Stratospheric Pollution: Multiple Threats to Earth's Ozone

Supersonic transports, aerosol sprays, and nuclear weapons are all examples of technological ability carried to excess, but they would not normally be considered in the same context. It now appears, however, that they do have something in common—they are all potential sources of catalytic agents that penetrate the earth's stratosphere and decompose the ozone that shields living things from the worst of the sun's ultraviolet radiation. The full extent of the environmental hazard associated with this phenomenon is still uncertain, despite several years of investigation. But it is increasingly clear that a wide range of human activities have the capability of disrupting the delicate photochemical balance on which the earth's ozone buffer, and perhaps life itself, depends.

The catalytic agents in question are oxides of nitrogen, released into the upper atmosphere by the jet engines of supersonic transports (SST's) and by nuclear explosions, and free chlorine, derived photolytically from chlorofluoromethanes such as those used as propellants in aerosol cans. Relatively small amounts of these agents are sufficient to destroy large quantities of ozone, itself an extremely unstable molecule (see box, page 336). The potential danger from SST's has been debated for at least 3 years now, but the even greater threat from nuclear war and the chlorofluoromethanes has only recently been recognized and is still largely unquantified. The most alarming of these threats is probably that from the chlorofluoromethanes because it now appears that civilization may already have produced enough of these halomethanes to cause an eventual reduction in the concentration of ozones in the stratosphere. This reduction, in turn, may well be sufficient to produce many unpleasant biological effects (see box, page 337).

The two most common halomethanes are $CFCl_3$ and CF_2Cl_2. The former is used primarily as a propellant in aerosol spray cans, the latter as a refrigerant. They are highly volatile and essentially inert to chemical reaction, properties that explain the near-exponential growth in their production during the last 10 years. Nearly 10^9 kilograms of the two halomethanes will be produced in the world this year, and about 5×10^9 kilograms have already been produced—most of which has already been released into the atmosphere.

The halomethanes are apparently ubiquitously distributed. John M. Swinnerton and Peter E. Wilkniss of the Naval Research Laboratory in Washington, D.C., for example, have found an average atmospheric concentration of the two halocarbons of 61 parts per trillion (ppt) at various points on a path from Los Angeles to the Antarctic. They have also measured an average concentration of 81 ppt at sites in the East Pacific Ocean and 120 ppt in the Arctic air near Spitsbergen, off Norway. Their results are consistent with those of James Lovelock of the University of Reading in England, who has found an average concentration of 52 ppt in the South Atlantic Ocean and 85 ppt in the North Atlantic.

High Concentrations above Cities

The concentrations appear to be even higher in populated areas. Swinnerton and Wilkniss have found average concentrations of about 160 ppt in the metropolitan Washington, D.C., area, but they observed concentrations as high as 700 ppt during a period of stagnant air last July. C. B. Farmer of the Jet Propulsion Laboratory in Pasadena has found concentrations of 650 ppt during similar conditions in the Los Angeles basin. Many scientists now think the observed concentrations indicate that nearly all the halomethanes which have been produced are still resident in the atmosphere.

The halomethanes have generally been assumed to be harmless. They do not react with other components of the atmosphere, even photochemical oxidants; they are relatively insoluble in water and apparently do not react with any chemicals in the ocean; and there are no known mechanisms for biological degradation involving them. Some atmospheric scientists have suggested, in fact, that their inertness would make them ideal tags for tracing the motion of large air masses.

But earlier this year, F. S. Rowland and Mario J. Molino of the University of California at Irvine reported that the halomethanes can be photolytically dissociated at wavelengths (190 to 210 nanometers) present only in the stratosphere. The products of this dissociation are the CX_3 radical (where X is either chlorine or fluorine) and free chlorine atoms.

Late last year, ironically, three different groups—Ralph J. Cicerone and Richard S. Stolarski at the University of Michigan, Ann Arbor; Steven C. Wofsy and Michael B. McElroy at Harvard University, Cambridge; and Paul Crutzen at the National Center for Atmospheric Research, Boulder—had investigated the potential role of free chlorine in the stratosphere. They independently concluded that small amounts of chlorine could catalyze the destruction of large amounts of ozone, but also that their findings were not important because there are no major sources of chlorine in the stratosphere. The results of Rowland and Molino indicate that there is such a source and that the threat to ozone is real.

