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NEWS

Pioneers of ozone study bag chemistry Nobel

The 1995 Nobel prize in chemistry has been awarded jointly to Paul J. Crutzen, Department of Atmospheric Chemistry and Biogeochemistry, Max-Planck-Institute for Chemistry, Mainz, Germany; Mario J. Molina, Department of Earth, Atmospheric and Planetary Sciences and Department of Chemistry at Massachusetts Institute of Technology, USA; and F. Sherwood Rowland, Department of Chemistry at the University of California, Irvine, USA.

The laureates are recognized for their pioneering work on the subject of formation and decomposition of ozone. Crutzen was instrumental in establishing the importance of nitrogen oxide chemistry. Rowland and Molina were the first to warn that chlorofluorocarbons (CFCs) released into the atmosphere were depleting the ozone layer. By explaining the chemical mechanisms that threaten to destroy the protective ozone screen surrounding the earth, the three scientists have contributed to our salvation from a global environmental damage that could have serious ill-effects.

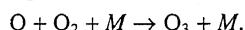
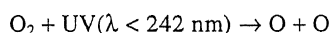
The ozone layer¹⁻³

Ozone, a three-atom molecule of oxygen, occurs naturally as a gas in trace amounts in the Earth's atmosphere. It is found primarily in a layer between about 12 and 50 km above the Earth's surface, in the region of the atmosphere called the stratosphere. The ozone layer is thin, fragile and almost invisible. Yet it plays an exceptionally fundamental role in determining the habitability of the Earth.

A one per cent decrease in ozone allows a two per cent increase in UV radiation that reaches the Earth. Effects from increased UV radiation include an increased risk of skin cancer, cataracts

and immune deficiencies in humans, as well as damage to crops and the plankton that supports marine life. While the stratospheric ozone plays a beneficial role, the surface-level tropospheric ozone is one of the most harmful pollutants, damaging plants and humans. The tropospheric ozone is produced through smog type of reactions⁴, a familiar problem in the atmosphere of many cities around the world.

The first qualitative photochemical theory for the formation and decomposition of ozone in the atmosphere was formulated by Sidney Chapman⁵ in 1930. According to this theory, ozone is produced in the middle and upper atmosphere through dissociation of molecular oxygen by sunlight; the free oxygen atoms combine with other O₂ molecules to form ozone.



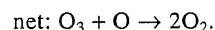
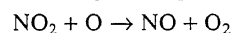
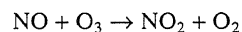
where *M* is a third body required to carry away the energy released in the combination reaction. The triple collision is rare at very high levels (above 60 km), because there are so few molecules. Thus, there is almost no ozone above 60 km. On the other hand, there is almost no atomic oxygen, O, below approximately 16 km, so the formation of ozone is unlikely there, too. These are the reasons most of the ozone is found in the stratosphere.

Early warnings

Chapman's theory, however, showed appreciable deviations from measurements. The calculated ozone contents were considerably higher than the observed ones. To account for this, Bates and Nicolet⁶ drew attention to the role

played by H, OH and HO₂ (products of UV photolysis of water vapour) in the catalytic reduction of odd oxygen above 60 km. But the calculations again showed very large concentrations of ozone than the observations.

Paul Crutzen⁷ in 1970 suggested that additional important processes must be taken into account in order to correctly describe the photochemistry of the atmospheric ozone. Crutzen uncovered an important aspect that nitrogen chemistry accounts for a significant fraction of ozone loss in the natural atmosphere, particularly above 25 km.

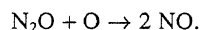


Using available satellite data, Crutzen provided a much more quantitative



Crutzen was born in 1933 in Amsterdam. He obtained his doctorate in Meteorology in 1973 from Stockholm University. He is a member of the Royal Swedish Academy of Sciences, the Royal Swedish Academy of Engineering Sciences and Academia Europaea.

understanding of the sources of NO_x via N_2O oxidation



The primary sources of N_2O include oceans, combustion of fossil fuels, fertilized agriculture fields, tropical and subtropical forests and woodlands. N_2O diffuses upwards from troposphere to the stratosphere to give NO which in turn reacts with ozone. The connection demonstrated by Crutzen⁸ between tropical biomass burning and the ozone concentration is one of the motives for the recent rapid development of research on global biogeochemical cycles.

