Fluorocarbons and the stratosphere

Observations and experiments are under way in response to the growing concern that widely used fluorocarbons might cause a depletion in Earth's protective ozone layer.

Gloria B. Lubkin

When the alarm was sounded last year that the ubiquitous fluorocarbon-propelled spray cans might be responsible for slowly removing Earth's protective ozone shield, reaction was widespread. Environmentalists urged an immediate ban, legislators held hearings and introduced legislation, government-sponsored study committees were formed, fluorocarbon-based industries defended their products and urged more definitive research (which they began to support in part). The concern, of course, is that the ozone layer shields life on Earth from harmful ultraviolet radiation. Much relevant research was already underway, sponsored by the Federal government, and by now workers in such disparate fields as atmospheric science, chemistry, physics and astronomy are working to answer the question, "Are the fluorocarbons depleting the ozone, and if so, how badly?"

Recently a Federal task force concluded that fluorocarbon 11 ($CFCl_3$) and fluorocarbon 12 (CF_2Cl_2) released to the environment are a "legitimate cause for concern." Half of the production of fluorocarbons 11 and 12 goes for aerosol propellants and another quarter goes for refrigerants. Fluorocarbon 22 (CHF_2Cl) is also widely used for refrigeration. Fluorocarbons are also used to produce foamed plastics, as solvents and fire extinguishers. (To be more precise, the fluorocarbons being discussed should be referred to as "chlorofluorocarbons.")

The alarm is sounded

In June 1974 Mario J. Molina and F. Sherwood Rowland (figure 1) of the University of California, Irvine postulated[1] that Earth's ozone shield in the stratosphere would be seriously depleted by the use of fluorocarbons 11 and 12. Although these fluorocarbons have been valued on Earth for their inertness, once they are released, they diffuse upward to the stratosphere, where they are decomposed by ultraviolet radiation from the Sun. This results in the release of fluorocarbon radicals and free chlorine atoms, which then act to decrease the average concentration of ozone through catalytic chain reactions.

More than a dozen groups have estimated the ozone reduction produced from the NO_x emitted by supersonic transports. Following Molina and Rowland's calculations some of these groups have also made model calculations for possible ozone reduction produced by the fluorocarbon release. Despite the variety of assumptions and parameters used, the results on ozone reduction of all the groups agree[2] within a factor of about two. The calculated global reduction of stratospheric ozone by fluorocarbons in 1975 is ½–1% and may be as large as 2%, according to H. Guyford Stever, chairman of the Federal Council for Science and Technology. Even if no more fluorocarbons 11 and 12 were added to the atmosphere, the ozone is theoretically expected to continue to decrease and eventually achieve as much as 1.3–3% reduction. If, on the other hand, we continue to release fluorocarbons at the 1972 rate, some calculations predict an eventual reduction of about 7% or more in the equilibrium concentration.

The reason for the delayed action of the fluorocarbons is that they diffuse very slowly into the stratosphere. Even if no additional fluorocarbons were released after a specified date, the average ozone concentration would continue to be reduced, reaching its lowest value in ten or more years.[2] It is expected that the effects of fluorocarbon release would last to some extent for as much as a century.

Once the fluorocarbon is dissociated by uv radiation into free chlorine and the fluorocarbon radical, it is expected[1] that the chlorine atoms would act as a catalyst to remove ozone. The catalytic chain reaction is:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

Each chlorine atom is believed capable of reacting with 10^3 ozone molecules, before forming less reactive hydrogen chloride, which then would diffuse downward to the troposphere. (Chlorine atoms can then be released again from HCl through reaction with the OH radical.) The Cl–ClO chain is expect-

