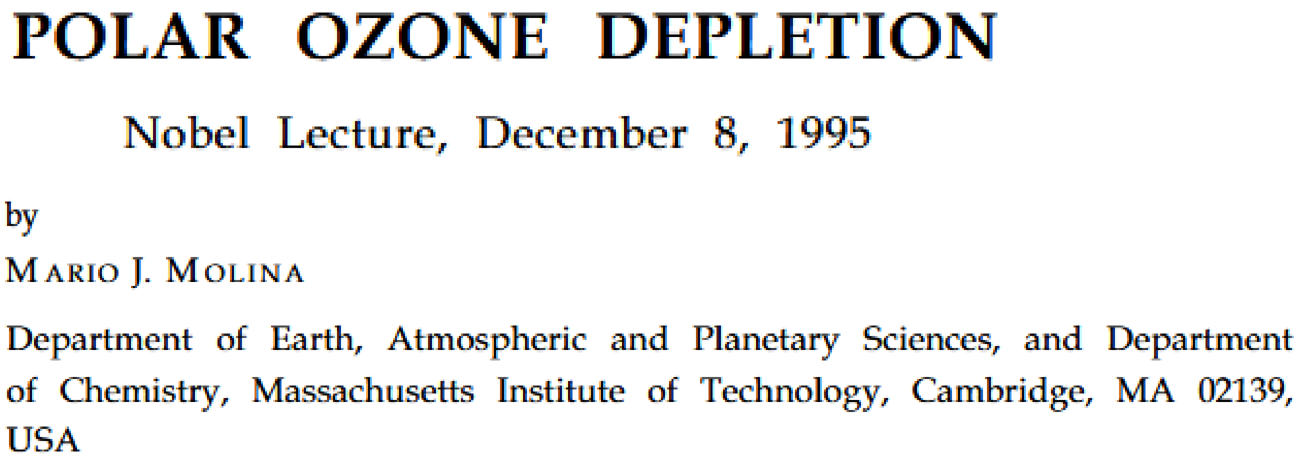
Classic Paper



POLAR OZONE DEPLETION

Nobel Lecture, December 8, 1995

by
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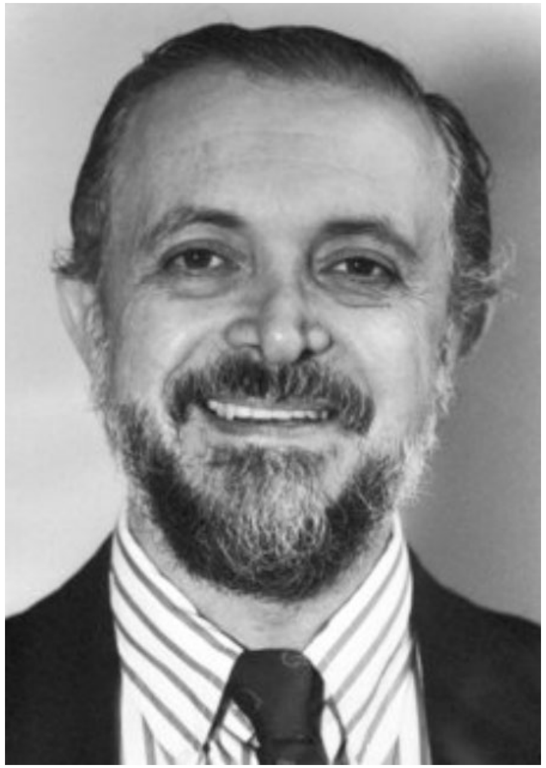


Anubhav Mahapatra
16-11-2024

The ozone layer acts as an atmospheric shield which protects life on Earth against harmful ultraviolet radiation coming from the sun. This shield is fragile: in the past two decades it has become very clear that it can be affected by human activities.

