The Ozone Layer: The Threat from Aerosol Cans Is Real

Release of chlorofluorocarbons into the atmosphere represents a definite hazard to the earth's ozone layer and entails the threat of "drastic" climate changes, according to a long-awaited report from the National Research Council. Because of these potential hazards, the NRC's Committee on Impacts of Stratospheric Change recommends that, unless new findings emerge to mitigate the threat, nonessential uses of the chemicals (which are also known as Freons, CFM's, or halocarbons) should be drastically curtailed. (A second report, prepared by the NRC's Panel on Atmospheric Chemistry and released at the same time, details the current state of knowledge about the ozone threat.) In effect, the committee recommends that halocarbons not be used in aerosol cans after January 1978. More important uses of halocarbons, such as in refrigerating units, would be phased out more slowly, but only if curtailment of other sources did not provide sufficient control and only if reasonable alternatives become available.

The recommendations probably represent the best compromise possible between the strongest opponents of halocarbons, who wanted an immediate ban on their use in aerosol cans, and the halocarbon industry, which has argued that delaying a decision for 2 years would allow time for a more accurate assessment of the potential danger. The report has been criticized by environmentalists for being too gentle with the industry, but the panel concluded, according to chairman John W. Tukey of Princeton University, that a much firmer estimate of the hazard could be obtained within a year or two. That extra time would allow industry time to minimize the impact of a ban on aerosols, but it would also allow Congress time to enact more thoughtful legislation. Furthermore, the committee concluded that even a 2-year delay in implementing the restrictions would increase the ultimate reduction in ozone by no more than 0.5 percent, and probably by much less. In a sense, then, the industry won the battle, but lost the war.

The report comes just 2 years after the initial prediction by F. Sherwood Rowland and Mario J. Molina of the University of California at Irvine that halocarbons could harm the ozone layer. These investigators postulated, in simplest terms, that the halocarbons would slowly migrate to the stratosphere where they would be photolyzed by ultraviolet light from the sun to liberate free chlorine atoms. These atoms would upset the normal balance between the formation and destruction of ozone—which shields the earth's surface from damaging ultraviolet radiation—and lead to a reduction in the concentration of ozone there.

Perhaps the most surprising aspect of the report is that, despite 2 years of intensive research in many laboratories, it pretty much confirms Rowland and Molina's original estimate about the extent of ozone destruction. The panel concludes that continued release of halocarbons at a rate corresponding to use in 1973 will eventually produce somewhere between a 2 and a 20 percent reduction in stratospheric ozone, with the most likely figure being 7 percent.

Such a reduction would, the committee says, produce a substantial increase in the amount of damaging ultraviolet light that reaches the surface of the earth. This would lead, in turn, to a larger increase in all forms of skin cancer, including life-threatening malignant melanoma. The increase in ultraviolet radiation would undoubtedly also have deleterious effects on plants and animals, although what these effects might be is not known.

The committee also concluded that halocarbons present a threat to the climate. This possibility was first suggested by Veerauhadran Ramanathan of the National Aeronautics and Space Administration's Langley Research Center. Halocarbons absorb infrared radiation in the wavelength region 8 to 13 micrometers, a region in which the atmosphere is relatively transparent. Ramanathan predicts that halocarbons anywhere in the atmosphere will absorb infrared radiation emitted from the earth and prevent it from radiating into space, thereby warming the atmosphere. This so-called greenhouse effect also occurs with carbon dioxide at different wavelengths.

It is quite difficult to assess the magnitude of the potential temperature increase because very little is known about the variables that affect climate. A simplified calculation cited by the committee, however, suggests that continued release of halocarbons at the 1973 rate might produce a global temperature increase of about 0.5°C in 50 years, or about half the effect predicted for carbon dioxide during the same period. Were the release of halocarbons to continue to increase at the same rate as in the past, the calculated effect on global temperature would be as large as that from carbon dioxide by the year 2000 and larger thereafter. These calculations are crude, but the important point, the committee emphasizes, is that the effects from halocarbons are additive to the effects from carbon dioxide and both should produce a temperature increase. Most climatologists agree that a global temperature increase of even 1°C would have a major effect on climate.

