More clues to the mysterious ozone hole

Satellite measurements indicate that ozone has once again started to disappear from the stratosphere above Antarctica, repeating a phenomenon that has intrigued and concerned scientists since it first came to light in 1985. While more than 100 researchers from around the world are currently staging two separate experiments to study this event (SN: 8/8/87, p.95), results from last year's experiments are pointing an ever-more-accusing finger at industrially produced chlorine chemicals as the cause of the ozone hole.

The newest information, reported in the Sept. 10 NATURE, comes from a group at the Jet Propulsion Laboratory (JPL) in Pasadena, Calif., which participated in the first National Ozone Expedition (NOZE I) last September and October at McMurdo Station in Antarctica. Using an interferometer, this group measured the atmospheric concentrations of certain gases thought to be critical to the stratospheric chemistry that might be at the root of the ozone disappearance.

The results from the JPL experiments confirm earlier reports that the chlorine chemistry of the Antarctic stratosphere is "perturbed" during the Antarctic spring, but the JPL report also contains measurements of some previously unstudied chemicals. According to group leader C. Bernard Farmer, the new measurements add to a growing pile of evidence that chlorine causes the depletions.

"The results don't constitute scientific proof yet, certainly not proof in any court," Farmer told Science News. "But the evidence is strongly circumstantial, and indeed what's more important is that the results are entirely consistent with the [proposed] chemical hypotheses."

The ozone hole is actually a large patch of ozone-depleted stratosphere that has appeared since the late 1970s over latitudes south of 45° during each Antarctic spring. Since they learned of its existence two years ago, atmospheric scientists have strived to identify the underlying causes and to determine if the global ozone layer is in jeopardy. They are currently debating whether the hole results from chemical reactions or a "dynamic" reorganization of winds over the Southern Hemisphere. Many scientists, although still unsure about the relative importances of chemistry and dynamics, believe both mechanisms are active.

The proposed chemical mechanisms have thus far focused on chlorine, which primarily reaches the stratosphere in chlorofluorocarbons (CFCs) — a class of chemicals used in refrigeration, aerosol sprays and foam production. When present in the stratosphere, chlorine and certain chlorine chemicals convert ozone (O_3) into molecular oxygen (O_2) .

Farmer's group measured the con-

centrations of the two "reservoir" species of chlorine: hydrochloric acid (HCl) and chlorine nitrate (CLONO₂). In the cold and darkness of the Antarctic winter, most of the chlorine readily assumes one of these two forms, both of which are innocuous and normally unreactive.

The researchers found that the chlorine level in the reservoir species was low throughout the period of greatest ozone loss in September, then returned to more normal levels in October when ozone depletion began to taper off. Where, then, was the missing chlorine during September?

One possible explanation is that some of the normally gaseous HCl and ClONO₂ had condensed onto cloud particles, called aerosols. When these reservoir chemicals are in this nongaseous form, the interferometer cannot detect them.

This scenario would seem to confirm the suspicions of scientists who believe chemistry is behind the ozone disappearance. Condensation must be occurring, they reason, because — as lab tests have shown — only in their condensed form on the surface of an aerosol do HCl and ClONO₂ react quickly enough to form ozone-destroying chemicals. According

to N. Dak Sze, who works with computer models of stratospheric chemistry at Atmospheric and Environmental Research, Inc., in Cambridge, Mass., the JPL data are "definitely indicative of the possibility" of such a scenario.

However, says Farmer, there is another explanation for the missing chlorine. Some of the chlorine could already be present in another, gaseous form, which actively destroys ozone. This explanation would match other results from NOZE I, which found abnormally high September levels of one such form, chlorine monoxide (ClO), a molecule active in ozone destruction (SN: 5/23/87, p.326).

While both explanations are possible, says Farmer, he is certain that ClO cannot account for all of the missing chlorine. "If it had all been in the form of ClO, we would definitely have seen it very clearly, and we didn't," he says. "So either it is frozen or there's some other chlorine species around."

Meanwhile, in the Antarctic this month, NOZE II scientists are again collecting ground-based measurements while others are studying the ozone hole from planes. And in Montreal this week, diplomats from more than 40 countries approved a protocol that establishes international limits on the production and consumption of CFCs. — R. Monastersky

X-ray snapshots of proteins in motion

Proteins are intimately involved in just about every biological system. Elucidating exactly how they perform their functions during chemical reactions has been a major goal for biochemists. Now a British team of scientists has demonstrated the potential of using the reflections of X-rays from a protein crystal to track the changes in the protein's form during a reaction. Their technique makes it possible to record three-dimensional motion pictures of a protein's chemical behavior and overcomes the problem of long data-collection times normally associated with Xray diffraction experiments.

"Despite its limitations," says chemist Dagmar Ringe of the Massachusetts Institute of Technology, "the technique of millisecond protein crystallography promises to extend the range of biochemical problems that can be studied by X-ray diffraction."

In a conventional X-ray diffraction experiment, an X-ray beam of a single wavelength shines on a crystal. Planes of atoms within the crystal reflect the X-ray beam and generate a pattern of spots on a nearby piece of photographic film. To ensure a complete sampling, many such exposures at different crystal angles are needed. The collection of sufficient data to deduce the crystal's atomic arrangement can take hours or

even days. As a result, the diffraction pattern represents an average atomic arrangement rather than the arrangement at a particular instant.

To avoid lengthy collection times, Janos Hajdu of Oxford University and his colleagues went back to an X-ray technique called Laué diffraction, first used 75 years ago. Instead of X-rays of a single wavelength, they used X-rays of extremely high intensity showing a broad spectrum between 0.2 and 2.1 angstroms. The wide range of X-ray wavelengths allowed the researchers to collect data quickly.

In their experiment, reported in the Sept. 10 NATURE, Hajdu and his team photographed the patterns produced by a crystal of the enzyme phosphorylase as it was bathed with maltoheptase, a molecule that binds with the protein enzyme. They were able to gather the necessary data in 3 seconds, and from the results they could detect structural changes in the protein.

The researchers conclude that there is no reason why consecutive X-ray images could not be taken at intervals of a few milliseconds. Furthermore, although the present technique depends on knowing the protein's crystal structure beforehand, a similar method can be used when the specimen's atomic structure is unknown. — I. Peterson

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