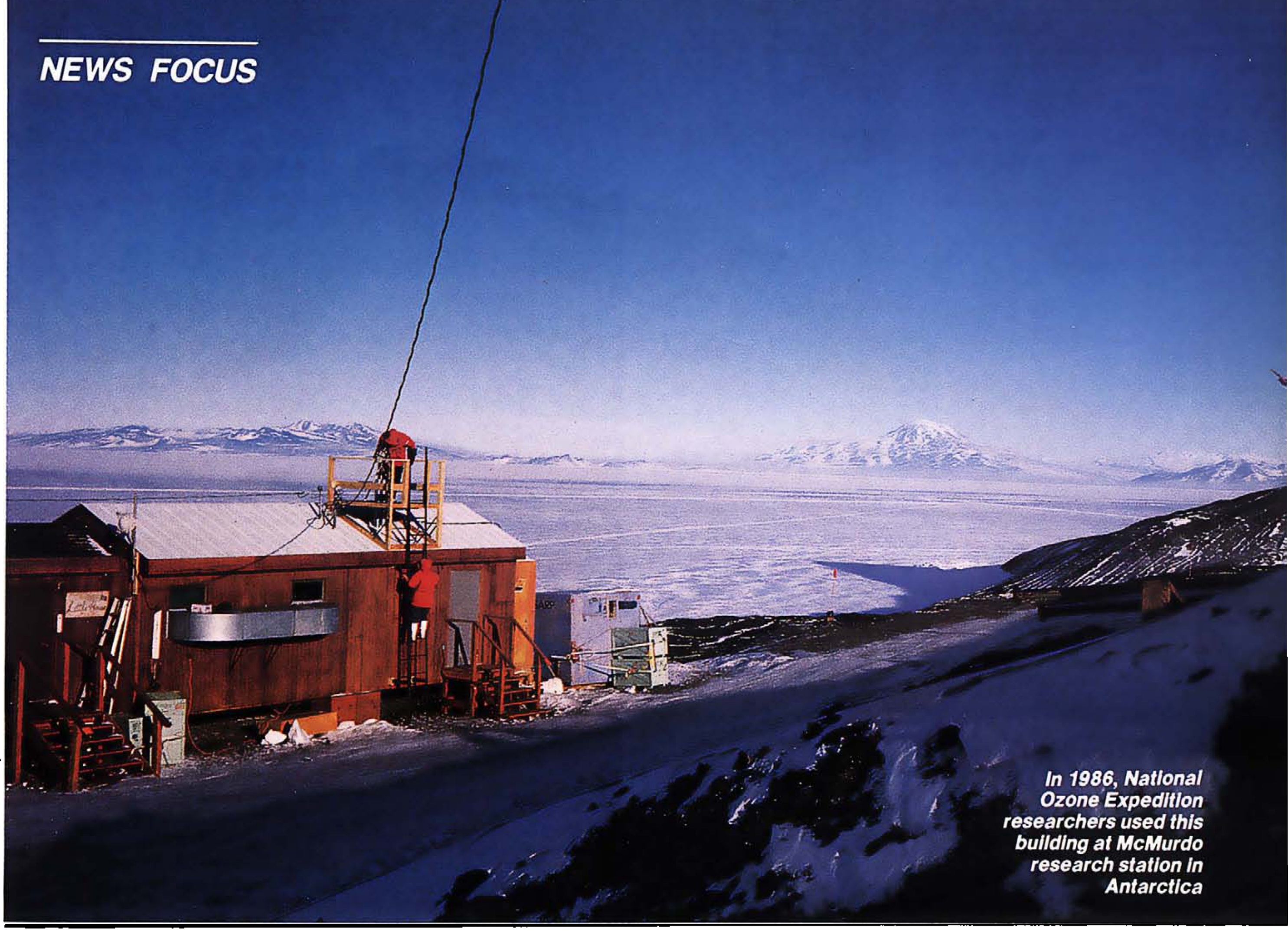
NEWS FOCUS



Robert L. de Zafra, SUNY Stony Brook

In 1986, National Ozone Expedition researchers used this building at McMurdo research station in Antarctica

Complex Mission Set To Probe Origins of Antarctic Ozone Hole

Pamela S. Zurer, C&EN Washington

There are 108 hotel rooms in Punta Arenas, Chile. For the next eight weeks, travelers looking for a room in that city near the southernmost tip of South America will have a rough time. An international group of 160 scientists, engineers, and technicians has commandeered virtually every space available. They are there to take part in the Airborne Antarctic Ozone Experiment.

