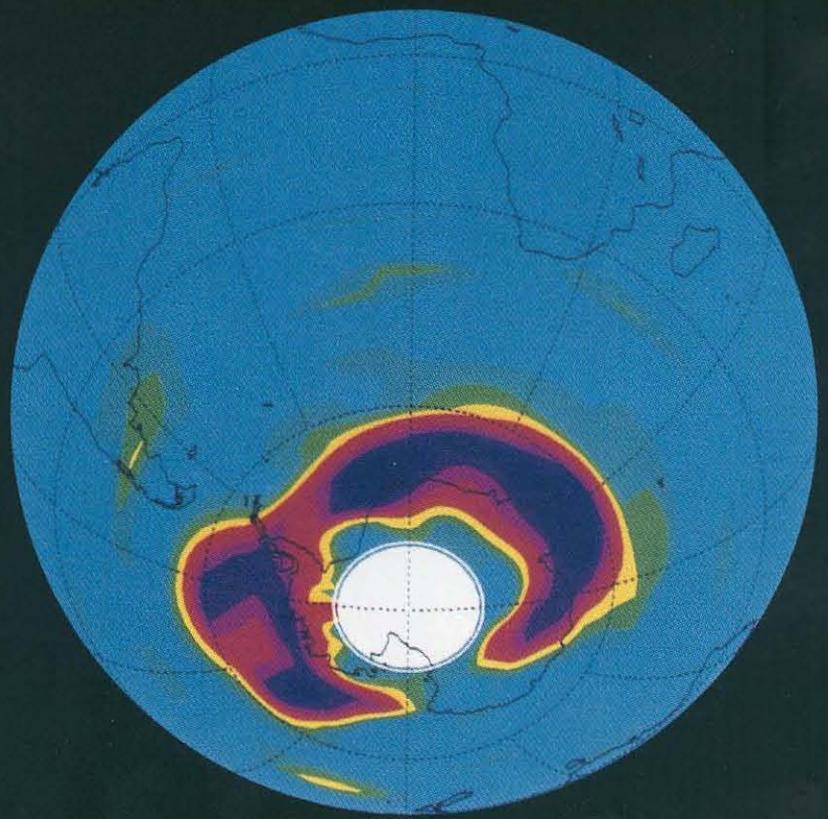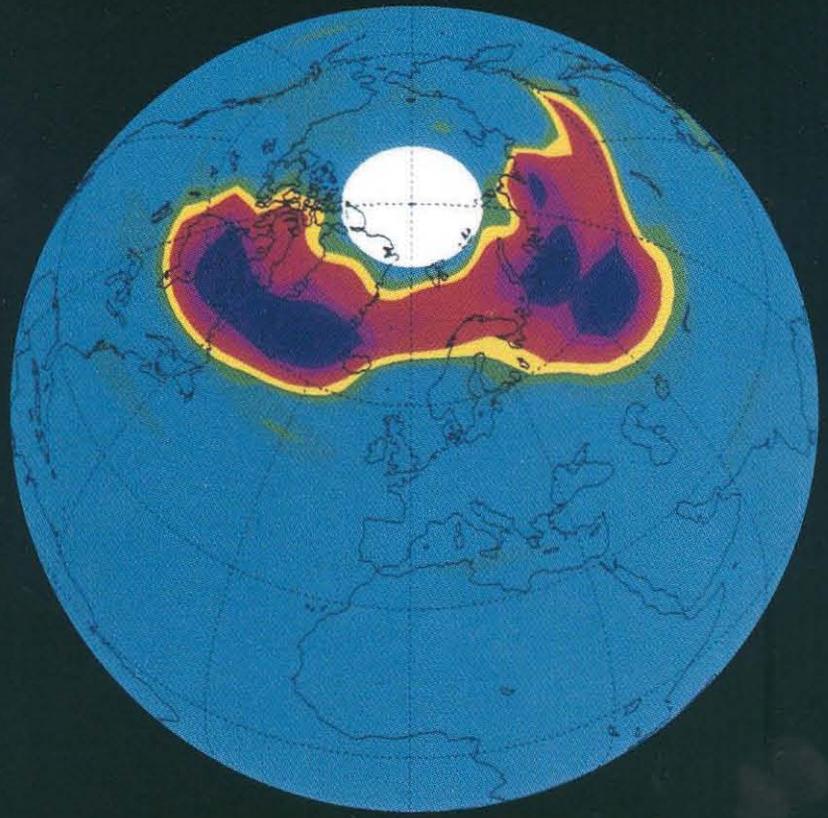# The Chlorine Threat to Stratospheric Ozone

Whether we're in for still more unpleasant surprises is a very difficult question to answer.

by Joe W. Waters

Chlorine monoxide (ClO), the form of chlorine mainly implicated in the destruction of stratospheric ozone, as measured on February 14, 1993, in the northern hemisphere, and on August 14, 1992, in the southern hemisphere, exhibits similar patterns of abundance around both poles. Red and darker colors indicate ClO abundances of one part per billion or greater. Data from JPL's Microwave Limb Sounder produced these maps.

Ozone has a split personality. Down near Earth's surface, it's a bad guy—an element of pollution and smog—which those of us who live in the Los Angeles area are all too familiar with. In the stratosphere, however, where most of the ozone resides, it's a good guy—in fact, its presence there is essential for life on Earth. Here I'm going to discuss only the good-guy ozone and how it's threatened by chlorine, currently a very active area of research. Tremendous progress is being made in understanding this phenomenon, but in the history of this research scientists have been unpleasantly surprised by the processes that can deplete ozone. Whether we're in for still more unpleasant surprises is a very difficult question to answer.

From space Earth's atmosphere appears as an eggshell-thin layer, visible along the horizon. The stratosphere is part of the upper atmosphere, above the region in which most of the clouds form, extending from about 10 to 15 kilometers to about 50 kilometers above Earth's surface. What is commonly called the ozone layer occurs around the region where ozone abundances peak, at about 20 to 25 kilometers above the surface.

Stratospheric ozone and life have a very special relationship. In the primeval atmosphere, before there was life, neither ozone nor oxygen existed in significant amounts in the atmosphere. Scientific theory holds that oxygen was produced by living organisms after life evolved in the sea or other bodies of water; oxygen entered the atmosphere and some of it went on to form ozone. Once the ozone layer was in place, life could then safely climb out of the water onto land. So without life,

there would be no ozone in the atmosphere, and reciprocally, that ozone now shields life from solar ultraviolet radiation.

A molecule of ozone consists of three atoms of oxygen bound together, represented as O_3. Its abundance in the stratosphere is relatively slight—only about 10 molecules per million total molecules at maximum. But that small abundance is a very effective absorber of solar ultraviolet radiation. Ultraviolet radiation, a very short wavelength of light, is very damaging to life, a principal manifestation in humans being skin cancer. It has been estimated that a 5-percent reduction in ozone would amount to about 100,000 additional skin-cancer cases a year in the United States. A striking effect of ozone depletion on the ecosystem has been observed in the marginal ice zone in the sea around Antarctica. The productivity of photoplankton there, the base of the food chain in the sea, has been observed to decrease by some 10 percent when the ozone hole is overhead.