There are few measurements of the concentrations of various species in the stratosphere, although Lovelock found halocarbon concentrations of 70 ppt at 32,000 feet (9.6 kilometers) over England, and it is not clear how much halomethane is already there. Most scientists, however, think that only a relatively small amount is in the stratosphere because of the long time—on the order of a few years—required for diffusion of halomethanes to the altitude of peak photolytic efficiency, about 25 to 35 kilometers. This amount is sufficient, perhaps, to produce a 1 percent reduction in ozone—a totally undetectable change. The major question, then, is what will happen when all of the halomethanes in the atmosphere attain equilibrium between the troposphere and the stratosphere, and what will happen if more are produced. The various groups have all calculated the possible effects on the ozone layer and their results are anything but reassuring.

The predictions of Wofsy and McElroy are, perhaps, typical. They find that even if the manufacture of halomethanes were to be halted immediately, the depletion of the ozone layer would reach 5 percent by 1990. If production were to continue with an annual increase of 10 percent, the ozone layer would show a 14 to 15 percent depletion by the year 2000. And if production were to continue to increase at the current annual rate of about 21 percent, the ozone layer would be depleted 7 percent by 1984 and 30 percent by 1994. Crutzen's calculations suggest less depletion of ozone but a greater shift in concentrations within the stratosphere. He predicts less biological effects and more climatic effects.

The Chemistry of the Stratosphere

The stratosphere is that portion of the earth's atmosphere, extending from an altitude of about 15 to 50 kilometers, in which temperature increases with increasing height. It accounts for about 12 percent of the mass of the atmosphere.

Ozone, O_3, is a natural trace ingredient of the atmosphere that occurs at an average concentration of about 3 parts per million. It is formed by photolysis of oxygen at wavelengths shorter than 242 nanometers, followed by reaction of free oxygen with oxygen molecules on the surface of particulates. The primary mechanisms for its natural destruction and their relative contributions, according to Harold Johnston of the University of California at Berkeley, are combination of free oxygen and ozone to form two oxygen molecules, 18 percent; interaction with hydroxide radical, 11 percent; destruction by naturally occurring nitric oxide, 50 to 70 percent; and unknown mechanisms, 0 to 20 percent.

Nitric oxide, NO, is formed in the stratosphere by the interaction of nitrous oxide (N_2O, which is formed by bacteria in the soil, is inert in the troposphere, and slowly diffuses into the stratosphere) with singlet oxygen. Smaller amounts are also produced by the interaction of cosmic rays with atmospheric gases; it is this phenomenon that explains the correlation between fluctuations in ozone concentration and the sunspot cycle, which controls the flux of cosmic rays to the earth. Nitric oxide diffuses slowly to the lower stratosphere, where it combines with other atmospheric components to form nitric acid, which is washed out of the atmosphere by rain.

While it is in the stratosphere, however, nitric oxide can destroy ozone through a catalytic cycle identified by Paul Crutzen, now at the National Center for Atmospheric Research, Boulder:

$$\begin{gathered} NO + O_3 \rightarrow NO_2 + O_2 \\ O_3 + h\nu \rightarrow O_2 + O \\ NO_2 + O \rightarrow NO + O_2 \end{gathered}$$

The net result is

$$2\,O_3 + h\nu \rightarrow 3\,O_2$$

The formation and destruction of ozone by these mechanisms are normally in equilibrium so that the concentration of ozone remains constant. The concern of many scientists is that injection of additional nitrogen oxides will upset the equilibrium.

A similar catalytic cycle involving free chlorine atoms was first described last year by Ralph J. Cicerone and Richard S. Stolarski of the University of Michigan, Ann Arbor:

$$\begin{gathered} Cl + O_3 \rightarrow ClO + O_2 \\ O_3 + h\nu \rightarrow O_2 + O \\ ClO + O \rightarrow Cl + O_2 \end{gathered}$$

This cycle produces the same net result as the nitric oxide cycle, but it is six times more efficient catalytically. Fluorine atoms can undergo the same reactions, but they are ineffective catalysts because the chain reaction terminates rapidly.