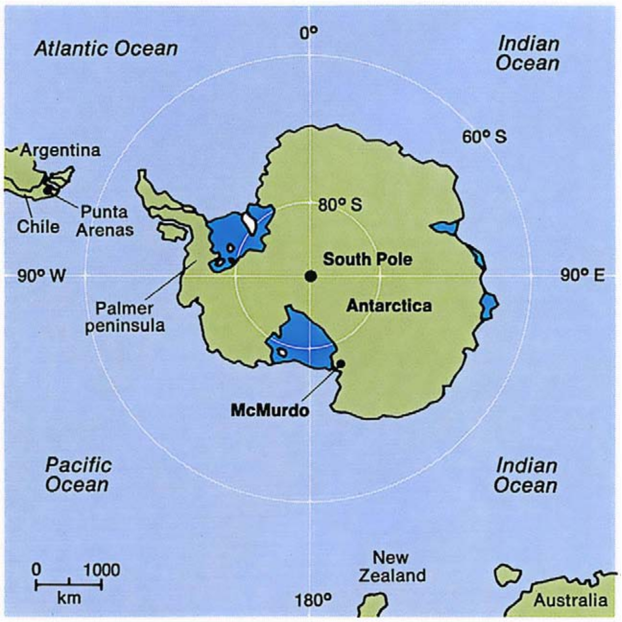
As the first sunlight since April strikes Antarctica this week, National Aeronautics & Space Administration aircraft will begin flying from Punta Arenas directly into the stratosphere above the polar continent. Atmospheric scientists hope data gathered on the flights will help explain the Antarctic ozone hole.

The term "hole" is shorthand for the phenomenon that has been recurring over Antarctica since the late 1970s. Each September and October, just as winter is ending there, the stratospheric ozone layer over the continent has mysteriously and dramatically shrunk. In October 1985—the worst case to date—the ozone layer was only half what it had been the same month a decade earlier. Later each year, as the sun warms the stratosphere and ends Antarctica's winter meteorological isolation, ozone levels return to near normal.

Last year, a team of scientists followed the development and disappearance of the hole from the ground at the National Science Foundation's research station at McMurdo, Antarctica. Before they arrived, the National Ozone Expedition (NOZE) researchers were not even certain their instruments would survive the trip. But the equipment performed admirably and they returned with a rich load of data. The NOZE observations, however, have raised as many questions as they answered.

This year's more ambitious research campaign, which benefits from an additional year's worth of planning, is attacking the problem with every weapon the atmospheric science community can muster. Two planes carrying a total of 21 experiments are scheduled to fly 10 data-gathering missions from Punta Arenas between Aug. 17 and the end of September. In addition to measuring ozone itself, instruments will determine the temperature profile and aerosol content of the

Research aircraft will fly from Chile into Antarctic ozone hole



stratosphere. Other experiments will measure the concentration of key chemical species. The experimental scientists—assisted by atmospheric modelers who are bringing their computers to Chile—aim to analyze and interpret the data as they are collected, modifying flight plans as the need arises.

"I believe this is probably the single most important Earth science project in a decade," says Robert T. Watson, NASA program scientist. The crucial question facing the expedition is whether the hole results from ozone destruction catalyzed by chlorine from chlorofluorocarbons (CFCs) and—if it does—what that means for the ozone layer covering the rest of Earth.

Many scientists think data collected last year by the NOZE team strongly support the case that CFCs cause the hole. Yet other researchers argue that the hole can be explained—at least in part and perhaps entirely—by natural fluctuations in the dynamical behavior of the atmosphere.

"Scientists—at least some of us—were getting complacent, thinking that they had started to understand the stratosphere and what controls ozone," Watson says. "This phenomenon in Antarctica was absolutely unexpected, absolutely unpredicted. We don't know if it's chemistry, we don't know if it's dynamics." The key question is whether it is caused by human activity, he says. Are the fluorocarbons involved? Will it have global ramifications?

With policy makers expected to impose international controls on CFC production at a diplomatic meeting in Montreal in late September (C&EN, May 11, page 5), the atmospheric science community is feeling pressure to come up with an answer to the Antarctic mystery. The scientists in Chile plan to spend their last week there thrashing out what their results mean.

"We hope by the end of September, by the time we come back, that we will have a statement as to what we think we have learned in Punta Arenas," Watson says. "We are going to try to use the intellectual capabilities of a hundred scientists down there to make as many statements as we can," he adds.

Besides NASA (which is organizing and managing the project), NSF, the National Oceanic & Atmospheric Administration, and the Chemical Manufacturers Association are involved in the program. Scientists from several U.S. universities, the U.K., Argentina, Chile, and France also are taking part. Argentina, Chile, and New Zealand are providing facilities.