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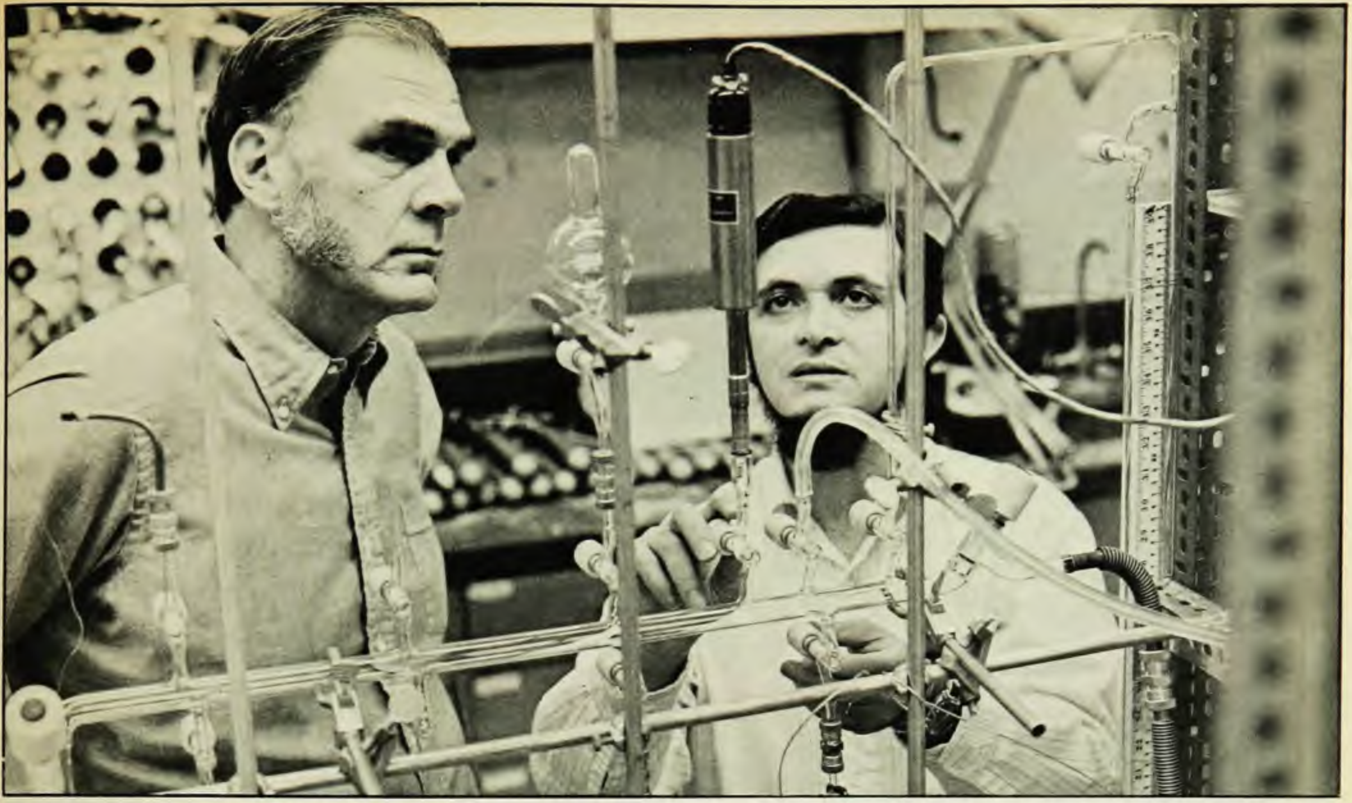


F. Sherwood Rowland (left) and Mario J. Molina postulated last year that Earth's ozone shield in the stratosphere would be depleted by fluorocarbons 11 and 12. They are shown with vacuum line used to determine the composition of a sample of stratospheric air. Figure 1

ed[3] to be comparable in efficiency to that of the NO–NO_2 chain in the catalytic conversion of $O_3 + O \rightarrow 2O_2$ per unit time per reacting chain. The NO–NO_2 chain (from microbiological sources) is the primary natural method for removal of ozone.