The two cycles can also interact in the following fashion:

$$\begin{gathered} ClO + NO \rightarrow Cl + NO_2 \\ NO_2 + O \rightarrow NO + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \end{gathered}$$

The net result is

$$O + O_3 \rightarrow 2\,O_2$$

The chain terminates only when hydrogen chloride, formed by abstraction of a hydrogen atom from hydrocarbons, diffuses to the lower atmosphere and is washed out by rain.—T.H.M. and A.L.H.

There are many uncertainties in these calculations. The most important is that they are all based on laboratory reactions whose occurrence in the atmosphere has never been confirmed. They are also based on one-dimensional models that only approximate conditions in the atmosphere. There are uncertainties in the initial concentrations of the reactants, the rates at which they are transported through the atmosphere, and their lifetimes in the upper atmosphere.

There may, moreover, be other reactive components of the stratosphere and other reactions—especially those occurring on the surface of particulates—of which we are unaware. And, finally, natural variations in the ozone concentration make it unlikely that we would detect any predicted depletion resulting from halomethanes until that depletion was of the order of 5 to 10 percent.

Even more uncertain are the effects of many nuclear bomb explosions on the stratosphere and the ozone layer. Nuclear war is to many persons an unthinkable, total event beside which the loss of ozone seems at first glance relatively trivial. That may or may not be true (and certainly the proliferation of these weapons raises the likelihood of regional or tactical use), but there now appear to be additional reasons to regard even limited nuclear war as a potentially global catastrophe.

Thermonuclear explosions heat the surrounding air to very high temperatures, dissociating oxygen and nitrogen and producing large quantities of nitrogen oxides (NO_x). Rapid cooling of the cloud as the fireball fades stabilizes the NO_x. Depending on the latitude and season, clouds from explosions in the range of hundreds of kilotons to megatons (TNT equivalent) will deposit most of their NO_x in the lower and middle stratosphere, where the ozone concentration is highest. What happens then is the subject of considerable speculation, but there is little doubt that the NO_x will catalyze the destruction of substantial amounts of ozone before it is itself destroyed or removed from the stratosphere. At issue are how much ozone depletion and whether other mechanisms—such as the production of additional NO_x by radiation from fission products trapped in the stratosphere—will enhance the effect.

The only source of what amounts to experimental data is the history of atmospheric testing of nuclear weapons—especially the period of heavy testing by the United States and the Soviet Union during 1961 and 1962, just before the ban on atmospheric tests went into effect. In the years that followed there were extensive measurements of the radioactive isotope carbon-14 in the atmosphere. Since nuclear bombs produce NO_x in proportion to carbon-14, the measurements give indirect evidence of the NO_x from the bomb clouds and hence a means of calculating what ozone depletion the bombs should have caused. Harold Johnston of the University of California at Berkeley, who along with Crutzen first pointed out the potential effects of nitrogen oxides on the ozone layer, estimated a 3 to 6 percent reduction of ozone in the Northern Hemisphere from the test series. On the basis of a different, time-dependent model of the stratosphere, J. S. Chang of the Atomic Energy Commission's Lawrence Livermore Laboratory found that the maximum ozone reduction was 4 percent and that it probably took 2.5 years for the ozone regenerating mechanisms to restore half of the loss.

The observed fluctuations of ozone tend to support the model calculations, but not unambiguously. The amount of ozone present in the stratosphere varies considerably (by as much as 30 percent from day to day and by as much as 10 percent over periods of years) in a way that is strongly coupled with the 11-year sunspot cycle. Ozone concentrations peaked in 1941 and again in 1952, but failed to do so as expected in 1963, after the extensive testing. Thereafter ozone levels rose gradually throughout most of the 1960's. H. M. Foley and Malvin A. Ruderman of Columbia University analyzed the data and found no effect of the weapons tests because, many investigators now believe, they did not take into account the time-dependent nature of the phenomenon. Johnston reanalyzed the data with more elaborate statistical techniques and did find a small but significant effect. He believes that ozone depletion due to the weapons testing accounts for the missing solar-cycle peak in the ozone data and that the increase during the 1960's represents the combined effects of recovery from

The Effects of Ozone Depletion

The diffuse layer of ozone that envelops the earth screens out more than 99 percent of solar radiation at wavelengths shorter than 320 nanometers. High intensities of this ultraviolet radiation are harmful to nearly all forms of life, and most scientists agree that surface life on the earth did not evolve until after the ozone layer was formed. But the effects of small increases in the intensity of ultraviolet radiation is still the subject of much research and debate.

