Research News

Ozone Hole Bodes Ill for the Globe

Nothing quite like the Antarctic ozone hole is likely to appear elsewhere, but the type of chemistry causing the ozone loss there may be behind the observed global ozone decrease

THE ANTARCTIC OZONE HOLE was a startling and ominous discovery. Theorists had not seen it in their maze of equations predicting the chemical behavior of stratospheric gases. And high-tech sensors in space picked up the hole, only to have that data expunged by computers as too incredible. Once recognized, the hole and the ease with which it consumed ozone were disquieting, to say the least.

Researchers are still not entirely comfortable with a phenomenon that surprised them so, and there is concern for the living things around Antarctica, but in many ways the hole has become less ominous than it might have seemed at first. At the same time, new understanding of the causes of the hole is raising concerns for the rest of the globe's stratosphere.

The Antarctic hole may be a beast with a voracious appetite for ozone, but for the time being the beast appears to be caged and to have limits to its hunger. During the 9 years of monitoring by the TOMS satellite, the springtime hole has always been about the size of the Antarctic continent or slightly larger, even though the loss of ozone has climbed to 50%. Researchers also doubt that the hole will get much deeper. The loss of half the ozone over Antarctica, or less than 5% of global ozone, in September and October 1987 is seen as a likely upper limit to ozone destruction in the hole. Losses in the layer between 15 and 20 kilometers altitude, where ice cloud particles mediate ozone destruction, approached 100%, but ice particles and ozone losses drop off rapidly with increasing altitude. By about 25 or 30 kilometers, increasing temperatures surpass the −80°C limit for the formation of the ice clouds, called polar stratospheric clouds. No ice, no ozone loss.

There is also evidence that the vortex of swirling wind that confines the hole forms a relatively secure container. If it leaked like a sieve, the hole would act as a flow-through reaction vessel, destroying the ozone in many times its own volume of air, rather than as a closed beaker. At the Polar Ozone Workshop in Snowmass, Colorado, last May, Dennis Hartmann of the University of Washington and his colleagues reported that they used certain gases as tracers to measure the flow of outside air through the hole as it formed. The vortex does leak, they concluded, but not much. It is unlikely that the amount of ozone brought in was greater than 30% of the observed ozone loss and it was more likely 15% of the loss, they reported. Confirmation awaits more fieldwork.

The Antarctic vortex does not leak much during the austral spring, but that does not last forever. By late October or November it falls apart, spewing blobs of its ozone-depleted air across the stratosphere of the Southern Hemisphere. That is not to the good; witness Melbourne's record December low in overlying ozone after last year's breakup. But preliminary analyses and modeling of the breakup reported at the Snowmass workshop suggest that any lingering ozone loss on a hemispheric scale is a modest one.

> ***"If those numbers are correct, they will produce significant changes in mid-latitude chemistry."***

For example, Michael Prather of the Goddard Institute for Space Studies in New York City and María García of Columbia University reported that, in their model, a year after breakup a depletion of only a few percent remained near the hole; the ongoing creation of ozone by solar ultraviolet radiation had made up the difference. Over several breakups, Prather reported, the depletion did not accumulate significantly.

The Antarctic ozone hole may not be poised to engulf the globe, but it has made researchers take an entirely new view of global ozone depletion. The place they reconsidered first was the Arctic stratosphere. It does have a vortex of its own, it can chill during the winter to the magic −80°C mark required for the formation of ice crystals, and TOMS has reported ozone losses at high Arctic latitudes during the spring. On their first try, researchers found a sign of ozone-destroying chlorine within last winter's vortex (*Science*, 27 May, p. 1144).

The Arctic may be harboring a combination of polar stratospheric clouds and potentially reactive chlorine, but the third element of the lethal mix, sunlight, has yet to be implicated. Unlike the Antarctic's vortex, the Arctic's version can break up and reform in midwinter and does not persist long into spring, when the pole begins to see the sun and chlorine can begin destroying ozone.

Researchers are now asking themselves, If chlorine released through the action of polar stratospheric clouds were destroying ozone in the Arctic, how bad could it get? The Antarctic hole went from unnoticeable to a 50% ozone loss in a decade. Current thinking on the causes behind that precipitous decline bodes ill for the Arctic.

One cause for the abrupt deepening of the Antarctic hole is presumed to be the increasing concentrations of chlorine-containing chlorofluorocarbons (CFCs) in the stratosphere. According to this reasoning, the approximate tripling of the concentration of CFCs between 1960 and 1985 gradually supplied more and more of the chlorine needed to tie up nitrogen in polar stratospheric cloud particles. It is nitrogen that normally combines with most free chlorine, reining in its destruction of ozone. In tying up the nitrogen as nitric acid in ice, ironically enough, the chlorine is released in an ozone-destroying form. But as long as some nitrogen remains free, it will dominate the chlorine and protect the ozone.