The effects of halocarbons on stratospheric ozone are better documented. When Rowland and Molina first predicted that there would be an effect, their theories were based almost entirely on laboratory experiments which indicated that halocarbons could be photolyzed and that many of the proposed reactions do occur in the laboratory. There was almost no evidence to prove that the process could actually occur in the stratosphere. Today, much of that evidence exists and more is being provided almost monthly from studies in many laboratories.

Among other things, these studies have provided fairly accurate rate constants for some 12 of the 19 most important reactions involved in the stratospheric chemistry. Most of the rate constants have been found to be very similar to those employed by Rowland and Molina in their original calculations. The largest uncertainty in calculating ozone depletions now, the panel says, are uncertainties in the rates of the seven remaining reactions. It is these values, among other things, that the committee hopes to obtain within the next year.

Perhaps the most important studies have been measurements of the actual concentrations of the various reactants in the atmosphere. These measurements are very difficult to make, both because the measurements must be made so far from the earth's surface and because the quantities are so small. The first problem is being solved with rocket soundings, balloon launchings, and remote sensing, but the second problem promises to remain particularly vexing. As an example of the difficulty involved, the report cites a recent effort at standardization in which identical samples of halocarbons were sent to various laboratories measuring atmospheric halocarbons.

The concentrations obtained in the laboratories varied from the actual concentrations by ± 30 percent for trichlorofluoromethane and dichlorodifluoromethane ($CFCl_3$ and CF_2Cl_2, the halocarbons implicated in ozone damage), ± 50 percent for methylene chloride, and over a fourfold range for carbon tetrachloride. With this kind of discrepancy in measurements, it is not surprising that the total amount of the two important halocarbons in the atmosphere is known only to within ± 40 percent.

Yet determination of the amounts of these compounds in the atmosphere is quite important, the panel argues, for only by comparing these amounts with the actual amounts released into the atmosphere will it be possible to tell if there are other destructive mechanisms for halocarbons. Halocarbon damage to the ozone layer is predicated on the premise that there are no important tropospheric sinks for the chemicals, so that all of them eventually reach the stratosphere. Any sink in the troposphere would reduce the amount of halocarbon that could interact with ozone, and thus would reduce the potential for damage.

The panel investigated many proposed mechanisms for destruction of halocarbons or their removal from the troposphere. They concluded that the only significant possibility for which there is supportive evidence might be an unidentified destructive mechanism in the ocean. Measurements of the halocarbons' solubility and their concentrations in oceanic surface waters indicate that the maximum possible effect from this mechanism would be a 20 percent reduction in the effect on ozone; this could lower the most probable ultimate ozone loss from 7.5 percent with no ocean effect to 6 percent. The panel settled on a compromise figure of 7 percent. Some scientists, such as J. Peter Jesson of the Du Pont Company, think that there are other destructive mechanisms in the troposphere that would reduce the effects on ozone, but these mechanisms have not been identified.

Uncertainties in the measurements have created other problems during the past year. This spring, for example, Allan L. Lazrus of the National Center for Atmospheric Research announced results from a balloon launch in which he found that there was substantially less hydrogen chloride in the stratosphere than had been predicted from the halocarbon theory. This suggested that the chemicals were not being photolyzed in the stratosphere to release free chlorine, and many scientists argued that the danger to the ozone layer had been grossly overestimated. This event contributed to the postponement of the NRC report, which had originally been scheduled for release in the spring. In June, however, Lazrus sent a letter to his fellow scientists stating that a mistake in calibration had occurred in the experiment and that the amount of hydrogen chloride in the stratosphere is, in fact, very close to the amount predicted by theory.

A similar misunderstanding nearly arose about chlorine oxide (ClO) recently, but many investigators seemed to have learned a lesson from their experience with hydrogen chloride and have avoided making a fuss about preliminary results. Chlorine oxide is a major intermediate in the reaction pathway through which chlorine is thought to destroy ozone. A demonstration that it is present in the stratosphere at predicted concentrations would provide definitive validation of the halocarbon theory.