Roughly 90% of the Earth's ozone resides in the stratosphere, which is the atmospheric layer characterized by an inverted - that is, increasing - emperature profile that rises typically from -210 K at its base at 10-15 km altitude, to roughly 275 K at 50 km altitude. The maximum concentration of ozone is several parts per million; it is continuously being produced in the upper stratosphere by the action of solar radiation on molecular oxygen, and continuously being destroyed by chemical processes involving free radicals. Work by Paul Crutzen in the early 1970's [1] established that nitrogen oxides of natural origin, present at parts per billion levels in the stratosphere, are responsible for most of this chemical destruction, which occurs by means of catalytic cycles. Harold Johnston pointed out in 1972 [2] that the large fleets of supersonic aircraft which were being considered at that time could have seriously affected the ozone layer through their emissions of nitrogen oxides.

In early 1974 F. Sherwood (Sherry) Rowland and I proposed that chlorofluorocarbons (CFCs) would decompose in the stratosphere, releasing chlorine atoms which would catalytically destroy ozone [3]. The CFCs are industrial compounds which have been used as refrigerants, solvents, propellants for spray cans, blowing agents for the manufacture of plastic foams, etc. The two important properties which make these compounds very useful are (1) they can be readily transformed from a liquid into a vapor under mild temperature and pressure conditions, as can be seen in Table 1, which displays vapor pressures and boiling points for some of the most common CFCs; and (2) they are chemically very inert, and hence are non-toxic, non-flammable, and do not decompose inside a spray can or a refrigerator.

Table 1. Physical Properties of Some Common CFCs

Compound	Formula	Vapor Pressure (atm)		Boiling Point
		260 K	300K	
CFC-11	$CFCl_3$	0.22	1.12	23.8°C
CFC-12	CF_2Cl_2	1.93	6.75	-29.8°C
CFC-113	$CFCl_2CClF_2$	0.08	0.47	47.7°C

Measurements reported by James Lovelock and coworkers [4] had indicated that the CFCs were accumulating throughout the Earth's atmosphere. In our 1974 paper we suggested that the CFCs will not be destroyed by the common cleansing mechanisms that remove most pollutants from the atmosphere, such as rain, or oxidation by hydroxyl radicals. Instead, the CFCs will be decomposed by short wavelength solar ultraviolet radiation, but only after drifting to the upper stratosphere - above much of the ozone layer - which is where they will first encounter such radiation. Upon absorption of solar radiation the CFC molecules will rapidly release their chlorine atoms, which will then participate in the following catalytic reactions [3,5]:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (2)$$

$$\text{Net: } O + O_3 \rightarrow 2\ O_2 \qquad (3)$$

These free radical chain reactions are terminated by reactions forming temporary reservoirs, the three most important ones being hydrogen chloride, chlorine nitrate, and hypochlorous acid:

$$Cl + CH_4 \rightarrow HCl + CH_3 \tag{4}$$
$$ClO + NO_2 + M \rightarrow ClONO_2 + M \tag{5}$$
$$ClO + HO_2 \rightarrow HOCl + O_2 \tag{6}$$

The free radicals are regenerated by reactions such as the following:

$$HCl + OH \rightarrow Cl + H_2O \tag{7}$$
$$ClONO_2 + h\nu \rightarrow Cl + NO_3 \tag{8}$$
$$HOCl + h\nu \rightarrow Cl + OH \tag{9}$$

Figure 1. The net effect of this chemistry is that the inorganic chlorine produced by the decomposition of the CFCs exists in free radical form - i.e., as "active chlorine" - only a few percent of the time. We have published more detailed reviews of stratospheric halogen chemistry; see, e.g., Abbatt and Molina [6] and Shen *et al.* [7]

