Jaffe

Ozone Depletion's Recurring Surprises Challenge Atmospheric Scientists

Despite a growing perception that the problem of ozone depletion is solved, scientists are still struggling to understand its complexities

Pamela S. Zurer, C&EN Washington

Last month, National Aeronautics & Space Administration scientists reported that global ozone levels for the second half of 1992 and for early 1993 were the lowest observed in the 14 years NASA has been monitoring the stratosphere from space. The decline was especially pronounced in the northern midlatitudes, where January 1993 ozone levels were 13 to 14% below normal.

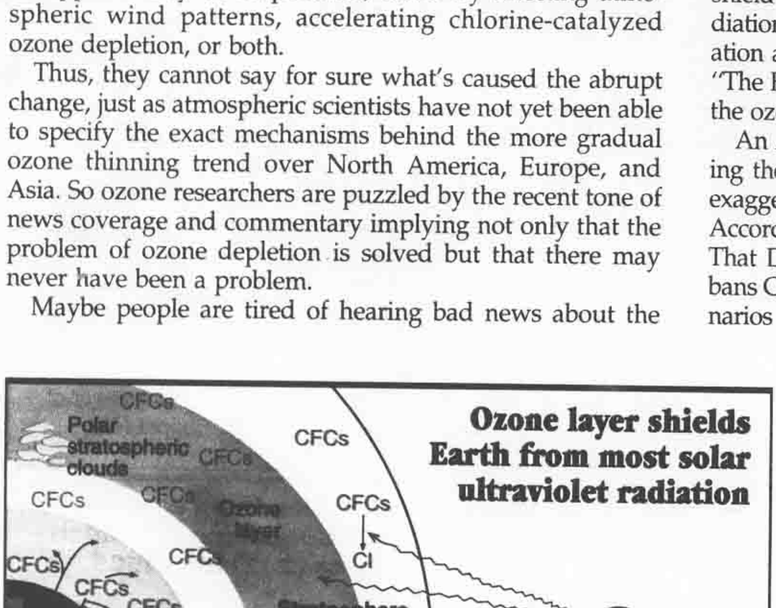
The researchers are unable to explain why ozone, which has been thinning at the average global rate of about 3% per decade, should suddenly decrease so much in one year. They suspect the 1991 eruption of Mount Pinatubo in the Philippines may be responsible, either by affecting atmospheric wind patterns, accelerating chlorine-catalyzed ozone depletion, or both.

Thus, they cannot say for sure what's caused the abrupt change, just as atmospheric scientists have not yet been able to specify the exact mechanisms behind the more gradual ozone thinning trend over North America, Europe, and Asia. So ozone researchers are puzzled by the recent tone of news coverage and commentary implying not only that the problem of ozone depletion is solved but that there may never have been a problem.

Maybe people are tired of hearing bad news about the environment. Or maybe the shrinking availability of chlorofluorocarbons (CFCs)—the ubiquitous chemicals being phased out because the chlorine they contain destroys stratospheric ozone—is beginning to cause people some pain. Whatever the reason, the chorus of voices expressing doubt about the significance of CFC-linked ozone depletion seems to be growing.

Talk show host Rush Limbaugh mockingly calls Vice President Al Gore "ozone man" on his national radio show. Dixy Lee Ray, former head of the Atomic Energy Commission and former governor of the state of Washington, writes in her new book "Environmental Overkill" that the scientific basis for banning CFCs is "flimsy and dubious." Even if the ozone shield that protects Earth from dangerous ultraviolet (UV) radiation is damaged, she argues, natural variations in UV radiation are so large the damage hardly matters. Another book, "The Holes in the Ozone Scare," claims to "demonstrate why the ozone depletion theory is a scientific fraud."

An April 15 *Washington Post* article, although not challenging the reality of ozone depletion, implies environmentalists exaggerated the problem, which it suggests is already solved. According to the *Post,* the Montreal Protocol on Substances That Deplete the Ozone Layer—the international treaty that bans CFCs and other halocarbons—has averted "the dark scenarios of environmental doom that were pronounced after discovery of the Antarctic ozone hole."



Ozone layer shields Earth from most solar ultraviolet radiation

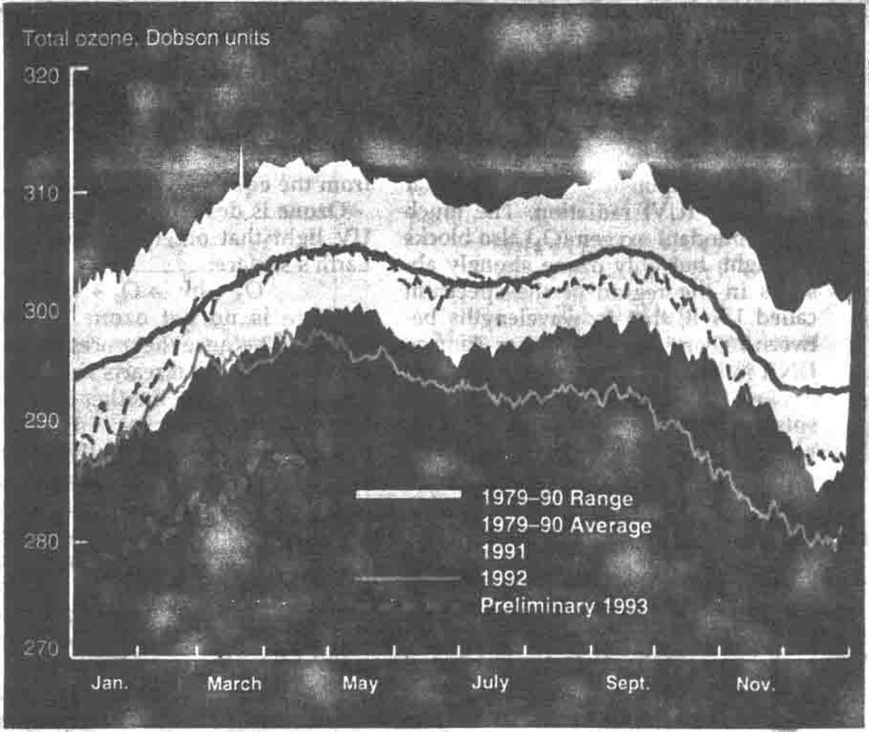
CFCs, released mostly in Northern Hemisphere, quickly disperse throughout troposphere and then slowly enter stratosphere

S. Fred Singer, director of the Washington, D.C.-based Science & Environmental Policy Project, goes further in a column in the April 21 *Washington Times.* Referring to Environmental Protection Agency Administrator Carol M. Browner's defense of measures to protect the ozone layer, he writes: "It seems not to have occurred to Ms. Browner that there might not have been a problem to begin with—so that all these international control measures are either superfluous or at best premature."

But the scientists actively involved in ozone research are convinced the problem of ozone depletion is real and will continue for decades to come. Since the 1985 discovery of the Antarctic ozone hole, the atmospheric science community has melded laboratory experiments, field observations, and computer modeling to vastly increase its understanding of stratospheric ozone. NASA has pumped some $200 million into research in the upper atmosphere, not counting nds spent on satellites, and the National Oceanic & Atmospheric Administration (NOAA) and National Science Foundation (NSF) have contributed lesser amounts.

Ozone researchers view the Montreal protocol and the revisions that have strengthened it as a triumph in which policymakers, by heeding the warnings of scientists, acted to ward off potentially dangerous ozone depletion. If the nations of the world comply with the protocol, the amount of ozone-depleting chemicals in the atmosphere will peak around 2000 before slowly beginning to decline. For the rest of this century, however, stratospheric chlorine will continue to increase beyond today's levels, which already are doing damage.

