The Nobel Prize in Chemistry 1995
Paul J. Crutzen, Mario J. Molina, F. Sherwood Rowland

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The Nobel Prize in Chemistry 1995 was awarded jointly to Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland *"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"*.

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

Press Release

11 October 1995

The Royal Swedish Academy of Sciences has decided to award the 1995 Nobel Prize in Chemistry to

Professor **Paul Crutzen**, Max-Planck-Institute for Chemistry, Mainz, Germany (Dutch citizen),

Professor **Mario Molina**, Department of Earth, Atmospheric and Planetary Sciences and Department of Chemistry, MIT, Cambridge, MA, USA and

Professor **F. Sherwood Rowland**, Department of Chemistry, University of California, Irvine, CA, USA

for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone.

The ozone layer - The Achilles heel of the biosphere

The atmosphere surrounding the earth contains small quantities of ozone - a gas with molecules consisting of three oxygen atoms (O_3). If all the ozone in the atmosphere were compressed to a pressure corresponding to that at the earth's surface, the layer would be only 3 mm thick. But even though ozone occurs in such small quantities, it plays an exceptionally fundamental part in life on earth. This is because ozone, together with ordinary molecular oxygen (O_2), is able to absorb the major part of the sun's ultraviolet radiation and therefore prevent this dangerous radiation from reaching the surface. Without a protective ozone layer in the atmosphere, animals and plants could not exist, at least upon land. It is therefore of the greatest importance to understand the processes that regulate the atmosphere's ozone content.

Paul Crutzen, **Mario Molina** and **Sherwood Rowland** have all made pioneering contributions to explaining how ozone is formed and decomposes through chemical processes in the atmosphere. Most importantly, they have in this way showed how sensitive the ozone layer is to the influence of anthropogenic emissions of certain compounds. The thin ozone layer has proved to be an Achilles heel that may be seriously injured by apparently moderate changes in the composition of the atmosphere. By explaining the chemical mechanisms that affect the thickness of the ozone layer, the three researchers have contributed to our salvation from a global environmental problem that could have catastrophic consequences.

How this knowledge evolved

Ozone is formed in the atmosphere through the splitting of ordinary oxygen molecules (O_2) by ultra-violet radiation from the sun. The oxygen atoms thereby liberated react with the molecular oxygen according to:

O_2+ uv-light -> 2O
O+O_2+M -> O_3+M

where M is a random air molecule (N_2 or O_2).

The English physicist Sidney Chapman formulated in 1930 the first photochemical theory for the formation and decomposition of ozone in the atmosphere. This theory, which describes how sunlight converts the various forms of oxygen from one to another, explains why the highest contents of ozone occur in the layer between 15 and 50 km, termed the ozone layer (Fig. 1). Later measurements, however, showed appreciable deviations from Chapman's theory. The calculated ozone contents were considerably higher than the observed ones. Thus, there must be other chemical reactions contributing to the reduction of the ozone content. Some years later the Belgian Marcel Nicolet contributed important

knowledge of how the decomposition of ozone was enhanced by the presence of the hydrogen radicals OH and HO_2.

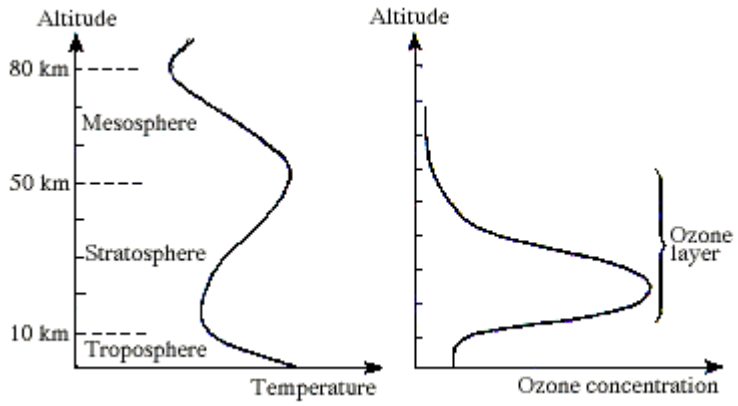

Fig. 1. Variation in temperature and ozone concentration up through the atmosphere

The scientist to take the next fundamental step towards a deeper understanding of the chemistry of the ozone layer was **Paul Crutzen**. In 1970 he showed that the nitrogen oxides NO and NO_2 react catalytically (without themselves being consumed) with ozone, thus accelerating the rate of reduction of the ozone content.

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2+O \rightarrow NO+O_2$
$O_3+\text{uv-light} \rightarrow O_2+O$

Net result: $2O_3 \rightarrow 3O_2$

These nitrogen oxides are formed in the atmosphere through the decay of the chemically stable nitrous oxide N_2O, which originates from microbiological transformations at the ground. The connection demonstrated by Crutzen between microorganisms in the soil and the thickness of the ozone layer is one of the motives for the recent rapid development of research on global biogeochemical cycles.