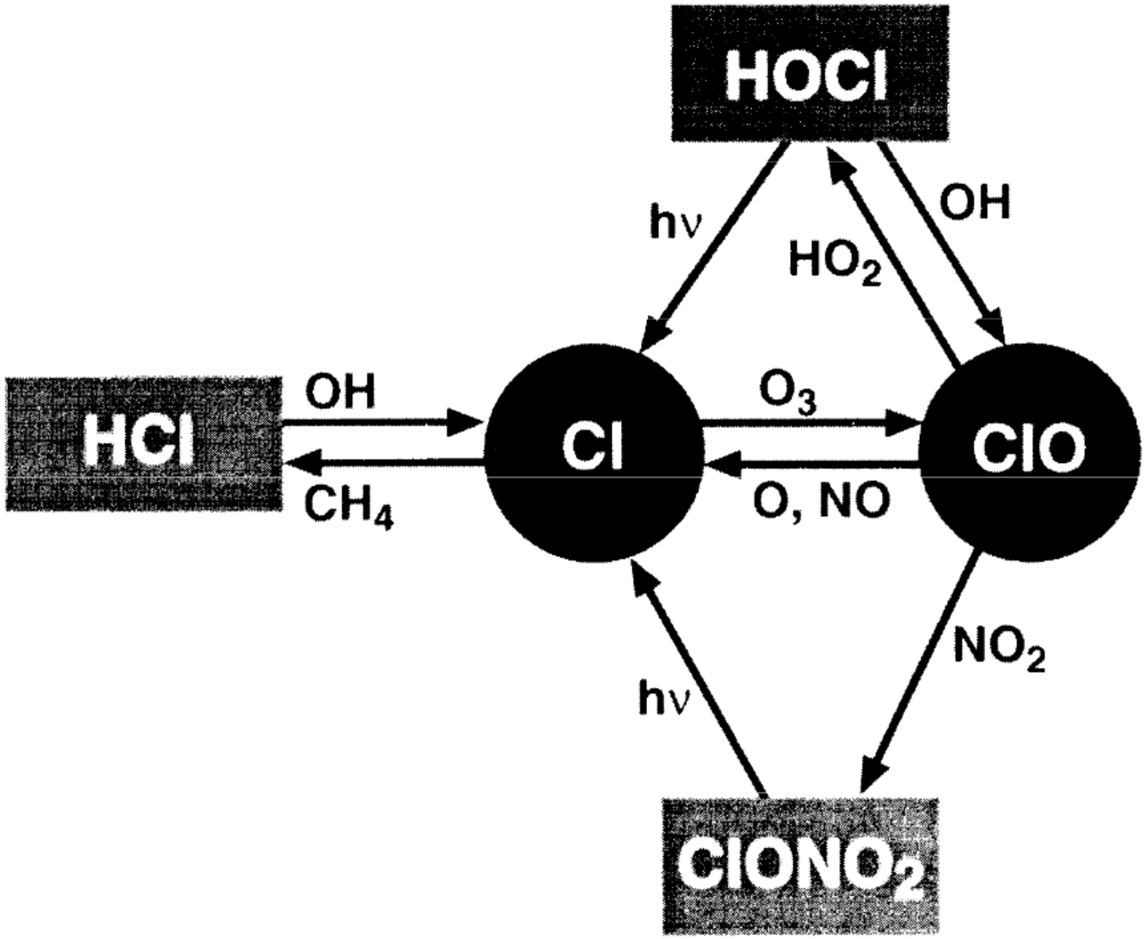


Fig I: Schematic representation of chlorine chemistry in the stratosphere at mid and low latitudes.

POLAR OZONE LOSS

The rapid seasonal decline of stratospheric ozone over the South Pole - the so called "Antarctic ozone hole" - is a startling phenomenon: a large fraction of the total column ozone - more than a third - disappears in the spring months over an area coinciding largely with the Antarctic continent (see Figure 2). In recent years it has become more severe: in October 1992 and 1993 more than 99% of the ozone disappeared at altitudes between about 14 and 19 km [8], where concentrations of this species are usually largest; and in 1995, in mid-September, the ozone hole was the largest ever recorded that early in the austral spring.

The initial question was, thus, whether the observed polar ozone loss was of human origin, or else merely a periodic natural phenomenon, only never before noticed. A prominent early theory put forth to explain this phenomenon had as a principal cause atmospheric dynamics driven by extreme cold temperatures: the hypothesis was that upon first sunrise in the spring, warming of the Antarctic stratosphere would lead to a net upward lifting of ozone-poor air from the troposphere or lower stratosphere. If so, no ozone destruction would be taking place; it would merely be redistributed periodically. Another theory suggested that the 11 year solar cycle was responsible for the effect: chemical destruction of ozone involving catalytic NO_X cycles would occur, with the catalysts being generated in the upper stratosphere by high energy particles or by ultraviolet radiation following enhanced solar activity. A third theory suggested that chlorine and bromine free radicals were the catalysts for the chemical destruction of ozone, the source of these radicals being compounds of industrial origin-CFCs and halons (these are compounds containing bromine which are used as fire extinguishers). This third theory is discussed next in more detail. It is based on our original CFC-ozone depletion hypothesis, but it is modified and extended to take into account the peculiar conditions prevailing over Antarctica: Figure 3 displays schematically the most important reactions of the modified theory (compare to Figure 1, the original chemistry).