Ozone in the stratosphere

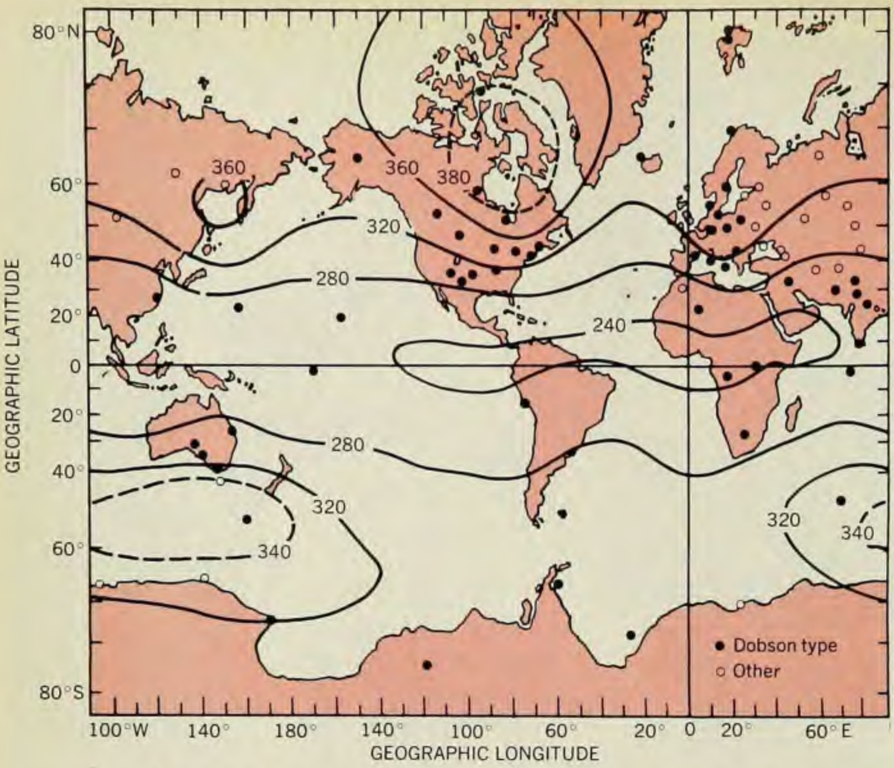
Ozone is in a dynamic equilibrium in the stratosphere. It is produced when ultraviolet radiation splits O_2 into free atoms, which each then combine with another O_2 to make O_3. It is destroyed by the interaction of ozone with oxygen atoms, with nitrogen oxides, with hydrogen species (H, OH, HO_2) and possibly other natural components in the stratosphere. An additional, though less important loss, occurs through transport of ozone to the troposphere.

The ozone content varies considerably with season, year and latitude.[2] At mid-latitudes the concentration fluctuates daily on the average 10% in winter, 5% in summer and 25% between seasons. Ozone is more concentrated over the poles than at lower latitudes (figure 2). Over the period 1955–70 total ozone levels in the Northern Hemisphere increased 5–10%. But since then, concentrations have declined about 2%. Many believe these fluctuations are primarily natural variations, influenced by the 11-year solar cycle. Harold S. Johnston of the University of California, Berkeley and Julius Chang, Lawrence Livermore Laboratory, believe that the ozone in the Northern Hemisphere was depleted by a few percent in the early 1960's by atmospheric nuclear-weapons testing. Some have argued that because these fluctuations occur naturally we should not worry about small additional changes. However, because of a reduction in average ozone, the total cumulative dose of uv radiation delivered to Earth will increase. It has been pointed out that some plants, animals and ecosystems may have difficulty in responding to such a change. Richard Garwin (IBM), who was involved in studies of SST-produced changes in the stratosphere, points out that even though we know that automobile accidents cause only a small percentage of the deaths that occur each year, this fact does not mean that we should not try to reduce automobile accidents.

Reducing the amount of ozone in the stratosphere would increase the amount of uv-B radiation (280–320 nanometers) reaching Earth. It is generally believed that this would cause harmful environmental effects. A major cause of concern is that a direct correlation has been found between latitude and the incidence of non-melanoma skin cancers. Solar uv radiation is more intense near the equator—both because the Sun is more nearly overhead and because there is naturally less ozone near the equator. Furthermore, skin cancers have been induced in animals exposed to increased uv radiation. A variety of possible biological and agricultural effects have been postulated,[2,4] including changes in physiological, biochemical, anatomical and growth characteristics of some plants; disturbances in aquatic and terrestrial ecosystems, changes in insect behavior, effects on agricultural chemicals, increased incidence of cancer in livestock, and reduction of crop yields produced by climatic changes. Some workers have suggested that reduction of stratospheric ozone would cause changes in temperature, wind patterns, and precipitation. V. Ramanathan (NASA Langley Research Center, Hampton, Virginia) has suggested[5] that fluorocarbons in the troposphere might block outgoing infrared radiation, thus causing a greenhouse effect, and raising Earth's temperature. An increase in temperature of even one degree might lead to a dramatic drop in food production.