Three different investigators, Robert W. Carlson of the Jet Propulsion Laboratory, Phillip A. Ekstrom of the Battelle Pacific Northwest Laboratory, and James C. Anderson of the University of Michigan, have attempted to measure the concentration of chlorine oxide. Carlson and Ekstrom used remote sensing techniques, while Anderson used a balloon-borne instrument package. Preliminary results from all three experiments suggested that the concentration of chlorine oxide was much higher than predicted, perhaps as much as 100 times higher. This would suggest that there is a large natural source of chlorine in the stratosphere, so that any effect from halocarbons would be small in comparison. Because of the importance of this measurement, all three investigators are now refining their techniques. Anderson, in particular, has recalibrated his instruments and performed another in situ measurement. His new results indicate that the actual concentration of chlorine oxide is no more than twice the amount predicted by theory. Fortunately, another false alarm has thus been avoided.

Another substance for which better measurements are required is chlorine nitrate ($ClONO_2$). At the beginning of this year, Rowland and Molina proposed that chlorine nitrate might be formed in the stratosphere from chlorine oxide and nitrogen dioxide. This reaction is potentially very important because both reactants are involved in the chain reactions that destroy ozone, and formation of

The Panel's Recommendations

The Committee on Impacts of Stratospheric Change actually made several recommendations. Among them:

▶ Regulation of halocarbons should be selective to produce the greatest immediate reduction in release. In simplest terms, this means that their use in aerosols could be banned by 1978, use in automotive air conditioners and industrial refrigerating units might be restricted several years later, and use in home refrigerators might never be restricted.

▶ In the meantime, all products that contain trichlorofluoromethane and dichlorodifluoromethane which could be released into the atmosphere should be so labeled. This would include aerosols and refill units for auto air conditioners.

▶ The United States should make every appropriate effort to encourage other countries to adopt similar restrictions. This country now accounts for only about half of the halocarbons released into the atmosphere.

▶ Restrictions on halocarbon use should be reviewed every 3 to 5 years, as the amount of knowledge about the climate increases, to determine if such restrictions are appropriate.

▶ A better knowledge of atmospheric chemistry and better measurements of atmospheric species should be obtained. There should also be developed better techniques for modeling both atmospheric and climatic change. Since so little is known in these areas, this should be an adequately financed long-term program.

▶ Better information should be obtained about the effects of ultraviolet radiation on humans, and particularly about its effects on plants and animals.

▶ Research should be undertaken to identify population groups with a drastically higher than normal susceptibility to malignant melanoma.

▶ More information should be obtained about preventive medicine procedures needed to protect humans against ultraviolet-induced skin cancers.

—T.H.M.

chlorine nitrate would temporarily remove them from the reaction chains. When Lazrus announced his mistaken results for hydrogen chloride, it was widely assumed that the missing chlorine had been incorporated into chlorine nitrate.

A closer investigation of the reaction rates involved indicates that chlorine nitrate is not as important a sink as halocarbon proponents had hoped, but the extent of its contribution to stratospheric chemistry is still in dispute. Rowland and Molina estimate that the formation of chlorine nitrate would reduce their original projections by about 30 percent. The NRC committee concluded that chlorine nitrate would reduce ozone damage by a factor of 1.85, and the figure of 7 percent reflects this reduction.

Unfortunately, the predicted concentration of chlorine nitrate in the stratosphere is lower than the sensitivity of measurements made so far. About all that can be said so far is that there is not much more there than is predicted by theory. But these measurements are interpreted by some investigators, such as Phillip Hanst of the Environmental Protection Agency, as indicating that chlorine nitrate is not important in stratospheric chemistry. In the unlikely event that this view should prove correct, the most probable reduction in ozone could be as high as 14 percent.

Because of all these uncertainties, it seems likely that the extent of the potential danger to the ozone layer will be the subject of dispute for many years. But there now seems little question that the theory is valid and that the danger exists, and it appears equally clear that the danger can be reduced only by eliminating unnecessary use of halocarbons.