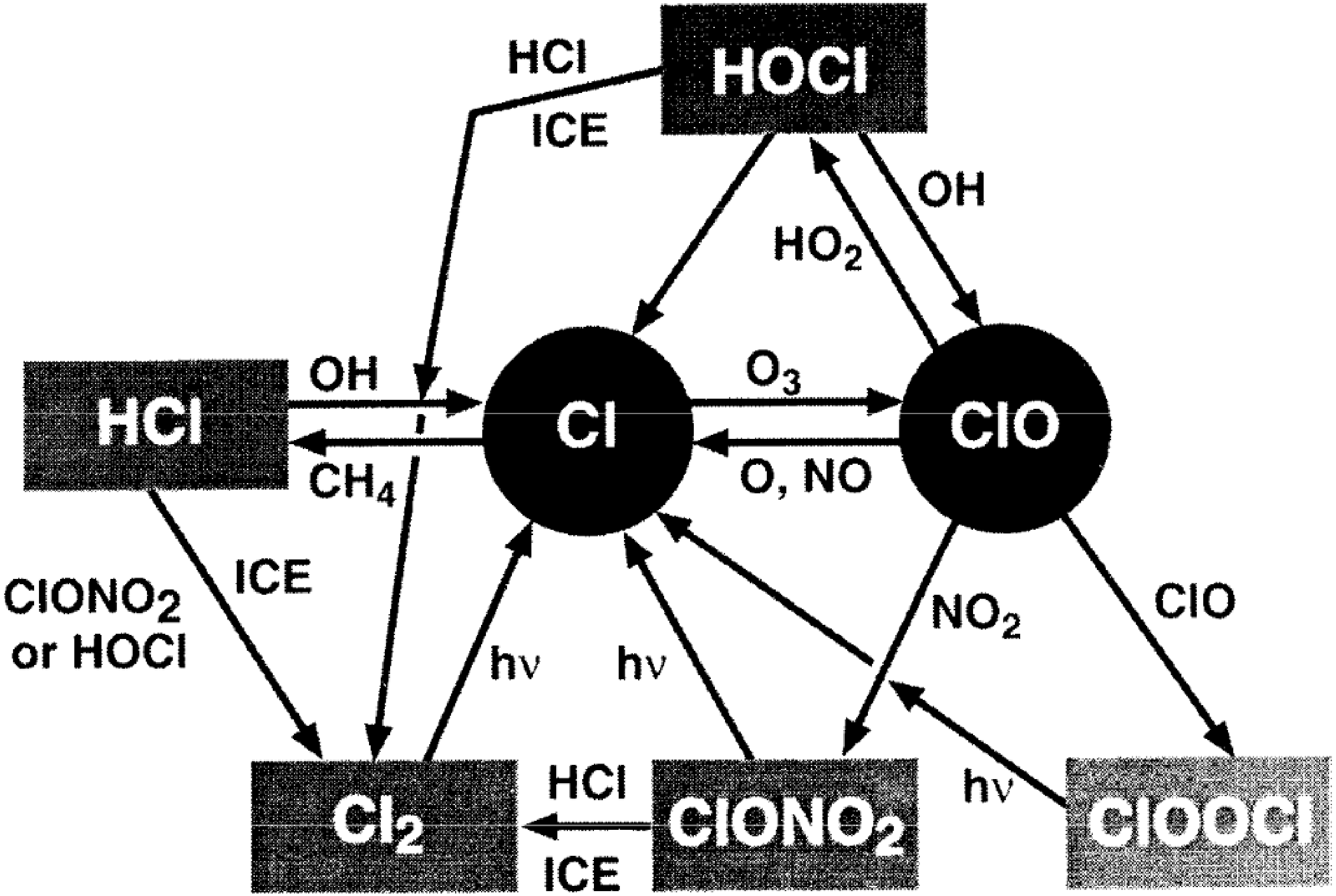


Fig. 3: Schematic representation of chlorine chemistry in the polar stratosphere.

