ARCTIC MEASUREMENTS INDICATE THE CHILLY PROSPECT OF OZONE DEPLETION

The North Pole warmed just in time this spring to avoid a possibly significant depletion of ozone. That conclusion is one outcome of the second Airborne Arctic Stratospheric Expedition, which reported on its findings at the end of April. Earlier, in the first days of February, the participating scientists had released some preliminary results because they were alarmed at seeing very high levels of chlorine monoxide, a reactive chlorine compound associated with ozone destruction. As shown in the figure below, which is based on satellite data, the levels and extent of ClO this January were comparable to those seen during the winter months in the Antarctic, where an "ozone hole" is known to develop at that time.

While a weaker vortex and milder temperatures in the North should prevent ozone loss severe enough to be termed a hole, the observers were nonetheless worried about the possibility of a substantial depletion. In one region, the ClO concentrations were the highest ever seen at either pole. Fortunately, the cold weather, which indirectly sustains the concentrations of ClO, broke in mid-January, sparing the Arctic—for this year. But the data collected on the mission indicated that the region might not be so lucky in winters to come. The expedition also provided new insight into the ozone losses that are occurring throughout the Northern Hemisphere.

The ozone hole

In the mid-1980s the world had indications that global ozone concentrations had fallen by perhaps a few percent. Though chlorofluorocarbons were suspected of somehow being responsible for the drop, there was no firm evidence to convict them. Then in 1985 British scientists identified a very dramatic drop in ozone levels that seemed to be occurring with increasing severity each successive winter over the South Pole. By 1987 the hole was so deep that ozone in some regions of the stratosphere virtually disappeared for a period in the early spring. Extensive scientific expeditions to the South Pole in 1986 and 1987 linked CFCs to the ozone depletion there by a chain that depends on the fine ice particles contained in the polar stratospheric clouds. (See PHYSICS TODAY, July 1988, page 17, and the article by Patrick Hamill and Owen Brian Toon, December 1991, page 34.)

After CFCs are injected into the atmosphere they remain there about 100 years, gradually making their way into the stratosphere. If the chlorine atoms are freed from these chemical compounds, they can catalyze the destruction of ozone. The important chain of reactions in the polar regions is as follows:

$$\mathrm{ClO} + \mathrm{ClO} \rightarrow \mathrm{ClOOCl}$$

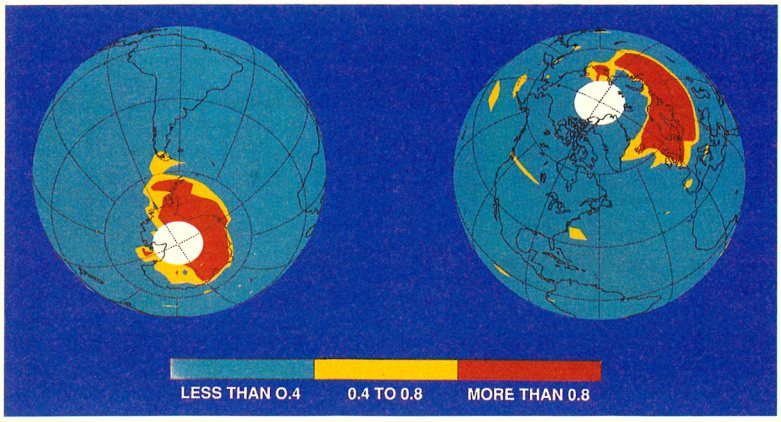
$$\mathrm{ClOOCl} + h\nu \rightarrow \mathrm{Cl} + \mathrm{ClOO}$$

$$\mathrm{ClOO} + M \rightarrow \mathrm{Cl} + \mathrm{O_2} + M$$

$$2(\mathrm{Cl} + \mathrm{O_3}) \rightarrow 2(\mathrm{ClO} + \mathrm{O_2})$$

where M represents a neutral molecule that has some momentum. This chain destroys two ozone molecules and frees the two ClO molecules to begin the cycle over again.