Johnston⁹ rediscovered the NO_x - O_3 sequence and made a connection to supersonic transport emissions. Supersonic civil aircraft can fly across the ocean at supersonic speeds, but cannot fly across land because of the sonic boom noise. These aircrafts would be capable of releasing nitrogen oxides right in the middle of the ozone layer at the 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. Since then, several multi-dimensional models¹⁰ have been developed to assess the potential environmental effects of aircraft operations in the stratosphere. But it must be pointed out that opposition to the 1970s supersonic fleet came primarily because of the very high development cost and not just the NO_x engine emissions.

The CFC affair

The next vital step towards a deeper understanding of ozone chemistry was in 1974, when Rowland¹¹ and his then postdoc, Molina, established the possibility of major stratospheric ozone depletion from CFCs. During the early seventies, CFCs were used as tracers in the troposphere because of their lack of reactivity. According to 'Rowland-Molina hypothesis' as it is now often described, the

release of atomic chlorine from the solar UV photolysis of CFCs triggers catalytic chain reaction that causes significant depletion of stratospheric ozone layer.

CFCs were invented in 1928 as safe alternatives to ammonia and sulphur dioxide refrigerants. Since then the uses of CFCs have been expanded to include aerosol propellants, air conditioning, refrigerants, foam-blowing agents, and as solvents in electronic industries¹². They are volatile, nonflammable, non-corrosive, nonexplosive, low toxic and chemically inert, and hence safe to work with. The very lack of chemical reactivity that makes CFCs commercially useful also allows them to persist for many decades in the Earth's atmosphere. The most important CFCs¹³ for ozone depletion are: trichlorofluoromethane - CFCl_3 (CFC-11), dichlorodifluoromethane - CF_2Cl_2 (CFC-12), 1, 1, 2 trichlorotrifluoroethane - $\text{CF}_2\text{ClCFCl}_2$ (CFC-113) and carbon tetrachloride (CCl_4).