Putting together this extraordinarily complex mission—which entailed diplomatic negotiations as well as the more mundane scientific and logistical groundwork—took scarcely more than a year. The project is costing about $10 million, not including the development cost of the instruments.

Punta Arenas, located just across the Strait of Magellan from Tierra del Fuego, is "as far south as we can get," says James J. Margitan, NASA program manager. During the Southern Hemisphere's summer, the city of more than 100,000 people is the hopping off point for tourists visiting Antarctica. It has a commercial airport with three big runways that can accommodate NASA's ER-2 and DC-8 research planes.

The ER-2, an updated version of Lockheed Corp.'s U-2 spy plane, will carry 14 experiments into the ozone hole at an altitude of 20 km—just the height where balloon-borne instruments found the ozone depletion to be most intense. The computerized instruments on board will be activated by the lone pilot flipping power switches.

It is a risky assignment. Although a proven aircraft, the single-engine plane soars right on the edge of space at the limits of where jets can fly. A slight mistake on the part of the pilot and the engine can stall. For that reason, the ER-2's flight path will traverse as little water as possible in getting to Antarctica. Once over the continent it will follow the Palmer peninsula into the ozone hole.

"The pilots realize they probably can't survive in the water for more than a few minutes," Margitan says. "It's very cold down there, very windy; wave heights are quite often 50 feet or so." Manned research stations on the Palmer peninsula at least offer the chance for an emergency landing or the hope of rescue if the plane goes down.

The ER-2's range is limited to about 3000 nautical miles, which means it will not always be able to reach the ozone hole. The roughly circular hole constantly is moving and changing shape. Satellite maps show the hole rotates around the South Pole at an offset, moving around the continent and back to its original position about once a week.

Data collected by instruments on NASA, NOAA, and European satellites will be relayed to the researchers in Chile to help in pinpointing the hole and finalizing flight plans. For example, ozone concentrations measured by the total ozone mapping spectrometer (TOMS) instrument on NASA's Nimbus 7 satellite will be relayed from NASA's Goddard Space Flight Center in Greenbelt, Md., to Punta Arenas within a few hours of the satellite's passing over Antarctica. Normally it takes months or more to analyze the TOMS data, but "people at Goddard are going to drop everything else and just do that," Margitan says.

The multiengined DC-8, a much heavier aircraft, cannot fly so high as the ER-2—only 12 km. NASA has just finished transforming the DC-8 from a commercial jetliner into a research plane. Several of the seven experiments it will carry consist of instruments that will probe the ozone hole from its lower edge. The DC-8's heavier payload means scientists will be able to accompany their experiments in flight.

What the DC-8 loses in altitude, it makes up in extended range. It can fly about twice as far as the ER-2. On two of its flights, the DC-8 is scheduled to fly across the continent to New Zealand. It will pass over McMurdo where scientists on the ground will be taking measurements that can be compared with those obtained in the air.

The researchers at McMurdo are scheduled to arrive there next week, flying in from New Zealand on ski-equipped planes. They are part of the second National Ozone Expedition (NOZE II), again cosponsored by NSF, NASA, NOAA, and CMA. As in 1986, they will be probing the ozone hole with ground-based and balloon-borne instruments.

The bulk of the results from last year's NOZE project are just beginning to appear in the research literature. But they have been making the rounds for some time in the atmospheric science community, generating spirited debates, to put it mildly. Proponents of competing theories were even shouting at each other at a meeting at NASA's Ames Research Center in June.

At the start of last year's research campaign, three distinct sets of theories had been offered to explain the Antarctic ozone hole. One blames high solar activity. Another, on dynamical theories, points to changes in atmospheric circulation as being behind the hole. The third set fingers ozone destruction catalyzed by chlorine.