Ozone researchers are uncomfortably aware that they cannot predict exactly what might happen during the period in which chlorine is still rising. Nor can they yet say how a proposed new generation of supersonic planes might affect stratospheric ozone—a question NASA and the aircraft industry want answered as quickly as possible. These researchers are worried about how much they still do not understand.

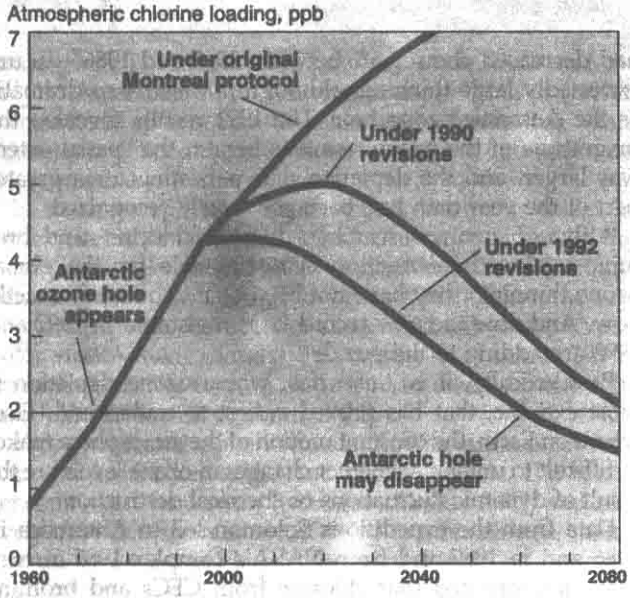


White area represents historic range of globally averaged daily ozone amounts as recorded by the Total Ozone Mapping Spectrometer (TOMS) on NASA's Nimbus-7 satellite. Ozone has remained below the historic range since May 1992

NASA photo

"What do [these critics] think would have happened without the Montreal protocol and the London and Copenhagen amendments?" asks Susan Solomon, a research chemist with NOAA's aeronomy laboratory in Boulder, Colo. Solomon led the 1986 expedition to Antarctica that returned with the first solid evidence linking CFCs to the ozone hole. "Without the controls we currently have, we would eventually have an enormous problem."

Chlorine may peak around 2000, but Antarctic ozone hole will persist



Note: Measured (1960–90) and projected (from 1990 on) abundances of chlorine in the atmosphere under the terms of the original 1987 Montreal Protocol on Substances That Deplete the Ozone Layer and under its 1990 London and 1992 Copenhagen revisions.
Source: World Meteorological Organization

"We have basically won a victory for this planet," says Joe W. Waters of NASA's Jet Propulsion Laboratory (JPL) in Pasadena, Calif. "Sometime after the turn of the century, chlorine is predicted to go down. The question is, have we done this soon enough? For 100 years, there is going to be as much or more chlorine in the stratosphere as [that which] caused the ozone hole. And it is going to be several centuries before chlorine decays back down to natural levels."

"We know unequivocally that CFCs are responsible for ozone destruction in the Antarctic," says James G. Anderson, professor of chemistry and earth and planetary sciences at Harvard University. "But if someone were to ask why the thinning of ozone in the Northern Hemisphere is accelerating as it is, the answer is: We aren't sure. Chlorine and bromine top the list of suspects, but determining the specific mechanism is our top research priority. We cannot predict at what rate the thinning will accelerate. We've learned often enough that every time we've thought things were reasonably predictable, that's when we get our next shock."

The first shock was the discovery of the Antarctic ozone hole. In the early 1980s, computer models of the atmosphere were suggesting ozone depletion from CFC use would amount to about 7% in 50 to 100 years. That estimated loss was significantly less than some earlier projections, which had varied widely since 1974 when F. Sherwood Rowland and Mario J. Molina of the University of California, Irvine, first hypothesized that chlorine from CFCs could destroy

Ozone and CFCs: basic photochemistry and dynamics

The intense concern regarding the fate of ozone (O_3) in Earth's atmosphere stems from its ability to shield Earth's surface from potentially harmful solar ultraviolet (UV) radiation. The much more abundant oxygen (O_2) also blocks UV light; but only ozone strongly absorbs in the region of the spectrum called UV-B, that is, wavelengths between 280 and 320 nm that can damage DNA in living systems.

The amount of ozone in the stratosphere isn't constant, but varies from place to place, month to month, and year to year. This natural variation can be as great as 25% at high latitudes. Other than in Antarctica—where ozone drops 50% within just a few weeks each spring—atmospheric scientists use statistical methods to reveal the long-term global thinning believed to be caused by halogen-catalyzed ozone destruction. Their analyses factor in seasonal variations, the 11-year solar cycle, and other complicating variables.

Ozone is produced continually in the upper stratosphere where solar UV radiation dissociates molecular oxygen to form atomic oxygen:

$$O_2 + h\nu \rightarrow O + O$$
$$O + O_2 \rightarrow O_3$$

These reactions occur very rapidly in the stratosphere over the tropics, where solar radiation is most intense. But even though most ozone is produced at low latitudes, it is not as abundant there as it is at higher latitudes, because circulation in the stratosphere constantly moves ozone away from the equator toward both poles.

Ozone is destroyed when it absorbs UV light that otherwise would reach Earth's surface:

$$O_3 + h\nu \rightarrow O_2 + O$$

There is no net ozone depletion, however, because the process produces atomic oxygen that reacts with molecular oxygen to form another ozone molecule.

Ozone also is continually being destroyed through reactions with families of naturally occurring radicals that contain chlorine, nitrogen, hydrogen, or oxygen atoms. Atmospheric scientists like to use an analogy of a bathtub to describe how natural production and destruction processes are roughly in balance: Even with the drain unplugged, the level of water in the tub will remain constant so long as water from the tap is entering as fast as water is flowing out.

If more holes are punched in the bathtub, however, the level of water will drop. That's exactly the trouble caused by chlorine and bromine carried into the stratosphere by chlorofluorocarbons (CFCs) and halons (fluorocarbons that contain bromine).

The Chemical Manufacturers Association began funding research into the possible environmental effects of CFCs in the 1970s, before these compounds were first implicated in ozone depletion. Two global networks of monitoring stations, now funded by the National Aeronautics & Space Administration and by the National Oceanic & Atmospheric Administration, have been measuring CFCs in the atmosphere since 1978.

That research confirmed that fully halogenated compounds are essentially inert in the troposphere, gradually floating unchanged into the stratosphere. In the past 50 or so years, chlorine concentrations in the stratosphere have increased from their background level of about 0.5 ppb to around 3.5 ppb today. Because of their long lifetimes, it will take several centuries, even after production stops, before the atmosphere is free of CFCs and halons.

Once CFCs and halons rise above the bulk of the ozone layer (which is most dense between 15- and 30-km altitude, depending on latitude), they are photolyzed by ultraviolet light, producing halogen atoms. For example:

$$CCl_2F_2 \text{ (CFC-12)} + h\nu \rightarrow CClF_2 + Cl$$

These chlorine atoms can abstract a hydrogen from methane to form hydrogen chloride (HCl). Or they can participate in catalytic cycles that destroy ozone, such as:

$$\begin{array}{c} Cl + O_3 \rightarrow ClO + O_2 \\ ClO + O \rightarrow Cl + O_2 \\ \hline O_3 + O \rightarrow 2O_2 \text{ (net)} \end{array}$$

ozone. Pressure to phase out the chemicals, which had been intense before the U.S. banned their use in aerosols in 1978, had largely faded by 1985.