Rowland and Molina realized that the chemically inert CFCs could be

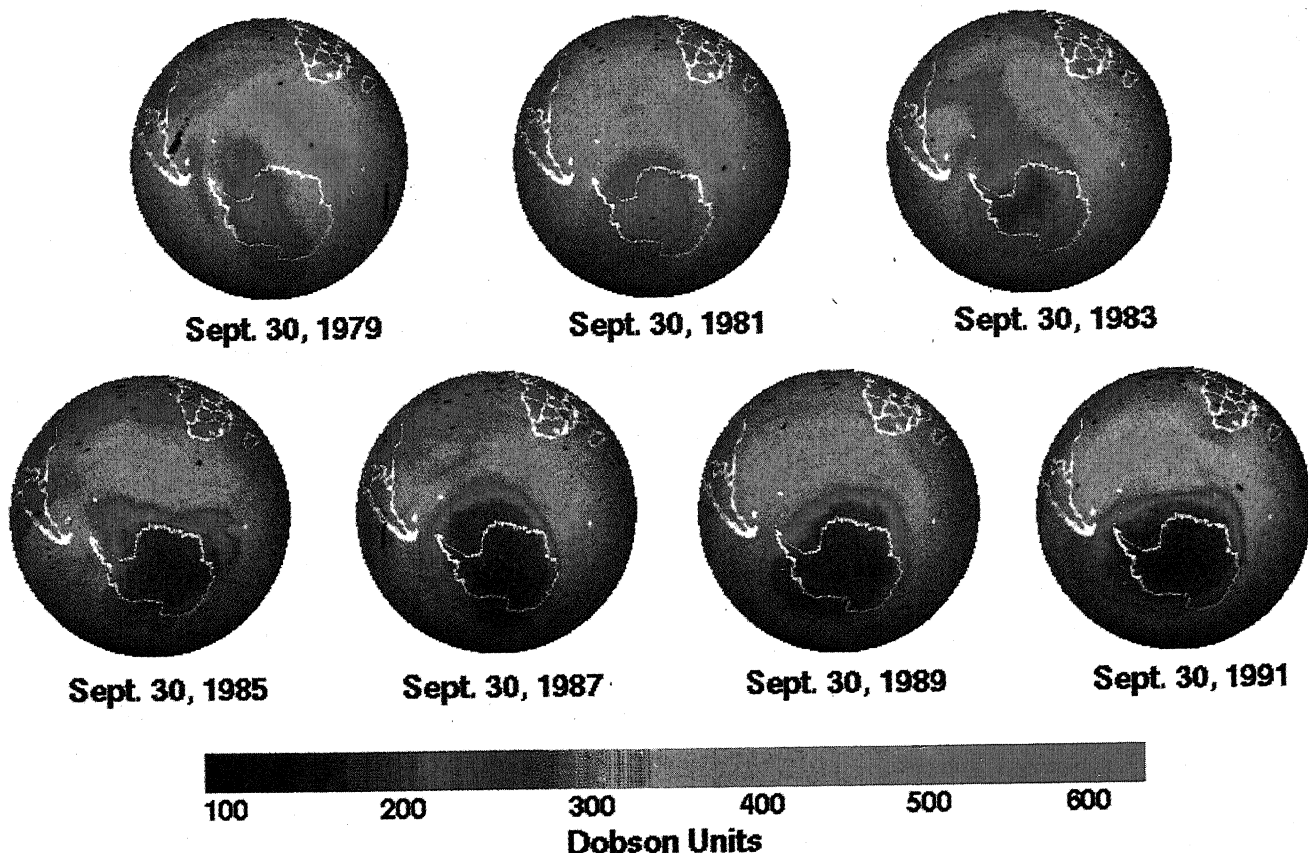
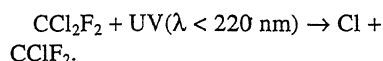
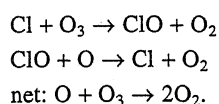


Figure 1. Progressive thinning of ozone layer as revealed by TOMS data.

transported to the stratosphere and decomposed by solar UV radiation.



After they are photolysed, most of the chlorine eventually ends up as hydrogen chloride, HCl, or chlorine nitrate, ClONO₂. These are called reservoir species. Alternatively, the chlorine atoms released could participate in the catalytic removal of ozone. The simplest mechanism suggested by Rowland and Molina is



Note that the role of chlorine atoms is that of a catalyst. Thus, an atom, once released, can participate in the O₃ removal as long as it stays in the atmosphere. The process is even more dramatic for bromine – it has no stable reservoirs; so the Br atom is always available to destroy ozone. On a per-atom basis, Br is 10–100 times as destructive as Cl. In contrast, fluorine is innocuous in the stratosphere. Most of it ends up as its reservoir – hydrogen fluoride (HF), which is extremely stable. Since chlorine and bromine radicals both cause ozone destruction, it comes as no surprise that iodine can also do so.

Hole in the ozone shield

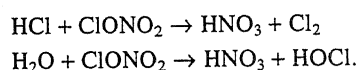
Antarctica is the southernmost continent of the world, and literally speaking, one of the most remote places on the Earth. But here occurred the first large-scale ozone loss. Public concern was aroused in 1985 when atmospheric scientists of the British Antarctic Survey¹⁴ announced their startling discovery of an 'ozone hole' over Halley Bay, Antarctica. Other scientists confirmed the discovery and reported that the region of ozone depletion was actually wider than the continent. These findings led to signing of a treaty in September 1987 on the protection of the ozone layer, known as Montreal Protocol, the first global environment protection agreement.

