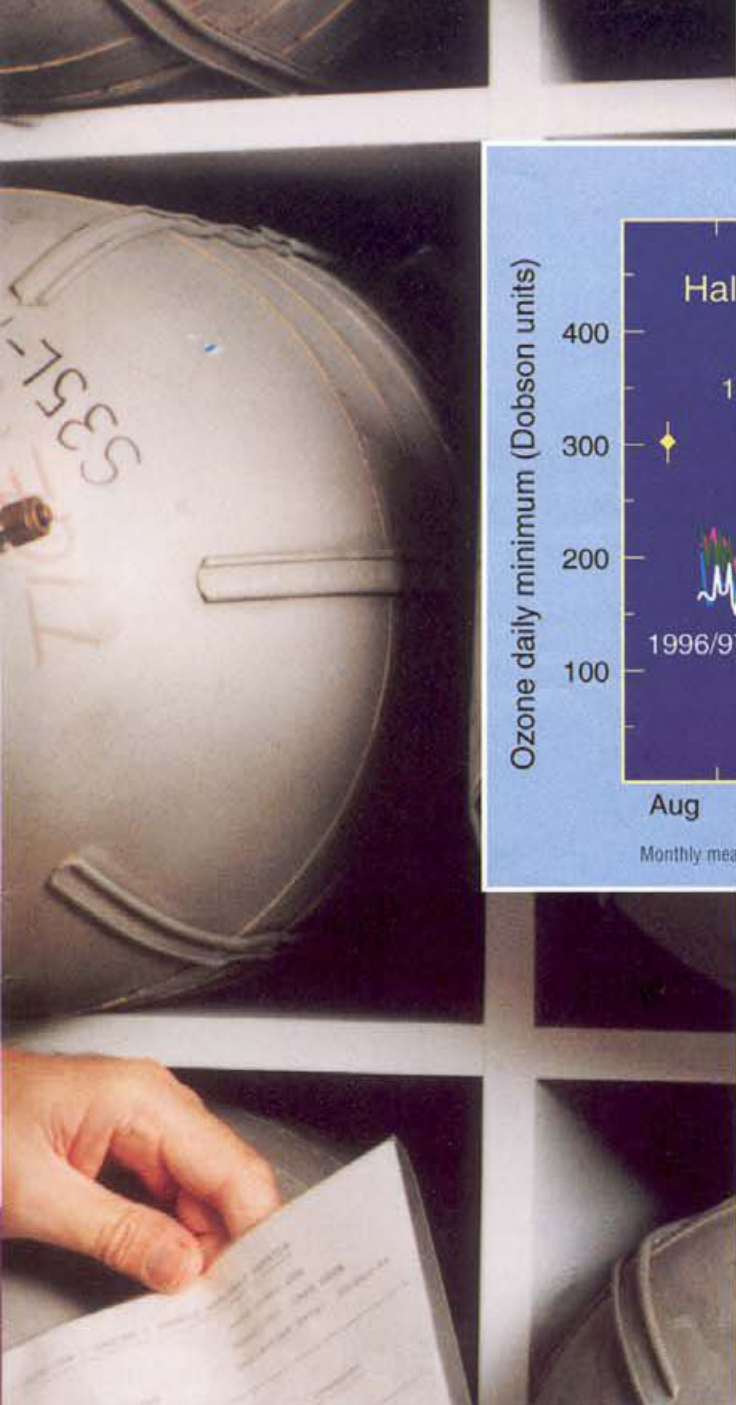




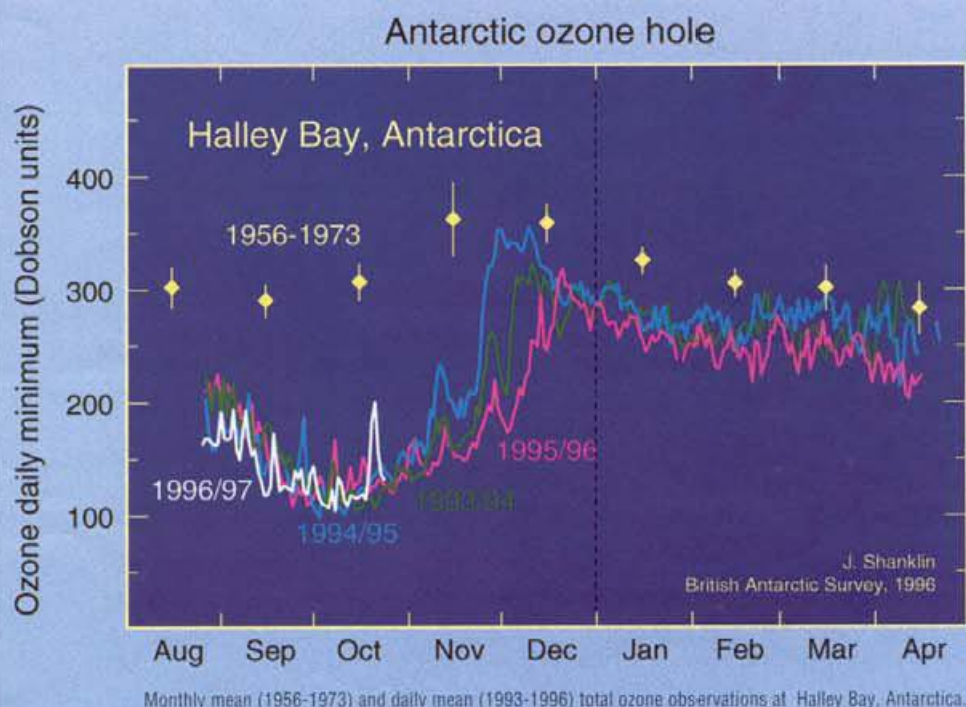
Dr Paul Fraser has been awarded two NASA Citations: in 1994 for participation in a northern hemisphere stratospheric photochemistry experiment in 1993, and in 1995 for the southern hemisphere 1994 stratospheric Antarctic ozone experiment. In 1995 he was awarded the Eureka Prize for environmental research for his contributions to ozone-depletion research and scientific advice to government, industry and public on CFCs and ozone depletion. In the same year he received a United Nations Environment Program Citation for his leadership in the 1994 international ozone assessment.