But that year scientists from the British Antarctic Survey reported that the ozone layer over Antarctica had mysteriously and precipitously shrunk each September and October since the late 1970s. Almost all the ozone at certain altitudes is destroyed within a few weeks as the spring Sun lifts Antarctica's winter darkness. No model had predicted that such enormous losses of stratospheric ozone could occur in such a short period of time.

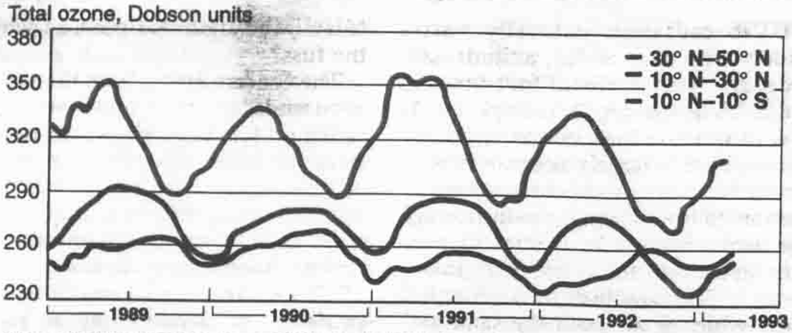
Another shock occurred in 1989 when the first comprehensive research expedition to probe the north polar regions returned with unexpected results: The Arctic stratosphere is loaded in winter with the same destructive chlorine species that cause the Antarctic ozone hole. Only the normally milder winters in the north have so far prevented massive ozone loss.

Then, in 1991, analysis of NASA satellite data indicated that the rate of destruction of the ozone layer over heavily populated latitudes was accelerating. Only three years before, an exhaustive review of all ground-based and satellite data had concluded that, averaged over the globe, ozone had decreased about 2.5% between 1969 and 1986—an unexpectedly large thinning, although not nearly so dramatic as the Antarctic ozone hole. The 1991 results revealed the magnitude of the ozone loss was bigger, the spatial extent was larger, and the depletion was persisting for a greater part of the year than had been previously recognized.

Although ozone researchers believe chlorine- and bromine-catalyzed destruction is responsible for the global ozone thinning, they have not been able to quantify exactly how. And now the new record lows registered in 1992 and 1993 are adding to the puzzle.

Paradoxically, it is Antarctica, where ozone depletion is most extreme, that has proved easiest to understand. Elsewhere on Earth, the constant motion of the atmosphere makes it difficult to untangle whether changes in ozone levels are the result of dynamic fluctuations or chemical destruction.

Data from the expeditions Solomon led to Antarctica in 1986 and in 1987 and from NASA's complex 1987 aircraft mission confirmed that chlorine from CFCs and bromine from halons (fluorocarbons that contain bromine) and methyl bromide are responsible for the ozone hole. At any given time, the total amount of chlorine and bromine in the



Note: Total daily ozone from January 1989 to March 1993 in three latitude bands from satellite monitoring.
Source: National Oceanic & Atmospheric Administration

Because the cycle regenerates the radicals that actually attack ozone, one chlorine atom can destroy hundreds of thousands of ozone molecules.

The simple chlorine-chlorine monoxide cycle can only occur at high altitudes where there are enough free oxygen atoms to allow the second step in the chain to run. A wealth of evidence has accumulated to show that these reactions are indeed destroying small amounts of ozone at about 40 km above Earth.

Different destruction mechanisms predominate elsewhere. The dramatic seasonal depletion of ozone known as the Antarctic ozone hole, for example, takes place at a time of year and in a region where essentially no oxygen atoms are present. The predominant destruction cycle there is one where chlorine atoms are regenerated by the reaction of chlorine monoxide with itself:

$$\begin{array}{c} 2(\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}) \\ \mathrm{ClO} + \mathrm{ClO} \rightarrow \mathrm{Cl_2O_2} \\ \mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{Cl} + \mathrm{ClOO} \\ \mathrm{ClOO} \rightarrow \mathrm{Cl} + \mathrm{O_2} \\ \hline 2\mathrm{O_3} + h\nu \rightarrow 3\mathrm{O_2}\ (\text{net}) \end{array}$$

Other families of radicals also participate in catalytic cycles that destroy ozone—nitrogen oxides, for example:

$$\begin{array}{c} \mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2} \\ \mathrm{NO_2} + \mathrm{O} \rightarrow \mathrm{NO} + \mathrm{O_2} \\ \hline \mathrm{O_3} + \mathrm{O} \rightarrow 2\mathrm{O_2}\ (\text{net}) \end{array}$$

The nitrogen oxide cycle lies behind concern over the effects that supersonic aircraft flying in the stratosphere may have on ozone. The planes' exhaust injects additional nitrogen oxide into the stratosphere, perhaps accelerating ozone depletion.

Until recently, nitrogen oxide cycles were thought to be the predominant natural loss process for ozone in the lower stratosphere. Recent research, however, suggests that the hydrogen radical family may be even more important:

$$\begin{array}{c} \mathrm{OH} + \mathrm{O_3} \rightarrow \mathrm{HO_2} + \mathrm{O_2} \\ \mathrm{HO_2} + \mathrm{O_3} \rightarrow \mathrm{HO} + 2\mathrm{O_2} \\ \hline 2\mathrm{O_3} \rightarrow 3\mathrm{O_2}\ (\text{net}) \end{array}$$

Members of the various families of radicals can react together, with varying effects on the fate of ozone. For example, when chlorine monoxide reacts with nitrogen dioxide, relatively inert chlorine nitrate is formed:

$$\mathrm{ClO} + \mathrm{NO_2} \rightarrow \mathrm{ClONO_2}$$

Like hydrogen chloride, chlorine nitrate is an example of a reservoir species that does not react with ozone, but that can break down into destructive free radicals. During the frigid Antarctic winter, chlorine nitrate reacts on the surface of polar stratospheric clouds to form molecules that dissociate into active radicals as soon as the Sun hits them. For example:

$$\begin{array}{c} \mathrm{ClONO_2} + \mathrm{HCl} \rightarrow \mathrm{Cl_2} + \mathrm{HNO_3} \\ \mathrm{Cl_2} + h\nu \rightarrow 2\mathrm{Cl} \end{array}$$

Similar heterogeneous reactions can also occur on sulfate aerosols that encircle Earth year-round. Heterogeneous chemistry, the importance of which has only begun to be understood since the discovery of the Antarctic ozone hole, shifts the balance between active and inactive chlorine from that which would exist if only gas-phase reactions took place.

stratosphere is virtually uniform worldwide. But—so far—only in Antarctica do all elements conspire both to convert halogenated species into the destructive forms that attack ozone and to keep them in those forms long enough to destroy massive amounts of ozone.

In the stratosphere, a stream of air known as the 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) first condense at about 193 K; water ice particles (type II clouds) form when the temperature falls still lower, to about 187 K.

These polar stratospheric clouds provide surfaces for reactions that are the key to the Antarctic ozone hole. The heterogeneous reactions convert hydrogen chloride (HCl) and relatively inert chlorine nitrate ($\mathrm{ClONO_2}$) to more reactive molecular chlorine ($\mathrm{Cl_2}$) and hypochlorous acid (HOCl):

$$\begin{array}{c} \mathrm{HCl} + \mathrm{ClONO_2} \rightarrow \mathrm{Cl_2} + \mathrm{HNO_3} \\ \mathrm{H_2O} + \mathrm{ClONO_2} \rightarrow \mathrm{HOCl} + \mathrm{HNO_3} \end{array}$$

The molecular chlorine and hypochlorous acid fly off into the gas phase, where both can be easily photolyzed by even weak solar radiation to produce chlorine radicals (active chlorine) that can catalyze ozone destruction.