The relation between ozone depletion and increases in ultraviolet radiation varies with latitude, time of year, and certain other factors. On the average, though, the percentage increase in radiation may be taken to be about twice the decrease in ozone concentration; that is, a 5 percent decrease in ozone would produce a 10 percent increase in radiation. This increase could produce many effects.

The most alarming effect might be an increase in the incidence of skin cancer. A 1973 report from the National Academy of Sciences suggested that a 5 percent depletion of ozone might produce an additional 8000 cases per year among the white population in the United States. This is probably very conservative.

A more recent estimate by Frederick Urbach of the Temple University School of Medicine, Philadelphia, is that the percentage increase in the incidence of skin cancers would parallel the increase in the intensity of radiation. But converting this estimate into numbers is difficult because estimates of the annual number of skin cancer victims in the United States vary from 200,000 to 600,000. A 5 percent ozone depletion (10 percent increase in radiation) might thus cause anywhere from 20,000 to 60,000 additional cases per year in the United States alone. Fortunately, 90 to 95 percent of such cancers are curable.

The effects of increased radiation on vegetation are less clear. Most scientists, says Martyn M. Caldwell of Utah State University, Logan, agree that there is not enough information available to predict the effects on major food crops. Some plants, such as tomatoes, lettuce, peas, and millet, appear to have their growth retarded when they are exposed to increased ultraviolet radiation, but in most cases the effects are more subtle. An increased incidence of mutation has been observed in certain experimental strains, says Caldwell, but the effects from prolonged exposure are very difficult to assess. There are also some indications that increased radiation will interfere with the growth of plankton in the ocean.

Ozone depletion might also produce climatological effects, but these are the most difficult of all to assess. Many scientists feel that there will be no important effects since the troposphere is the primary regulator of climate and there are few inputs from the stratosphere to the troposphere. Others, such as Robert Dickinson of the National Center for Atmospheric Research, Boulder, suggest that there could be several effects. An increase in ultraviolet radiation might, for example, lead to an increased melting of polar ice. Alternatively, a redistribution of ozone in the atmosphere might lead to a reduction in average global temperature. A sustained 1°C drop, Dickinson says, might be sufficient to initiate a new ice age.

Other potential effects in man that have been cited include an increased incidence of sunburns, an increased incidence of premature aging of the skin in white populations, and an increased incidence of allergic reactions resulting from the effects of ultraviolet light on chemicals in contact with the skin. Increased intensities of ultraviolet radiation might also disrupt many activities in certain insect species that are able to perceive it visually.

Clearly, most of the potential effects from disturbance of the ozone layer are highly speculative and much more needs to be known. Some of the research is currently being conducted, but it will be a long time before we will know with any assurance the effects of our interference with the atmosphere.—T.H.M. and A.L.H.

the weapons tests and restoration of the normal 11-year cycle.

The controversial evidence is thus that the 1961–1962 bomb tests resulted in a moderate, transient reduction of ozone, enough to suggest that nuclear war would cause vastly greater reductions. Virtually the only study of what the total effect would be is a research effort headed by Michael MacCracken and Chang at Livermore. In accord with the AEC's penchant for secrecy, the study was originally classified (the classification guidelines have since been changed, however), although the modeling techniques and the mechanisms being investigated are not. One difficulty is that atmospheric models developed to describe the small perturbations of the ozone layer which a fleet of SST's might cause are not adequate to describe the more extensive, time-dependent changes associated with nuclear war. Nuclear explosions in the stratosphere, for example, destroy some ozone in the immediate vicinity of the bomb, but the more important ozone reduction is delayed, according to MacCracken, with the maximum effect coming some months after the explosion. By that time the spread of NO_x through the atmosphere ensures that the impact will be hemispheric, and ultimately global.

High Altitude Explosions

Another cause for concern is the possibility of disproportionate effects from very high altitude bomb explosions (above 50 kilometers) that might continuously inject NO_x produced by fission products over periods of 10 years or more. MacCracken does not think this possibility is very likely because the atmosphere at these levels is thought to be in such strong photochemical equilibrium that excess NO_x would be rapidly destroyed by solar radiation. But the mechanism has not yet been adequately studied. And there is always the possibility that the amount of stratospheric debris a nuclear war would leave behind could, as one weapons scientist put it, "do some things we don't even know about."