Another aspect of ozone is that its absorption of ultraviolet radiation heats the upper stratosphere. Ozone largely determines the temperature structure of the upper atmosphere, which, in turn, determines its circulation. Since the stratosphere is heated from above, it's a relatively stable layer—and therefore relatively comfortable for airplanes. But the troposphere, the layer of the atmosphere nearest Earth's surface, is heated from below (mainly by visible radiation absorbed by the surface), which creates relatively turbulent air and the weather patterns we experience.

The amount of ozone in the stratosphere is
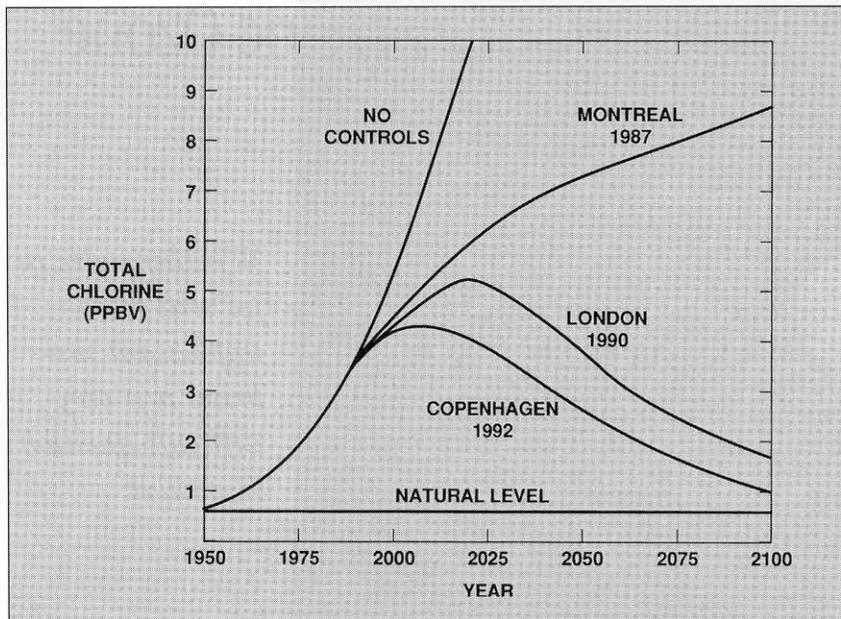
Levels of chlorine in the stratosphere from 1950 projected through the next century, given the controls on CFCs that have been proposed under various international agreements. The total amount of chlorine (whose natural level is 0.6) is represented along the vertical axis in parts per billion. (From _WMO and the Ozone Issue_, World Meteorological Organization, Geneva, 1992.)

Essentially all of that additional chlorine has come from the production of chloro-fluorocarbons (CFCs).

maintained by a dynamic balance. Ozone is being produced and destroyed continually, and the net difference between those effects determines how much there is. So let's consider in more detail how that process works. Ozone is produced from molecular oxygen, O_2, a form that is much more abundant in the atmosphere— about 21 percent. Ozone is produced when an energetic photon from the sun breaks some of the O_2 molecules into two atoms of oxygen. The resulting oxygen atoms react with some of the remaining O_2 molecules to form O_3. A tremendous amount of energy from the sun goes into producing ozone—approximately 2×10^{13} watts, about three times the total power consumed by humankind. It's entirely unfeasible for us to replenish ozone because of the energy required.
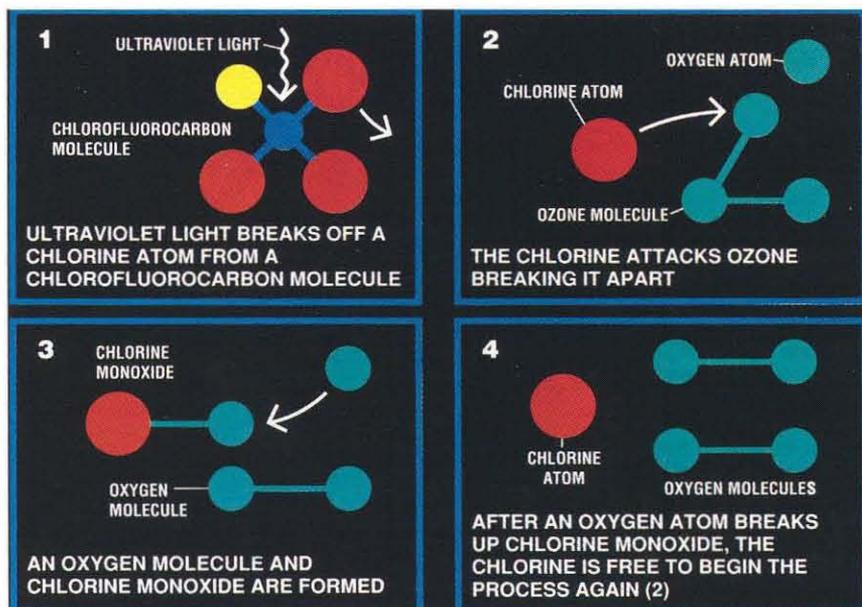
Ozone in concentrated form, however, is about as explosive as dynamite. So, although it's extremely difficult to produce ozone, it's very easy to destroy it. This can happen in several ways. For the first 20 years or so of research in this field, which started around 1930, the only known ozone-destroying mechanism was the interaction of O_3 with an oxygen atom to create two oxygen molecules. It turns out that this is a very slow process, and is now thought to account for only about 10 percent of the total destruction of ozone. But since 1950 several catalytic cycles have been discovered that can speed up the destruction of ozone very rapidly. Four chemical families are involved in these speeded-up reactions—hydrogen, nitrogen, chlorine, and bromine. A major source of the latter two is industrial production down on Earth's surface.

Chlorine, in particular, is known to be a serious threat to stratospheric ozone.

The graph above shows the total amount of chlorine in the stratosphere, plotted over a 150-year time period with projections forward for various future scenarios. The vertical scale represents the total chlorine in parts per billion. The natural level has been measured at about 0.6 parts per billion, and we know that the source molecule for this natural chlorine is methyl chloride (CH_3Cl), produced, for example, from sea salt. Currently, the total amount of chlorine in the stratosphere is about 3.6 parts per billion—six times the natural amount. Essentially all of that additional chlorine has come from the production of chlorofluorocarbons (CFCs). The curve on the graph that goes up out of sight represents what would happen if there were no controls, no cutbacks in the industrial production of these molecules. The other curves show what would happen under various international agreements or proposals, the first of which is the Montreal Protocol of 1987, which was established after chlorine had been proven to be a threat to the stratosphere, but before the cause of the ozone hole had been discovered. This agreement cut back the production of chlorine from industrial sources, and was strengthened in London in 1990, as a result of proof that the ozone hole was due to chlorine. Just this past year, even tighter restrictions were suggested at an international meeting in Copenhagen.

But even with these cutbacks, there's going to be a lot more than the natural amount of chlorine in the stratosphere for a very long time. The

CFCs (carbon atoms surrounded by chlorine and fluorine atoms) diffuse intact into the upper stratosphere, where ultraviolet radiation can rip off a chlorine atom, setting it free to combine with ozone to form chlorine monoxide (CIO) and O_2. A single oxygen atom can break up CIO, freeing the chlorine atom again to continue its ozone-destroying cycle.