O Defending the zone

Graeme O'Neill talks to Australia's own CFC expert about discoveries that prompted a timely response to ozone depletion.



David Whittas



Chlorine atoms destroy ozone by removing an oxygen atom, forming chlorine monoxide (ClO) and an oxygen molecule (O₂). Chlorine monoxide reacts quickly in the atmosphere with oxygen atoms, liberating atomic chlorine. The chlorine atoms are again free to react with ozone. In this way, a single chlorine atom can destroy thousands of ozone molecules, a process terminated when chlorine atoms react with a source of hydrogen such as methane.

Ozone depletion is severe over Antarctica due to rapid release of molecular chlorine (Cl₂) from reactions on the surface of ice crystals within polar stratospheric clouds. The chlorine comes from compounds absorbed on the ice such as chlorine nitrate (ClONO₂) and hydrochloric acid (HCl) which originates from the breakdown of CFCs. In spring, the reappearance of sunlight over Antarctica splits chlorine molecules into single chlorine atoms that destroy ozone.

In 1985, a British Antarctic Survey team discovered that the stratospheric ozone layer over Antarctica had thinned alarmingly, allowing increased levels of damaging ultraviolet-B radiation to reach the Earth's surface.

Dr Paul Fraser of CSIRO's Division of Atmospheric Research received the news with surprise and excitement. He had been aware of the possibility since 1974, the year that Californian research chemist Professor Sherwood Rowland became concerned about spray-can products because he calculated that the chlorofluorocarbon (CFC) propellant in them could destroy the Earth's ozone layer (see story on page 34).

Fraser, who had been recruited to study the greenhouse gas carbon dioxide, saw the research paper by Rowland and Professor Mario Molina, and made the career switch

that was to make him an international authority on CFCs. The now-classic *Nature* paper, for which the authors won the 1995 Nobel Prize for Chemistry, described a self-sustaining cycle of chemical reactions by which a lone chlorine atom, prised free of the tenacious grasp of a chlorofluorocarbon molecule by ultra-violet radiation, in theory could destroy up to 100 000 ozone molecules in the stratosphere.

'It seems a long time ago, and the chemistry was an over-simplification of what actually happens to chlorine and bromine in the stratosphere,' Fraser says. 'But in the crudest sense, it approximated what happens in the Antarctic stratosphere during winter and spring. All the chlorine and bromine atoms originating from CFCs and halons are available to destroy ozone: that's why we see pronounced ozone loss in Antarctica, and not

over the rest of the globe, where only a small fraction are available.'

Rowland and Molina predicted that ozone depletion would be global, but Fraser says it is now known that ozone-depleting reactions are greatly enhanced in the unique environment of polar stratospheric clouds, on super-cooled water droplets or ice crystals nucleated by tiny, frozen droplets of nitric acid solution.

Ozone levels over Antarctica have plunged by 25-30% during the past two decades. In the same period, ozone has declined by about 6% over temperate regions. Over Antarctica in spring there is near complete destruction of ozone at the altitudes where polar stratospheric clouds occur (15-20 km).

The mid-latitude decline was largely unexplained until recently, when scientists identified another culprit for enhancing ozone destruction by CFCs: supercooled droplets of

A Nobel effort



THE fact that the world is likely to survive the CFC-initiated assault on our protective ozone layer is largely thanks to Nobel prize-winning chemists, Professors Sherwood Rowland (pictured) and Mario Molina.

On a recent visit to CSIRO's Division of Atmospheric Research in Melbourne, Rowland explained that his interest in stratospheric ozone was stirred by a 1972 *Nature* paper by English scientist James Lovelock describing results from his invention, the electron capture detector which can measure meta-trace concentrations of atmospheric gases.

'We had been using CFCs as inert sources of chlorine in nuclear reactors. So we knew something about their lack of chemistry,' Rowland says. 'When Lovelock reported finding CFCs in the atmosphere it caught my eye.'

