Environmental Chemists Share the 1995 Chemistry Nobel Prize

An Honour for Unearthing the Secrets of our Ozone Roof

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> "The whole of my remaining realizable estate shall be dealt with in the following way: the capital, invested in safe securities by my executors, shall constitute a fund, the interest on which shall be annually distributed in the form of prizes to those who, during the preceding year, shall have conferred the greatest benefit on mankind."
>
> — *from the will of Alfred Nobel.*

The 1995 Nobel prize for chemistry to the trio — Paul Crutzen, Mario Molina and Sherwood Rowland — is the first chemistry Nobel for any environmentally related work. While the announcement came as a surprise to many, the Nobel committee had clearly adhered to the will of Alfred Nobel. By detailing the delicate balance that maintains the ozone layer and showing how human activity on the earth is perturbing it, "the three researchers contributed to our salvation from a global environmental problem that could have catastrophic consequences," reads the citation from the Royal Swedish Academy of Sciences.

Leaky Roof over the Living Room

Ozone (O_3), a molecule composed of three oxygen atoms, is found primarily in the stratosphere between 12 and 50 km above the Earth's surface. The formation of ozone from molecules of oxygen in the upper atmosphere is part of a cyclic series of chemical reactions that prevents the sun's ultraviolet (UV) radiation from reaching the earth. The steps are illustrated in the following mechanism, proposed by Chapman in 1930.

$$O_2 + UV\ (\lambda < 242\ nm) \longrightarrow, O + O$$
$$O + O_2 + M \longrightarrow, O_3 + M$$
$$O_3 + UV \longrightarrow, O + O_2$$
$$O + O_3 \longrightarrow, O_2 + O_2$$

where M represents another molecule of oxygen or nitrogen that is unchanged in the reaction.

Why worry about the ozone layer? Without it human beings would suffer serious biological effects from solar radiation, including a large increase in the incidence of skin cancer and irritating eye disorders. Light-skinned people, especially children, are most at risk. Closer to the earth, however, ozone is a harmful pollutant that causes damage to lung tissue and plants.

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1995 Nobel Laureates in Chemistry


Paul J Crutzen (1933-)


Mario J Molina (1943-)


F S Rowland (1927-)

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After years of observation and experimentation, it seems clear that the ozone layer is affected by natural and man-made activities. Scientific measurements have documented a downward trend in the total column amount of ozone over mid-latitudes, as well as substantial ozone loss over polar regions during the spring seasons.

Theories to Explain the Ozone Thinning

Theoreticians came up with three competing models to explain the ozone depletion. One group of scientists blamed the 11-year solar cycle — the periodic waxing and waning of the sun's energy output. A second group suggested that natural changes in stratospheric winds were responsible. But a third theory held man-made chemicals as the culprits. The fast paced research of the last two decades proved that ozone in the stratosphere is removed predominantly by catalytic cycles involving gas phase reactions of active free radical species in the HO_x, NO_x, ClO_x, and BrO_x families.

Crutzen was instrumental in establishing the nitrogen oxide chemistry in 1970. The following year, Johnston made the connection between supersonic transport emissions and the ozone layer. Until then, it had been thought that the radicals H, OH and HO_2 (collectively called HO_x) were the principal catalysts for ozone loss. The next leap towards a better understanding of ozone chemistry was in 1974, when Rowland and Molina first suggested that chlorine from chlorofluorocarbons (CFCs) was destroying the ozone layer. At that time, several papers had been published indicating that CFCs were excellent tracers in the troposphere.