1 ULTRAVIOLET LIGHT
CHLOROFLUOROCARBON MOLECULE
ULTRAVIOLET LIGHT BREAKS OFF A CHLORINE ATOM FROM A CHLOROFLUOROCARBON MOLECULE

2 OXYGEN ATOM
CHLORINE ATOM
OZONE MOLECULE
THE CHLORINE ATTACKS OZONE BREAKING IT APART

3 CHLORINE MONOXIDE
OXYGEN MOLECULE
AN OXYGEN MOLECULE AND CHLORINE MONOXIDE ARE FORMED

4 CHLORINE ATOM
OXYGEN MOLECULES
AFTER AN OXYGEN ATOM BREAKS UP CHLORINE MONOXIDE, THE CHLORINE IS FREE TO BEGIN THE PROCESS AGAIN (2)

The chlorine level at which the ozone hole is generally considered to form is about two parts per billion, and the chlorine in the stratosphere will remain above that level for at least 100 years.

chlorine level at which the ozone hole is generally considered to form is about two parts per billion, and the chlorine in the stratosphere will remain above that level for at least 100 years. Even if we completely ceased production of CFCs today, the reservoir of chlorine in the lower atmosphere, which takes time to diffuse upward to the upper stratosphere, would continue to increase for about 10 years. So, no matter what we do, the problem is going to be around for a long time.

How does chlorine actually destroy ozone? Chlorine enters the stratosphere in the form of CFCs. Economically, these are extremely important molecules, used in refrigeration systems, for example. CFC molecules consist of a carbon atom (colored blue in the illustration above) surrounded by chlorine (red) and fluorine (yellow) atoms. They are extremely stable chemically, and it's this chemical stability that makes them dangerous to ozone, even though that sounds like a paradox. They're initially released in the lower atmosphere, where they don't interact chemically to form other substances that would get removed from the atmosphere naturally. And they're not soluble in water, so they don't get rained out. Eventually they diffuse upward, intact, into the stratosphere, a process that takes some 10 years. If for the first 10 or 20 years of their existence we can assume that these molecules resided in refrigeration systems or other industrial products before being released into the atmosphere, then much of the chlorine that we're looking at now in the stratosphere was actually produced some 20 or 30 years ago.

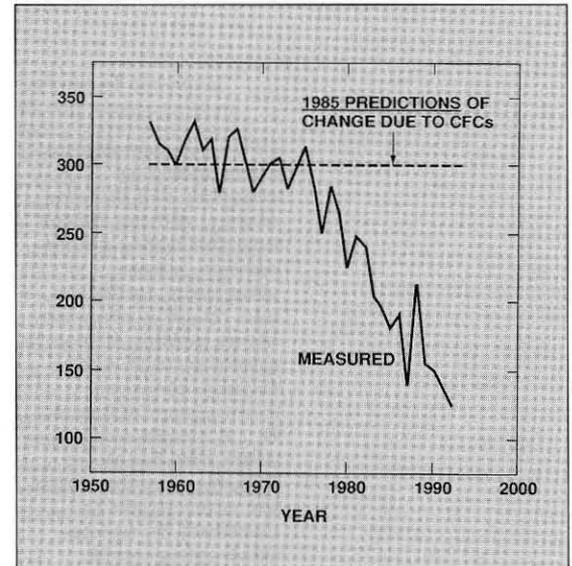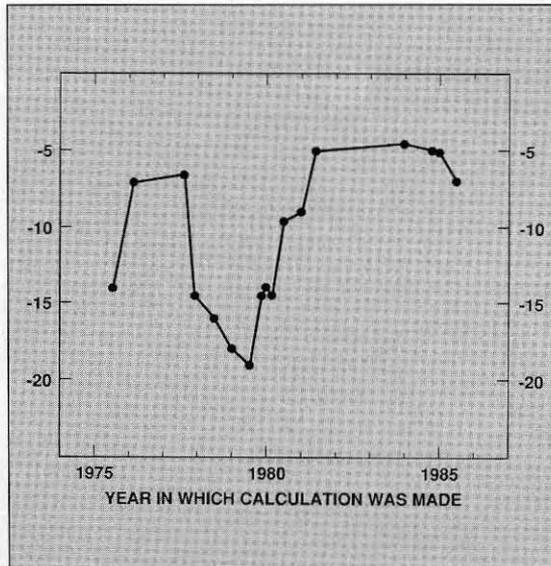Because their upward diffusion takes such a long time, the CFCs get mixed around by winds and are horizontally distributed uniformly around the globe. We think they enter the stratosphere mostly through the tropics. Once they get above the ozone layer, they're no longer protected from solar ultraviolet radiation. This radiation breaks loose a chlorine atom, which then attacks the ozone. The chlorine atom rips off one of the oxygen atoms from ozone to form an intermediate molecule—chlorine monoxide (CIO)—and leave an oxygen molecule (O_2). Chlorine monoxide is extremely short-lived. It's very reactive and interacts with the atomic oxygen that is naturally present there. The atomic oxygen rips the O off the CIO to create another oxygen molecule and leaves the chlorine atom free. So this chlorine atom can then go on to attack another ozone molecule and repeat the cycle. That's what makes it so effective: if a chlorine atom destroyed only one ozone molecule, it wouldn't be a problem. But because the cycle repeats over and over, a little chlorine goes a long way.

What breaks this cycle? Eventually the chlorine atom, instead of interacting with ozone, will interact with methane (CH_4) in the atmosphere to form hydrochloric acid (HCl). The HCl diffuses downward, and because it's soluble in rain the chlorine is finally washed out, closing the cycle. This "washing chlorine out of the atmosphere" is a very slow process, taking 100, maybe even 200, years. The ozone destruction cycle can also be broken when CIO interacts with nitrogen dioxide (NO_2) in the atmosphere to make chlorine nitrate ($ClONO_2$).

For about 10 years after the chlorine threat to

ozone was discovered (in 1974 by Mario Molina and F. Sherwood Rowland of UC Irvine), this process was thought to be the whole story. Based on laboratory measurements of the rates of chemical reactions, predictions were made. How much ozone would this process be expected to destroy? How much would this process change the equilibrium of ozone and reduce its natural abundance? The graph above shows the predicted depletion—the new equilibrium that would be set up after the chlorine had done its stuff. In 1974 it was predicted that the ozone depletion would be about 15 percent and that this depletion would be reached after more than 100 years. In the graph, the horizontal axis represents the years the calculations were made, and the curve fluctuates up and down as laboratory measurements of reaction rates improved. After about 1980, it tended to stabilize at about 5 to 7 percent. This gave us a sense of complacency; we thought we knew what was happening. That ozone would diminish 5 to 7 percent was still a serious problem, but because this was supposed to occur over such a long time the problem didn't command any real sense of urgency. It would happen slowly enough for us to have time to think about what to do.