The quantitative aspects of the ozone hole, however, could not be explained by dynamical processes or by gas phase chemical reactions. In fact, atmospheric models employing the gas-phase chemistry estimated only a 1–2% loss of ozone, significantly less than what has

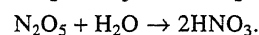
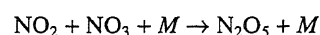


Rowland was born in Delaware, USA in 1927. He earned his B S degree from Ohio Wesleyan University and his M S degree from University of Chicago. In 1952, Rowland received his Ph D from the University of Chicago and taught at Princeton University and the University of Kansas before going to Irvine in 1964 as founding Chairman of its chemistry department. Before the publication of the Rowland–Molina papers on CFC problem, his research centered on the chemical reactions of radioactive isotopes. Currently, Rowland is Emeritus Professor in the University of California and he is also Foreign Secretary of the US National Academy of Sciences.

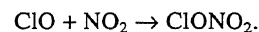
been observed. Such findings prompted the ozone researchers to suspect that an alternative mechanism must exist that could accelerate the decomposition of ozone. As it turned out, Rowland¹⁵ along with Solomon, Garcia and Wuebbles identified this mechanism as chemical reactions on the surface of cloud particles in the stratosphere. The clouds convert two so-called reservoir species of chlorine, HCl and ClONO₂, into more reactive chlorine (Cl₂) and hypochlorous acid (HOCl):



The nitric acid that is produced sticks to cloud particles whereas the Cl₂ and HOCl fly off into the gas phase. Further, Crutzen¹⁶ and Arnold emphasized that the clouds absorb nitrogen oxides and thus it allows the abnormally high chlorine to persist.



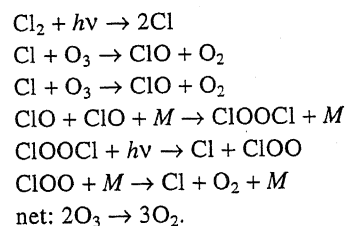
That is, the conversion blocks the following reaction



As a consequence of these studies, an exciting new branch of atmospheric chemistry has emerged: 'heterogeneous' chemical reactions on particle surfaces.

In the stratosphere, a stream of air known as polar vortex circles Antarctica in winter. Air trapped within this vortex becomes extremely cold during the polar night. Temperatures drop low enough to form clouds even in the very dry stratosphere. Particles of nitric acid trihydrate (type I polar stratospheric clouds (PSCs)) first condense at about 193 K; water ice particles (type II clouds) form when the temperature falls still lower, to about 187 K. These clouds freeze-out water vapour (dehumidification) and remove nitrogen oxides (de-nitrification) by adsorption of HNO₃ into the PSCs¹⁷. As mentioned earlier, the PSCs provide a reaction surface for transferring inactive chlorine to an active stable form ready to react once sunlight appears in the spring. The arrival of UV radiation photolyses the Cl₂ to radicals that can catalyse ozone destruction.

Several proposals have been made for the catalytic mechanism linking halogen radicals to the chemical destruction of ozone¹⁸. For example, McElroy¹⁹ and coworkers suggested ClO–BrO mechanism while Solomon¹⁵ and colleagues proposed ClO–HO₂ sequence in addition to the classical catalytic couplet originally introduced by Molina and Rowland. Nevertheless, a chlorine chain²⁰ suggested in 1987 by Mario Molina and his wife Louisa J. Molina, involving ClO dimer formation at low temperatures followed by photolysis and thermal decomposition is now thought to account for the massive ozone destruction. The proposed mechanism follows.



