

Nobel Chemistry Prize Gives a Stratospheric Boost to Atmospheric Scientists

After identifying mechanisms for atmospheric ozone depletion, Crutzen, Molina and Rowland have continued to strengthen our understanding of such processes.

Reaching out in an interdisciplinary direction, the Royal Swedish Academy of Sciences has awarded the 1995 Nobel Prize in Chemistry to Paul Crutzen, Mario Molina and F. Sherwood Rowland for "their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone." The award comes on the eve of the 1996 global ban on ozone-depleting chemicals, mandated by the 1987 Montreal Protocol and its later updates.

Crutzen is the director of the division of atmospheric chemistry at the Max Planck Institute for Chemistry in Mainz, Germany; Molina is the Lee and Geraldine Martin Professor of Environmental Sciences at MIT; and Rowland is the Donald Bren Research Professor of Chemistry and Earth System Science at the University of California, Irvine. All three have explored the impact of emissions on the atmosphere, primarily those of man-made origin.

Susan Solomon of the National Oceanic and Atmospheric Administration's Aeronomy Laboratory in Boulder, Colorado, who led two Antarctic expeditions to study the ozone hole in the 1980s, told us that the evidence for ozone depletion is stronger than ever, despite some public misconceptions to the contrary: The South Pole

continues to lose more than 60 percent of its ozone each austral spring. After this past winter even the normally milder North Pole developed a hole about half as deep as that at the South Pole.

Catalytic cycles

The thin layer of naturally occurring ozone is primarily concentrated between 15 and 50 kilometers above sea level, at which altitudes the molecules intercept much of the Sun's ultraviolet radiation, shielding Earth's flora and fauna from the harmful effects of the Sun's uv radiation.

Crutzen, as a meteorology student at Stockholm University in the late 1960s, tried to explain why there was not as much ozone observed in the atmosphere as one would calculate from the photochemical reactions involving only oxygen. Some researchers had proposed that the ozone was being destroyed by catalytic reactions with the hydrogen radicals OH and HO₂, through which a small concentration of radicals might promote the destruction of a great number of ozone molecules. But no one knew what the actual rates of these reactions were.

Crutzen did not feel that hydrogen radicals were the whole story; he suspected there was another catalytic cycle, involving the nitrogen oxides, NO and NO₂ (collectively, NO_x). In the late 1960s Crutzen learned about measurements of HNO₃ in the stratosphere, from which he deduced how much NO_x might be present. The result was a 1970 paper in which Crutzen showed that, with a certain

level of NO_x, one could account for the discrepancy between observed and calculated ozone concentrations.¹

But how could the NO_x get into the stratosphere? Crutzen knew from studies in 1965 that they could result from the photochemical breakdown of nitrous oxide, N₂O, which comes from microbiological processes within the oceans and soil. In a 1971 paper² Crutzen proposed that the N₂O released from the biosphere, being largely inert, stays in the troposphere until it is carried by air currents into the stratosphere, where it decomposes into NO_x. Before Crutzen, no one had realized that reactive chemicals could be transported to the stratosphere in an inert form, said Ralph Cicerone of the University of California, Irvine.

Although most public concern today focuses on the chlorofluorocarbons, nitrous oxide emissions are growing because of man's use of fertilizers and other activities (see the article by Ann P. Kinzig and Robert H. Socolow in *PHYSICS TODAY*, November 1994, page 24).

Independently of Crutzen, Harold Johnston at the University of California, Berkeley, had also called attention to the possible catalytic destruction of ozone by nitrogen oxides—especially those that would be created by combustion in supersonic aircraft.³ By the time he completed his study, Johnston told us, Congress had already ruled against supersonic transports in this country.

CFCs: inert tracers

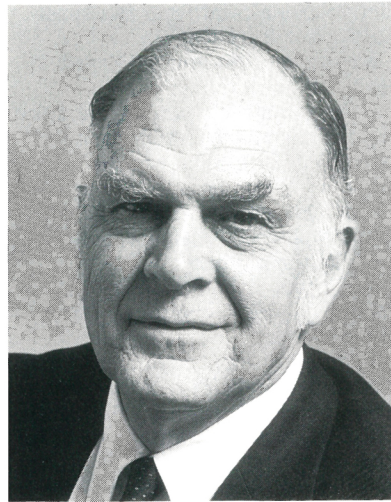
Yet another catalytic cycle for the de-



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struction of ozone was that involving chlorine atoms. In 1974 Rowland and Molina, who at the time was a postdoc in Rowland's lab at Irvine, uncovered this threat by tracing what becomes of the chlorofluorocarbons being added to the atmosphere as a consequence of uses such as refrigerants and aerosol propellants. Using a highly sensitive instrument he had developed, James Lovelock, an independent scientist who lives in Cornwall, UK, had demonstrated in 1973 that roughly all the CFCs produced up to that point were still around and had spread globally throughout the lower atmosphere. CFCs had been selected by industry largely because they were chemically inert, and it was interesting to speculate just what in the atmosphere might eventually cause the CFCs to break down.