What was really happening over Antarctica, however, was another story, which is shown compared with the prediction (dashed line) in the graph above right. The vertical scale shows the total amount of ozone in the stratosphere above Antarctica in October, as measured by the researchers who discovered the Antarctic ozone hole. These were members of the British Antarc-

tic Survey team, who began making measurements at the start of the International Geophysical Year of 1957. In the mid-seventies ozone over Antarctica really started taking a nosedive. By 1985 it was down by about a factor of two. This is a tremendous effect. At the outset, few really expected that chlorine could be the cause of the Antarctic ozone decrease; three hypotheses were put forward to explain it. One hypothesis ascribed it to the increase in solar activity: the greater the solar activity, the more nitrogen oxides are produced, which can destroy ozone. Another theory had to do with circulation: perhaps the circulation pattern over Antarctica is changing, causing an upwelling of ozone-poor air from below. The third theory had to do with the chlorine. We knew that chlorine was increasing in the stratosphere during this period, but what was being measured was so out of line with the ozone levels that had been predicted that this explanation was difficult to accept.
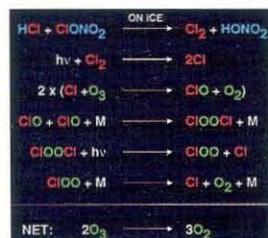
So after this work was published in 1985, scientists led by Susan Solomon of the National Oceanic and Atmospheric Administration (including a JPL group under Barney Farmer and Geoff Toon) hastily organized an Antarctic expedition to test these hypotheses. Measurements indicated that neither the solar activity nor the circulation could explain the dramatic decrease in ozone, but that it was due to chlorine chemistry, which is enhanced in the meteorological conditions over Antarctica. Observations also showed that it's in the lower portion of the stratosphere that the ozone is being lost.

The clincher to implicating chlorine as

Right: The correlation between a rise in chlorine monoxide and a drop in ozone was measured in the lower stratosphere over Antarctica in September 1987 by James Anderson and colleagues. The left vertical axis represents ClO in parts per billion, and the right vertical axis is ozone in parts per million.
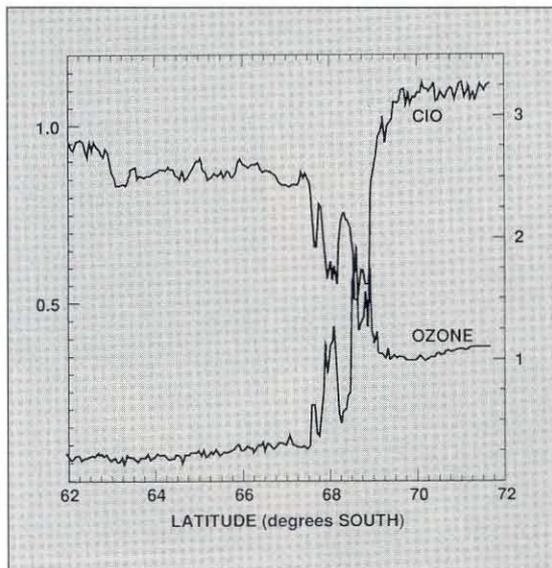
Below: The cause of the unexpectedly high amount of ClO turned out to be a chemical reaction taking place on the particles (both water ice and nitric acid trihydrates) of the polar stratospheric clouds that form in cold temperatures. The end result is the conversion of two ozone molecules to three oxygen molecules.

The abundance of the chlorine monoxide molecule is a direct measure of the rate at which chlorine destroys ozone.

responsible for the ozone hole, certainly the one that has received the widest recognition, is the measurements made by James Anderson and colleagues at Harvard (earlier measurements by ground-based microwave techniques had also provided similar information). They had previously developed a technique for measuring the chlorine monoxide molecule, then put their instrument on a converted U2 spy plane in 1987, and flew from the tip of South America into the ozone hole. At the same time that they hit the ozone hole and the ozone abundances went down, the ClO abundances shot up. The abundance of the chlorine monoxide molecule is a direct measure of the rate at which chlorine destroys ozone. The oxygen atom in ClO has to have been ripped out of ozone, and for ClO to be there in any appreciable abundance, that process must be cycling because ClO is short-lived. In the curve at left you can see some of the impressive anti-correlations between measured ClO and ozone. Although this proved beyond any shadow of doubt that the ozone hole is due to chlorine, there was still a problem. All the theories at the time maintained that it was absolutely impossible to have this amount of ClO in the lower stratosphere. It just "couldn't happen." The theories predicted that the natural abundance would be almost 100 times lower than what was measured.
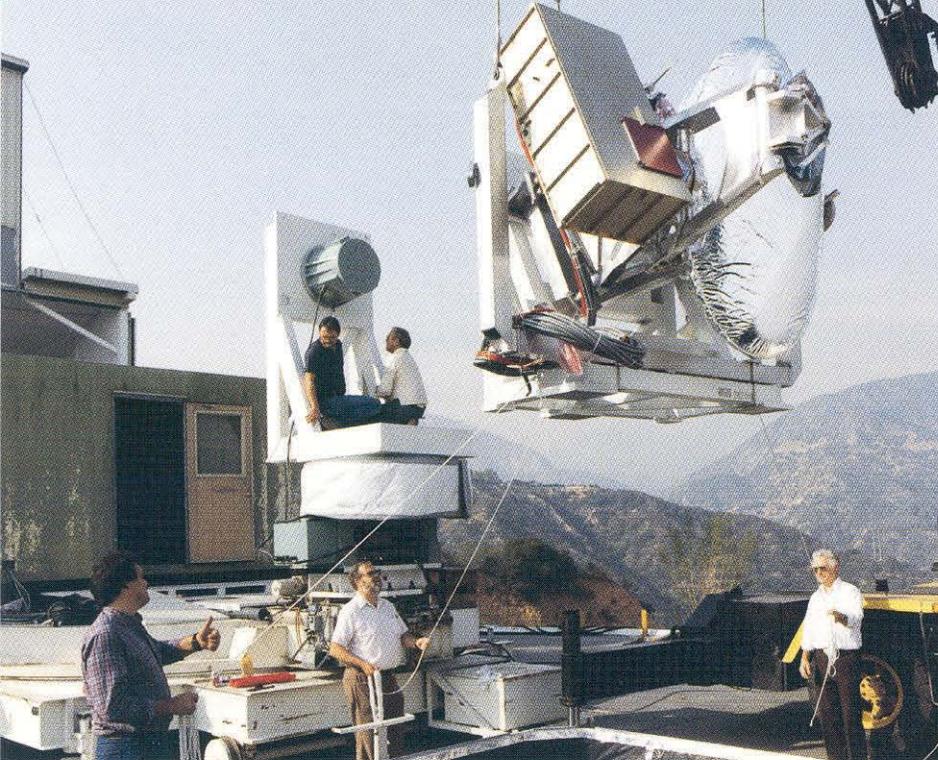
Something was obviously missing. And it turned out to be that the theoretical models included only the chemistry that occurs in the gas phase of molecules. We now know that additional reactions, which don't occur in the gas phase, take place on particles in the polar stratospheric

clouds that form in the cold temperatures over Antarctica. HCl and $ClONO_2$ combine on the surface of these ice clouds to form Cl_2, which is released, and nitric acid ($HONO_2$), which stays on the ice clouds. Even rather weak sunlight breaks up the Cl_2 into chlorine atoms, which can then go on to attack ozone, forming ClO plus O_2. In the upper stratosphere the ClO can get recycled into chlorine atoms through interaction with atomic oxygen, as mentioned earlier, but in the lower stratosphere there isn't enough atomic oxygen to free up the chlorine again. There is, however, another mechanism in which two ClO molecules combine to form ClOOCl. This ClOOCl can then be broken down by sunlight to form ClOO plus Cl, and the ClOO can also be broken up by sunlight or collisions with other molecules to free the remaining chlorine atom. These reactions have the net effect of converting two ozone molecules to three oxygen molecules, and were initially investigated in the laboratory by Mario Molina in 1987 when he was at JPL.

