). The troposphere has very efficient cleansing mechanisms: it has clouds and rain, which remove particles and water-soluble pollutants on a time-scale of a few weeks at most. 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 several years before being removed by finding their way into the troposphere.

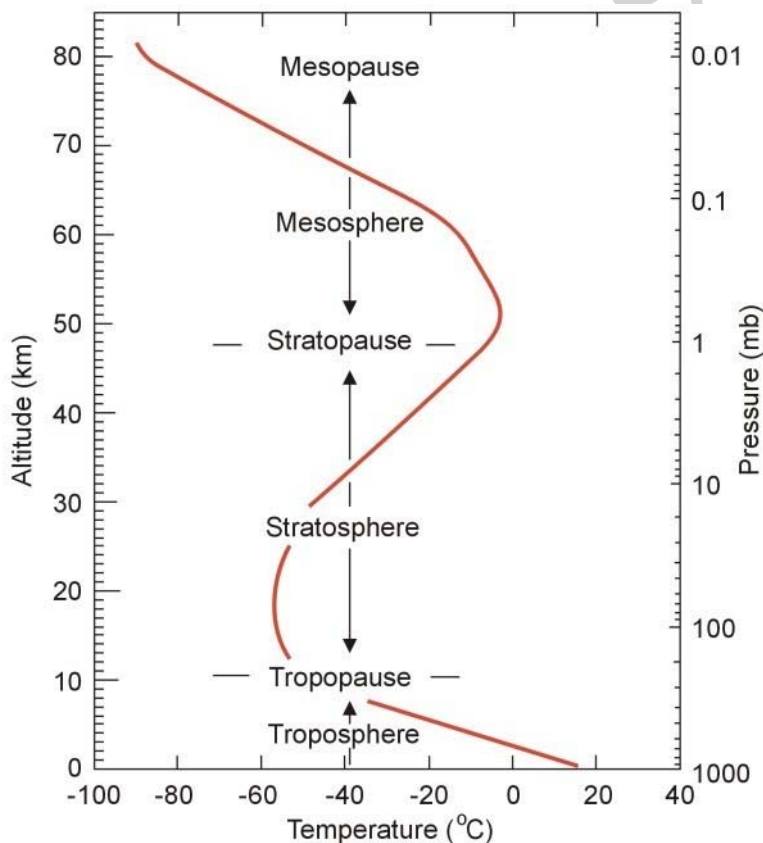


Figure 1: Typical atmospheric temperatures and pressures as a function of altitude

## 2. Stratospheric Ozone

The atmosphere is heated mostly from below, at the earth's surface, which explains why temperature decreases with altitude. However, in the stratosphere, temperature increases with altitude because this layer has a constituent that absorbs some fraction of the incoming solar radiation. This constituent is ozone, molecules of which consist of three oxygen atoms bound together ( $O_3$ ), instead of the two found in the normal oxygen molecules ( $O_2$ ) that make up 21% of the air we breathe. The average concentration of

ozone in the atmosphere is about 300 parts per billion—that is, there are about three molecules of ozone for every ten million air molecules. On the other hand, about 90% of the ozone is contained in the stratosphere, where its concentration reaches several parts per million. 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. The Swiss chemist C. F. Schönbein discovered ozone in 1840 while observing electrical discharges; he noted its distinctively pungent odor and named it “ozone”, which means “smell” in Greek. Early suggestions that atmospheric ozone was the result of lightning discharge led to the idea that ozone was present mostly in the lower atmosphere. However, in the 1880s British chemist W.N. Hartley concluded that ozone is a normal constituent of the higher atmosphere. He also realized that ozone shields the earth’s surface from high-energy ultraviolet radiation from the sun.

In the 1930s, English physicist Sydney Chapman formulated the first theory for the formation and destruction of ozone in the atmosphere, describing how solar radiation converts the various forms of oxygen from one to another. However, measurements of the ozone concentration in the stratosphere were found to be considerably lower than the calculated values based on the Chapman mechanism, which is not surprising since ozone is a rather unstable species that can be destroyed by a variety of chemical reactions. In the early 1970s Paul Crutzen and Harold Johnston independently suggested that trace amounts of nitrogen oxides (NO and NO<sub>2</sub>, jointly referred to as NO<sub>x</sub>), which are naturally present in the stratosphere, control the ozone abundance through a chain of catalytic reactions. A catalyst is a chemical substance that participates in a chemical reaction and influences its speed without undergoing permanent change itself. The species NO and NO<sub>2</sub> have an odd number of electrons; they are free radicals and are chemically very reactive. 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 various chemical processes. The nitrogen oxides are formed in the stratosphere through the decay of chemically stable nitrous oxide (N<sub>2</sub>O), which originates predominantly from soil-borne microorganisms.

Ozone is also present in the troposphere; some of it is generated there by photochemical reactions and some is transported from the stratosphere. The ingredients for its photochemical formation in the lower atmosphere are NO<sub>x</sub>, hydrocarbon fragments, and solar radiation; thus, NO<sub>x</sub> plays a dual role, destroying or generating ozone depending on the altitude. Ozone is a key component of urban smog. It is produced by air pollution in amounts that are relatively small on a global scale, but very significant on a local scale because of the human health effects resulting from breathing air containing ozone at levels above a few tenths of a part per million. Ozone can cause eye, nose, and respiratory problems in humans and animals; it can also cause serious damage to crops and other vegetation.

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### Biographical Sketch

**Mario J. Molina** is Institute Professor at the Massachusetts Institute of Technology (MIT). He has been involved with the chemistry of the stratospheric ozone layer and with the chemistry of air pollution in the lower atmosphere. He was a co-author, with F. S. Rowland, of the 1974 publication in the British magazine *Nature*, of their research on the threat to the ozone layer from chlorofluorocarbon (CFC) gases that were being used as propellants in spray cans, as refrigerants, as solvents, etc. Professor Molina was

born in Mexico City, Mexico. He holds a Chemical Engineer degree (1965) from the Universidad Nacional Autónoma de México, a postgraduate degree (1967) from the University of Freiburg, West Germany, and a Ph.D. in Physical Chemistry (1972) from the University of California, Berkeley. He went to MIT in 1989 with a joint appointment in the Department of Earth, Atmospheric and Planetary Sciences and the Department of Chemistry and was named MIT Institute Professor in 1997. Prior to joining MIT, he held teaching and research positions at the Universidad Nacional Autónoma de México; the University of California, Irvine and the Jet Propulsion Laboratory at the California Institute of Technology. He was elected to the National Academy of Sciences in 1993 and the Institute of Medicine in 1996. Currently he serves on the President's Committee of Advisors in Science and Technology, the Secretary of Energy Advisory Board, National Research Council Board on Environmental Studies and Toxicology, and on the boards of US-Mexico Foundation of Science and other non-profit environmental organizations. He has received several awards for his scientific work including the 1995 Nobel Prize in Chemistry, which he shared with Professors F. S. Rowland and P. Crutzen for their work in atmospheric chemistry.

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