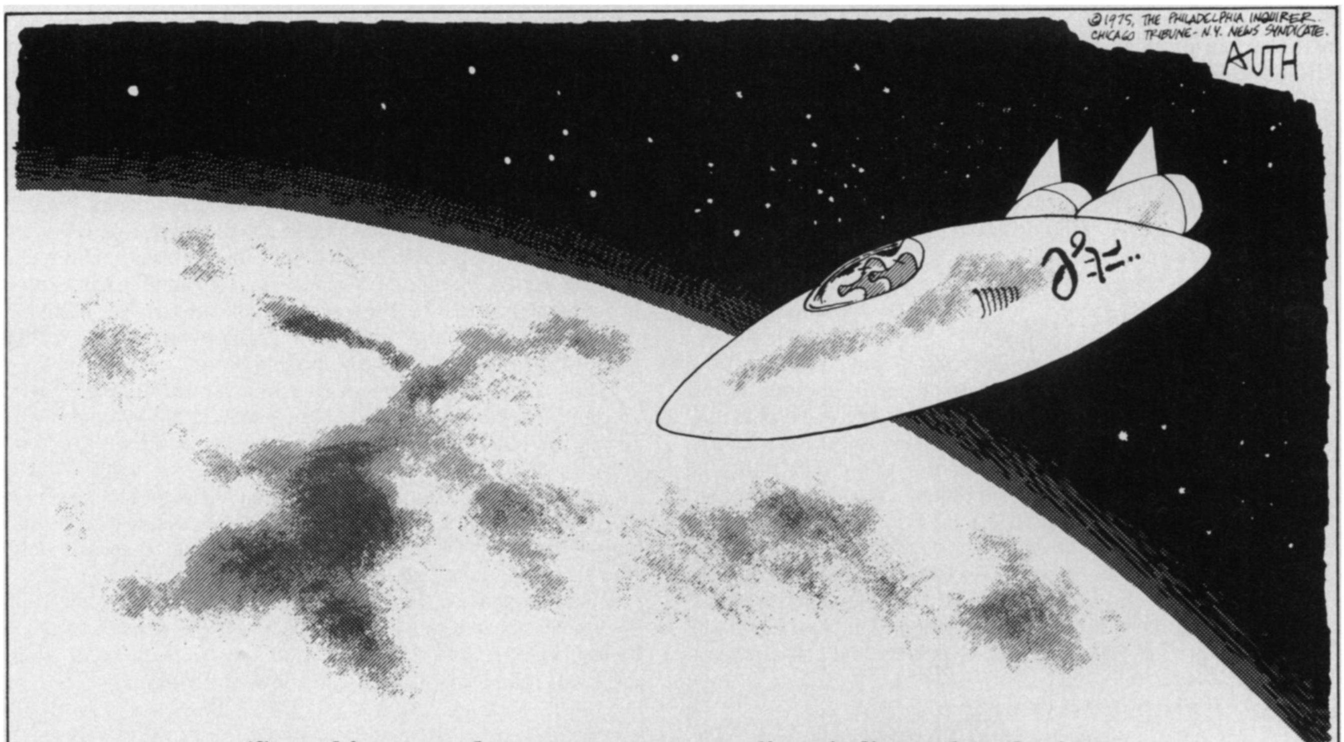
Ozone Verdict: On Faith or Fact?



'Something must be wrong . . . my readings indicate that they've decided to destroy their ozone shield with deodorant sprays . . .'

When, if ever, is there enough data to confirm an unpopular scientific theory? Fluorocarbons stand accused; when can an indictment be handed down?

BY JANET H. WEINBERG

Some have called it a scientific controversy: Are fluorocarbon aerosol propellants and refrigerants destroying the ozone layer or are they not? According to one highly respected atmospheric researcher, there is no scientific controversy.

University of California at Berkeley chemist Harold S. Johnston, the earliest theorist of ozone destruction stemming from man's activities, believes the controversy is really a philosophical one: When, if ever, is there enough data to confirm an unpopular scientific theory, one that could put a halt to a major industry and change the habits of millions of consumers? Fluorocarbons stand accused. But how much does the scientific community need to know before an indictment can be handed down?

Many prominent researchers vote for indictment now. Many others, including industry scientists, want to see the results of several more years of study before drawing any conclusions. Herein, Johnston says, lies the controversy.