CFCs set the Chlorine Atoms Free

CFCs is the name traditionally given to the group of fully halogenated methanes. They were invented in 1928 as safe alternatives to ammonia and sulphur dioxide refrigerants. Rowland and Molina recognized that once CFCs are released into the troposphere, they will remain there until transported to the

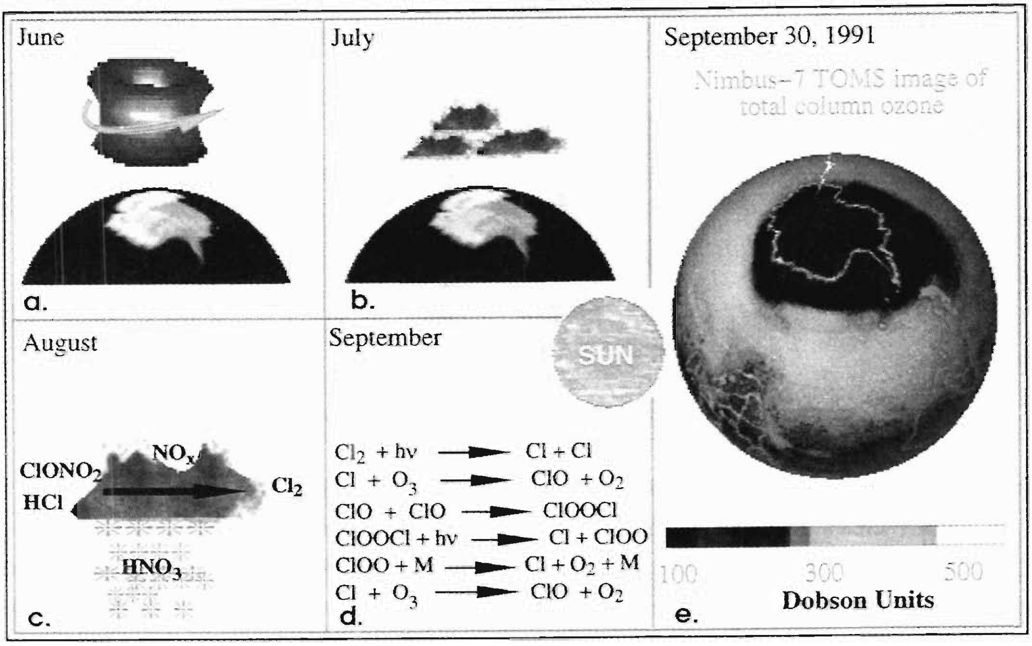

***Figure 1** The sequence involved in the formation of the ozone hole. a) Polar vortex circles Antarctica in winter. b) Temperatures drop low enough to form clouds known as polar stratospheric clouds (PSCs). c) PSCs denitrify and dehydrate the stratosphere through precipitation and convert HCl and $ClONO_2$ into more reactive chlorine. d) The arrival of the sun photolyses the Cl_2 to radicals that can catalyse ozone destruction. e) The ozone hole is completely established in September and October (1 Dobson Unit = 2.69×10^{16} molecules of ozone cm^{-2}). The polar vortex breaks down in November and the ozone level attains normal values in December (not shown in the figure).*

stratosphere and decomposed by solar UV radiation.

$$CCl_2F_2 + UV\ (\lambda < 220\ nm) \longrightarrow CClF_2 + Cl.$$

The atomic chlorine released reacts with ozone as follows:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2 .$$

The chlorine atom thus freed, can participate once again in the breakup of ozone molecules. The net effect of this pair of reactions is the conversion of atomic oxygen (O) and ozone into molecular oxygen (O_2).

$$O + O_3 \longrightarrow 2O_2 .$$

The quantitative aspects of the ozone hole, however, could not be explained by this cycle. As a result, several other proposals have been made for the catalytic mechanism linking halogen radicals to the chemical destruction of ozone. The catalytic cycle that is considered

Milestones in Ozone Research

1839 - Schonbein discovered ozone using a chemical test with potassium iodide paper.

1880 - Hartley recognized that the 293nm cutoff in the solar UV radiation at the Earth's surface corresponds very closely with the UV absorption spectrum of O_3.

1926 - Dobson developed an ultraviolet spectrophotometer to measure the total column ozone.