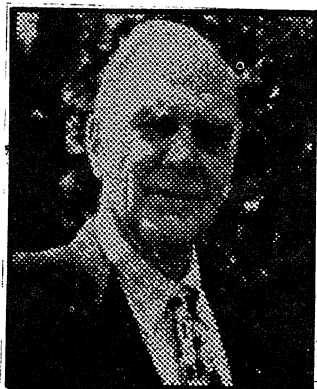
Molina²¹ and coworkers also proposed a variation on this sequence in which the

photolysis of ClOOCl was replaced by thermal decomposition.

Basically, the overall effect of all these processes is to pre-condition the Antarctic stratosphere so that when sunlight returns to the stratosphere in spring two ozone molecules can be transformed into three molecules of oxygen through the above sequence of reactions. Once the spring is well-on, the Sun induces a dynamical breakdown of the stable vortex, and the 'chemical containment vessel', as it is sometimes called, is broken down and mixing of air with lower latitude occurs. PSCs evaporate and the atmosphere returns to a normal state.

Hence, in late winter, regions of ozone depletion around the pole begin to appear. Within a few weeks, the ozone hole is completely established. The hole disappears when the polar vortex finally breaks down after the spring Sun warms the air over Antarctica. Air then sweeps in from low latitudes, bringing nitrogen oxides that tie up the active chlorine and ozone that fills up the hole. The depletion first identified over Antarctica is now being observed to a lesser extent over the Arctic too, and is also much more evident at middle latitudes than has ever been predicted.

The Total Ozone Mapping Spectrometers (TOMS) aboard the NASA's Nimbus-



Mario Molina – the first Mexican to receive a scientific Nobel – was born in 1943 in Mexico City, Mexico. He received his Ph D in Physical Chemistry from the University of California, Berkeley. His wife Louisa is a Chinese and she is also a physical chemist. Mario is a member of the US National Academy of Sciences.

7 spacecraft (launched on 24 October 1978) measures the total column ozone density of stratospheric ozone by observing back scattered solar UV radiation. The results of such measurements are usually presented in Dobson Units (1 DU = 2.69×10^{16} molecules of ozone cm^{-2}). Time series of TOMS images are shown in Figure 1, which illustrates the changes in total ozone over Antarctica at the beginning of every austral spring. The colour scale at the bottom shows the total ozone values in Dobson units. As a matter of fact, the roughly circular ozone hole rotates around the south pole at an offset, moving around the Antarctic continent and back to original position about once a week.

Skeptics, CFCs, and the ozone layer

When Rowland and Molina predicted in 1974 that chlorine from CFCs could chew away the ozone layer, some skeptics did not want to believe it at first. Further, the critics claimed that only small amounts of CFCs could enter the stratosphere because they are heavier than air (the molecular weight of CFC-11 (CCl_3F) is 137.5; that of air 29), adding that the chlorine is vented into the atmosphere by evaporation of sea water and eruptions of volcanoes.

Rowland made a broad attempt to confront the controversy and tackled the misconceptions concerning CFCs and ozone depletion. He argued that indoor experience with mass-dependent molecular diffusion is not applicable in the wind-driven atmosphere, in which the mixing process does not distinguish molecular masses²². If atmospheric gases segregate by weight, then the heavier molecules should dominate at lower altitudes. In reality, however, the relative proportions of Helium-4, Nitrogen-14, and Krypton-84 are unchanged from ground-level to about 100 km, despite the variation in molecular weight. Concerning the chlorine from sea water, it is in the form (NaCl) that is rapidly removed from the troposphere by rain. Volcanoes do eject chlorine as HCl during eruptions. But again, HCl is washed out by rain in the troposphere. Only rarely are eruptions so violent that they inject material directly into the stratosphere.

At last, the fierce debate is now over and the researchers are convinced that

chlorine from CFCs is responsible for the ozone loss. Thanks to pioneering research by many researchers, among them Crutzen, Molina and Rowland, as well as Susan Solomon, James Anderson, Richard Stolarski, Ralph Cicerone and Donald Wuebbles.

Deservedly rewarded...