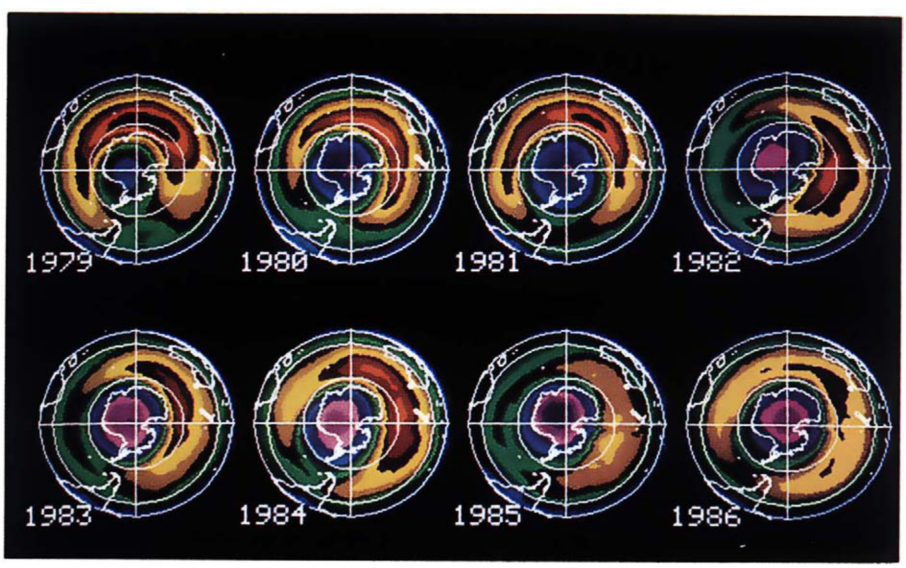
On one thing most everyone agrees: The solar activity theory is dead—at least as far as explaining the dramatic ozone drop in Antarctica is concerned. (It may still be relevant to ozone depletion on a global scale.) That theory proposes that ozone destruction is catalyzed by abnormally high levels of active nitrogen species, which collectively are called odd nitrogen and include nitrogen oxides (NO_x).

At the top of the atmosphere, odd nitrogen is produced by blasts of energetic particles from the sun interacting with nitrogen molecules, according to Linwood B. Callis, an atmospheric scientist at NASA's Langley Research Center. Callis is one of the authors of the solar theory. The solar particles—electrons and protons—tend to zoom in at the poles because of Earth's magnetic field. During the polar night, the odd nitrogen species sink down into the stratosphere where they persist for three or four years, Callis says.

The solar theory linked the current Antarctic ozone phenomenon to a maximum in the sun's cycle of energy output which occurred in 1979. The theory predicted high concentrations of NO_x over Antarctica and also that the ozone loss should peak near the top of the stratosphere, closest to the source of the extra odd nitrogen.

The researchers at McMurdo in 1986 found just the opposite. "The nitrogen dioxide abundances inside the ozone hole are the lowest we have observed anywhere in the world," says NOAA's Susan Solomon, who led last year's NOZE expedition and is again heading this year's. Also, balloon measurements by David J. Hofmann and his coworkers from the University of Wyoming found the ozone depletion to be occurring between about 12 and 20 km altitude, far lower than the solar theory had predicted.

Although the data from last year's expedition eliminated the solar theory, they bolstered the chlorine theories. The concentrations of some key chemical species were found to be highly perturbed in the direction that the CFC-based hypotheses predict.



NASA photo

The average concentration of ozone in October of each year is shown in these maps of measurements taken by the total ozone mapping spectrometer (TOMS) aboard the Nimbus 7 satellite. The spectrum of colors represents varying abundances of ozone. The South Pole is at the center of each polar projection, surrounded by Antarctica outlined in white. The rim of each map represents the equator. From 1979-85, the average amount of ozone over Antarctica declined from October to October. That deepening of the ozone hole can be seen on the maps by the change in color at the center from blue in 1979 through pink to deep purple in 1985. Ozone concentrations in the hole were slightly higher in October 1986 than in 1985. A crescent-shaped area of relatively high ozone levels surrounds the hole. The amount of ozone there also has been dropping

However, "the dynamical theory is still hanging in there," says Jerry D. Mahlmann, director of NOAA's Geophysical Fluid Dynamics Laboratory in Princeton.

"The quantitative aspects of the ozone hole can't be explained by either the chemical or the dynamical theories," Mahlmann says. "Both groups can come up with hand-waving explanations but neither can quantify them."

It's likely that the answer will turn out to be some combination of the two. "I think that probably—this is my purely personal opinion—both the dynamics and the chemistry play a role," says Adrian Tuck, a dynamicist from NOAA's Aeronomy Lab. Tuck is mission scientist for the airborne expedition.

Dynamicists point out that the ozone concentration at a given time and place is not just a function of photochemistry but of the forces in the atmosphere that move ozone around. For example, ozone is formed most abundantly at high altitudes in the tropics. Atmospheric motions carry it downward and toward the poles so there is actually less ozone over the equator than at higher latitudes.

The circulation of air in the Southern Hemisphere is quite different than in the northern, where there is much more land. Up in the stratosphere a stream of air known as the polar vortex tends to circle Antarctica in winter. Air trapped within the vortex gets extremely cold during the polar night because warm air from the mid-latitudes rarely breaks through. Stratospheric temperatures drop below −90 °C, cold enough to form clouds even in the very dry stratosphere.