The Livermore scientists believe that the problem is a serious one and deserving of further study, although they decline to give specific estimates of ozone depletion until their report, now under review within the AEC, is released. The report is unlikely to settle all the uncertainties, however, because its authors describe their results as preliminary, and many academic scientists are skeptical that present techniques are adequate to the task of modeling drastic shifts in the stratosphere.

One effect of the uncertainty is to give all nations, even the most remote, a greater stake in the prevention of nuclear war. According to Jim Hartzler of the Arms Control and Disarmament Agency in Washington, D.C., noncombatant peoples in a nuclear war might well suffer more from increased ultraviolet radiation as a result of ozone depletion than from direct radioactive fallout. Thus the bomb may well have more of the character of a doomsday device than had previously been supposed, although the effects of the higher ultraviolet radiation are still uncertain.

The origin of the concern over chlorofluoromethanes and nuclear explosions—and the source of much of the modeling information about the stratosphere used to make assessments of these hazards—was the debate over NO_x emissions from SST's. That debate spawned the Climatic Impact Assessment Program (CIAP) of the Department of Transportation, in what has turned out to be an unusual example of an agency supporting research that has tended to severely restrict one of its own long-cherished projects. At least nine different investigators or groups have now modeled the ozone changes due to SST's, and their results are in reasonably good agreement. A 50 percent increase in NO_x, the consensus seems to indicate, would decrease ozone levels by between 7 and 12 percent.

Most of these numerical models assume that latitudinal and longitudinal variations of ozone and other stratospheric species can be neglected, and they describe the vertical distribution of these quantities and some of their chemical interactions. Even in the vertical dimension a number of simplifying assumptions are made—in particular, the vertical transport of trace constituents by small-scale turbulent motions (inherently a three-dimensional process) is approximated with formulas analogous to those that describe diffusion. If these approximations are incorrect, the calculated ozone effect could be either larger or smaller than the models indicate. A comparison of results obtained with one-dimensional models to those obtained with the huge, three-dimensional general circulation models used for weather forecasting indicates, according to J. D. Mahlman of the Geophysical Fluid Dynamics Laboratory (Department of Commerce) in Princeton, that the diffusion approximations are only good within a factor of 2 or 3.

The models used to predict ozone depletion also constrain many of the chemical variables. The distribution of NO_x, for example, is often specified by the investigator rather than calculated by the model, and observations of this species in the stratosphere are scattered and possibly unreliable. Consequently, Mahlman believes, the degree of uncertainty associated with these model calculations is much larger than might appear from the generally similar results, although he does not doubt that ozone depletion would occur.

A Better Model

A recent three-dimensional model of the atmosphere constructed at the Massachusetts Institute of Technology by Fred Alyea, Derek Cunnold, and Ronald Prinn represents some progress toward overcoming these limitations. They find that NO_x released from a fleet of 500 SST's in the Northern Hemisphere not only would cause a 16 percent reduction in ozone in the Northern Hemisphere, but also would cause an 8 percent reduction in the Southern Hemisphere. They calculate an ultraviolet flux reaching the ground in the United States during the summer that would be roughly equivalent to the normal flux 15 degrees of latitude to the south, which would give New York State the sunburn potential of the Caribbean.

Despite the uncertainties, the Department of Transportation has taken the preliminary model results seriously enough to plan for strict limitations on flight paths and schedules and to encourage research on engine modifications that might cut down on NO_x emissions. Ironically, however, the CIAP itself faces a reduction in funds just as the full extent of the threats to stratospheric ozone are becoming apparent. In addition to SST's, bombs, and chlorofluoromethanes, for example, the space shuttle will inject small but nonnegligible amounts of chlorine into the stratosphere from the ammonium perchlorate used as an oxidizing agent in its rocket engines. It seems obvious that a search for additional stratospheric pollutants ought to be continued. The discovery of these previously unsuspected sources of catalytic agents in 3 years of research does indeed lead one to ask, as McElroy puts it, "What the hell else has slipped by?"

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