Studies on Ozone Destruction Expand Beyond Antarctic

With proof in that chlorine from CFCs destroys Antarctic ozone, scientists now find signs of perturbed chlorine chemistry in the Arctic

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The evidence now is irrefutable: Chlorine from chlorofluorocarbons (CFCs) destroys ozone in the stratosphere above Antarctica every spring. Elsewhere, scientists searching for signs of the chemical processes that cause the Antarctic ozone hole have found some indications of perturbed chlorine chemistry in the Arctic stratosphere. Also, results from laboratory experiments suggest key reactions involved in ozone depletion could be taking place on sulfuric acid aerosols above more temperate regions of the globe.

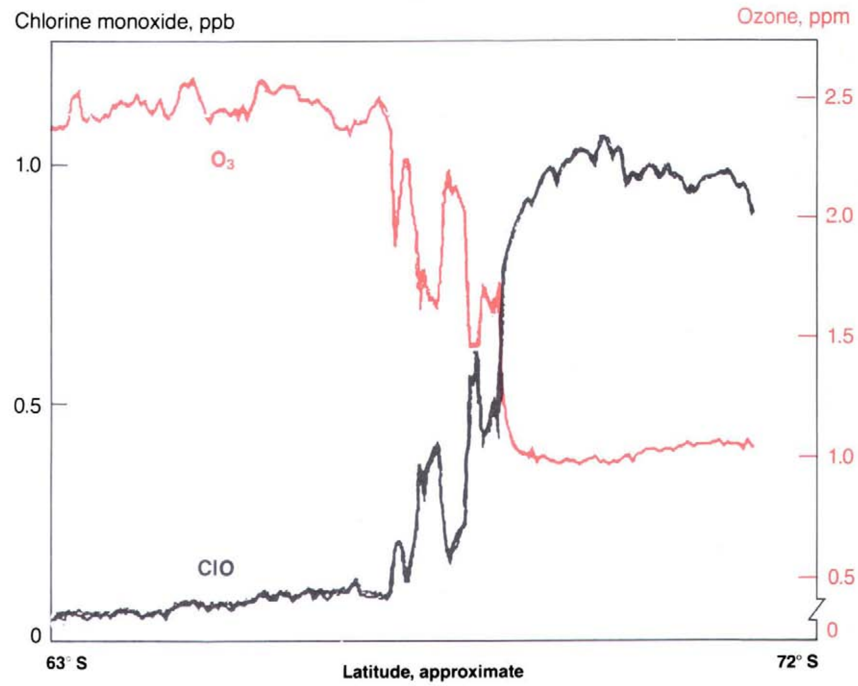
Such was the verdict of an international group of atmospheric scientists who met in Snowmass, Colo., earlier this month to weigh the latest findings on ozone in the polar regions. So many of the key researchers in stratospheric chemistry, physics, and meteorology gathered for the week-long polar ozone workshop that morbid jokes began to circulate. "If the roof caved in, it would end all the discussion of ozone depletion," one wag cracked. "There'd be nobody left to worry about it."

The worry, of course, is that long-lived halocarbons are reducing the concentration of ozone in the stratosphere, thereby exposing humans, animals, and plant life to harmful levels of ultraviolet radiation. Large changes in ozone may also affect climate unpredictably. Many of the scientists at the meeting were clearly troubled by the evidence that human activities have drastically changed the behavior of the atmosphere in Antarctica—and perhaps elsewhere.

The conference—jointly sponsored by the National Aeronautics & Space Administration (NASA), the National Oceanic & Atmospheric Administration (NOAA), the National Science Foundation (NSF), the Chemical Manufacturers Association (CMA), the World Meteorological Organization, and the United Nations Environment Program—was primarily intended to be the first public airing of detailed findings from last year's Airborne Antarctic Ozone Experiment (C&EN, Nov. 2, 1987, page 22). That expedition had set out to explore the massive loss of ozone that has been recurring over Antarctica each spring for the past decade, the so-called ozone hole.

In 1987, the ozone hole was larger than ever. More than half of the total ozone column was wiped out and essentially all ozone disappeared from some regions of the stratosphere. The hole also persisted longer than it ever did before, not filling up until the end of November.