In recent years, Crutzen²³ has continued to make many other important contributions to the current understanding of atmospheric chemistry, both in the troposphere and stratosphere. Molina's²⁴ work at MIT (and University of California, Irvine and Jet Propulsion Laboratory before going to MIT) has mainly emphasized laboratory studies of heterogeneous reactions in relevance to atmospheric chemistry. Rowland's²⁵ work has primarily involved grab sample measurements of tropospheric gases, such as methane, hydrocarbons and halocarbons. Equally important, he urged scientists to reach beyond their subspecialties and attempt the difficult job of communicating sound science to the public.

Without a doubt, ozone researchers are all delighted and pleasantly surprised by the selection of environmental sciences for recognition by the Nobel committee. The Nobel prize to the trio of atmospheric scientists has elevated the whole area of ozone research. Indeed, it is the first Nobel prize for any environmentally related work. The Nobel committee, perhaps, is starting a trend to recognize scientists who have made fundamental contributions in applied sciences!

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S. Parthiban, Department of Aerospace Engineering, Indian Institute of Science, Bangalore.

The 1995 Nobel Prize in Medicine: A tribute to the power of formal genetics

One of the most remarkable areas of achievements in biology during the past few decades has been the elucidation of the mechanisms that an apparently unstructured egg cell uses to transform itself into a complex-patterned multicellular organism. The first glimpse of this genetic blue-print was obtained through genetic studies with the fruit fly *Drosophila*. Fortunately, these results were obtained at a time when the recombinant DNA and molecular biological techniques were spreading like wild fire and therefore, even these esoteric genetic studies with *Drosophila* attracted the imaginations of biologists working with all kinds of organisms. Very soon the commonality of organization of all living organisms was reaffirmed and scientists could hope to decipher the genetic programme that controls development of as complex an organism as *Homo sapiens*.

Therefore, the committee for this year's coveted Nobel prize in Medicine has very rightly selected three *Drosophila* geneticists for their pioneering work on the genetic control of embryonic development and differentiation using simple but powerful tools of conventional genetic analysis. They are Edward B. Lewis of The California In-

stitute of Technology, USA, Christiane Nüsslein-Volhard of the Max-Planck Institute for Entwicklungsbiologie, Tübingen, Germany and Eric Wieschaus of Princeton, USA. Lewis has been working with *Drosophila*, mostly by himself, for more than 50 years and published¹ a summary and analysis of the data collected by him over many years in his well-known *Nature* paper in 1978; Nüsslein-Volhard and Wieschaus published² their seminal paper, also in *Nature*, in 1980 when both were at the EMBO Laboratory in Heidelberg, Germany. These two papers have changed the course of contemporary biology in more than one way by allowing a new look at the transformation of a seemingly structureless egg into a complex, patterned and organized organism. The concepts generated in these papers have found very wide applications in studies dealing not only with animals but plants as well. It is remarkable indeed, that these two papers were based on simple methodologies of 'pure' or formal genetics with no 'sophisticated' or 'advanced' molecular biological techniques being employed. As is the wont of geneticists, they simply obtained a large number of mutations, selected those that affected early development,

mapped the mutations on linkage maps and characterized the consequences of either individual mutations or specific combinations of the different mutations on the developmental phenotype of the individual. The only 'advanced' analytical techniques employed by these scientists were scanning electron and/or dark-field microscopy! It was the systematic analysis and a foresight in rationalization of the phenotypic effects of the various mutant genes that led them to formulate general principles of Nobel prize-winning consequence.

Study of embryonic development has fascinated biologists for a long time. Curiosity to know how a single-celled egg develops into a complex organism led to the growth of the whole field of Embryology to describe the morphological and anatomical changes taking place in a developing embryo. In biology it is often necessary to examine the abnormal so that the normal may be understood. Thus a conventional experimental embryological approach to the study of a complex process has been to disrupt one step in the chain of events and follow its consequence. This path was followed by generations of eminent embryologists during this century and their efforts did help in providing some