POLAR STRATOSPHERIC CLOUDS

In contrast to the troposphere, the stratosphere is extremely dry and practically cloudless - the concentration of water vapor is measured in parts per million, and is, in fact, comparable to that of ozone. Normally, there is a thin layer of aerosol throughout the lower stratosphere - a haze - first described in 1961 by Junge and co-workers [17]. The aerosols droplets are mostly liquid and consist of supercooled aqueous sulfuric acid solutions - about 75% H_2SO_4 by weight at mid and low latitudes, with radius roughly 0.1 µm. The "background" number density falls typically in the 1-10 cm^{-3} range, but it may increase between one and two orders of magnitude following the injection of SO_2 directly into the stratosphere by major volcanic eruptions, such as El Chichon in 1982 and Mount Pinatubo in 1991. The SO_2 is oxidized in the stratosphere to form H_2SO_4 on a time scale of months, and the excess particles decay over a period of a few years. SO_2 emitted at the earth's surface by processes such as the combustion of coal is mostly oxidized and removed from the atmosphere (as acid rain) before reaching the stratosphere. The background aerosols arise mainly from COS, which is also emitted at the earth's surface but is sufficiently stable to reach the stratosphere, where it photooxidizes to yield SO_2 and subsequently H_2SO_4.

Polar stratospheric clouds (PSCs) form seasonally over the polar regions. Satellite-based instruments have been monitoring these clouds long before the discovery of the ozone hole by observing the attenuation of sun light, which is scattered at wavelengths characteristic of the size of the cloud particles. In the winter and spring months, sharp increases in the attenuation resulting from the presence of PSCs are evident, followed by a decrease in the summer after the cloud particles evaporate or sediment out.

The PSC particles form by condensation of vapors on the pre-existing sulfuric acid aerosols. Observations have also indicated the existence of different types of clouds, the two most common ones being often referred to as Type I and Type II PSCs. The later ones are present only when the temperatures fall below the frost point of water, which is typically about 185-187 K the particles are roughly 10 micrometer in diameter and are composed principally of water-ice crystals. These Type II clouds are more prevalent over Antarctica, because of its lower temperatures compared to the Arctic. Type I PSCs are observed more frequently, forming at temperatures above the frost point of water but below 190-195 K, with particle diameters of roughly one micrometer. Thermodynamic considerations coupled with laboratory experiments indicate that Type I PSC particles consist most likely of nitric acid trihydrate (NAT), which is the most stable condensed phase under the conditions which lead to the formation of these clouds. However, more recent laboratory experiments indicate that the aerosol particles are not likely to freeze at temperatures above the water frost point [18]. Furthermore, investigations performed in the field [19] and in the laboratory [20, 21] indicate that the liquid sulfuric acid droplets should absorb significant amounts of nitric acid and of water vapors under polar stratospheric conditions, with a very rapid change in composition - and hence size - occurring over a narrow temperature range [22, 23], thus explaining the formation of Type I clouds below a certain temperature threshold. Hence, it appears that Type I PSCs are sometimes liquid - particularly over the Arctic - and sometimes solid.

CHEMISTRY ON CLOUD PARTICLES

Laboratory experiments, field observations and atmospheric modeling calculations have now established that chemical reactions occurring on PSC particles play a central role in polar ozone depletion. These reactions have two separate effects, referred to as chlorine activation and nitrogen deactivation: first, chlorine is transferred from the relatively inert reservoir compounds HCl and $ClONO_2$ into forms that can be readily photolyzed (mostly Cl_2); and second, nitrogen oxides are removed from the gas phase, through incorporation of nitric acid into the PSCs, thus preventing the formation of $ClONO_2$, a species that interferes with the catalytic chlorine cycles which destroy ozone. In fact, some PSC particles grow large enough to precipitate, permanently removing nitric acid from the stratosphere; this is the process labeled denitrification.