As reactive chlorine increases, Antarctic ozone decreases



Instruments aboard NASA's ER-2 research airplane measured concentrations of chlorine monoxide and ozone simultaneously as the plane flew from Punta Arenas, Chile (53° S), to 72° S. The data shown above were collected on Sept. 16, 1987. As the plane entered the ozone hole, concentrations of chlorine monoxide increased to about 500 times normal levels while ozone plummeted.

Source: James G. Anderson, Harvard University

But discussion at the ozone workshop ranged far beyond Antarctica. The scientists also exchanged ideas on laboratory studies of heterogeneous reactions believed to be the key to unexpectedly fast ozone loss, the ozone hole's effect on the rest of the Southern Hemisphere, observations of key chemical species in the Arctic made in January and February, and the recently uncovered global decrease in ozone (C&EN, March 21, page 6).

The fierce debate over chemistry versus dynamics in regard to Antarctica is over. Scientists who a year ago were insisting that natural fluctuations in the dynamical behavior of the atmosphere could account for the hole—at least in part and perhaps entirely—have bowed to the accumulated evidence that chlorine chemistry is responsible for the ozone loss.

In retrospect, all the key data needed to reach that conclusion were available more than a year ago from the observations of the first NSF-organized National Ozone Expedition (NOZE), which went to Antarctica in August 1986 (C&EN, March 16, 1987, page 6). However, it took the overwhelming weight of evidence gathered by 1987's much more complex NASA-led aircraft expedition—in which two research aircraft flew a total of 25 missions over Antarctica last August and September—to convert many skeptics.

The single most convincing aircraft experiment was the measurement of huge amounts of chlorine monoxide by Harvard chemistry professor James G. Anderson and his research associate William H. Brune. Chlorine monoxide has been dubbed the "smoking gun" of ozone depletion, because chain reaction mechanisms proposed to destroy ozone depend on chlorine monoxide to carry the chain.

The Harvard researchers' resonance fluorescence instrument was carried directly into the ozone hole by NASA's ER-2 research plane, where chlorine monoxide concentrations 500 times larger than those found at comparable altitudes at mid-latitudes were measured. Two other instruments on the aircraft, those of NOAA's Michael Proffit and NASA's Walter Starr, simultaneously measured ozone concentrations. They observed that ozone over Antarctica emerged from the polar night essentially unaltered. Once the sun came up and triggered chlorine chain reactions, however, ozone began to rapidly disappear.

"Within three weeks ozone dropped precisely within the region defined by high chlorine monoxide," Anderson says. "There was a very clear relationship between ozone and chlorine monoxide, a dramatic anti-correlation."

A chlorine chain first proposed by Mario J. Molina and coworkers at NASA's Jet Propulsion Laboratory (JPL) in Pasadena, involving both chlorine monoxide and its dimer, is now thought to account for about 80% of the ozone loss:

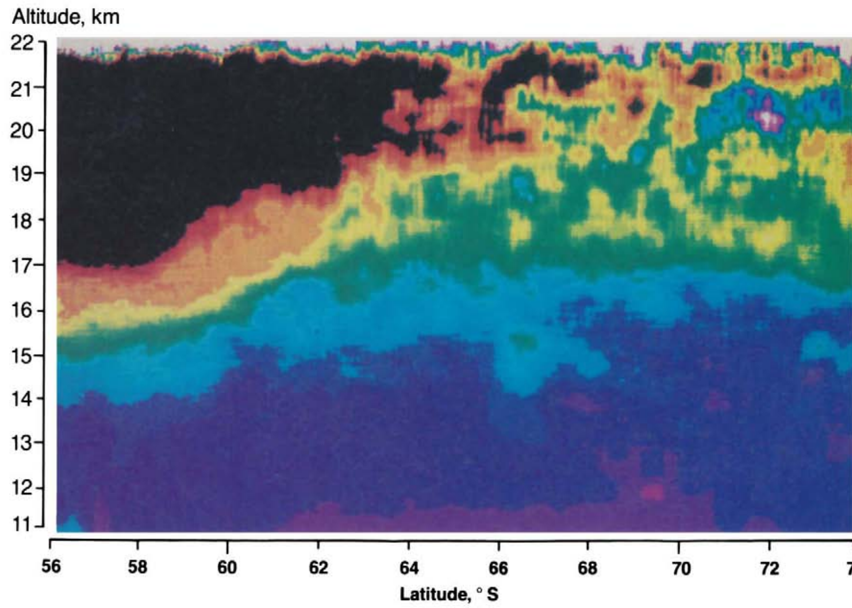
$$ClO + ClO + M \rightarrow Cl_2O_2$$
$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$$
$$ClOO + M \rightarrow Cl + O_2 + M$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$\text{Net: } 2\,O_3 \rightarrow 3\,O_2$$

where *M* represents another molecule that is unchanged in the reaction. Anderson and coworkers also found evidence for a significant amount of chlorine monoxide dimer within the Antarctic ozone hole.