It appears that in the late 1970s chlorine exceeded some critical level at which it finally overwhelmed the nitrogen, consigning most of it to ice particles. Chlorine had short-circuited ozone's protective system with the help of the ice and the hole began deepening in earnest. If this helped trigger the Antarctic hole, then this trigger has already been pulled in the Arctic.

As became apparent at the workshop, there is increasing evidence that once chlorine freed itself to destroy ozone each austral spring, it went about it in a particularly virulent fashion. Both laboratory experiments and observations show that ozone-destroying chlorine is part of a catalytic cycle including chlorine monoxide. They also suggest that in this cycle two chlorine monoxides combine to form the dimer of chlorine monoxide, which in turn breaks down to yield the free chlorine that actually destroys

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The lovely agent of destruction. *Polar stratospheric clouds become obvious at the horizon when the sun has set.*

the ozone. As chlorine does its damage, it also completes the cycle by regenerating the two chlorine monoxides.

Final laboratory data are still awaited, but if this is the particular catalytic cycle involved, the reaction whose rate limits the rate of ozone destruction will be the formation of the dimer. Because dimer formation requires that two molecules come together, its rate varies with the square of the concentration of chlorine monoxide. Such a nonlinear dependence of the rate means that the Antarctic's stratosphere, and presumably the Arctic's, are on a slippery slope indeed. Doubling free chlorine would mean a quadrupling of the rate of ozone destruction each spring.

Some such heterogeneous chemistry involving ice particles is clearly behind the formation of the Antarctic hole each spring and is probably involved in its year-to-year deepening, but there may be more to the observed long-term trend. Ross Salawitch of Harvard University is one of the modelers who sees a need for an additional explanation. He is not sure just what it is, but the possibilities that come to his mind all involve the temperature of the stratosphere.

At the workshop, analyses of observations of the past 30 years showed that the hole has cooled about 10°C during the past decade and is now 15°C colder than during the 1960s. The less ozone in the hole, the colder it has been, the longer stratospheric clouds persisted, and the later the hole broke up.

The implication is that the hole could be self-reinforcing through connections between ozone and temperature. One connection between ozone and temperature is straightforward enough—the absorption of solar ultraviolet by ozone warms the stratosphere. Less ozone, less heating and deeper cold.

The more speculative connection, which would make ozone loss self-reinforcing, is made through polar stratospheric clouds. In a general way, it might be assumed that they could complete a loop that begins with an initial ozone loss, which produces greater cold. The greater cold in turn produces more and longer-lasting ice clouds, which lead to more ozone loss. The beast could feed upon itself. By such a feedback, any Arctic ozone depletion, once begun, might intensify much as the Antarctic hole has.

Over the long haul, there are additional worries. The greenhouse effect warms the lower atmosphere, but it cools the stratosphere, perhaps as much as 10°C by the middle of the next century. And Sherwood Rowland of the University of California at Irvine has pointed out that stratospheric water, a scarce component of ice clouds, could double by the middle of the next century due to the oxidation of the increasing amounts of atmospheric methane.

Polar ozone seems to have plenty of problems, but it is the 80% of stratospheric ozone that lies outside the polar regions that is the ultimate concern. News at the workshop concerning global ozone was not encouraging. Researchers have been looking for the cause of a global ozone decrease, one especially evident during the cold of winter, that exceeds any predicted by models lacking heterogeneous chemistry. The answer would not be ice clouds. Outside the polar regions, temperatures are 20° to 30°C too warm. But there are plenty of surfaces in the global stratosphere, in the form of sulfuric acid–water droplets.

Sulfuric acid aerosols had seemed harmless until the Antarctic hole prompted laboratory experimenters to reexamine them under realistic stratospheric conditions. Old, scattered measurements at higher temperatures suggested that only one nitrogen-containing molecule in a million striking a sulfuric acid droplet would "stick," that is, dissolve in it or react with it. That discouraged making any connection between aerosols and ozone loss. But the workshop attendees heard from three groups that the fraction of nitrogenous molecules sticking to sulfuric acid under stratospheric conditions is more like one in a hundred or one in ten than one in a million. And the lower the temperature, the more efficient the sticking.

"If those numbers are correct," says Susan Solomon of the National Oceanic and Atmospheric Administration in Boulder, "they will produce significant changes in midlatitude chemistry. It is fair to say that that would accelerate ozone loss; whether it would be enough to account for the observed loss is unclear." As if more bad news were needed, David Hofmann of the University of Wyoming is now saying the background levels of aerosols have been increasing during the past several decades. On the bright side, researchers might still be laboring in ignorance without the jolt that the Antarctic ozone hole gave them.

■ RICHARD A. KERR