The following are the key chlorine activation reactions:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (23)$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (24)$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O \quad (25)$$

The most important reaction is (23), the first one among these three. Our early laboratory experiments indicated that this reaction does not occur in the gas phase at significant rates [24a]. However, we noticed in those experiments that this and other reactions involving chlorine nitrate are very sensitive to surface effects; similar observations had been reported by Sherry Rowland's group [24b]. In 1986 Solomon *et al.* [10] suggested that reactions (23) and (24) would be promoted by PSCs, setting the stage for efficient ozone depletion over Antarctica. In 1987 we carried out a series of laboratory measurements showing that indeed reaction (23) is remarkably efficient, requiring only a few collisions of the reactant $ClONO_2$ with ice exposed to HCl vapor [25]. This peculiar chemical reactivity of ice was surprising; in contrast to liquid water - and the well-established chemistry of aqueous ions - reactions promoted by ice at temperatures down to 180 K were unprecedented. Our results were subsequently corroborated by several other groups (for a review, see Kolb *et al.* [26]).

MEASUREMENTS OF KEY SPECIES OVER ANTARCTICA

Beginning in 1986, a series of field experiments were designed to test the various hypothesis which had been put forth to explain the Antarctic ozone hole. For example, observations of upward flow in the polar stratosphere would have verified the "dynamics only" theory. The solar cycle theory would have been supported by observations of high NOx levels in regions where ozone was being depleted; furthermore, according to this theory in years of low solar activity the polar stratosphere would recover to normal pre-ozone hole conditions. In contrast, expectations from the halogen theory were low levels of nitrogen oxides, and high levels of active chlorine.

The first observational campaign designed to test these theories - the National Ozone Experiment (NOZE) - was mounted in the winter of 1986. The NOZE scientists, based on McMurdo, Antarctica, and led by Susan Solomon, performed remote sensing measurements of key stratospheric species such as NO_2, O_3, and chlorine free radicals. Their findings provided the first evidence that the chemistry of the Antarctic stratosphere was highly perturbed, with the halogen chemistry mechanism appearing most likely. A second NOZE campaign, as well as the Airborne Antarctic Ozone Experiment (AAOE) were conducted in 1987. This expedition was based on Punta Arenas, Chile: the results from flights conducted over a six week period largely confirmed and extended the results from the NOZE experiment. The observations provided very clear evidence of a strong downward flow within the Antarctic polar vortex, which is the region of the stratosphere where the ozone hole develops: contrary to predictions based on the dynamics only theory, the levels of tracers such as the CFCs, CH_4 and N_2O were typical of air coming from higher altitudes - "aged" air which had been exposed to short-wavelength ultraviolet radiation. Furthermore, the concentration of NOx was remarkably low, in contrast with expectations from the solar cycle theory.

The unique instruments required for all these experiments - as well as the halogen hypothesis itself - were developed in a relatively short amount of time’: the community was well prepared for these new developments, since it had vigorously continued for over a decade the pursuit of scientific research on the stratospheric ozone issue.