Aerosol propellants and refrigerants are no small target for an accusing scientific theory. Almost every home has refrigeration and air conditioning equipment, and just about every consumer product that is sprayable is aerosol-packaged. A million Americans work in fluorocarbon-related industries, DuPont's research director, Ray McCarthy, estimates, and the annual contribution to the gross national product from the production and sales of these products is nearly $8 billion. But, many are saying now, whether fluorocarbons are big business or not, if the theories of ozone depletion are correct, the irony would be too great to continue—the irony of endangering human health and world climates through the use of a convenience packaging system or the current refrigeration technology.

At a recent all-day symposium on the fluorocarbon-ozone problem at the American Chemical Society meeting in Philadelphia, the main researchers met to compare evidence and postulates. Several who now stand ready to indict the chemicals on the basis of current evidence laid out their reasons for believing the ozone destruction model to be true. Two in particular were Johnston and F. Sherwood Rowland.

Although the propellant problem has only recently come to light with a report last June in NATURE by Rowland and Mario J. Molina, there is a large body of data "directly applicable to the problem," Johnston says. From 1971 to 1974, the Department of Transportation's Climatic Impact Assessment Program directed $50 million worth of research on atmospheric chemistry and the possible perturbations of the ozone by supersonic jets. In the light of this information, the caveat that the new model is "just a theory" should

Freon $\xrightarrow{uv}$ Cl	(1)
$Cl + O_3 \rightarrow ClO + O_2$	(2)
$ClO + O \rightarrow Cl + O_2$	(3)

be considered carefully, Johnston says.

There are "exact parallels" between what happens when nitrogen oxides from natural sources and jet engine exhausts destroy ozone and what happens when chlorine radicals are released from propellants. "We have to 'change the labels' in our equations," Johnston says, "but we don't have to redo all of the basic work." The chlorine model, he says, is "virtually proven by analogy."

Rowland, who has already called for a ban of fluorocarbons 11 and 12, stresses several points. First, laboratory tests and preliminary direct measurements have so far confirmed the chlorine model. "Industry has had a year already to come up with a major error in the model and has been unable to do this," he says. He emphasizes that because of its long stratospheric lifetime, virtually all of the fluorocarbons 11 and 12 ever released is still hanging in the stratosphere or floating slowly toward it. And, unfortunately, all of those fluorocarbons eventually are released, even those contained within closed systems; within two months by aerosol cans, two years by car air conditioners and 15 years by home refrigerators.

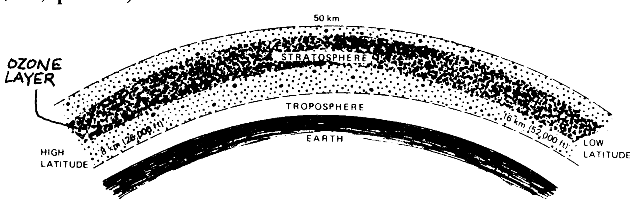
Rowland calculates that 800,000 tons of fluorocarbons are being released each year, and from that, 500,000 tons of active chlorine molecules are freed. If his ozone-destruction model and reaction rates are correct, this is about 25 times more chlorine atoms than would be allowed if an upper limit of 0.5 percent ozone depletion were established. (The Department of Transportation CIAP study mentions 0.5 percent ozone depletion as a possible acceptable limit.) Many have suggested that the search for problems with the model continue for three to five more years. That much time might be necessary to determine a precise limit to set for chlorine released in the stratosphere, Rowland says, but not for proving the model correct. "What is the likelihood that the model is off by a factor of 25, so that the current 500,000 tons will be permissible?" he asks. "I think that possibility is negligible, and that we ought to put an immediate ban on fluorocarbons 11 and 12."

The lack of serious challenges to the Rowland-Molina model, combined with strong press and public interest, has given momentum to the anti-propellant movement. Two or three aerosol valve manufacturers have closed plants or cut shifts because of flagging orders, including the Yonkers, N.Y., plant of spray valve inventor Robert Abplanalp. DuPont spokesmen declined to cite sales figures, but one industry observer sees a downswing and attributes it to consumer concern and the beginning of a shift by producers to other

Ozone destruction: A blue-sky problem

Miles above the earth, where the air is thin and sharp and silent, there is a layer of ozone (O_3), a bluish gas that protects the earth from the ravages of too much sunlight. It is formed when sunlight strikes oxygen (O_2), and it filters out harmful ultraviolet light having wavelengths shorter than about 295 billionths of a meter. The ozone layer is dynamic and changing. The amount that hangs in the stratosphere (12 to 50 kilometers above the earth) varies with the time of day, the season and the latitude. There is more ozone during the day, for example, than at night; more over northern latitudes, less over southern. (This last fact has been correlated with the larger numbers of skin cancer cases in southern latitudes.) Scientists know that the formation and destruction of ozone are part of a natural, dynamic balance. And this balance, they are discovering, is easily disturbed.