In summary, what's happening over Antarctica is that the cold temperatures in the Antarctic winter cause ice clouds to form, which activates the chlorine—converting it from safe to dangerous forms. The ozone hole then occurs in September because the spring sunlight comes around and breaks up the chlorine, which is necessary to maintain the cycle. (Our recent satellite experiments, to be discussed later, show that this process is actually going on long before September.)

Now, here one might ask a very reasonable question. If the ozone hole is due to the low
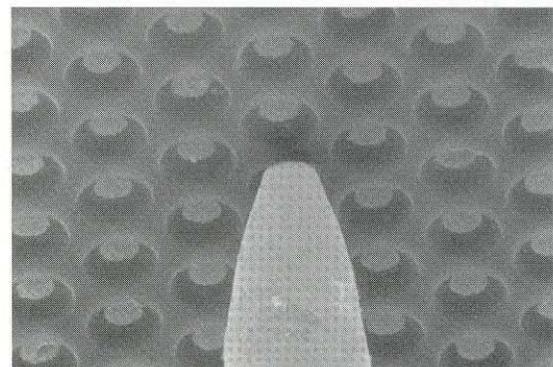
temperatures causing activation of chlorine, isn't global warming a wonderful thing? Unfortunately, it doesn't work that way. When we speak of global warming, we mean warming near Earth's surface. This is because of the increase in CO_2, which puts a greenhouse blanket over us. But that greenhouse blanket is effectively below the stratosphere, and this causes the stratosphere to cool. So the net effect of "global warming" is to aggravate the ozone-destroying process.

For almost two decades my group at JPL has been developing techniques for making measurements of the stratosphere. We do radio astronomy of the Earth. Through the wonders of quantum mechanics, a large number of molecules in the stratosphere—one of them being this culprit, ClO—naturally broadcast at particular frequencies. We can build sensitive receivers at these wavelengths and listen to the signals given off by the molecules. The intensity of the signal allows us to determine the molecule's abundance. Our work at JPL has not just concentrated on ClO, but is devoted to sorting out the spectrum of all the other molecules in the stratosphere as well. We not only have to know where our target molecules are, but also where there might be interfering lines that could mess up our measurements. A JPL group led by Herb Pickett and Ed Cohen is providing the enormous spectroscopy data needed for this task. We sent instruments up on balloons and aircraft before investing in satellites. Our first balloon launch, in 1980, laid a firm foundation for the satellite experiments to follow.

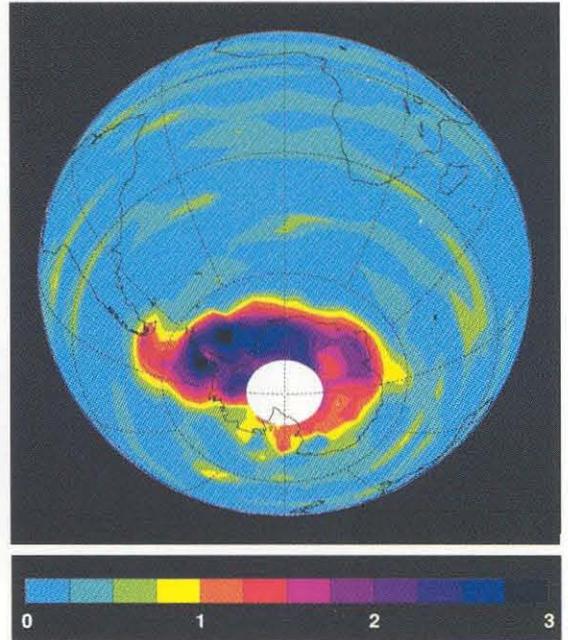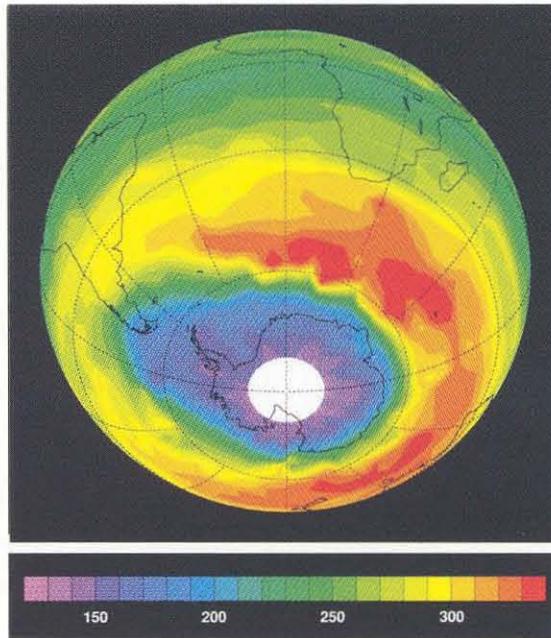We currently have data coming in from the Upper Atmosphere Research Satellite (UARS), a project established by NASA to perform a comprehensive study of the upper atmosphere, particularly the ozone layer. Our group is responsible for one of 10 instruments on that satellite—the Microwave Limb Sounder (MLS). It picks up microwaves from the edge, or limb, of the atmosphere (seen tangentially through it). The heart of the instrument is the tiny "whisker" semiconductor diode junction (above), which transforms the very short wavelengths (about one and a half millimeters, or 1,000 times shorter than FM radio wavelengths) that the atmosphere is emitting to much longer wavelengths, or much lower frequencies. Then we amplify those signals to a level that can be detected with conventional electronics. Since nothing quite like the MLS experiment had ever flown in space before, it took a tremendous amount of skill and sophisticated design to put it together. MLS follows a long history of JPL microwave experiments in space, starting in 1962 with one going to Venus; Frank Barath and Jim Johnston, who led the overall management of MLS, first "cut their teeth" on the 1962 Venus instrument.

UARS was launched precisely on schedule from the space shuttle *Discovery* on September 12, 1991—an important deadline to make because the ozone hole forms in September. After launch and instrument turn-on, we had a few days to look south at the ozone hole. The UARS orbit is designed to switch observation directions every month; one month we would look mostly south (to 80° south latitude and 34° north) and then switch to looking mostly north the next month. On the next page, top left, is a map, looking

south, made from data taken less than 10 days after launch. This picture of the ozone hole (purple indicates a very low amount of ozone) is what we expected to see. But what our instrument mapped for the first time was ClO in the stratosphere. The ClO map (above, right) was made at the same time as the ozone measurements, with red and darker colors indicating high ClO abundances. You can see that the ClO is concentrated where the ozone is depleted; there's an almost exact coincidence.