Fortunately, most of the year and over most of the globe, the chlorine atoms are largely sequestered in so-called reservoir species, either hydrochloric acid (HCl) or chlorine nitrate ($\mathrm{ClONO_2}$). Chlorine rarely exists in a reactive form. However, scientists studying the Antarctic ozone hole found evidence that the polar stratospheric clouds, which form during the Antarctic winter, are the sites for highly efficient heterogeneous reactions that liberate the chlorine from these reservoir species, converting it largely to $\mathrm{Cl_2}$. At the same time, the reactions leave the nitrogen oxides essentially frozen into the clouds as nitric acid, so that the reactive chlorine can not easily be bound up again



Chlorine monoxide concentrations (in parts per billion) measured by the Microwave Limb Sounder aboard the Upper Atmosphere Research Satellite. Abundances of this chemical in the Northern Hemisphere in January (right) were at times as great as those in the Southern Hemisphere at the end of its winter last September (left). In the red regions levels of ClO are sufficiently high to destroy ozone molecules at the rate of 1% per day.

in a reservoir species. These heterogeneous reactions tend to occur in the deep of the Antarctic winter, when there is no sunlight. When the Sun shines for longer periods, photolysis can convert molecular Cl_2 to atomic Cl, which forms ClO by reaction with O_3. Sunlight then drives the reaction cycle that ravages the ozone. One piece of evidence that strongly linked CFCs to ozone depletion was the strong anticorrelation between concentrations of ClO and ozone.

Can it happen up north?

It was only natural to wonder whether an ozone hole could develop at the other pole, although there was reason to suspect that the situation there would not be as bad. The Arctic winters are not as cold as those in the Antarctic, and the circumpolar circulation is considerably weaker. So the polar stratospheric clouds that form at the North Pole are neither as abundant nor as persistent as those that develop within the frigid, isolated vortex of the South. But the consequences of a significant ozone depletion in the Arctic might be more severe, because of its proximity to populated regions.

The Airborne Arctic Stratospheric Expedition was organized to explore the potential for ozone depletion at the North Pole by understanding the stratospheric photochemistry and dynamics there. The first expedition, based in Stavanger, Norway, collected data in January and February 1989. AASE II operated largely out of Bangor, Maine, and Fairbanks, Alaska, and ran from October 1991 through March 1992. It involved 80 observers and drew its support from NASA, the National Oceanic and Atmospheric Administration, NSF and a number of universities: the University of California at Irvine, the University of Colorado, the University of Denver, Harvard, MIT, Pennsylvania State University, San Jose State University and the University of Washington. The expedition was also supported by the chemical industry's Alternative Fluorocarbon Environmental Acceptability Study.

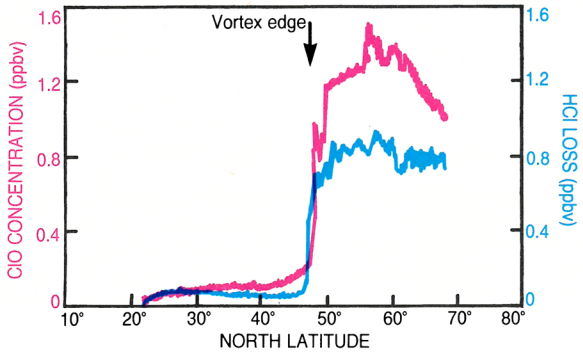
The planners of AASE II expanded the mission in several ways. First, they collected data from late fall, before the appearance of polar stratospheric clouds, to late spring, after the clouds had gone. Next, they added the kinds of measurements that would possibly enable researchers to distinguish changes brought about by chemical processes from those resulting from dynamical transport of air masses. Finally, they extended the region of data collection by including flights over much of the Northern Hemisphere, not just the Arctic. They did this to explore the causes of the decreases in the stratospheric ozone at mid-latitudes that had been seen from late fall through early spring over the past decade in ground-based and satellite observations. The data at mid-latitudes also enabled the researchers to examine the impact of the aerosols from the eruption of Mount Pinatubo in June 1991.

Like the massive data-gathering attack on the South Pole, the Arctic mission relied heavily on instruments aboard two aircraft: An ER-2 plane, which can fly as high as 20 km, collected samples *in situ* to measure ozone, atmospheric chemical tracers, and chemical species such as ClO, BrO, HCl and $ClONO_2$; and a DC-8, which flew across the North Pole from Bangor to Stavanger, carried remote sensing instruments such as lidar (light detection and ranging) and Fourier-transform infrared spectrometers. The data from these instruments are complemented by meteorological predictions and analyses as well as by data from the Total Ozone Mapping Spectrometer aboard the Nimbus-7 satellite, which has been surveying worldwide ozone levels for 13 years.