In contrast, the nitric acid ($\mathrm{HNO_3}$) produced by those heterogeneous reactions sticks to cloud particles. That immobilization ties up the nitrogen family of compounds that—if free—would react with the active chlorine to re-form chlorine nitrate. During the winter, some cloud particles grow larger and sink to lower altitudes. This process, called denitrification, physically removes nitric acid from the neighborhood of the active chlorine.

By spring, the stage is set for chlorine to chew up ozone as the Sun rises and ends the long Antarctic polar night. Sunlight splits molecular chlorine into chlorine atoms that attack ozone, yielding molecular oxygen and chlorine monoxide (ClO). The chlorine monoxide forms a dimer that, in turn, is photolyzed to chlorine atoms, which begin the cycle anew by attacking more ozone.

Bromine from halons and methyl bromide also destroys ozone over Antarctica. Although bromine is much less abundant in the stratosphere than chlorine, it is more reactive and so accounts for a significant fraction of ozone depletion.

Enhanced UV radiation linked to skin cancer, plant damage

Significant losses of ozone in the stratosphere will increase the amount of ultraviolet-B (UV-B) radiation (280 to 320 nm) reaching Earth's surface. Such an increase has been observed in Antarctia, where UV levels under the springtime ozone hole increase to summerlike intensity. Although the damage to humans from long-term exposure to UV radiation is well known, the consequences of increased exposure for plants and marine life are just beginning to be explored.

The most recent United Nations Environment Program (UNEP) assessment of the environmental effects of ozone depletion estimates that for every 1% decrease in ozone, biologically damaging UV radiation will increase 1.3%. In trying to evaluate the impact of any increases, however, one needs to consider not only how much ozone is lost, but also where and when.

UV-B radiation naturally varies widely with time of day, altitude, latitude, and season. About four times as much UV-B reaches Philadelphia at 10 AM in summer than in winter, for example. That is largely because in winter the Sun's low slant angle means radiation follows a longer path through the ozone layer than it does in summer. In Denver, the radiation in July is about 12% greater than in Washington, D.C., which is at about the same latitude, because of Denver's clearer skies and higher altitude. And, all other things being equal, southern localities such as Miami experience much more UV radiation than northern locations.

Those natural variations lie behind the contention that ozone depletion on the order of 5%, 10%, and 15% should not be of any concern. People live happily and healthily in both Denver and Miami, the argument goes, so why all the fuss?

The concern stems from the fact that even under an intact ozone shield, UV radiation has been shown to have effects on human health that worsen with increased exposure. "There is overwhelming evidence that the primary cause of nonmelanoma skin cancers is chronic long-term exposure to UV," says Frederick Urbach, emeritus professor of dermatology at Temple University Medical School in Philadelphia. "In any [Northern Hemisphere] country, as you move from north to south such skin cancers become more prevalent." Urbach served as an expert reviewer for the 1991 UNEP report.

Australia has the highest incidence of skin cancer in the world, he says—a clear example of what can happen when light-skinned people whose ancestors were from northern regions

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"You start with something like 250 Dobson units of ozone at the end of August," says NOAA's Solomon. "You can actually watch the ozone disappear—we sit there and measure it—and by the time you get to the end of September four weeks later you have about half as much. The satellite view shows it's happened over a very broad region so you've got a hole."

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.

Atmospheric scientists believe the data implicating CFCs as the cause of the Antarctic ozone hole are unequivocal. The key chemical species have been observed over Antarctica. The rates of the crucial heterogeneous reactions have been measured in laboratory studies on ice particles that mimic polar stratospheric clouds. And computer models that include heterogeneous reactions and Antarctica's unique dynamics can roughly simulate the hole's formation.

Among the wealth of observations—the results of NSF's 1987 National Ozone Experiment and NASA's 1987 Airborne Antarctic Ozone Experiment are collected in a special issue of the *Journal of Geophysical Research* [**94,** 11,181 (1989)]—the single most convincing are the chlorine monoxide measurements by Anderson's group. In 1987, they found 1.3 ppb of chlorine monoxide within the polar vortex, two orders of magnitude greater than normal levels. And by mid-September they saw a clear inverse correlation between the two species: the more chlorine monoxide, the less ozone.

Ozone researchers were stunned when the same instrument measured almost that much chlorine monoxide in the winter Arctic stratosphere during 1989's Airborne Arctic Stratospheric Expedition. They had thought that only during Antarctica's frigid winter could so much chlorine be converted to the destructive form.

Just as in the Southern Hemisphere, a polar vortex of winds circles the dark North Pole in winter. But the Antarctic vortex is much colder and more stable, persisting for about five months, well into spring. In the Arctic, the minimum temperatures tend to be about 10 K warmer. The Arctic vortex holds together for only a few months, usually breaking up by late February or early March before the north polar regions are fully sunlit.

Although polar stratospheric clouds are a constant feature of the Antarctic winter, they occur only sporadically in the warmer Arctic. The clouds that do form are mostly type I nitric acid trihydrate; water ice type II particles are rare. The differences between the two regions reflect the greater land mass in the Northern Hemisphere, which results in more dynamic activity in the atmosphere.

The abundant chlorine monoxide observed in the Arctic indicates that simply passing through nitric acid trihydrate clouds is enough to process chlorine nitrate and hydrogen chloride into the active radicals that destroy ozone. That finding was confirmed during a second Arctic aircraft expedition that took place in the winter of 1991–92.

Among the instruments NASA's ER-2 aircraft carried directly into the stratosphere on those flights was one that measured hydrogen chloride. "We saw a very dramatic and sudden loss of HCl in air that had just passed through polar stratospheric clouds," says JPL's Christopher R. Webster, whose group developed the instrument. As the hydrogen chloride decreased, chlorine monoxide simultaneously increased.

"We found the HCl loss was exactly half the amount of [active chlorine] produced," Webster says. "No more or no less. That stoichiometry tells you immediately that HCl's reacting with another molecule that contains chlorine," namely chlorine nitrate. Those observations by Webster and his coworker Randy D. May confirmed for the first time move to lower latitudes where UV radiation is more intense.

UV light is also believed to be a factor in the more deadly melanoma skin cancer and in cataracts, although the evidence is less clear-cut, Urbach says. And the UNEP report cites research that suggests exposure to UV radiation weakens the immune system, even among dark-skinned people who seldom suffer from skin cancer.

But humans are not the only creatures that live under the damaged ozone layer. Increased levels of biologically damaging UV radiation penetrate the ocean surface under the Antarctic ozone hole and inhibit photosynthesis by phytoplankton, according to research by Ray C. Smith and coworkers of the University of California, Santa Barbara. They observed that the growth of some types of phytoplankton—which form the bottom of the marine food chain—were much more affected than other types.

Phytoplankton, like most organisms, have protective mechanisms such as natural sunscreens or enzymatic pathways that repair UV damage, says Deneb Karentz, assistant professor of biology at the University of California, San Francisco. But in terms of ecological effects, she says, it isn't yet known if there is a threshold level beyond which the repair mechanisms can't keep up with the UV damage.

"The fact that these UV protective and repair mechanisms exist is good news," she says. "But we don't have any way of knowing how effective they are—especially in Antarctica, where the creatures are suddenly exposed to summer-level ultraviolet intensities after being in the dark all winter."