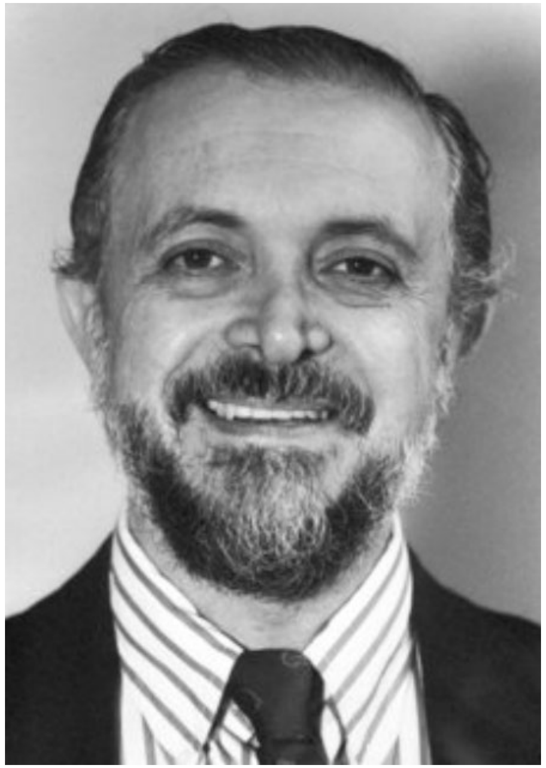
CONCLUSIONS

Much remains to be learned about stratospheric chemistry - and, in more general terms, about the physics and chemistry of the global atmosphere. On the other hand, the cause-effect relationship between human-produced chemicals and ozone depletion is rather well established now: the signals connected with the Antarctic ozone hole are very large indeed. The stratospheric ozone issue has shown us that mankind is quite capable of significantly affecting the atmosphere on a global scale: the most striking effects of CFCs, which are emitted mostly in the north, are seen as far away as possible from the sources, namely over the South Pole. This global problem has also shown us that different sectors of society can work together - the scientific community, industry, environmental organizations, government representatives and policy makers - to reach international agreements: the Montreal Protocol on Substances that Deplete the Ozone Layer has established a very important precedent for the solution of global environmental problems.

ACKNOWLEDGEMENTS

Many colleagues and collaborators have contributed to the work described above; while only some of them have been mentioned here, I would like to express my appreciation to all of them. I am grateful to my past and present students and associates for their dedication in carrying out research in my laboratory. I am especially indebted to my wife, Luisa, who has been my closest collaborator for many years. I also want to acknowledge the sponsors of our research, which have included the National Aeronautics and Space Administration and the National Science Foundation.

Biography



Mario J. Molina
The Nobel Prize in Chemistry 1995

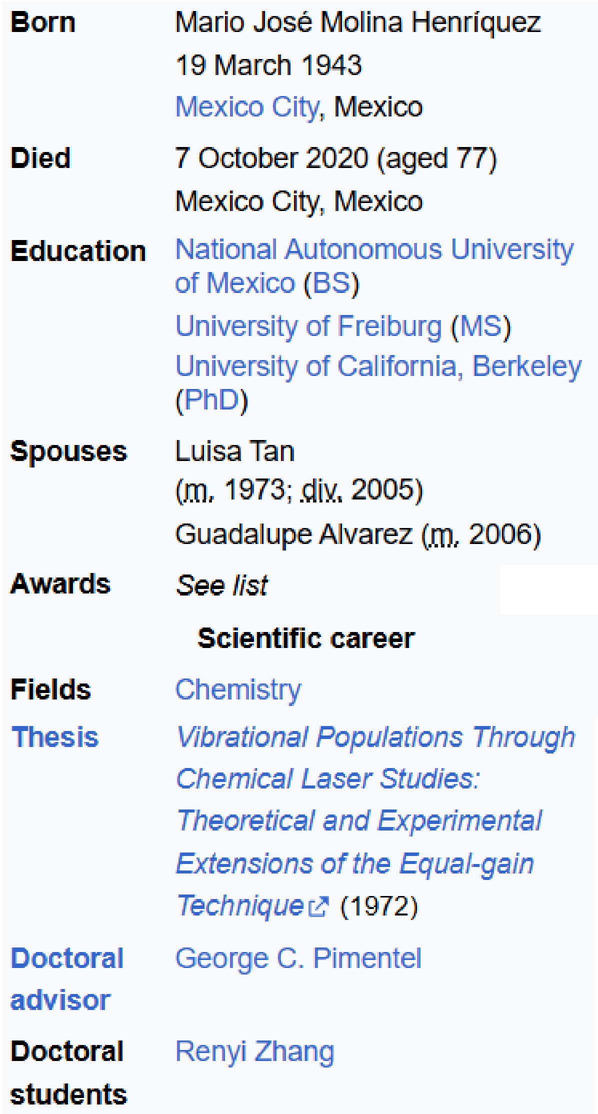
Born: 19 March 1943, Mexico City, Mexico

Died: 7 October 2020, Mexico City, Mexico

Affiliation at the time of the award: Massachusetts Institute of Technology (MIT), Cambridge, MA, USA

Prize motivation: “for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone”

Prize share: 1/3



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Scientific career	
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Doctoral advisor	George C. Pimentel
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-Thank you