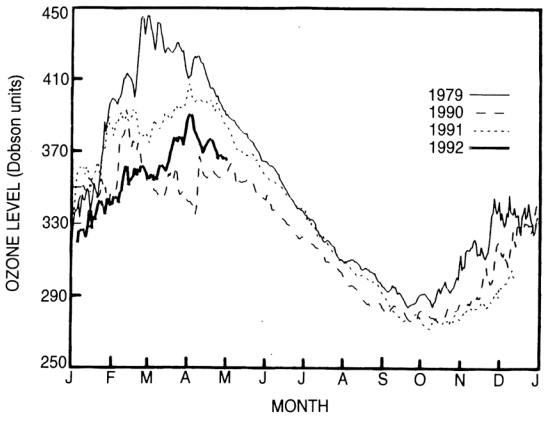
Additional data have come from the Microwave Limb Sounder on NASA's Upper Atmosphere Research Satellite, which was launched just last September. The MLS, the only instrument of the nine aboard UARS that is able to measure the reactive chlorine, can provide global mapping of ClO to supplement the detailed, more regional aircraft measurements from AASE II. As it orbits, the MLS peers through the atmosphere and detects the microwave emissions from ClO, hydrogen peroxide, water vapor and ozone emanating from a slice about 300 km across. Joe Waters of the Jet Propulsion Laboratory, principal investigator for the MLS, told us that the instrument covers a large portion of the globe every day, measuring a vertical profile of ClO from 15 to 50 km every minute, with a resolution of about 3 km.

Findings

This year's mission found levels of ClO even higher than those of three years ago, with concentrations reaching a record level of 1500 parts per trillion by volume at 20 km by the third week of January. (ClO concentrations vary widely, but normal values at mid-latitudes in the summer are on the order of 20 pptv.) Scientists from the expedition point out that these levels represent a large fraction of the available inorganic chlorine in the stratosphere. Similarly, about 40% of the bromine in the stratosphere was found in the form of BrO. James Anderson (Harvard), who is the mission scientist, commented to us that the record ClO levels were especially surprising because they occurred under relatively benign conditions. As shown in the figure below, wherever the ClO levels were high, concentrations of HCl—the only reservoir species directly measured—were low. AASE II participants traced the history of air parcels with high values of ClO and low values of HCl and found that these parcels had experienced temperatures below that at which polar stratospheric clouds form, −78 °C. Conversely, the temperatures for the air parcels with more normal levels of both chemicals had never dipped below this value. As the weather warmed in late January and the clouds disappeared, ClO concentrations fell and the reservoir species became more prominent. These data strengthen the case already made by



Anticorrelation of HCl and ClO. Concentrations of ClO (red, in parts per billion by volume) are higher at latitudes where losses of HCl (blue) are greater, indicating that the former, reactive form of chlorine is being freed from the latter, reservoir species. This conversion occurs primarily inside the Arctic vortex. (Data courtesy of Darin Toohey, University of California at Irvine, and Christopher Webster, Jet Propulsion Laboratory.)



Total ozone levels, integrated over the Northern Hemisphere, as measured by the Total Ozone Mapping Spectrometer on the Nimbus-7 satellite. Shaded region indicates the range of data taken over 13 years. The data indicate that between 40° and 50° N ozone levels have declined as much as 8% over the past decade.

measurements in the Antarctic for the role of polar stratospheric clouds in the buildup of ClO.

Over substantial regions, levels of ClO were high enough at times to reduce the number of ozone molecules at a rate of at least 1% per day. But this winter was a short one: There was a 39-day period during which the temperatures were intermittently low enough for polar stratospheric clouds to form, compared with a 68-day range during an average winter. Scientists from the expedition warned that a more extensive ozone loss was very likely during some future, more severe winter.

The scientists also monitored ozone levels throughout the mission. Direct determination of any winter loss of stratospheric ozone is complicated, because ozone concentrations normally *increase* in the winter due to an influx of ozone from low latitudes and higher altitudes. But researchers were still able to distinguish a decrease in ozone superimposed on this increase by comparing ozone levels with those of tracers such as N_2O and CFC-11, which travel in the same circulation patterns. The ozone loss determined this way was about 20% in the altitude range from 16 to 17 km. These measurements agree with the model calculations.