The first threat noted: supersonic aircraft

The power of nitrogen oxides to decompose ozone was also noted early by the American researcher Harold Johnston, who carried out extensive laboratory studies of the chemistry of nitrogen compounds. In 1971 he pointed out the possible threat to the ozone layer that the planned fleet of supersonic aircraft and supersonic travel (SST) might represent. These aircraft would be capable of releasing nitrogen oxides right in the middle of the ozone layer at altitudes of 20 km. Crutzen's and Johnston's work gave rise to a very intensive debate among researchers as well as among technologists and decision-makers. This was also the start of intensive research into the chemistry of the atmosphere which has made great progress during the past several years. (The subsequent cancellation of

plans for a large SST fleet had other reasons than the environmental risks they involved.)

Spray cans and refrigerators damage the ozone layer

The next leap in our knowledge of ozone chemistry was in 1974, when **Mario Molina** and **Sherwood Rowland** published their widely noted *Nature* article on the threat to the ozone layer from chlorofluorocarbon (CFC) gases - "freons" - used in spray bottles, as the cooling medium in refrigerators and elsewhere and plastic foams. Molina and Rowland based their conclusions on two important contributions by other researchers:

- James Lovelock (England) had recently developed a highly sensitive device of measuring extremely low organic gas contents in the atmosphere, the electron capture detector. Using this he could now demonstrate that the exclusively man-made, chemically inert, CFC gases had already spread globally throughout the atmosphere.
- Richard Stolarski and Ralph Cicerone (USA) had shown that free chlorine atoms in the atmosphere can decompose ozone catalytically in similar ways as nitrogen oxides do.

Molina and Rowland realised that the chemically inert CFC could gradually be transported up to the ozone layer, there to be met by such intensive ultra-violet light that they would be separated into their constituents, notably chlorine atoms. They calculated that if human use of CFC gases was to continue at an unaltered rate the ozone layer would be depleted by many percent after some decades. Their prediction created an enormous attention. For the CFC gases were used in many technical processes and their very chemical stability and non-toxicity were thought to render them environmentally ideal. Many were critical of Molina's and Rowland's calculations but yet more were seriously concerned by the possibility of a depleted ozone layer. Today we know that they were right in all essentials. It was to turn out that they had even underestimated the risk.

Ozone content over Antarctica

Molina's and Rowland's report led to certain restrictions on CFC release during the late 1970s and early 1980s. Not until 1985, when the real shock came, was there any real urgency in the international negotiations on release restrictions. Then the Englishman Joseph Farman and his colleagues noted a drastic depletion of the ozone layer over the Antarctic, the "ozone hole" (Fig. 2). The depletion was, at least periodically, far greater than expected from earlier calculations of the CFC effect. The debate among researchers now intensified. Was this a natural climatic variation or was it chemical decomposition brought about by mankind? Thanks to pioneering research by many researchers, among them Crutzen, Molina and Rowland, as well as Susan Solomon and James Anderson, both from the USA, the picture has now cleared. The depletion is caused chiefly by ozone reacting chemically with chlorine and bromine from industrially manufactured gases.

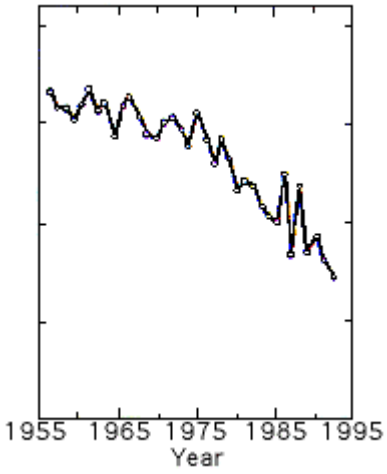

Fig 2. Thickness of the ozone layer (mean monthly value for October) over Halley Bay, Antarctica. Note the drastic depletion since the end of the 1970s.

The surprisingly rapid depletion of the ozone layer over Antarctica could not be explained by transport processes or by gas phase chemical reactions. An alternative mechanism must exist which could accelerate the decomposition of ozone. Crutzen and colleagues identified this mechanism as chemical reactions on the surface of cloud particles in the stratosphere. Thus, the Antarctic ozone depletion appears to be connected with the extremely low prevailing temperatures, which lead to condensation of water and nitric acid to form "polar stratospheric clouds" (PSCs). The ozone-decomposing chemical reactions are greatly reinforced by the presence of cloud particles. This understanding has led to an exciting new branch of atmospheric chemistry: "heterogeneous" chemical reactions on particle surfaces.