At the University of Maryland, College Park, botany department chairman Alan H. Teramura has found that increased UV radiation adversely affects many, but not all, plant varieties. In a six-year field study of soybeans, his group found decreased yields in sensitive varieties but no effect in others that were UV-tolerant. "That gives us hope that we can mitigate the UV problem through crop breeding, but there are still a lot of unknowns," Teramura says.

In trees, the damage from UV radiation accumulates over time, the Maryland researchers find. "It may not be significant in one or two years, but over 50 years the injury could be severe," says Teramura.

Teramura is also concerned about native plants: "UV-sensitive species may not be able to compete. All else being equal, we could see changes in biodiversity as the competitive balance between various plant species is altered."

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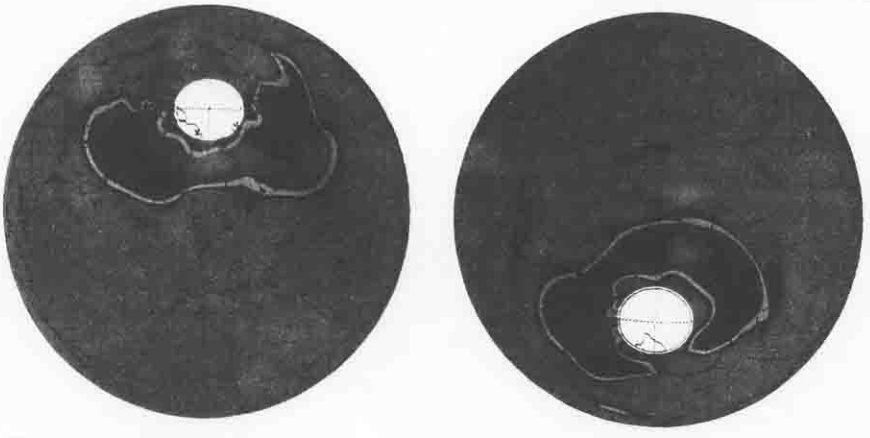
that the heterogeneous reaction of hydrogen chloride with chlorine nitrate was taking place in the stratosphere.

In January 1992, during the course of those Arctic experiments, the NASA scientists observed 1.5 ppb of chlorine monoxide in the stratosphere north of Bangor, Me., a concentration even higher than they had seen in Antarctica. They interrupted their experimental flights to announce their results.

The conditions they found could destroy ozone at a rate of 1 to 2% per day, said Harvard's Anderson, chief scientist for the mission—as fast as in the Antarctic hole. "Should the vortex persist under these conditions of high ClO and low nitrogen oxides, we're going to be extremely surprised if we . . . do not see measurable ozone loss," said Michael J. Kurylo, manager of NASA's upper atmosphere research program. The probability was good, they said, that severe ozone depletion would occur in the far north—if not in 1992, then sometime in the next decade.

The press conference led to a storm of publicity, much of it claiming a northern ozone hole was imminent. Within a few days, then-President Bush unilaterally moved up the U.S. deadline for phasing out CFCs from 2000 to 1996. (The international community adopted the same advanced deadline in November 1992 when it strengthened the Montreal protocol.)



Jet Propulsion Laboratory photo

Maps of ozone-destroying chlorine monoxide in the stratosphere reveal similarities between the north (left) and south polar regions in winter. Red and darker colors indicate chlorine monoxide abundances of 1 ppb or more as observed by the microwave limb sounder on NASA's Upper Atmosphere Research Satellite. White circles at pole are where no measurements are made

The press conference also generated a wave of criticism, most conspicuously in the *Wall Street Journal*. NASA didn't bother to publicize that chlorine monoxide levels had dropped from their peak level and that no Arctic hole had appeared, the paper editorialized. NASA's alarmist warning, it said, was "setting science policy via press releases."

Even some of the scientists who took part in the Arctic mission tell C&EN they wish that press conference had never been held. But Anderson has no second thoughts. "We had no doubt about what we saw," he says. "We'd flown the experiments 50 times and all the calibrations had been stabilized. At 1600 ppt of ClO, ozone disappears with a time constant of three weeks. If we see enough ClO to take out significant amounts of ozone in a three-week period, we must announce it."

Most press accounts missed the subtlety that active chlorine concentrations not only must be large but must remain high for several weeks while being exposed to sunlight if they are to destroy massive amounts of ozone. That is, although the rate of ozone loss depends on chlorine monoxide, the total amount of ozone destroyed depends not only on chlorine monoxide concentration but also on how long it persists in sunlight.

As it turned out, the extremely high Arctic chlorine monoxide levels did not last long in 1992. An unusually early warming in late January allowed the region to escape dramatic ozone depletion. When the stratosphere warms up, the polar stratospheric clouds evaporate and stop processing hydrogen chloride and chlorine nitrate into active chlorine. The chlorine monoxide that's already present reacts with nitrogen dioxide and is trapped as chlorine nitrate. By mid-February 1992, chlorine monoxide levels had decreased substantially.

"We believe these elevated abundances of chlorine monoxide essentially will be a permanent feature of the Arctic winter hemisphere for the next one to two decades, until overall atmospheric chlorine abundances have decreased," Kurylo says. "The actual ozone loss associated with that will be driven largely by the meteorological conditions of any one particular winter. We were very fortunate in 1991–92 that the cold temperatures abruptly ceased at the end of January."

Researchers aghast at misconceptions about CFCs, ozone depletion

According to some skeptics whose voices have lately been growing louder, ozone depletion is not a serious environmental problem but a scientific fraud. To the working atmospheric science community, such ignorance of 20 years of intense research, coupled with the constant repetition of misrepresentations and half-truths, is frustrating and insulting.

Conservative radio talk show host Rush Limbaugh is one of the more prominent individuals responsible for propagating the idea that concern over ozone depletion is much ado about nothing. On the air and in his best-selling book, "The Way Things Ought to Be," he says "environmentalist wackos" unhappy with the American way of life are behind the effort to ban chlorofluorocarbons (CFCs).

Although not so well known as Limbaugh, S. Fred Singer is another persistent scoffer at the seriousness of ozone depletion. An atmospheric physicist, Singer is no longer an active researcher but is the director of the Washington, D.C.-based Science & Environmental Policy Project. Lately, he has retreated from his assertion in the June 30, 1989, issue of *National Review* that "evidence is firming up that volcanoes ... contribute substantially to stratospheric chlorine, and thus dilute the effects of CFCs." Like Limbaugh, he has said that scientists driven by a hunger for grants and publicity are behind the "hype" about ozone.

Limbaugh often cites Dixy Lee Ray, the former governor of Washington State who once headed the Atomic Energy Commission. Ray's latest book, "Environmental Overkill," devotes two error-ridden chapters to ozone depletion. She says only small amounts of CFCs could enter the stratosphere because they are heavier than air. The Antarctic ozone hole was first observed in the 1950s, she claims, so could not be caused by CFCs, whose emissions were quite small at that time.

Ray, in turn, cites a book called "Holes in the Ozone Scare: The Scientific Evidence That the Sky Isn't Falling," by Rogelio A. Maduro and Ralf Schauerhammer. Maduro—who previously published magazine articles arguing the same points—is an associate editor of *21st Century Science & Technology* magazine, which often is linked with jailed political activist Lyndon LaRouche. LaRouche has no formal connection with the magazine, according to staff there, although it has published some of his articles and he served on the board of directors of the foundation that published its predecessor, *Fusion*.

Publicity materials for "Holes in the Ozone Scare" say the ozone scare benefits "the global chemicals cartel"—including ICI and Du Pont—"which financed and supported the movement to ban CFCs" in order to profit from marketing replacements. "The book proposes an alternative: the overthrow of the murderous environmentalist regime now ruling our schools, government institutions, and media."