Although chlorine chemistry is ultimately responsible for the ozone destruction, dynamics play a role in setting up the unique meteorology of Antarctica. 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 fall below −90 °C, cold enough to form clouds even in the very dry stratosphere.

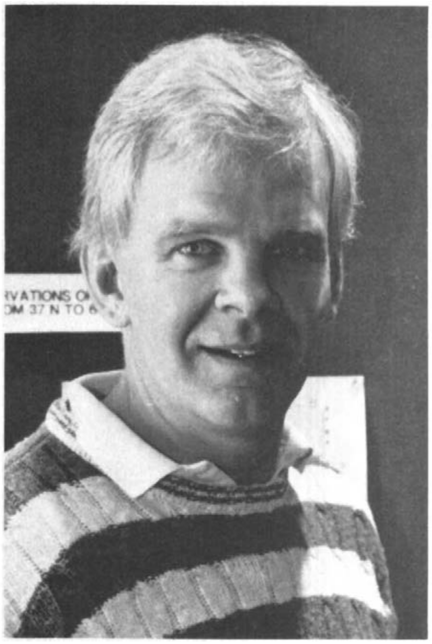
These polar stratospheric clouds provide surfaces for heterogeneous reactions that are the key to the Antarctic phenomenon. The reactions convert chlorine nitrate ($ClONO_2$) and hydrogen chloride—molecules that are relatively inert—to active

Ozone is lost above 15 km in Antarctic hole



On flights across Antarctica, an airborne lidar (laser radar) system was used to measure ozone concentrations. The computer plot above shows ozone levels on Sept. 26, 1987. The black areas in the upper left corner represent ozone concentrations of more than 2.5 ppm by volume outside the ozone hole. As the plane flew further south, much lower amounts of ozone were recorded between 15 and 22 km altitude. Orange represents ozone concentrations of about 2.0 ppm; yellow, about 1.5 ppm; green about 1.0 ppm; and blue about 0.5 ppm.

Source: Edward V. Browell, NASA Langley Research Center



C&EN staff photo

Anderson: chlorine monoxide studies

forms of chlorine that can catalyze the destruction of ozone. They also tie up nitrogen species, which could react with active chlorine to reform inert chlorine nitrate, as nitric acid (HNO_3) that becomes incorporated in the cloud particles (C&EN, Nov. 30, 1987, page 25):

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

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

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

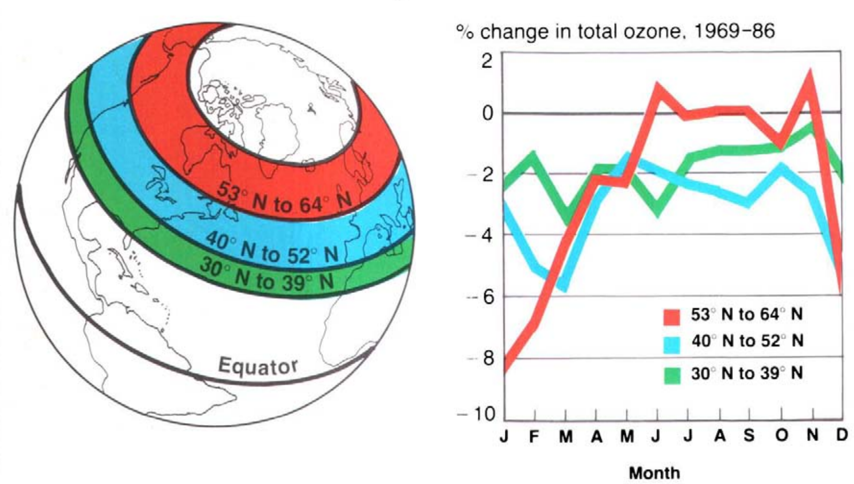
Many of last year's aircraft and ground-based experiments probed the nature and frequency of polar stratospheric clouds. Two types of clouds form as the stratospheric temperature falls in winter. The most commonly occurring clouds are composed of nitric acid trihydrate particles, which condense around sulfuric acid aerosols that are ubiquitous all year long. Larger water ice particles form less often, when the temperature drops lower still.