The AASE researchers wondered if the aerosols from Mount Pinatubo might have a significant impact on the chemical composition of the atmosphere. But no evidence of a substantial impact in the Arctic region was found. While the scientists believe that reactions on liquid aerosols such as those composing the Pinatubo cloud are important, conversion of inorganic chlorine to ClO in polar stratospheric clouds is substantially faster. Air moving through warm air laden with Mount Pinatubo aerosols was hardly perturbed chemically, whereas air only briefly exposed to polar stratospheric clouds exhibited large depletions in $ClONO_2$ and HCl.

Mid-latitude measurements

While the ozone hole has attracted a lot of attention, there is growing evidence of a slow but steady ozone depletion over the rest of the globe. The Total Ozone Mapping Spectrometer monitors the total amount of ozone contained in a vertical column of the atmosphere. The trends determined by TOMS are depicted in the figure above. (There, ozone is measured in Dobson units. One DU is equivalent to the amount of ozone that would occupy a 0.01-mm-thick column at standard temperature and pressure.) The figure shows that the ozone levels from 1990 to 1992 were considerably below those in 1979. That the curve for 1991 is higher than those for the surrounding two years reflects normal quasibiennial variations. Analysis of the data from an $11\frac{1}{2}$-year period ending in May 1990 reveals[1] that ozone levels have declined globally by 3% since 1978. However, this decrease is much greater in certain regions, such as the southern high latitudes and the northern mid-latitudes. Between 40° and 50° N, the TOMS data indicate a decline as large as 8% per decade.

The data collected by TOMS for AASE II this year indicate that the average ozone levels in the Northern Hemisphere this past winter were lower than those during any other year in the TOMS record. The seasonal maximum in ozone concentration, which occurs in the late winter and early spring, was 10–15% lower than it had been in previous years.

Anderson told us that one of the chief findings of AASE II was that the erosion of ozone at mid-latitudes was at least as serious as that at the high latitudes. The expedition scientists measured levels of both ClO and BrO that were high enough to contribute to a significant ozone loss. Anderson admitted that they "have not yet connected cause and effect from a scientifically defensible position," but said that "the gap is being bridged."

One of the first surprises of the expedition was the early measurement of low levels of NO_x (NO and NO_2, collectively) in the stratosphere. These low levels indicate that NO_x cannot be playing as large a role in catalyzing the destruction of ozone as are ClO and BrO. The measured concentrations of NO_x were significantly below the levels predicted by models based on chemistry that occurs only in the gas phase. The AASE II scientists now believe that NO_x is converted to other nitrogen oxides by heterogenous chemical reactions that can occur on sulfuric acid aerosols in the stratosphere. These reactions can simultaneously explain the high observed levels of ClO, because in the absence of NO_x, ClO cannot be sequestered as $ClONO_2$.

Both the rates of ozone depletion and the abundances of ClO are greater than those predicted by models that include only homogeneous gas-phase reactions. Those models have often been used as the basis for policy decisions. It now appears that the data are in general agreement with models that also include the reactions that can occur on atmospheric aerosols.

The aerosol burden of the atmosphere was of course greatly increased this year by the Mount Pinatubo output, which may have enhanced the surface area of atmospheric particulates by a factor of 20–30 at mid-latitudes. However, because the background aerosols might have already converted most of the NO_x, the additional aerosols from Mount Pinatubo may not have had a proportional effect, at least at high latitudes and altitudes below 20 km. At lower latitudes and higher altitudes, sunlight frees more of the NO_x, and the contribution from Mount Pinatubo aerosols becomes important. This year measurements of the NO_2 column—that is, NO_2 at *all* altitudes—were significantly lower outside the polar vortex than those in 1989. It is still not clear how much the Mount Pinatubo volcano will worsen an ozone depletion that is already bad enough.

—Barbara Goss Levi

Reference

1. R. S. Stolarski, P. Bloomfield, R. D. McPeters, J. R. Herman, J. Geophys. Res. Lett. **18**, 1015 (1991). ■