These critics' supposedly scientific debunking of the current understanding of the ozone issue often relies on misreadings of old scientific literature. They ignore more recent research that leads to different conclusions than the ones they promote. To researchers who keep up in the field, critics' arguments appear so patently incorrect and out-of-date that it has hardly seemed worth taking the time to rebut them.

That attitude among atmospheric scientists is changing, however, as such misinformation gains wider currency. National Aeronautics & Space Administration research scientist Richard S. Stolarski, for example, would like to see the community collaborate on a book. Carefully documented with scientific references, it would explain how scientists have drawn the conclusions they have about ozone.


C&EN staff photo

Rowland: communicate to public

F. Sherwood Rowland—the University of California, Irvine, chemistry professor who with Mario J. Molina in 1974 first linked CFCs to ozone depletion—already is speaking out. In a speech he delivered last February as president of the American Association for the Advancement of Science, he urged scientists to reach beyond their narrow subspecialities and attempt the difficult job of communicating sound science to the public.

In his talk, Rowland tackled some of the major misconceptions concerning CFCs and ozone depletion. Similarly, he published a broad attempt to confront the controversy in the December 1992 *ASHRAE Journal*, a publication of the American Society of Heating, Refrigeration & Air-Conditioning Engineers.

The following discussion addresses a few of the most common myths and draw heavily on conversations with Rowland and on his writings.

- Myth: CFCs are heavier than air and do not rise into the stratosphere.

CFCs indeed are heavier than air. CFC-11 (CCl_3F), for example, has a molecular weight of 137.5 and tends to sink toward the floor if spilled in a still room. But the atmosphere is more like a room stirred by a fan: Winds mix light and heavy molecules until they are evenly dispersed, independent of molecular weight.

Rowland and Molina early on addressed the issue of whether heavy molecules such as CFCs could rise into the stratosphere [*Rev. Geophys. Space Phys.*, 13, 1 (1975)]. They cite work done in the 1960s by researchers at the National Center for Atmospheric Research (NCAR) n Boulder, Colo., who used rockets to mple air up to 50 km above Earth. The researchers found no variation in the ratio of krypton-84 to neon-20 from ground-level to the highest altitude, despite the four-fold variation in molecular weight. Other measurements with other molecules confirm that result.

Furthermore, since the mid-1970s, CFCs and other halocarbons have been measured in thousands of stratospheric air samples collected by balloons and aircraft. This research has been evaluated and summarized with authoritative references in the World Meteorological Organization's Global Ozone Research & Monitoring Project Reports: "Atmospheric Ozone 1985" (1986); "Report of the International Ozone Trends Panel 1988" (1989); "Scientific Assessment of Stratospheric Ozone 1989" (1990); and "Scientific Assessment of Stratospheric Ozone Depletion: 1991" (1992).

- Myth: Natural sources of chlorine, such as seawater and volcanoes, add far more chlorine to the stratosphere than is carried there by CFCs.

Sodium chloride (NaCl) from sea spray does enter the lower atmosphere in large amounts. Because it is water soluble, however, rain removes it rapidly from the troposphere—the region of the atmosphere that is closest to Earth's surface and is where weather takes place. CFCs, by contrast, do not dissolve significantly in water and are not washed out by rainfall.

Volcanoes do spew hydrochloric acid (HCl), not only during eruptions but also in the steamy plumes many give off almost constantly. But again, hydrogen chloride is washed out by rain in the troposphere. Only rarely are eruptions so violent that they inject material directly into the stratosphere. Even when they do, little hydrogen chloride reaches that high. For example, NCAR researcher William G. Mankin and coworkers, who measure hydrogen chloride in the stratosphere, saw little change after the huge eruption of Mount Pinatubo in 1991 [*J. Geophys. Res. Let.*, 19, 179 (1992)]. Apparently, steam in the volcanic plume rapidly condenses to water, scrubbing out the hydrogen chloride [*Science*, 260, 1082 (1993)].

The amount of chlorine in the stratosphere today is about 3.5 ppb—twice what it was in the 1970s and five times the level of the 1950s—paralleling the growth in use of CFCs. Just as stratospheric concentrations of CFCs have increased, so have the stratosphere's abundances of hydrogen chloride and hydrogen fluoride—just as would be expected from the decomposition of CFCs in the stratosphere. The correlation between the amounts of fluorine- and chlorine-containing species in the stratosphere is further evidence that CFCs are the source [*J. Atmos. Chem.*, 15, 171 (1992)].

- Myth: The ozone hole was first discovered in 1956, before CFCs were in wide use, and thus must be a natural phenomenon.

Gordon M. B. Dobson, the British ozone pioneer after whom the units in which ozone is measured are named, and colleagues began monitoring ozone over Halley Bay in Antarctica in 1956. They expected to find September ozone levels of about 450 Dobson units (DU), equivalent to March or April ozone levels in the Arctic. Instead they recorded levels of about 300 DU—not unusually low values on a global scale, but different from what they had anticipated [*Appl. Opt.*, 7, 387 (1968)].

Dobson had discovered not the ozone hole, but the very strong Antarctic polar vortex that isolates air over Antarctica all winter long. The much weaker Arctic polar vortex, in contrast, allows greater exchange of air between the north polar region and lower latitudes during winter.

For almost two decades, the pattern of ozone amounts Dobson first observed did not change. In contrast, in the late 1970s ozone abundances over Antarctica began to decline each September before recovering in November. By the mid-1980s, the September decrease had become a dramatic plunge that wiped out half of Antarctic ozone within a month. For the past few years, values within the ozone hole have fallen below 125 DU. In 1991, they bottomed out at a record low 111 DU In 1992, the extent of the hole was the largest on record.

Only rarely in the Arctic are temperatures cold enough for polar stratospheric clouds to last all winter—about one year in every 10. But should such a frigid Arctic winter occur while the amount of chlorine in the stratosphere is still large—as will be the case for the next several decades—scientists believe a tremendous amount of ozone will be wiped out.

"There have been some years, as in 1975–76, when the Arctic in March had temperatures comparable to what the Antarctic etimes has in September," Solomon says. "Under that sce- io it's hard to imagine why you wouldn't have massive ozone loss. ... I expect it's going to happen in my lifetime."

But even massive ozone loss in the Arctic likely would not produce anything as dramatic as the Antarctic ozone hole. In Antarctica, ozone concentrations are normally at a stable minimum in the spring. It's easy to detect sizable variations from that baseline.

The situation is very different at the equivalent time of year in the Arctic, however. There ozone normally increases noticeably in spring, as waves of ozone-rich air move in from the tropics. Atmospheric scientists must try to tease apart any chlorine-caused decrease in ozone from the natural dynamical increase.

"You're in a situation where, instead of watching ozone drop, you are trying to decide if it is going up as fast as it normally would," Solomon says. "Even if ozone stays at a constant level in the Arctic, that doesn't mean it's not being destroyed."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Solomon (left to right), Waters, and Anderson: still much left to understand

Ozone researchers try to get a handle on that problem by measuring not just ozone but also "tracers" in the same parcel of air. Tracers are gases that are relatively inert in the stratosphere, such as nitrous oxide, methane, and CFCs.

The correlation between the amount of ozone and a particular tracer at a given altitude is approximately constant in the absence of chemical ozone depletion. So, if the scientists know the abundance of a tracer and know its usual relationship to ozone, they can calculate how much ozone should have been in a certain block of air. Using such techniques, researchers calculate ozone losses of 10 to 20% occurred in the Arctic winters of 1988–89 and 1991–92, the two years for which some data on tracers are available from aircraft experiments.