Both kinds of polar stratospheric clouds could serve to denitrify the stratosphere (that is, remove nitrogen species from the vapor phase), an essential condition for large-scale ozone depletion. Michael B. McElroy of Harvard University's department of Earth and planetary sciences suggests that the extent of denitrification, which may be less in warmer years when fewer clouds form, may be a key to the severity of the ozone loss in a given year.

"It's most important to understand how variable the denitrification rate is and what controls it," McElroy says. Indeed, polar stratospheric clouds persisted for an unusually long time in 1987—the worst year yet for the ozone hole—according to observations by NASA Langley Research Center atmospheric scientist M. Patrick McCormick and his coworkers.

Laboratory research groups are trying to determine if nitric acid trihydrate clouds catalyze heterogeneous reactions as water ice particles have already been found to do (C&EN, Nov. 30, 1987, page 25). Preliminary work from both JPL and SRI International in Menlo Park, Calif., indicates such nitric acid trihydrate particles may well play an important role in creating active chlorine species in the Antarctic stratosphere.

Ozone has decreased at high latitudes in winter



Source: NASA Ozone Trends Panel report

Sulfuric acid aerosols also catalyze the key heterogeneous reactions, two research groups told the workshop—a finding that could have implications for global ozone loss. Although polar stratospheric clouds only occur during winter in the polar regions, sulfuric acid aerosols are present in the stratosphere worldwide throughout the year.

SRI's Margaret A. Tolbert reports that both water and hydrogen chloride react with chlorine nitrate on 65% sulfuric acid at −63 °C. The reactions are very dependent on temperature and the percentage of water in the sulfuric acid solutions. Similarly, Jane Van Doren of Boston College and Aerodyne Research in Billerica, Mass., finds both temperature and composition of sulfuric acid aerosols are very important in determining how significant heterogeneous reactions will be in the stratosphere outside Antarctica.

One unresolved aspect of the ozone hole is whether the polar vortex acts like a beaker that contains the unusual chemical processes over Antarctica. Some scientists at the workshop suggested the system instead resembles a flow reactor, in which air enters the vortex, is transformed, and then moves out. "The system is a chemical processor, with the effects of chlorine-induced ozone loss being spread out to latitudes outside," hypothesizes NOAA's Adrian Tuck.

Other researchers, however, presented evidence that the system is more like a containment vessel, with very little leakage of air across the walls of the polar vortex. "There are a lot of smart people here who can't agree," commented Du Pont atmospheric scientist Mack McFarland.

However, there's no doubt that air over Antarctica mixes freely with that from higher latitudes once the polar vortex breaks up in mid-spring. Atmospheric modelers are attempting to calculate whether the ozone-poor air from near the South Pole "dilutes" ozone at regions away from the vortex. Such dilution might explain a decrease in ozone since 1979 of about 5% or more at all latitudes south of 60° south latitude that has been measured by satellite.

Dilution can account for the observed loss, according to calculations by both Malcolm K. W. Ko and his coworkers from Atmospheric & Environmental Research Inc., Cambridge, Mass., and Michael J. Prather and coworkers from NASA/Goddard Institute for Space Studies, New York City. Both groups note that the exact magnitude of the dilution effect and how far north it extends depend upon the assumptions built into their models.

Ozone-depleted air from Antarctica may have been carried north to inhabited regions late last year, according to Roger Atkinson of the Australian Bureau of Meteorology. Three out of five Australian ozone-monitoring stations observed a sharp drop in ozone last December, shortly after the polar vortex broke up. The abnormally low ozone values persisted for three weeks over Melbourne, resulting in the lowest December mean ozone levels on record.

"We're investigating to see if this could be related to dilution of ozone," Atkinson says, stressing that the low ozone values need careful analysis to make certain they are not artifacts. "But given the timing, it's possible that this is the first sign of depletion extending over Australia."