When we switched to looking north in early October, we saw a different picture (right, top). Blue indicates ClO abundances below our detectable level. While the northern part of the planet looked pretty clean in regard to ClO in early October, by the middle of December we started seeing ClO signals that were definitely above our noise level. By the middle of January (bottom), our observations gave quite a spectacular picture: about the same abundances of ClO that we had seen in the ozone hole over Antarctica and here occurring over populated areas of the planet. Aircraft measurements had been done before in the north, and we knew that there would be enhanced ClO, but we were very surprised to see so much over such a large area. Now, the first thing we do when we see something like this is to make sure it's real. Examining the raw signals from the instrument made it clear that the abundance of ClO over Moscow on January 11 was comparable to that over Antarctica in the depths of the ozone hole.

Why was the ClO along one side of the planet in the north on January 11? Why was there
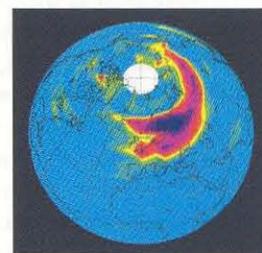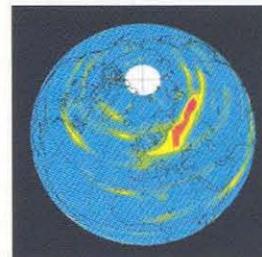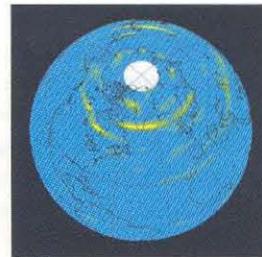

Aircraft measurements had been done before in the north, and we knew that there would be enhanced ClO, but we were very surprised to see so much over such a large area.

The maps above show lower stratospheric ClO measured on October 2, 1991 (top), December 14 (center), and January 11, 1992 (bottom) in the northern hemisphere.

Right: In the same January 11, 1992 map of ClO as on the previous page, the black contour marks the edge of daylight, poleward of which the ClO is expected to be transformed into ClOOCl. The green contour indicates where it was cold enough for polar stratospheric clouds to form, a condition ripe for conversion of chlorine to ClO. This daylight portion coincides with the highest levels of ClO. The white contour indicates the approximate boundary of the Arctic vortex, which serves to contain the ClO.
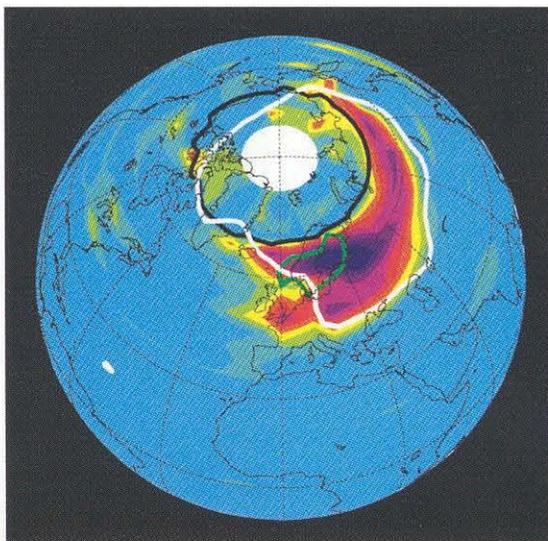
Far right: A comparison of temperature, ClO, and ozone in the 1991-92 northern winter vortex shows clear correlations between the three. The dashed line is the threshold for the polar stratospheric clouds. As temperatures dip below that line, ClO shoots up, and ozone decreases. The crosshatched line indicates the ozone loss calculated from the ClO; the gap in the two lower curves represents the satellite's switch to the southern view.
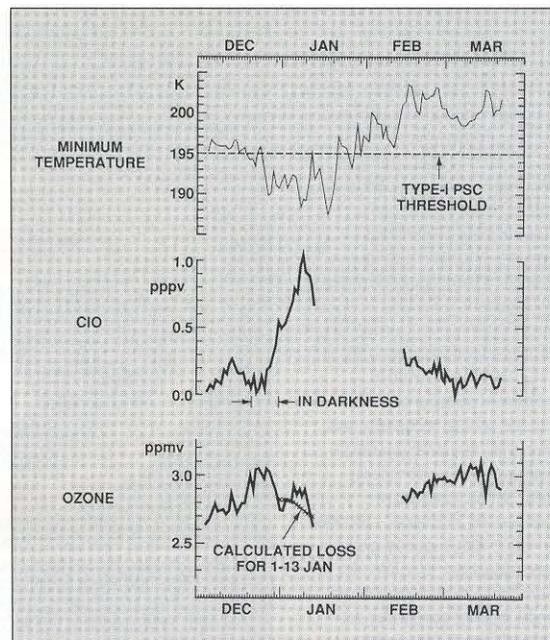
nothing nearer the pole? (Our satellite can't see higher than 80°, but the ClO clearly ends south of that.) We can now explain this. The black contour in the map above marks the edge of daylight; poleward of that contour is winter darkness. Theory predicts that ClO goes into the ClOOCl form in darkness, which explains the ClO decrease toward the north. The green contour marks out the general region in which the temperatures were cold enough for the polar stratospheric clouds to form and trigger the conversion of chlorine to ClO—and that's just where we see the largest abundances of ClO. Another important contributor to this distribution pattern is air motion. The white contour roughly marks the edge of the Arctic vortex, a swirling mass of air about the size of Asia. The air moving around inside this vortex is pretty much contained (just *how* much is currently somewhat controversial), and inside it much of the chlorine in the atmosphere has been converted to the reactive forms, which include ClO.

We might expect to see ozone depletion where we see all this chlorine monoxide, but when we compare this picture with a map of the ozone in the same place at the same time, we actually see *more* ozone. It turns out that two processes are occurring in the vortex. One is the cold temperatures that can activate chlorine to ClO. The other is the descent of ozone-rich air from above. Ozone transported up from the tropics into the polar regions is apparently descending into the lower stratosphere, and a race is going on between the rate at which the ozone is being destroyed by the chlorine and the rate at which

it's being replenished by descending air. It's interesting to look at the evolution of that situation over the winter. The chart above shows temperatures, chlorine monoxide, and ozone during the four-month period from December 1991 to March 1992. The white, dashed horizontal line in the top column is the threshold below which the polar stratospheric clouds can form, and you can see that it gets cold enough for them to form in the middle of December. When that happens, the ClO shoots up, and ozone, which normally increases at this time of year due to transport from the tropics, starts to decrease. There are fluctuations in the ozone decrease, and it's difficult to just pull out the ozone loss by itself. The gap in the curves occurs because we had to switch to the southward view—a very frustrating period for us, because we really wanted to see what was happening in the north. By the time we looked back north, the temperatures had risen above the cloud threshold. Nitrogen is expected to come out of the evaporating polar stratospheric clouds and quench the chlorine, and that's consistent with the observed decrease in ClO.