After its formation, the natural destruction is catalyzed by nitrogen oxide, one of many compounds that floats in the stratosphere. When it was announced several years ago that large fleets of supersonic transport planes were being planned, a University of California at Berkeley professor, Harold Johnston, theorized that nitrogen oxide exhausts from the jets could interfere with the natural balance of ozone formation and depletion and cause a net deficit. This, he reasoned, would allow more solar radiation to penetrate to the earth's surface, and would ultimately lead to more cases of skin cancer. Skin cancer has been correlated to exposure to light of the wavelengths that are absorbed by ozone. Several years of study have confirmed the Johnston hypothesis and both the Department of Transportation and the National Academy of Sciences have warned in recent reports that jet engines will have to be redesigned or their flight limited (SN: 4/5/75, p. 220).



Last year, University of California at Irvine chemists F. Sherwood Rowland and Mario Molina were pondering the environmental fate of fluorocarbons, better known as the inert propellants in aerosol cans and refrigerants. Direct sampling by atmospheric chemists had earlier revealed growing levels of the two most prevalent compounds, fluorocarbon 11 ($CFCl_3$) and 12 (CF_2Cl_2). These compounds are so inert to the attack of reactive species in the lower atmosphere, such as OH hydroxyl radical, that they must be floating to the stratosphere unchanged, Rowland and Molina reasoned. There, exposed to strong sunlight, they would be photodissociated, releasing chlorine atoms. And these, the team hypothesized, could act as catalysts to the destruction of ozone just as would the nitrogen oxides from SST exhausts. Chlorine would be an even stronger catalyst, though, and each chlorine atom would destroy thousands of ozone molecules. And to make matters worse, the effects of a fluorocarbon buildup would be delayed and long lasting due to the inertness of the compounds and their slow movement upward. The maximum effects of today's release, therefore, will not be felt for perhaps 10 years, and then the effects will continue for a century.

The current best estimate, based on computer models, is that if fluorocarbon use continues to grow as it has in recent years and there is no halt to production, the ozone layer will have been depleted by 13 to 20 percent by the year 2000. This depletion would cause thousands of new cases of skin cancer, perhaps a 20 to 40 percent increase in the incidence of new cases, would damage plants and phytoplankton and might possibly affect the weather adversely.

There is an urgency about the study of this problem; the longer scientists study before action is taken, the stronger will be the damaging effects of increased UV light and the longer will the effects be felt if the model is true. Many would like to wait until ozone depletion can be measured and definitely linked to fluorocarbons before action is taken. But now, the natural fluctuations in total ozone in the stratosphere are greater than the estimated 1 percent reduction from fluorocarbons, making direct ozone depletion hard to measure. And waiting a decade for a measurable increase to be manifest could increase the biological and environmental damage unnecesarily. So scientists are searching hard for chemical evidence in the stratosphere that will confirm or refute the Rowland-Molina model.

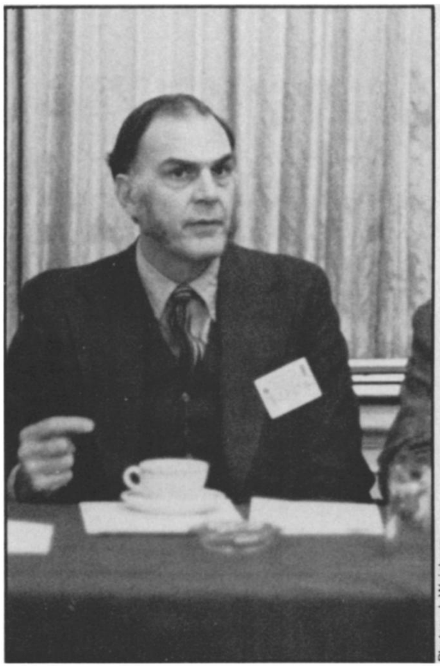
—Janet H. Weinberg

packaging alternatives. Those alternatives could be roll-on containers, spray pumps or possibly other fluorocarbons, Rowland says. Fluorocarbon 22, for example, is already used in refrigerators by itself or in combination with other fluorocarbons. It degrades faster, according to the model, and could be used in refrigerators and be less of an environmental threat. "I don't offer fluorocarbon 22 as a specific suggestion or the only alternative," Rowland says, "but just to point out that there might be fluorocarbon alternatives." Industry spokesmen during legislative hearings tend to dramatize the impact of a fluorocarbon ban, Rowland says, by suggesting it would necessitate a throwback to sulfur dioxide and ammonia refrigeration. He contends this does not have to be the case.