Atmospheric scientists are wondering if the chlorine chemistry that is responsible for the massive ozone depletion that has been occurring over Antarctica each spring for the past decade is also taking place to a lesser extent in the Arctic. Significant losses of ozone at high northern latitudes in winter have recently been uncovered (C&EN, March 21, page 6).

A polar vortex also forms in the Arctic regions in winter, but it is much weaker and shorter-lived than over Antarctica. Consequently, air within the north polar vortex is not so well isolated and often encounters warmer air from the mid-latitudes. Polar stratospheric clouds do occur in the Arctic stratosphere, although less often than in the colder south polar region.

Some indications of perturbed atmospheric chemistry in the Arctic have already been observed. A team of scientists led by chemist Susan Solomon of the NOAA's aeronomy laboratory in Boulder spent three weeks in January and February of this year in Thule, Greenland, (76.5° N) recording visible and near-ultraviolet spectra of stratospheric species.

Concentrations of chlorine dioxide—a useful proxy for the free radicals involved in ozone loss—were elevated, the scientists found. They also measured very low levels of the key species nitrogen dioxide. "I think that strongly indicates that some kind of heterogeneous chemistry is going on," Solomon says, although to a much lesser extent than in the Antarctic.

Chlorine monoxide concentrations in northern high latitudes also are greater than found closer to the equator, according to Harvard researchers Anderson and Brune. Their resonance fluorescence instrument was flown from California to Great Slave Lake, Canada, (61° N) in February aboard NASA's ER-2 research plane. The researchers found chlorine monoxide levels increased as the plane flew further north. The highest value measured was about 55 ppt by volume—only $^{1}/_{20}$th the maximum observed over Antarctica, but five times what they measured at 35° N.

"We've been kind of numbed by the 1300 ppt of chlorine monoxide we saw in Antarctica," Anderson says, "but there's definitely unusual chlorine in the Northern Hemisphere."

Such glimpses of anomalous chlorine chemistry have prompted NASA to plan a research expedition to probe the Arctic stratosphere next January and February, similar to the one the agency coordinated in Antarctica last year. The research planes will begin flying from Stavanger, Norway, (59° N) as soon after the first of the year as weather permits.

"We're very eager for international cooperation," says Michael P. Kurylo, NASA program manager for the project. Danish scientists may take part by making simultaneous ground-based observations from Greenland. And Soviet scientists and planes may also participate, although negotiations for cooperation with the U.S.S.R. have not yet been finalized.

Strong criticism of the NASA report that concludes ozone has declined significantly in the Arctic region and elsewhere beyond Antarctica was voiced at the workshop. Wayne F. J. Evans, of Canada's atmospheric environment service in Ontario, objected to the method by which ground-based (Dobson) ozone measurements were revised.

"Modifications to the Dobson data are politically unacceptable and scientifically unacceptable," Evans said. "NASA put a lot of money into this—you would have thought they could have done it right."

The report in question was prepared by a panel of more than 100 scientists assembled by Robert T. Watson, manager of NASA's upper atmospheric research program. The goal was to critically examine a 1986 report that global ozone had been dropping an average of about 1% a year for several years, based on data from ozone-measuring instruments aboard the Nimbus 7 satellite, launched in 1978.

Because changes of that magni-

Adequacy of ozone protection treaty is under scrutiny

The Montreal Protocol on Substances That Deplete the Ozone Layer has not yet gone into effect. But bad news about stratospheric ozone has been accumulating so rapidly of late that the United Nations Environment Program (UNEP) is already making plans to speed up reassessment of the international agreement restricting production of chlorofluorocarbons (CFCs).

The Montreal protocol, carefully shepherded by UNEP through two years of complex negotiations, was signed by 24 countries and the European Community last September. It will freeze consumption of CFCs at 1986 levels on July 1, 1989. Later cuts will reduce CFC consumption first by 20% by mid-1993, then an additional 30% by mid-1998. Consumption of halons (fluorocarbons that contain bromine atoms) is to be frozen at 1986 levels.

The agreement will go into force on Jan. 1, 1989, if it has been ratified by at least 11 countries accounting for two thirds of world consumption. So far, only the U.S. and Mexico have ratified it.

"The ozone layer has little protection at the moment from destruction by chlorine," says Peter Usher, program manager of UNEP's global environmental assessment project. "Our highest priority is to get the protocol implemented on time." Usher expects that Japan and the European Community member nations will ratify the accord this summer, satisfying the conditions for the agreement to go into effect.