Polar stratospheric clouds are central to the chlorine-based theories of ozone loss. Those hypotheses propose that certain crucial heterogeneous reactions take place on the surface of the cloud particles. The spectacular depletion is showing up in Antarctica, according to the argument, because it doesn't get cold enough elsewhere on Earth for such stratospheric clouds to form for long periods.

However, although the drop in ozone has been largest within the frigid polar vortex, the seasonal decline is not limited to the area in which polar stratospheric clouds form. The TOMS satellite data show a sizable decrease in ozone in the southern mid-latitudes.

"People refer to the Antarctic ozone hole," Watson says. "In reality it is not just a hole over Antarctica. There seems to have been a reduction of ozone all the way to at least 45° south—the southern tip of both South America and Australia."

"There's a large decline at mid-latitudes," Mark R. Schoeberl says. Schoeberl, an atmospheric scientist at NASA Goddard, is a forceful defender of the dynamical theories. "How do you explain that decline chemically? There's no polar stratospheric clouds there and yet there's been a significant change in ozone."

Proponents of a dynamical cause suggest that changes in stratospheric circulation in the Southern Hemisphere over the past decade can explain the loss of ozone over both Antarctica and the mid-latitudes. Ka Kit Tung, a dynamicist from the department of mathematics and computer science at Clarkson University, points to a strong correlation between trends in ozone and temperature. Everywhere ozone has declined there has been a drop in temperature, and the greater the drop in temperature, the greater the decrease in ozone. Essentially, atmospheric waves that carry heat and ozone to the Antarctic have been getting weaker, the dynamicists assert.

"Stratospheric circulation is driven by waves coming out of the troposphere, large-scale waves like the highs and lows you see on the weather map," Schoeberl says. "We have seen a major decrease in that wave activity since 1979. We think it is a result of changes in sea-surface temperature.

"The origin of the ozone change may be a weak climatic shift in the troposphere that is being felt in the stratosphere first, because the stratosphere's got very little mass. It's like the tail on the dog. The dog shakes itself a little and the tail goes all over the place," he says.

Dynamicists propose that the dramatic drop in ozone over Antarctica occurs in early spring because the sun hitting the continent after the winter night causes ozone-poor air from the troposphere to rise. That air displaces air parcels that would normally be ozone-

Research mission to attack ozone hole on all fronts

ER-2 aircraft measurements
Ozone
Bromine monoxide
Chlorine monoxide
Nitric acid on filters
Nitric oxide
Nitrous oxide
Total odd nitrogen
Water vapor
Whole air samples
Aerosol size distribution
Condensation nuclei
Particle chemistry and size
Pressure, temperature, winds
Temperature lapse rate

DC-8 aircraft measurements
Ozone
Aerosols
Bromine monoxide
Chlorine monoxide
Chlorine dioxide
Chlorine nitrate
Nitric acid
Hydrogen chloride
Water vapor
Whole air samples

Satellite measurements
Ozone
Aerosols
Nitrogen dioxide
Polar stratospheric clouds
Weather

Ground-based measurements
Ozone
Aerosols
Bromine monoxide
Chlorine dioxide
Chlorine monoxide
Chlorine nitrate
Hydrogen chloride
Nitric acid
Nitrogen dioxide
Nitrous oxide
Polar stratospheric clouds
Temperature

Balloon measurements
Ozone
Aerosols

Computational support
Dynamical modeling
Photochemical modeling
Trajectory modeling

rich. Polar stratospheric clouds, which would have been increasing in number as the winters became colder, could help drive the rising motion by absorbing solar energy, Mahlmann says.

However, last year's NOZE researchers said they found no evidence for the kind of upward motion needed to support the dynamical theory. Hofmann's group's balloons carried aerosol counters on several flights. Their measurements showed the aerosols were sinking, not rising.

"The dynamical theory holds that ozone is supposed to be transported in rising air," Hofmann says. "But we don't see aerosols being moved up. The hole could be caused only by uplift if ozone were lifted alone through 'immaculate transport'—transport that only moves ozone," he jokes.

Hofmann's data are not convincing to Mahlmann. "Aerosols aren't good tracers," he says. "They tend to form rapidly and sink relative to air."

Measurements of another species—nitrous oxide (N_2O)—at McMurdo last year also have proved contentious. Nitrous oxide can be used as a tracer of atmospheric air motions. The gas is produced at Earth's surface and its concentration drops off with increasing altitude. If tropospheric air were rising over Antarctica as the dynamicists propose, the concentration of nitrous oxide ought to be higher than normal in the stratosphere.

In 1986 NOZE researchers Robert L. de Zafra, Philip Solomon, and their coworkers from the State University of New York, Stony Brook, measured nitrous oxide at McMurdo with their millimeter-wave spectrometer. In early reports, the researchers concluded they had measured surprisingly small quantities of nitrous oxide within the ozone hole (C&EN, June 1, page 6).