Of prime interest now, however, is what happened during the prolonged cold winter that just ended, when temperatures cold enough for polar stratospheric clouds lasted until late February. No NASA aircraft were probing the Arctic stratosphere during the winter of 1992–93, but satellites were watching from the sky.

A powerful instrument called the microwave limb sounder aboard NASA's Upper Atmosphere Research Satellite (UARS) has been collecting daily maps of chlorine monoxide and ozone concentrations since the satellite was launched 20 months ago. JPL's Waters and coworkers found that high concentrations of chlorine monoxide in the far north lasted much longer this past winter than in 1991–92 [*Nature*, **362,** 597 (1993)].

UARS observed chlorine monoxide abundances beginning to increase in the Arctic regions in December 1992. By mid-February, the satellite was recording huge amounts of chlorine monoxide: about 2 ppb, as much as the instrument had seen over Antarctica six months earlier just before the Antarctic hole opened up. The polar vortex containing the active chlorine was expanding, contracting, and wobbling around the North Pole, Waters says, "slipping down over Europe and completely engulfing Great Britain and the Riviera" on certain days in February. Chlorine monoxide abundances remained as high as 1 ppb as late as March 4.

The key question, of course, is what happened to Arctic ozone during the period chlorine monoxide was so high. Some appears to have been chemically destroyed, Waters says. It's difficult to tell just how much ozone was lost, however, because ozone concentrations normally would be increasing at that time of year. That is, destruction of ozone by chlorine could have been masked by the influx of ozone from low latitudes. Waters' instrument is not capable of observing tracers, and without that data the chemical loss could not be separated from dynamical changes. It is possible UARS observed ozone decreasing in February because less ozone was coming in from the tropics than normal, rather than because it was being chewed up by chlorine monoxide.

Ozone depletion in and around the north polar vortex during the past winter may have contributed to the record low global ozone levels recorded in early 1993 by the Total Ozone Mapping Spectrometer (TOMS) on another NASA satellite. But loss in the Arctic caused by polar stratospheric clouds could not account for all the unusually low values. For one thing, the strikingly depressed ozone first showed up about the middle of 1992.

Until it developed serious problems May 7, TOMS had been observing Earth's ozone layer since late 1978. Every day it scanned the globe, recording the abundance and distribution of ozone. Data from TOMS indicate that between 1979 and 1991 ozone decreased 6 to 8% at high latitudes and 3 to 5% at midlatitudes, with no change near the equator. A major thrust of current ozone research has been to try to explain quantitatively this long-term thinning.

Averaged over Earth as a whole (excluding the poles, which TOMS could not see when they are in the dark in winter), the thinning amounts to about 3% during the 12-year period. But in 1992, average global ozone suddenly dropped another 2 to 3% in one year. And preliminary data from 1993 show global ozone still way below normal.

"In the second half of 1992 global ozone was 2 to 3% lower than we had ever measured before," said James F. Gleason at a press conference last month. "In May 1992, it began to drop well below the historic range." Gleason, an ospheric scientist with the Universities Space Research Association in Columbia, Md., works at NASA's Goddard Space Flight Center in Greenbelt, Md. He and his NASA colleagues recently published a paper on the record low global ozone levels [*Science,* **260,** 523 (1993)].

The biggest decreases are in the northern midlatitudes, the region that encompasses most of North America, Europe, and Asia. In December 1992, ozone abundances were 9% below the average at those latitudes. They dropped to 13 to 14% below normal in January and remained significantly below average well into April.

These values are so much lower than expected that the NASA scientists were worried at first that their instrument, which since may have failed (see page 6), was faulty. The orbit of the aging Nimbus 7 satellite on which TOMS flies had started to decay, complicating the in-flight calibration of the instrument. But comparisons with data from other satellites and from ground-based instruments confirmed TOMS' observations. Indeed, both Environment Canada and the World Meteorological Organization have independently reported record low levels of ozone over Canada and Europe this past winter.

The researchers say they can only speculate why ozone levels have dropped so much in the past year. Everyone's first guess, however, points to the June 1991 eruption of Mount Pinatubo. The biggest difference between 1992 and 1993 and earlier years is the increased sulfate aerosol layer in the stratosphere resulting from that eruption.

The stratosphere holds a permanent thin veil of sulfate sol droplets, which form when sulfur dioxide from volcanic eruptions and carbonyl sulfide emitted by bioorganisms are oxidized in the stratosphere to sulfuric acid. Mount Pinatubo injected 15 million to 30 million tons of sulfur dioxide directly into the stratosphere. Within several months of the eruption, sulfate aerosol particles from Mount Pinatubo had spread from the tropics throughout the stratosphere, increasing the aerosol layer some 20 to 50 times over its usual levels. Although the aerosol concentration is now only about half what it was immediately after the eruption, t will take several more years before it returns to normal.

The extra aerosol could affect ozone concentrations in everal ways. For example, sunlight absorbed by the aero-ol particles can heat the stratosphere, altering its usual cirulation patterns. Or the aerosols could increase chlorine- and bromine-catalyzed ozone depletion by providing surfaces for heterogeneous reactions.

Atmospheric scientists have been worrying about heterogeneous reactions on sulfate aerosols ever since they learned that reactions on polar stratospheric clouds are responsible for the Antarctic ozone hole. Although heterogeneous reactions on sulfate aerosols are not nearly as efficient as those on polar stratospheric clouds, researchers believe they account for a significant part of the global ozone thinning. And the extra aerosol from Mount Pinatubo is probably responsible for the intensification of the thinning this past year.

Solomon and NOAA's David J. Hofmann pointed out in 1989 that volcanic eruptions could exacerbate the destruction of o by chlorine and bromine. They noted that heterogeneous chemistry on sulfate aerosols was probably responsible for the drop in ozone that occurred after El Chichon erupted in Mexico in 1982. "I think it's highly likely that [low ozone in 1992 and early 1993] is due in part to Pinatubo," Solomon says.

Solomon also believes aerosols from Mount Pinatubo are responsible for the increase in size of the Antarctic ozone hole this past year [*Nature,* **363,** 245 (1993)]. The area of the 1992 hole was the largest on record, about 25% bigger than average. And the altitude range in which ozone was destroyed over Antarctica was greater than usual last year as well.

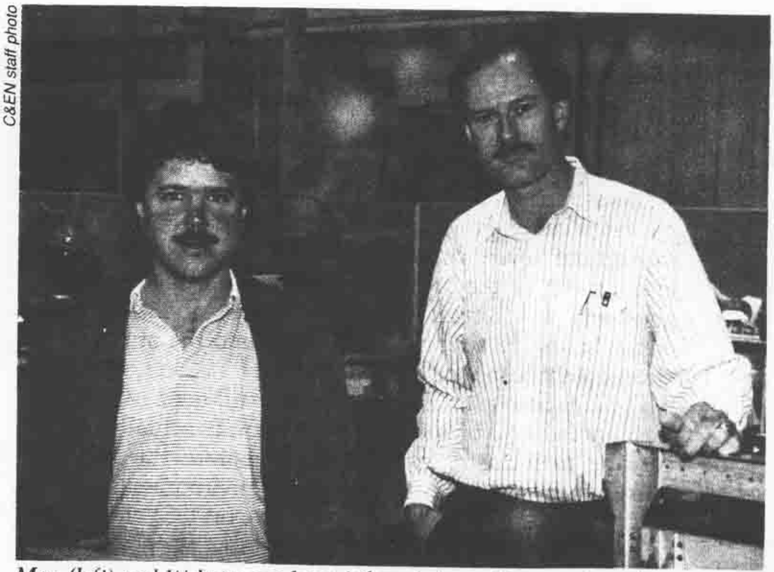
"Last year there was a collar of depleted ozone outside the normal extent of the ozone hole where it wasn't cold enough for PSCs [polar stratospheric clouds] but there were lots of volcanic particles," she says. "PSCs only occur in a certain height range, and yet the ozone depletion extended over a much broader altitude range than it had before. It certainly looks like another mechanism than the usual one was contributing to the Antarctic hole in 1992."