The ozone layer and the climate

The ozone problem also has interesting connections with the issue of how mankind is affecting the climate. Ozone, like carbon dioxide and methane, is a greenhouse gas that contributes to high temperatures at the surface of the earth. (CFC gases have a similar effect). Model calculations have shown that the climate is specially sensitive to changes in the ozone content in the lower layers, the troposphere. Here the ozone content has increased markedly during the past century, chiefly because of the release of nitric oxide, carbon monoxide and gaseous hydrocarbons from vehicles and industrial processes and from the combustion of biomass in the tropics. The elevated ozone content in lower atmospheric layers is itself an environmental problem for the damage it can cause to crops and human health. Paul Crutzen has been the world's leading researcher in mapping the chemical mechanisms that determine the ozone content at these levels.

What can we expect in the future?

Thanks to our good scientific understanding of the ozone problem - and very largely to Crutzen, Molina and Rowland - it has been possible to make far-reaching decisions on prohibiting the release of gases that destroy ozone. A protocol on the protection of the ozone layer was negotiated under the auspices of the United Nations and signed in Montreal, Canada, in 1987. Under the latest tightening-up of the Montreal Protocol, the most dangerous gases will be totally banned from 1996 (developing countries have a few years' grace to introduce substitutes that do not harm the ozone layer). Since it takes some time for the ozone-destroying gases to reach the ozone layer we must expect the depletion, not only over Antarctica but also over parts of the Northern Hemisphere, to worsen for some years to come. Given compliance with the prohibitions, the ozone layer should gradually begin to heal after the turn of the century (Fig. 3). Yet it will take at least 100 years before it has fully recovered.

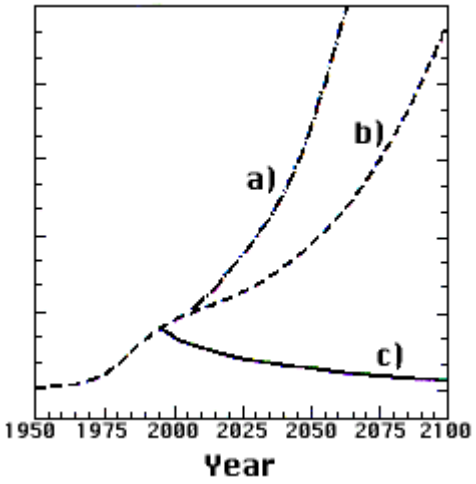

Fig 3. Change in the chlorine content in the stratosphere up to the present and three different future scenarios: a) Without restrictions on release, b) Limitations according to the original Montreal Protocol of 1987 c) The release limitations now internationally agreed. (Chlorine content is a measure of the magnitude of ozone depletion.)

Mario Molina was born in 1943 in Mexico City, Mexico. PhD in physical chemistry, University of California, Berkeley. Member of the US National Academy of Sciences.

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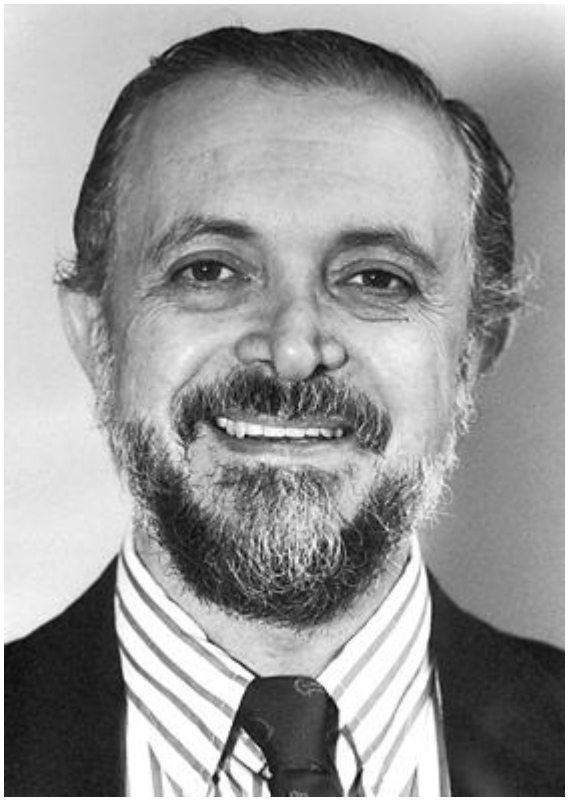
The Nobel Prize in Chemistry 1995
Paul J. Crutzen, Mario J. Molina, F. Sherwood Rowland
Mario J. Molina

Born: 19 March 1943, 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"

Field: Atmospheric and environmental chemistry



Award Ceremony Speech

Presentation Speech by Professor Ingmar Grenthe of the Royal Swedish Academy of Sciences

Translation of the Swedish text

Your Majesties, Your Royal Highnesses. Ladies and Gentlemen,

About thirty years ago, for the first time, we humans were able to view our planet from space. We saw white cloud formations, blue oceans, green vegetation and brown soils and mountains. From space, we could view and study the earth as a whole. We have come to understand that we influence and are influenced by our biosphere, our life zone. One of the tasks of science is to describe and explain how this happens. In their research on the chemical reactions occurring in the earth's atmosphere, the 1995 Nobel Laureates in Chemistry - Paul Crutzen, Mario Molina and Sherwood Rowland - have adopted this global perspective.