It is interesting to compare the levels of ClO and ozone in the south polar region on July 11, 1992, with those of its seasonal equivalent—the same "solar day"—on January 11 in the north polar region (opposite). Just as in the north, there is more ozone in this layer of the lower stratosphere in polar regions. At the same time, chlorine has already been activated to ClO. (These are the first measurements ever made of ClO in the south at this time of year.) We're

| JUNE 1 | JULY 11 | 17 AUGUST | 17 SEPTEMBER |

ClO

OZONE

In the Antarctic winter of 1992, ClO was already at enhanced levels by the beginning of June and remaining high all winter. More ozone was coming in, however, in the early winter than was being eaten up by the ClO. By mid-August the ozone in the vertical layer shown here had begun to decrease, and the formation of the ozone hole had started.


ClO

Ozone

ClO

Ozone
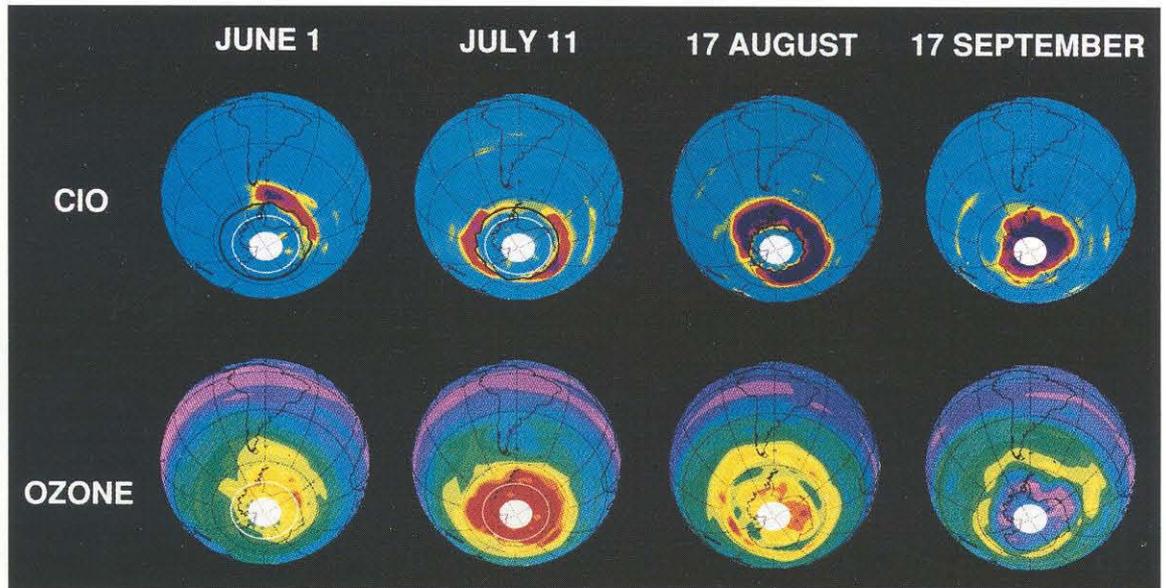
On the same "solar day"—January 11, 1992, in the north and July 11, 1992, in the south—there is more ClO (top) in the north than in the south. More intense planetary waves in the north shift the vortex off the pole more than in the south. This brings air processed by polar stratospheric clouds into sunlight, which is needed to maintain the high abundances of ClO. These planetary waves also cause a warmer winter stratosphere in the Arctic, which is the reason that the ClO doesn't stay around as long in the north and that no Arctic ozone hole has (yet) formed.
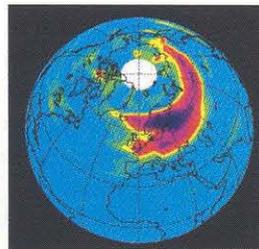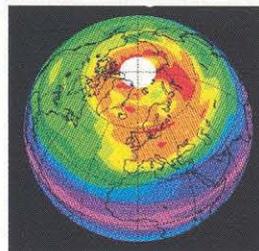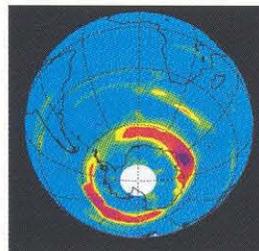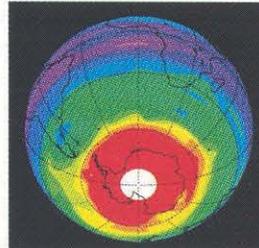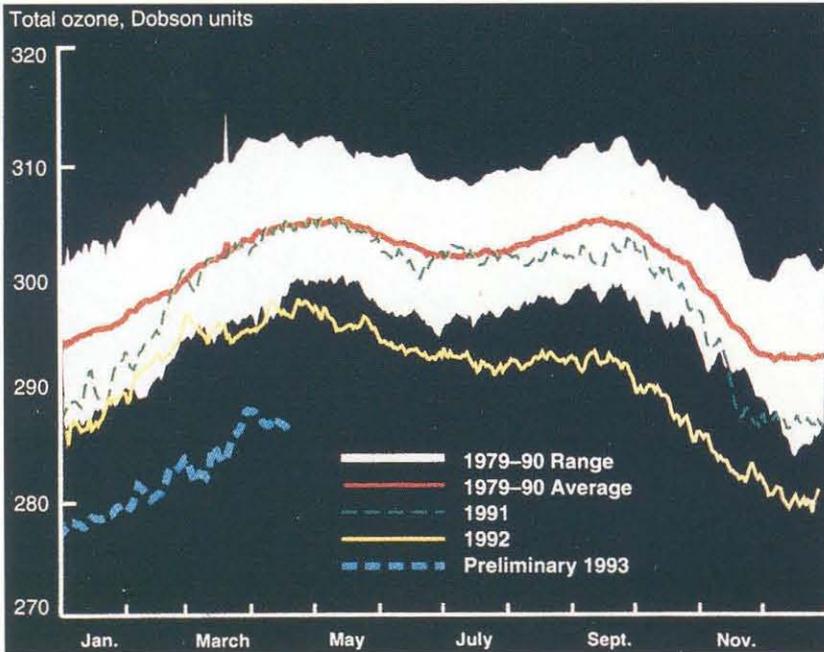
seeing the same processes in the south as in the north, although the distribution of ClO in the south is more symmetric about the pole, than in the north, where it's very asymmetric. The northern hemisphere has a much richer distribution of sea and land than the south, causing differential heating of the atmosphere and creating more intense planetary waves. Planetary waves, for example atmospheric wind patterns such as the jet stream, meander back and forth around the planet. The more intense planetary waves in the north shift the vortex off the pole, which is the reason for the asymmetry, and also cause a warmer winter stratosphere. The Arctic stratosphere generally tends to be about 10 degrees warmer than Antarctica, and that's why there's no ozone hole (yet) over the Arctic.