Shortly after, Rowland learned of new findings showing that

chlorine atoms destroy ozone. With Molina, who had joined his research group, Rowland achieved the breakthrough that would earn them both the Nobel Prize. The two reported in a now-famous *Nature* paper that CFCs would find their way into the stratosphere. There, intense sunlight would split the molecules, liberating active chlorine. The resultant chlorine would catalytically reduce ozone levels by several per cent.

Sherwood recalls the nervous night he spent waiting to hear from the Nobel Prize Committee. There was a whisper on the scientists' grapevine that he, Molina, and Dutch-born ozone chemist Paul Crutzen were favoured to win the prize. 'I was told that if successful, I would get a phone call at 3.30 am,' he says. Sherwood woke the next morning and glanced at his bedside clock. It was 6.30. 'I thought, oh well ...' The phone rang five minutes later.

The 1995 Nobel Prize shared by the three chemists marks the first time that the Swedish Academy has honoured research into anthropogenic impacts on our environment.

Paul Holper

sulfuric acid resulting from volcanic eruptions and from carbonyl sulfide from the world's oceans. In the three years after the massive 1991 eruption of Mt Pinatubo in the Philippines, ozone levels at mid-latitudes plummeted by an additional 2%, a third of the long-term decline.

Fraser says that when ozone researchers looked back through data gathered since 1979, they detected another dip in stratospheric ozone concentrations, in the aftermath of the 1982 eruption of Mexico's El Chichon volcano.

The 1996 Antarctic ozone hole was similar to the deep holes of the previous three years. Pinatubo's influence has faded, but chlorine and bromine concentrations in the stratosphere have continued to rise, and are likely to do for the next few years, despite the speedy reaction of scientists, governments and business to the 1985 ozone crisis. However stratospheric chlorine and bromine levels should stop rising by the end of this decade.

'When international concerns about ozone surfaced in 1975, governments and industry didn't know what was going on, but they were prepared to fund research,' says Fraser. 'By the early 1980s, there was a greatly enhanced knowledge of the stratosphere, so when the ozone hole was discovered in 1985, we were able to propose a mechanism that we could test and confirm experimentally.'

'In the early 1980s there was no proof of any global ozone loss. There was a small downward trend, but we couldn't tell if it was significant, or blame CFCs. Ozone levels fluctuate naturally by 1-2%, tracking the 11-year sunspot cycle; the fewer sunspots, the less ozone is produced in the stratosphere.

'By 1986 we were able to say that CFCs were probably responsible for the Antarctic ozone hole. Fortunately policymakers had met in Vienna in 1985 and drawn up the Vienna Convention, which was basically a philosophical statement about the need to protect the global ozone layer.'

Two years later, philosophy was translated into action: the Montreal Protocol imposed strict and revisable controls over ozone-depleting chemicals, including the CFCs variously used as solvents, propellants and refrigerants, and bromine-containing halons widely used in fire-extinguisher systems.

Fraser says ozone researchers knew the original version of the Montreal Protocol would not protect the ozone layer, but also knew it was important to have a protocol acceptable to governments and industry. Subsequent meetings in London (1990), Copenhagen (1992) and Vienna (1995) tightened restrictions on CFCs and halons even further with industrialised nations agreeing to a total phaseout of CFC and halons by the end of 1995.

The measures had already begun to bite: in 1992 all four stations in the atmospheric baseline CFC-monitoring network (at Cape Grim in Tasmania, in Ireland, Barbados and American Samoa) showed that the total concentration of the major ozone-depleting species in the lower atmosphere had stopped growing and by 1996 were declining.

In 1996 the trend is running about three years ahead, and 10% below that predicted by the Montreal Protocol. But Fraser says optimism may be premature. The downward trend is dominated by methyl chloroform, a relatively short-lived chemical that is expected

to vanish from the atmosphere within a decade or so. A large pool of much longer-lived ozone-eating chemicals remains in the atmosphere and will continue diffusing into the stratosphere. As these long-lived species come to dominate the chemical spectrum 'we may see some hiccups along the way', he says.

And the terrestrial tap is leaking. Large amounts of CFCs still exist in refrigerators and in poorly-sealed airconditioning systems of older motor vehicles. Fraser is more concerned, however, about the delayed impact of 'vast tonnages' of halons stored in large buildings around the world which will not enter the atmosphere until the buildings' firefighting systems are decommissioned or fail catastrophically. 'Some of these systems are leaking and there's not much we can do about it,' he says.

The volume of bromine-containing chemicals may be small compared with those containing chlorine, but bromine has 40 times or more the ozone-depleting potential of chlorine, so bromine from halons and other bromine-containing chemicals such as the fumigant methyl bromide, account for about 20% of the ozone-depleting potential remaining in the atmosphere.

When will the ozone layer begin to recover? It could be soon after the turn of the century, but ozone researchers will not be able to confirm that any recovery is significant until about 2010, and the models predict stratospheric ozone may not return to its pre-CFC levels until about 2030 or beyond.

'I hope I will be around to confirm that the ozone layer is recovering, but only my children will see it fully repaired,' Fraser says