That result astounded most atmospheric scientists, as there was no ready explanation as to where the nitrous oxide could have gone. Since then, however, the Stony Brook scientists have re-examined their results and concluded the concentrations were not so low as they first reported. Infrared measurements by a different NOZE team, headed by C. Barney Farmer of NASA's Jet Propulsion Laboratory, indicate a more normal, if slightly reduced, abundance of nitrous oxide. The findings are probably inconclusive as far as the dynamical theory goes.

N. Dak Sze, an atmospheric modeler who is president of Atmospheric & Environmental Research Inc., in Cambridge, Mass., points out that last year's experiments were designed to test the photochemical hypotheses and can't shed much light on the dynamics of the atmosphere in Antarctica. Sze is among the modelers now in Punta Arenas.

"The problem with the McMurdo experiments is that they were in one place looking up," Sze says. "We need information from different points in space to understand dynamics. I have high hopes for this year's aircraft missions that will be flying all around."

Even the strongest proponents of the dynamical theory have to admit, however, that strange chemistry takes place over Antarctica in late winter and early

David J. Hofmann, University of Wyoming

Veil of polar stratospheric clouds 20 km above McMurdo

spring. Strange, that is, when compared with the better—if not completely—understood chemistry of the stratosphere in the temperate zones.

The NOZE researchers last year found that, compared with the temperate zones, there were very low amounts of nitrogen dioxide above Antarctica. They also reported extremely high concentrations of chlorine monoxide. And they observed one species—chlorine dioxide ($OClO$)—that had never before been detected anywhere in the world.

Advocates of the chemical theories think that Antarctic ozone is not just being redistributed but is actually being destroyed. To explain the spectacular ozone decrease, the hypotheses invoke large concentrations of chlorine in the active forms—chlorine atoms and chlorine monoxide—that can catalyze destruction of ozone. Several different chain mechanisms have been proposed and each one depends on chlorine monoxide to carry the chain.

It appears that large amounts of chlorine monoxide are in the ozone hole. De Zafra and the other Stony Brook researchers measured the species last year at McMurdo. At the altitude where they were looking, chlorine monoxide gives a very broad signal so they had to undertake some complex manipulation of their raw data. However, they conclude that the concentration of chlorine monoxide within the ozone hole in September is somewhere between 0.5 and 2 ppb.

That is two orders of magnitude larger than what is typically found in the lower stratosphere (15 to 20 km) above North America, where abundances of chlorine monoxide are on the order of 0.01 ppb. And considering that total chlorine content of the atmosphere is only about 3 ppb, the Stony Brook group's figure places a huge amount in chemically active form.

To some, the chlorine monoxide figures are as good as a smoking gun in indicting CFCs as the culprit behind the ozone hole. "Every other place in the world you have high ClO you have loss of ozone," says F. Sherwood Rowland, professor of chemistry at the University of California, Irvine. "I think the purpose of this year's Antarctica trip is not to see whether chlorine is contributing to ozone loss, but to see exactly what the contributions of the various chlorine chains are."

Unfortunately, the Stony Brook researchers' revision of the amount of nitrous oxide they found in Antarctica has caused some critics to be suspicious of their chlorine monoxide data. The abundance of chlorine monoxide is so crucial to understanding what is going on in Antarctica that a major goal of this year's aircraft expedition is to measure it accurately by several independent methods.

A key experiment on the ER-2 is Harvard chemistry professor James G. Anderson's instrument for determining chlorine monoxide concentrations on the fly. Anderson and his research associate William Brune have flown their resonance fluorescence instrument previously on balloons.

The unusually high amounts of chlorine monoxide the Stony Brook researchers found in the ozone hole can be explained—qualitatively at least—by the chemical theories. At the altitudes (12 to 20 km) where most of the ozone is being lost in Antarctica, chlorine monoxide normally reacts with nitrogen dioxide to form chlorine nitrate ($ClONO_2$). Chlorine nitrate and hydrogen chloride are dubbed reservoir species because, although they themselves don't take part in chain reactions that destroy ozone, they are a storage pool for active chlorine.

The chemical hypotheses propose that, under the uniquely cold conditions of the Antarctic night, polar stratospheric clouds provide a surface for heterogeneous reactions that free chlorine from these reservoir species. Until recently, these heterogeneous reactions were not included in the computer models that are used to simulate the chemical behavior of the stratosphere.