Solomon thinks the enhanced aerosols from Mount Pinatubo are accelerating ozone depletion at high latitudes primarily through the reaction of chlorine nitrate with water. Laboratory studies have shown that this reaction proceeds on sulfate aerosols. However, the rate of the reaction varies dramatically depending on the percent of sulfuric acid in the aerosol, according to Margaret A. Tolbert, associate professor of chemistry at the University of Colorado, Boulder. The colder the temperature, the greater the water content of the aerosol, and the faster the reaction proceeds. So the chlorine nitrate plus water reaction is most likely to trigger extra ozone depletion in the coldest regions of the stratosphere near the poles.

But the reaction of chlorine nitrate on sulfate aerosols is not the one that has been implicated as underlying the long-term global ozone thinning that was identified well before Mount Pinatubo erupted. The culprit there appears to be the reaction of dinitrogen pentoxide (N_2O_5) with water to form nitric acid, which proceeds readily on sulfate aerosols regardless of temperature. The normal sulfate aerosol layer already consumes dinitrogen pentoxide about as fast as it forms, so the increased aerosols from Mount Pinatubo don't make that much difference:

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

Dinitrogen pentoxide is formed from nitrogen oxides, the



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May (left) and Webster use laser infrared absorption spectrometer to measure hydrogen chloride, other species compounds that act as brakes on ozone depletion by tying up reactive chlorine and bromine as less reactive nitrates:

$$\begin{gathered} NO_2 + NO_3 \rightarrow N_2O_5 \\ NO_2 + ClO \rightarrow ClONO_2 \end{gathered}$$

By transforming dinitrogen pentoxide into the less reactive nitric acid, the sulfate aerosol reaction removes nitrogen oxides, allowing chlorine monoxide and bromine monoxide concentrations to rise. The active halogen species can then catalytically destroy ozone:

$$\begin{gathered} ClO + BrO \rightarrow Cl + Br + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \\ Br + O_3 \rightarrow BrO + O_2 \\ \hline 2O_3 \rightarrow 3O_2 \text{ (net)} \end{gathered}$$

NASA's 1991–92 aircraft expedition confirmed that the conversion of dinitrogen pentoxide to nitric acid on the sulfate aerosol layer siphons off reactive nitrogen, allowing chlorine monoxide levels to increase. NOAA research chemist David Fahey and coworkers measured surprisingly low amounts of nitrogen oxides even at midlatitudes. And Anderson's group observed chlorine monoxide at about 100 ppt or more over a large part of North America—much lower than the whopping amounts that occur at high latitudes when polar stratospheric clouds are at work, but still much higher than the 15 to 20 ppt that would be expected in the absence of the sulfate aerosols.

The realization that sulfate aerosols suppress the amount of nitrogen oxides in the stratosphere has wide-ranging ramifications, atmospheric scientists are finding. Most strikingly, it completely changes the calculated impact on the ozone layer of nitrogen oxide emissions from supersonic aircraft.

Computer models that don't include heterogeneous chemistry predict that a fleet of proposed new supersonic planes flying in the stratosphere would decrease ozone significantly. But when the reaction of dinitrogen pentoxide on sulfate aerosols is included in the calculations, the models predict the planes would hardly damage ozone at all.

Since 1990, NASA has been funding research to try to answer the question of how a second generation of supersonic planes would affect the ozone layer. Market studies indicate that new supersonic aircraft—dubbed high-speed civil transport (HSCT)—that fly farther and carry more passengers than the British-French Concorde could be economically viable in the next century.

The project to develop HSCTs fits well with the Clinton Administration's goal of shifting resources from defense to civilian technology. NASA is spending about $400 million throughout seven years in its High Speed Research Program, much of the funds directed toward developing engines with low nitrogen oxide emissions. About one tenth of the funds are supporting research into the atmospheric effects of stratospheric aircraft.

The U.S. aerospace industry would still need to spend at least another $10 billion before any HSCTs actually fly, according to industry estimates. But before the industry makes that kind of investment, the environmental issues that helped scuttle the supersonic transport (SST) in the early 1970s must be resolved. The atmospheric science community is not ready to give definitive answers.

"If we lived in the models, we could be sure we could fly the airplanes based on what we already know," says Harvard University's Steven C. Wofsy. "But because we live in the atmosphere, we have a lot more to learn."

Wofsy served as project scientist for the just-completed Stratospheric Photochemistry, Aerosols & Dynamics Expedition (SPADE). For a month this spring, NASA's instrument-laden ER-2 aircraft flew flights out of California, taking measurements that will help better define the lower stratosphere.

For the first time, Wofsy says, the researchers were able to observe all the important families of radicals that affect ozone—chlorine, bromine, nitrogen, and hydrogen. A new instrument from Anderson's group measured hydroxyl (OH) and hydroperoxyl (HO_2) radicals as the plane crisscrossed the stratosphere, a feat that's never before been done. "OH is the driver of a lot of transformations," Wofsy says. "Until now we've been relying on calculations of OH without having ever made systematic measurements."

By flying at sunrise and sunset, the researchers were able to test some of their assumptions about stratospheric chemistry. "There are some tip-offs, some clues the atmosphere gives us about heterogeneous chemistry that are most apparent at the day-to-night and night-to-morning transitions," Wofsy says. "In particular, at night the heterogeneous reactions will tend to continue or even speed up while the gas-phase reactions shut off."

Other experiments on the plane, including a new instrument to measure carbon dioxide as a tracer, were designed to provide information about circulation in the atmosphere and about how species move between the troposphere and stratosphere. The effect of the HSCT exhaust will depend on jus where in the atmosphere the plane's emissions end up. "We don't really know what the distribution of the exhaust will be whether it will stay here, go there, or what," Wofsy says.

Most of the scientists who took part in SPADE will als participate next year in a major campaign in the Souther Hemisphere. For six months beginning in March 1994 NASA's research aircraft will fly out of New Zealand, turn ing south to probe the stratosphere over Antarctica an north to assess the stratosphere over the tropics.

If all goes well, the campaign will see the first full flights Perseus, a new remotely piloted aircraft that can carry instru ments much higher into the stratosphere than can NASA ER-2. Perseus is the brainchild of Harvard's Anderson, who anxious to gather data from those high altitudes.

"We have pockets of information from the ER-2's fligh over Antarctica and the Northern Hemisphere, but thos are only glimpses up to 19 km in altitude," he says. "Mo of the destruction of ozone is occurring between 19 and or 27 km. We must be able to lay out the catalytic cycles th are destroying ozone at all altitudes all over the globe— from its production region in the tropics to the higher la tudes and the polar regions."

Knowing they are missing so much information preven atmospheric scientists from believing they are anywhe near fully understanding the complexities of the ozone la er. "The Antarctic ozone hole didn't catch us off guard b cause there was more chlorine in the stratosphere than thought," says JPL's Waters. "It caught us completely guard because we hadn't thought of the heterogeneous pr cesses that turned out to be so important. I can't help w rying what processes we may be overlooking now."