So these planetary waves are our friends; they can warm the stratosphere in the Arctic winter, thereby helping prevent an ozone hole from forming. Once the temperatures do drop below the threshold for polar stratospheric cloud formation, however, the planetary waves work against us by circulating the air out of the polar night into sunshine, which is needed to maintain the ozone destruction cycle. You can see that in the ClO maps: on the same "solar" day, much more of the ClO is present in the north than in the south. But in the north the ClO doesn't stay around as long, because it doesn't stay cold enough for very long in the winter. We can trace what happened through the southern winter in 1992 (above) and again, this picture came as somewhat of a surprise to us. The ClO reaches enhanced levels as early as June 1. The abundance

Total ozone, Dobson units

Legend:
- 1979–90 Range
- 1979–90 Average
- 1991
- 1992
- Preliminary 1993

of chlorine monoxide is enhanced all winter, but in the early winter ozone is still increasing, because more ozone is coming in than is being destroyed. By mid-August the ozone has started to decrease, indicating that chemical destruction of ozone has become the dominant process, and the ozone hole has started to form.
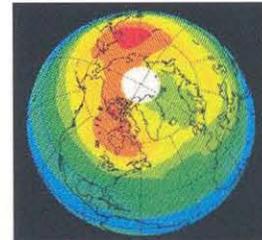
Our observations in the northern hemisphere continued through the winter of 1993. We saw enhanced ClO as early as December 4 over Russia. The vortex, elongated over Canada and Russia, stayed pretty much centered on the pole throughout December and January. On January 8, before we had to switch to looking southward, it was mostly over Canada. But when we looked back north in February, we saw a very different picture from what we had observed in February 1992. In 1993 ClO was enhanced through the end of February into early March. The temperature was a few degrees colder in February 1993 than in the previous year, and this made a tremendous difference because 1993 temperatures were below the point where the polar stratospheric clouds form. We also observed significantly less ozone in 1993 than in 1992, although this was distributed throughout the northern hemisphere. Over the northern hemisphere this past winter it was some 10–20 percent below what it was the previous winter.

The Total Ozone Mapping Spectrometer (TOMS), on another NASA satellite, has been making measurements for 15 years and can put the low 1992–93 ozone in better historical context than our satellite, which has been making measurements for only two years. Above is a
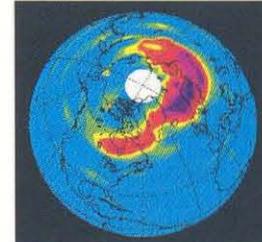
February 1992
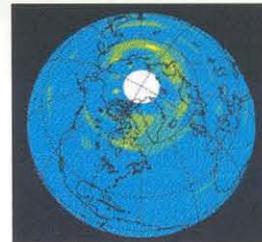
ClO
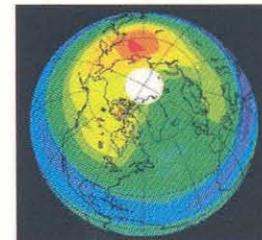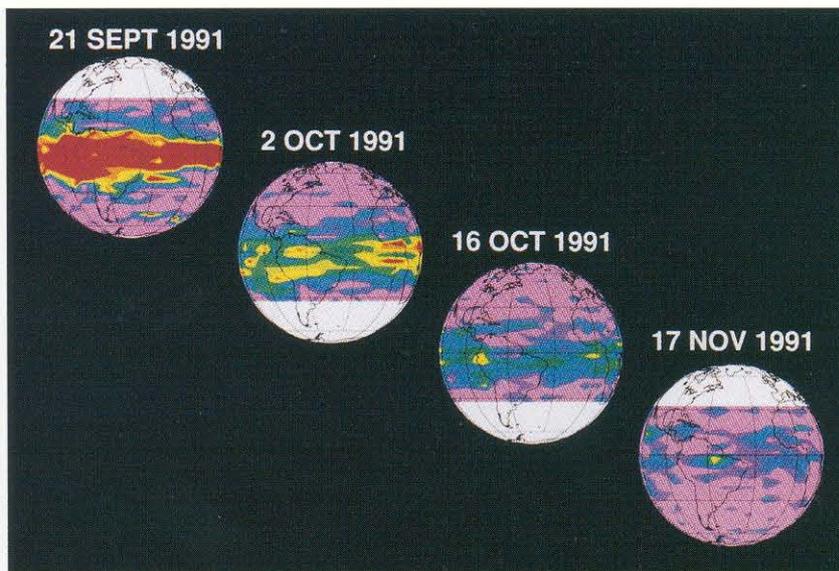

Ozone

February 1993

ClO

Ozone

Temperatures just a few degrees colder in the northern hemisphere in 1993 resulted in significantly more ClO than in the previous year. Ozone was observed to be significantly lower in 1993.

MLS measurements of sulfur dioxide in the atmosphere following the June 15, 1991, eruption of Mount Pinatubo show a significant amount still around in September and then diminishing. Red indicates 10 parts per billion, and purple indicates zero. Sulfur dioxide decay leads to formation of the small sulfate particulates where chemical reactions can take place that shift stratospheric chlorine toward ozone-destroying forms.

Discoveries of qualitatively new effects that destroy ozone do not appear to be slowing down.

plot of the yearly cycle of total global ozone between 65° south and 65° north from TOMS, made by James Gleason (of NASA's Goddard Space Flight Center) and colleagues. The white area indicates the extreme ranges of ozone for the 11-year period between 1979 and 1990. The yellow curve is 1992, and the blue curve segment is 1993. In 1993 ozone is at unprecedented low values when viewed throughout the world. We know that part of the cause is the chlorine activated by polar stratospheric clouds. We are not sure of all the reasons for ozone being low throughout the hemisphere, but Mount Pinatubo, the Philippine volcano that erupted on June 15, 1991, is thought to be a contributor. Measurements showed that while Pinatubo did not inject a significant amount of chlorine into the atmosphere, the volcano did inject a lot of sulfur dioxide (SO_2) into the stratosphere. In the maps above of SO_2 from our instrument, red indicates high sulfur dioxide, about 10 molecules per billion. It's estimated from the TOMS data that Pinatubo originally injected about 20 million tons of sulfur dioxide into the stratosphere. The SO_2 gradually decays as it forms sulfuric acid, which coagulates into tiny particulates called aerosols. Laboratory measurements have shown that heterogeneous chemical reactions can take place on particulates of this sort and can shift the balance of chlorine in the atmosphere toward forms that are detrimental to ozone. So we expect that Mount Pinatubo contributed to the low values of ozone this past winter. Pinatubo would not, however, have been a problem for ozone, had not the stratosphere already been loaded with

chlorine. It's the chlorine that's already there, which can be converted on these Pinatubo particulates, that causes the problem.

Now we *hope* we know everything about the processes that deplete ozone, but it's really not certain how much of the whole picture we have at the present time. Discoveries of qualitatively new effects that destroy ozone do not appear to be slowing down. But even though there's still a lot of uncertainty, there is also a much greater sensitivity now to the planet's problems. More effort is being put into understanding the Earth and what we're doing to it. For our own part, an enhanced follow-on experiment is being planned for long-term measurements on NASA's future Earth Observing System (EOS), both to continue studies of ozone depletion and to measure parameters important in climate change. □

Joe Waters is a senior research scientist at JPL, where he holds joint appointments in the Earth and Space Sciences Division and in the Observational Systems Division. He received his PhD in electrical engineering in 1970 from MIT, where he also earned his BS and MS degrees. After working as a research associate at MIT (where he analyzed microwave data from the first Earth-orbiting microwave spectrometer), Waters joined the JPL staff in 1973 to establish a capability in microwave remote sensing there. He led teams that first detected carbon monoxide in Earth's mesosphere and in the atmospheres of Venus and Mars, and he has twice been awarded NASA's Medal for Exceptional Scientific Achievement. This article was adapted from Waters's Watson Lecture on May 19, 1993.