After eliminating a number of possible reactions, Molina and Rowland calculated that the CFCs would eventually be wafted up to the stratosphere before ultraviolet rays would break up the molecules. They estimated the mean atmospheric lifetime of these compounds to be 40–80 years for CFC-11 (CCl_3F) and 70–150 years for CFC-12 (CCl_2F_2), compared with current estimates of about 50 and 100 years, respectively. Molina and Rowland next explored what would happen to the chlorine atoms, deducing that they would catalyze the destruction of ozone molecules.⁴

After they completed their studies, Molina and Rowland learned from Johnston that Richard Stolarski (now at the NASA Goddard Space Flight Center) and Cicerone had proposed the chlorine-based catalytic cycle at a conference several months earlier.⁵ But Stolarski and Cicerone had focused on the possible threat of chlorine emissions from volcanoes and from the space shuttle, not from CFCs.

Molina and Rowland predicted that if CFCs continued to be produced in the steady state at the 1974 rate, the ozone layer would be depleted by 7–13%. The forecast caused a big stir, because the potential uv increase was large—and so were the potential economic costs of a ban on the products.

The Irvine hypothesis rested on scanty evidence at the time. But it was increasingly strengthened as more data came in: Balloon-borne instruments found CFCs in the stratosphere and confirmed that they photodissociate; further stratospheric measurements found ClO , which is the rate-limiting radical in the catalytic chain reaction; and systematic studies, some done by Rowland and

Molina themselves, ruled out additional sinks for the CFCs.

The evidence was convincing enough by 1976 to prompt the US, as a precautionary measure, to ban the use after 1978 of CFCs as aerosol sprays, an application for which there were available substitutes. Because of the growth in other uses of CFCs, the total commercial production worldwide remained constant from 1974 to 1990, at about 1 million tons annually.

The ozone hole

Far greater urgency was added to the concern over ozone depletion in 1985, when Joseph Farman and his colleagues from the British Antarctic Survey, who had been tracking ozone levels at the South Pole for many years, found that the mean value measured in October 1984 had dropped to nearly half of what it had been in the early 1970s. Since 1984 the ozone hole has continued to deepen, with ozone virtually disappearing at altitudes of 15–21 km each spring.

Clearly a new explanation was needed for this dramatic effect, and by the mid-1980s there was a large and active atmospheric science community poised to attack the problem. (See the news story about this so-called “ozone hole” in *PHYSICS TODAY*, July 1988, page 17, and a correction in *PHYSICS TODAY*, August 1988, page 21.) The answer was found in chemical reactions that are facilitated by the polar stratospheric clouds that form during the Antarctic winter. Through reactions on the cloud-particle surfaces (heterogeneous rather than purely gas-phase reactions), diatomic chlorine molecules are liberated from the reservoir species, hydrochloric acid (HCl) and chlorine nitrate (ClONO_2). When the Sun emerges at the start of the Antarctic spring, its visible rays dissociate the diatomic molecules and the stratosphere becomes loaded with free chlorine atoms, ready to attack the ozone.

To piece together this scenario required the hypotheses, measurements and calculations of a good many people. In the words of the Swedish Royal Academy of Sciences, the picture has now cleared, “thanks to the pioneering research by many researchers, among them, Crutzen, Molina and Rowland, as well as Susan Solomon and James Anderson [of Harvard University].”

Continuing activities

Crutzen has also studied abnormal ozone production in the troposphere as a result of reactions involving pollutants. He continues to worry about

nitrous oxide emission from manure and has most recently studied chemical reactions in the marine boundary layer. Born in Amsterdam in 1933, Crutzen earned his PhD from Stockholm University in 1969. After a postdoc at the Clarendon Laboratory at the University of Oxford, he returned to Stockholm in 1971 to work at the university there. In 1974 he moved to the National Center for Atmospheric Research in Boulder, Colorado, becoming director of the division of atmospheric chemistry in 1977. Crutzen joined the Max Planck Institute for Chemistry in 1980.

Molina said he is still studying the impact of CFCs on the Northern Hemisphere, the potential consequences of a new fleet of SSTs now being explored by NASA and the impact on ozone of particulates from volcanoes. Molina was born in 1943 in Mexico City and received a PhD in physical chemistry from the University of California, Berkeley, in 1972. After working at Irvine as a postdoc (1973–75) and faculty member (1975–82), he became a senior research scientist at Caltech's Jet Propulsion Laboratory. Molina went to MIT in 1989.

Rowland has looked at mid-latitude ozone concentrations by season to discern downward trends not seen in annually averaged data. Together with Don Blake of Irvine, he regularly monitors concentrations of various atmospheric species. Born in Ohio in 1927, Rowland earned a PhD in radiochemistry under Willard Libby (himself a Nobel laureate) at the University of Chicago in 1952. He taught first at Princeton (1952–56) and then at the University of Kansas (1956–64) before going to Irvine.

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References

1. P. Crutzen, *Q. J. R. Meteorol. Soc.* **96**, 320 (1970).
2. P. Crutzen, *J. Geophys. Res.* **76**, 7311 (1971).
3. H. Johnston, *Science* **173**, 517 (1971).
4. M. J. Molina, F. S. Rowland, *Nature* **249**, 810 (1974); F. S. Rowland, M. J. Molina, *Rev. Geophys. and Space Phys.* **13**, 1 (1975).
5. R. S. Stolarski, R. J. Cicerone, *Can. J. Chem.* **52**, 1610 (1974). ■

The award of the Nobel Peace Prize to Joseph Rotblat and the Pugwash Conferences on Science and World Affairs is reported on page 61.