Further evidence that unusual chemistry is taking place in the ozone hole stems from the observation of chlorine dioxide last year at McMurdo. Susan Solomon and her coworkers from NOAA's Aeronomy Lab in Boulder, Colo., used both sunlight and moonlight to determine the amount of chlorine dioxide in the ozone hole by visible absorption spectroscopy. They had earlier tried to measure that molecule over Boulder, but found none.

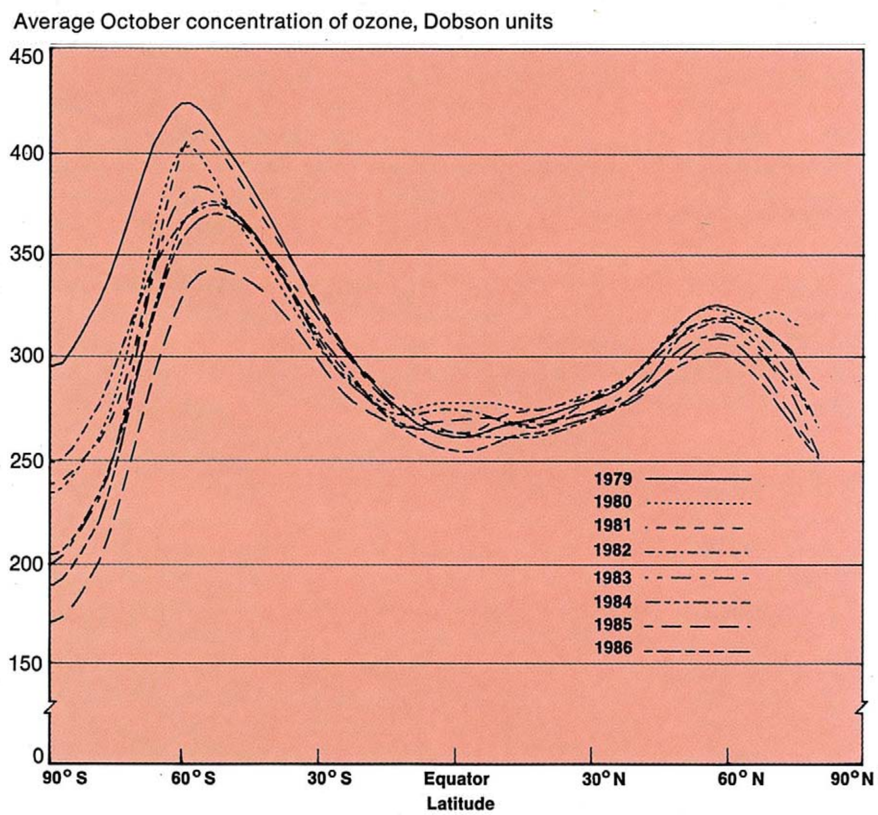
Chlorine dioxide is an indirect indicator that heterogeneous chemistry is at work in Antarctica, because the mechanism that forms it is unlikely to occur with purely homogeneous chemistry. It is one of the products of the reaction between chlorine monoxide and bromine monoxide. The occurrence of chlorine dioxide also shows indirectly that bromine monoxide is present.

Bromine monoxide, which itself can take part in a catalytic cycle that destroys ozone, has never been measured in the atmosphere. Anderson and his coworkers have looked for it in balloon flights over Texas, but were not able to detect any. They will try to measure it over Antarctica with the same instrument on the ER-2 that is monitoring chlorine monoxide.

Rowland notes that the same heterogeneous reactions thought to be of crucial importance in the Antarctic ozone hole could account for the less dramatic loss of ozone that has been observed over the mid-latitudes. He answers the dynamicists' argument that there are no polar stratospheric clouds in those warmer regions by pointing out that aerosols could provide the surfaces for the reactions.

"Our concern about heterogeneous reactions predates our awareness of the Antarctic ozone phenomenon," Rowland says. "There are stratospheric aerosols present everywhere. You can't conclude they are not important."

Springtime ozone drop extends well north of Antarctica



Note: One Dobson equals an atmospheric concentration of ozone of about one molecule in every 10^9 molecules. **Source:** Mark R. Schoeberl, NASA

Chlorine-based ozone hole theories depend on heterogeneous reactions

Ozone is formed when ultraviolet radiation dissociates molecular oxygen:

$$O_2 + h\nu \rightarrow 2O$$

$$O + O_2 + M \rightarrow O_3 + M$$

where *M* represents another molecule of oxygen or nitrogen that is unchanged in the reaction.