Once the protocol is in force, UNEP's next step will be to organize a reassessment of the scientific understanding of ozone depletion. Such a reconsideration of whether the treaty is strong enough to protect the ozone layer is required every four years under the terms of the protocol. The first reassessment was to have taken place in 1990, but Usher says the new data on Antarctica and global ozone trends are prompting UNEP to speed things up. The agency now aims to complete the reassessment by mid-1989.

C&EN staff photo

Usher: implement protocol on time

"This meeting is telling us there is good reason to believe the Montreal protocol is not sufficient to repair the Antarctic ozone hole," Usher said earlier this month at the polar ozone workshop. "The hole is occurring now with about 3 ppb of chlorine in the atmosphere. Under the protocol, the concentration of chlorine will increase to 6 or 7 ppb. If we want to repair the ozone hole, we must bring the atmosphere back to pre-CFC conditions, requiring almost a total ban."

Usher points out that UNEP's role is only to present the most up-to-date scientific understanding to government decision makers. After that, it is up to the nations of the world to decide if the protocol's control measures are adequate and timetable sufficient. However, he says, UNEP will recommend policies that protect the ozone layer.

"Despite major advances in atmospheric science we are still continually being surprised by things," Usher says. "That confirms our belief that pollution of the atmosphere, given our limited understanding, is not acceptable."

tude are much larger than scientists have been predicting using computer models of the atmosphere, the panel wanted to determine if the satellite-measured losses really were occurring or were an artifact of instrument degradations in space. The scientists exhaustively re-evaluated all available Dobson and satellite data on ozone concentrations.

What the panel found was that the satellite values had drifted significantly as the instrument degraded, but could be normalized by comparing the satellite data to ozone values measured at Dobson stations on the ground. The report concluded that the ozone layer worldwide shrank an average of about 2.5% during the past decade, even after accounting for natural variability. The decline has been most precipitous in winter months at high latitudes.

In reaching that conclusion, however, the panel noted that the quality of data varied significantly from Dobson station to Dobson station. Some instruments clearly had been carefully maintained and read, while others had not. The panel threw out data from some stations and retroactively corrected data from others to take into account recalibration or replacement of the Dobson instruments. It was this manipulation of Dobson data that Evans suggested could be "fudging."

Evans was the most vocal critic at the workshop, but some other scientists also are not completely comfortable with the report. "Industry silence doesn't mean we agree with the ozone trends panel," says Allied-Signal's S. Robert Orfeo. "We may wind up agreeing with the conclusion but we want to analyze the raw data ourselves."

Orfeo is chairman of CMA's fluorocarbon program panel, 19 CFC producers who fund research to determine the effects of CFCs on the atmosphere. The CMA panel recently obtained the raw data that went into the ozone trends report and is carrying out an independent evaluation. Most atmospheric scientists at the meeting, however, accept the data evaluation that went into the ozone trends panel report as well within the bounds of good science.

The polar ozone workshop ended with a tribute by John Lynch, manager of NSF's polar atmospheric sciences program, to Molina and F. Sherwood Rowland, professor of chemistry at the University of California, Irvine. Rowland and Molina first proposed in 1974 that chlorine from CFCs can catalyze ozone depletion.

"I've never seen any scientific problem attacked so rapidly and come out with such high-quality results," Lynch said of the Antarctic ozone hole. "The scientific community was preconditioned by Rowland and Molina's warning to be in a position to move fast when it had to." □

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News of the Week

Cover: Researchers at South Pole launch balloon carrying ozone-measuring instruments. Photo by NSF's John T. Lynch

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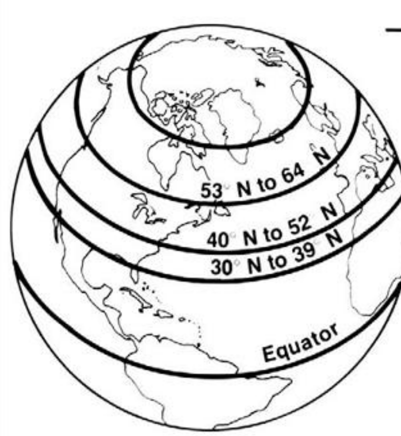

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