1930 - First qualitative photochemical theory for the formation and decomposition of ozone in the atmosphere was formulated by Sidney Chapman.

1950 - Bates and Nicolet drew attention to the role played by H, OH and HO_2 (products of photolysis of water vapour) in the catalytic reduction of odd oxygen above 60km.

1970 - Paul Crutzen suggested that additional important processes must be taken into account in order to correctly describe the photochemistry of the atmospheric ozone.

1971 - Johnston made a connection to supersonic transport emissions. This resulted in a very intensive debate among researchers as well as among technologists and decision makers.

1974 - Rowland and Molina established the possibility of major stratospheric ozone depletion from CFCs.

1978 - Nimbus-7 satellite was launched. It contains the 'Total Ozone' Mapping Spectrometer that measured the daily ozone concentration globally till 1993.

1985 - The British Antarctic Survey announced their startling discovery of an 'ozone hole' over Halley Bay, Antarctica.

1987 - Molina and his wife Louisa proposed a chlorine chain involving ClO dimer formation which is now thought to account for the massive ozone destruction.

1995 - Crutzen, Molina and Rowland were jointly awarded the Nobel Prize in Chemistry for their pioneering work on the subject of formation and decomposition of ozone.

currently involves the formation of ClO dimer at low temperatures followed by photolysis or thermal decomposition (*Figure 1d*) proposed by Molina and his wife Louisa.

A Hole has Opened in the Southern Sky

Anxiety deepened when a continent-sized hole (as wide as the United States of America and as deep as Mount Everest) which had eroded the ozone from 40 km above the Earth and eventually extended downwards to 15-20 km in the ozone layer was detected in the 1980s over Antarctica by a British team. Unravelling the reasons for this massive destruction of ozone has involved a vast collaborative effort, in which the three laureates have remained active. The series of processes currently seen as responsible for the ozone hole formation are presented in *Figure 1*. Some of them occur simultaneously in parallel stages.

The Antarctic ozone hole, once a mystery, is now one of the best understood aspects of the entire subject thanks to the pioneering research by Crutzen, Molina, Rowland and several others. It is now accepted that chlorine chemistry is responsible for the ozone depletion. Yet chlorine photochemistry alone cannot explain the entire ozone loss; chemists believe that Antarctica's unusual meteorology is also responsible for setting up conditions that allow photochemical ozone destruction.

Early Sign of Coming Doom

Although a fairly solid picture has emerged about the global ozone loss, many pieces of the ozone puzzle are still missing. Will new ozone problems develop in the near future? Despite the complexities and uncertainties, almost everyone agrees on the following: Chemistry is central to understanding any phenomenon associated with ozone layer depletion.

Under the auspices of the United Nations, the major industrial countries have agreed to cease production of CFCs. The United Nations Environment Programme and the Ozone Secretariat invited the world community to observe 16 September, 1995 as the first-ever International Day for the preservation of the ozone layer. This day was designated to commemorate the signing, in 1987, of the Montreal Protocol on substances that deplete the ozone layer.

At last, the world is waking up to protect the ozone shield for future generations! Scientists are now involved in developing safe substitutes for CFCs. It is only fitting that the 1995 Nobel prize in chemistry has been awarded to the researchers who played a key role in identifying the chemicals and mechanisms by which the ozone destruction occurs.

Men and women carry on:
making more of self is fun.
But before all world is gone
something drastic must be done.
Is there still a little chance
of putting end to doomsday dance?

(-L.O. Bjorn)

Suggested Reading

M.J Molina and F S Rowland. *Nature.* 249: 810-812, 1974.

P.J Crutzen and F Arnold. *Nature.* 324: 651-655, 1986.

L T Molina and M J Molina. *J. Phys. Chem.*, 91: 433-436, 1987.

P.J Crutzen and M O Andreae, *Science.* 250: 1669-1678, 1990.

F S Rowland. *Ann. Rev. Phys. Chem.*, 42: 731-768, 1991.

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