Although industry scientists will concede privately that major efforts are under way to design new packaging alternatives—aerosols included—they remain, on the surface, unconvinced of Rowland's model. DuPont's McCarthy points to recent downward revisions in the computer model predictions of ozone depletion made by Harvard atmospheric scientists Michael McElroy and Steven Wofsy as evidence that the propellant scare may be hasty and the threat small. McCarthy also points to measurements of chlorine in the stratosphere that suggest sources other than fluorocarbons. Carbon tetrachloride (CCl_4) and methylchloride (CH_3Cl) are probably reaching the stratosphere, too, and adding more free chlorine atoms. In the case of methylchloride, which forms during the evaporation of sea water, these chlorine molecules might be a part of the dynamic natural balance of ozone creation and depletion, as are nitrogen oxides, McCarthy says. If chlorine is a part of the natural ozone cycle, he says, then perhaps the addition of more through fluorocarbons would not represent a major problem. (Rowland points out the addition of small amounts of nitrogen oxides against a large natural background of nitrogen oxides has already proven damaging, and he thus disagrees with McCarthy's analysis.)

All of this is not to say that industry scientists are unconcerned about the problem. Industry, Government and academic scientists alike are calling for more data, and the Manufacturing Chemists Association is footing a good part of the bill—$3 million to $5 million over the next few years. Atmospheric researchers in several laboratories are preparing to measure the levels of critical chemicals in the stratosphere, including the ClO radical, chlorine and the OH (hydroxyl) radical. These chemicals would, theoretically, take part in the rate-limiting step of the chlorine reaction, and measurement of them would help confirm or refute the model.

Measurements of free chlorine in the stratosphere at altitudes of 30 to 50 kilometers will be taken this year from outside the atmosphere by NASA's OAO-3 Copernicus satellite. A high-flying balloon to be launched from White Sands, N.M., this fall will measure stratospheric compounds. Several researchers, many of them funded by the Manufacturing Chemists Association, will use stationary devices to measure chemicals. Among them, Douglas Davis of the University of Maryland will use tuned laser fluorescence to measure the ClO radical. Donald H. Stedman of the University of Michigan will do the same using chlorine fluorescence. Allan Lazrus of the National Center for Atmospheric Research will continue to measure HCl. His preliminary measurements have been consistent with the Rowland-Molina model. Researchers in dozens of other laboratories are beginning to make direct atmospheric measurements. They are also studying simulated reactions in the laboratory and are working on mathematical models to predict reaction and ozone-depletion rates.


Photos: J. Weinberg

Rowland: Calling for an immediate ban.

McCarthy: Up front and unconvinced.

It is obvious from all of this that the field is in a state of flux and that data are being produced, revised and retuned continually. During the past eight or nine months, scientists have devoted six full days to the propellant-ozone question at sessions such as ACS Philadelphia symposium. As an indication of the ferment, even during the presentation and discussion of scientific papers in Philadelphia, small groups of scientists huddled together in the corners of the meeting room, whispering and scratching equations down on the backs of envelopes.

Two groups, one sponsored by the Government and the other by the National Academy of Sciences, are meeting now, charged with collecting and assessing the information as it develops and determining the environmental and legal ramifications of the fluorocarbon problem.

So, for the present, most scientists involved in the propellant-ozone question are content to hasten back to the lab benches and amass data. Six months or a year from now, however, that might not be the case. Rowland thinks rapid and accurate measurement of the critical chemicals is possible, and that confirmation of the model could be reached experimentally within about six months. But McCarthy and other industry scientists are talking about three to six years for proper proof of the theory. "I hope," McCarthy said in Philadelphia, "that the measurements now planned and under way will prove effective in *unequivocally* providing information on the reaction of chlorine in the stratosphere. If not, we will seek other methods which will give us that unequivocal proof." Unequivocal is a subjective term, Johnston responded. Many are already convinced. "How many decimal places must we go before the model is proven to industry satisfaction?"

Ralph Cicerone of the University of Michigan, another early contributor to the ozone-destruction theory, thinks that scientists and public policymakers have little time or room for error on this issue. "Decision makers do not have much room to hedge their bets." Maybe they have the luxury with SST's, he says, of building them, flying them and waiting to measure ozone depletion as a result. The ozone layer would return to normalcy after three years or so. "But whatever the effects of fluorocarbons will be, the full impact will not be felt for a decade after release and it will persist for many decades."

"Complete scientific proof to everyone's satisfaction will take years, so we are faced with a benefit-risk analysis. I have come to the reluctant conclusion that the risks are greater than the benefits, and the evidence is already strong." □