The sun is the engine of life. Solar radiation is the source of energy for nearly all living organisms. But only some of the sun's rays are beneficial. It also emits ultraviolet radiation that harms living beings. Many of us have painful experience of excessive sunbathing. Life in the forms we are familiar with is the result of photosynthesis in green plants, which transforms the carbon dioxide in the air into biomass and oxygen. It has taken hundreds of millions of years for the biosphere to develop the atmospheric composition we have today. In the upper atmosphere, or stratosphere, solar radiation can transform oxygen into ozone. The highest ozone concentrations are found at an altitude of between 15 and 50 km. This ozone layer absorbs the sun's ultraviolet radiation very effectively, thereby reducing hazardous radiation on the earth's surface. This, in turn, makes efficient photosynthesis possible. Here we see an example of a feedback mechanism between the chemistry of the biosphere and the atmosphere. If it is disrupted, there may be serious consequences for life on our planet.

This year's laureates have made a series of major contributions to our knowledge of atmospheric chemistry. This has included studying how ozone is formed and decomposes and how these processes can be affected by chemical substances in the atmosphere, many of them the result of human activity. In 1970 Paul Crutzen demonstrated that nitrogen oxides, formed during combustion processes, could affect the rate of ozone depletion in the stratosphere. He suggested that dinitrogen monoxide, popularly known as "laughing gas" and formed through microbiological processes in the ground, could have the same effect. He has also studied the formation of ozone in the lower atmosphere. Ozone is one ingredient of "smog," which is formed by the influence of solar radiation on air pollutants, especially exhaust gases from motor vehicles and other combustion systems. Whereas stratospheric ozone is a prerequisite for life, tropospheric ozone is strongly toxic and harmful to most organisms, even in small quantities.

In 1974 Mario Molina and Sherwood Rowland showed that chlorine compounds formed by the photochemical decomposition of chlorofluorocarbons (CFC or "Freon" gases) could decompose the stratospheric ozone. They presented detailed hypotheses on how these complicated processes occurred.

The discoveries of the three researchers have an unusually close connection with the consequences of modern technology. Supersonic aircraft release nitrogen oxides in the stratosphere. Motor vehicles and stationary combustion plants release the same substances into the lower atmosphere. CFC gases from refrigerators and air conditioners, and in the form of aerosol spray propellants - combined with a "throwaway culture" - result in large-scale emissions of chlorine compounds into the atmosphere. The findings presented by this year's laureates in chemistry have had an enormous political and industrial impact. This was because they clearly identified unacceptable environmental hazards in a large, economically important sector. Their models were also subjected to very rigorous examination which eventually confirmed the main features of their original hypotheses. One obvious result is an international agreement known as the Montreal Protocol, which regulates the manufacture and use of CFCs.

Perhaps the most spectacular observation of changes in the stratospheric ozone content was made in 1985 over Antarctica by Joseph Farman and his colleagues. They observed a rapid and dramatic depletion of ozone in the polar region when sunlight returned after the polar night. The ozone content then built up to more normal levels during the subsequent polar summer and winter, after which the process was repeated. This recurring "ozone hole" was completely unexpected. Eventually a scientific explanation was found, mainly through the research of Susan Solomon, with important contributions from this year's laureates in chemistry as well.

Professor Crutzen, Professor Molina, and Professor Rowland,

You have demonstrated the importance of homogeneous and heterogeneous chemical processes in the earth's atmosphere. You have developed models that combine these data with knowledge of the large-scale transport processes in the atmosphere, and how these models can be utilized as a forecasting tool to evaluate the consequences of emissions of anthropogenic substances of various kinds. You have thereby not only created a clearer understanding of fundamental chemical phenomena, but also of the large-scale and often negative consequences of human behavior. In the words of Alfred Nobel's will, your work has been of very great "benefit to mankind." It is a privilege to congratulate you on behalf of the Royal Swedish Academy of Sciences, and I now ask you to receive your Nobel Prizes from the hands of His Majesty the King.

From *Nobel Lectures, Chemistry 1991-1995*, Editor Bo G. Malmström, World Scientific Publishing Co., Singapore, 1997

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Nobel Lecture

Nobel Lecture, December 8, 1995

Polar Ozone Depletion

The Lecture in Text Format

Pdf 296 kB

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