—THOMAS H. MAUGH II

Coal Research (IV): Direct Combustion Lags Its Potential

Burning coal directly to generate electricity accounts for most of the energy now derived from this material—but contributes less than 15 percent of the U.S. energy supply. It is a use that could in theory be rapidly expanded to replace declining domestic supplies of oil and gas. In practice, means of burning coal cleanly are either not yet available or troublesome enough that environmental standards for sulfur dioxide emissions pose a considerable barrier to more widespread use. Two principal technologies are being developed to overcome this barrier: stack gas scrubbing, a technique for removing pollutants after combustion in conventional boilers, and fluidized bed combustion, a new and potentially cleaner method of burning coal and other fuels. In the past few years there has been considerable progress with both technologies in this country and elsewhere. Nonetheless, the U.S. R & D program on direct coal combustion is hindered by being split between two agencies with differing missions, by the resistance of the electric utility industry to coal clean-up efforts, and by what many observers believe to be unresolved technical problems in the experimental and demonstration equipment now being built. Overall, the impression is of a program given inadequate priority and of technologies lagging behind their potential to make a very substantial contribution to clean energy supplies far sooner than coal-based synthetic fuels.

The Environmental Protection Agency (EPA), for example, has been the principal supporter of research on stack gas scrubbers. Indeed, the Energy Research and Development Administration (ERDA) has been constrained, under the terms of an informal agreement extracted by Senator Edmund Muskie (D–Maine), from engaging in scrubber R & D. But the EPA is primarily a regulatory agency and its approach to scrubber development has been halfhearted. Having carried the work far enough to set sulfur dioxide emission standards and to establish to its own satisfaction that several different scrubber techniques are workable, the agency is phasing out its R & D support of this technology (the current budget is about $5 million). EPA spokesmen ascribe numerous failures in demonstration projects to lack of effort on the part of utility companies in making the equipment work, and the agency position is that further development of the technology is up to industry.

It is no secret that the power industry has, to varying degrees, been reluctant to adopt scrubbers. The equipment is expensive—$75 to $125 per kilowatt, a substantial fraction of the cost of the power station itself—and increases costs but not profits. Scrubbers also consume as much as 5 percent of the power output of a generating plant and introduce a whole new order of complexity, that of chemical processing, into its operation. Most of the scrubbers now planned or in operation on coal-fired boilers in the United States utilize an aqueous slurry of lime, $Ca(OH)_2$, or limestone, $CaCO_3$, as the scrubbing agent. Both are throwaway processes that consume hundreds of thousands of tons of the scrubbing reagent per power plant per year and produce even larger quantities of a wet sludge, principally calcium sulfate, which must be disposed of. Also under development are several processes in which the scrubbing agent can be regenerated and the sulfur recovered in the form of a useful by-product. The principal contenders here seem to be the Wellman-Lord, magnesium oxide, aqueous carbonate, and citrate processes.

From the utility point of view, claims that scrubbing technology has been commercially demonstrated and its problems solved are greatly exaggerated. Part of the problem is the great variability of impurities in coal and water and of operating constraints across the United States. Most successful experience so far has been with low-sulfur coals found in the western United States. No commercial equipment has yet proved able to cope with typical high-sulfur, high-chlorine coal in the eastern United States without discharging large volumes of polluted waste water. Moreover, the first trouble-free commercial unit is not yet on line, according to Gerald Hollinden, head of scrubber R & D for the Tennessee Valley Authority (TVA), a utility that has co-operated with EPA in developing scrubber technology. Designs for scrubbing equipment are still in flux, and Kurt Yeager of the Electric Power Research Institute (EPRI) says that any given unit must still be considered a prototype.

The problems encountered with lime and limestone scrubbers illustrate the complexity of the stack gas cleaning process. Combustion gases from a boiler are piped to a reactor vessel where most of the sulfur dioxide is removed. In one configuration, for example, lime or limestone slurry is sprayed from the top of the vessel while the gases enter from the bottom, to afford maximum opportunity for the absorbent liquid to react with the SO_2. The liquid is drained off to a holding tank, where more lime or limestone is added to precipitate the sludge. If the operating conditions are not held within narrow bounds, however, solids are are deposited within the scrubber vessel, eventually plugging it.

From the scrubbing vessel, the stack gas is passed through equipment known as mist eliminators, where moisture and