Ozone can be destroyed by ultraviolet light or by reaction with a number of free radicals, including chlorine atoms. The chlorine content of the atmosphere has been increasing because of the use of chlorofluorocarbons. These compounds are dissociated by ultraviolet light in the upper stratosphere, yielding free chlorine atoms:

$$CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl$$

$$CCl_3F + h\nu \rightarrow CCl_2F + Cl$$

Chlorine can destroy ozone through the four following catalytic cycles:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$O + ClO \rightarrow Cl + O_2$$

$$\text{Net: } O + O_3 \rightarrow 2O_2$$

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$HO_2 + ClO \rightarrow HOCl + O_2$$

$$HOCl + h\nu \rightarrow OH + Cl$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + ClO + M \rightarrow (ClO)_2 + M$$

$$(ClO)_2 + h\nu \rightarrow Cl + ClOO$$

$$ClOO + M \rightarrow Cl + O_2 + M$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$ClO + BrO \rightarrow Cl + Br + O_2$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

The reaction of chlorine monoxide and bromine monoxide also can produce bromine and chlorine dioxide:

$$ClO + BrO \rightarrow Br + OClO$$

If only homogeneous gas-phase chemistry is considered, these chain reactions are not very effective at the altitude where the unusual ozone loss is occurring in Antarctica (12 to 20 km) because very little of the chlorine there is in the form of chlorine atoms, chlorine monoxide, or hypochlorous acid (HOCl). Instead the chlorine species react with methane or nitrogen dioxide to form hydrogen chloride and chlorine nitrate ($ClONO_2$), reservoir molecules that are inert toward ozone:

$$Cl + CH_4 \rightarrow HCl + CH_3$$

$$ClO + NO_2 \rightarrow ClONO_2$$

The chlorine-based theories of the ozone hole propose that in Antarctica, heterogeneous reactions convert a large portion of the reservoir species to the active forms of chlorine:

$$H_2O + ClONO_2 \rightarrow HNO_3 + HOCl$$

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$$

These reactions are slow in the gas phase, but could be important on surfaces such as the polar stratospheric clouds in Antarctica.

Whatever the contribution of aerosols at other locations, polar stratospheric clouds are the focus of intense speculation with regard to Antarctica. Very little is known about them, other than that they exist.

Atmospheric scientist M. Patrick McCormick and his coworkers from NASA Langley first started observing the clouds about a decade ago with a satellite-based instrument designed to measure stratospheric aerosols. Most aerosols in the stratosphere are tiny sulfuric acid droplets formed from sulfur dioxide injected into the atmosphere by volcanic eruptions.

"In the Antarctic we saw large layers at about 20 km in very cold temperatures," McCormick says. "They just didn't belong there. They didn't look at all like the normal background volcanic aerosol."

The Langley researchers find that the clouds form in winter in Antarctica—and occasionally in the Arctic too—when the stratospheric temperature drops below about −80 °C. They thought at first that the clouds were ice particles that condensed very suddenly on sulfuric acid aerosols when the temperature got cold enough.

Since McCormick and his coworkers published those observations in the early 1980s, however, they have come to believe the clouds are more complex. They recently probed Arctic polar stratospheric clouds with a laser radar (LIDAR) instrument carried on a plane.

The researchers' new measurements suggest that as the temperature drops, nitric acid first condenses as a trihydrate. Then ice particles form as it gets colder still. That is, polar stratospheric clouds may be a combination of nitric acid trihydrate and ice particles.

McCormick's observations fit strikingly well with proposals by several scientists that polar stratospheric clouds contain condensed nitric acid, hydrochloric acid, or both. "If nitric acid were condensing it would remove NO_x from the atmosphere," says O. Brian Toon, research scientist at NASA Ames and deputy project scientist for this year's airborne expedition. That would allow high amounts of active chlorine in the stratosphere because the formation of chlorine nitrate would be inhibited.

Several experiments flying on the NASA aircraft will gather data on the clouds. "If the ER-2 can get into a polar stratospheric cloud, we'll be able to say something about what's in the particle," says McCormick.

Among the experiments on the ER-2 is a setup by Bruce W. Gandrud, a chemist at the National Center for Atmospheric Research, that will attempt to determine if stratospheric nitrate is present in the solid or vapor phase. Other instruments will measure the particle size distribution in the clouds.

Undoubtedly the wealth of data that will be collected by aircraft, balloon, satellite, and ground-based instruments over the next few months will lead to a better understanding of the Antarctic ozone hole and what the phenomenon means for the rest of the world. It's unlikely, however, that a definitive answer can emerge in such a short time. □

CHEMICAL & ENGINEERING

NEWS

Volume 65, Number 33
CENEAR 65 (33) 1–40
ISSN 0009-2347

AUGUST 17, 1987

News of the Week

Business

Government

Science

ACS News

Cover: Erebus glacier, Antarctica. Photo by Robert L. de Zafra, SUNY Stony Brook

News Focus