Models of ozone depletion

Fortunately for those concerned about the fluorocarbon effect on stratospheric ozone, many estimates of the NO_x effect on stratospheric ozone had already been made. Most of the global NO_x models are one dimensional; some are two and even three dimensional. Variations among the individual models occur in the choice of values for the so-called "eddy-diffusion coefficients" in the one-dimensional models. Inclusion of variations in latitude and longitude does not appreciably change the overall



Average annual global distributions of total ozone. The ozone amounts are given in milliatmosphere-cm. Note that the yearly average shows a minimum straddling the equator and an increase as one moves towards the poles. Figure based on R. Gebhart, R. Bojkov, J. London, Contributions to Atmospheric Physics **43,** 209 (1970). Figure 2

estimates of average ozone reduction.[2] When the effect of chlorine is considered, the same transport processes are used and the chemical reactions of all the chlorine species are added.

For the fluorocarbons, at least five full one-dimensional calculations have been made (figure 3): by Steven Wofsy, Michael McElroy and N. D. Sze[6] (Harvard University), by Paul Crutzen[7] and by Crutzen and Ivar Isaksen (National Center for Atmospheric Research, Boulder, Colo. and NOAA), by Richard Turco (RDA Associates, Santa Monica, Calif.) and Robert Whitten (NASA Ames Research Center, Mountain View, Calif.), by Ralph Cicerone, Thomas Donahue, Shaw Liu and William Chameides (University of Michigan) and by Julius Chang, Donald J. Wuebbles and William H. Derewer (Lawrence Livermore Laboratory). A two-dimensional calculation has been done by R. Vupputuri and B. W. Boville[8] (Atmospheric Environmental Services, Ontario, Canada). Each group independently estimated solar flux as a function of altitude, and used different methods for handling the chemistry and for doing the calculation.

All of the calculations are subject to change as new data come in on rate constants. Last fall, shortly after the first predictions of ozone depletion from the fluorocarbons were made, one of the rate constants, the attack of hydroxyl on hydrogen chloride, was reevaluated at stratospheric temperatures. When this new value was introduced into the models, Rowland says, the ozone depletion became more severe (by a factor of about 1.4). Then two more rate constants were reevaluated: chlorine plus ozone and chlorine plus methane. Both these constants caused the predicted ozone depletion to become less severe. (The combined effect is about a factor of two). Minor changes have been made in some other rate constants. Rowland argues that the net result of the changes in rate constants is that the predictions are essentially unchanged. He stands by his original prediction that if we continue introducing fluorocarbons into the atmosphere at 1972 rates, we will deplete the ozone by 7–13% in the steady state.

When the alarm was first sounded last year, Rowland remarks, there were no measurements in the literature of any chlorine compound in the stratosphere. Now there are two types of measurements. The first is a balloon- or aircraft-borne filter, coated with a basic substance to trap gaseous acids. Alan Lazrus (National Center for Atmospheric Research) has reported[9] that the mole fraction of hydrogen chloride increases with altitude. Lazrus says this means that a source of chlorine is being introduced into the stratosphere. In the model calculations, as altitude increases, the amount of hydrogen chloride from fluorocarbons and other organic chlorine compounds (such as CCl_4 and CH_3Cl) increases, agreeing with Lazrus's observation, Rowland notes.

A second relevant measurement has been done by two groups, who used balloons and aircraft to measure the fluorocarbons as a function of altitude (figure 4). These have been done by Dieter Ehhalt (then at the National Center for Atmospheric Research) and his collaborators[10] (who also made rocket measurements at 50 km) and by Eldon Ferguson and his collaborators[11] at the NOAA laboratory in Boulder. They find that fluorocarbon 11 is being removed at a lower altitude than fluorocarbon 12. Rowland has compared these results with theoretical predictions using several different eddy diffusion coefficients, and he remarks that the agreement is good with all of them, indicating that the photochemical processes are dominant over stratospheric transport processes in determining the profile of figure 4.

Additional data on fluorocarbon distribution in the lower stratosphere have been collected from airplane observations by P. W. Krey and R. J. Lagomarsino (Health and Safety Laboratory of ERDA, New York). They find[12] a decrease in concentration with altitude from about 12 to 19 km in the stratosphere. In addition they observe concentrations of fluorocarbon 11 in the stratosphere commensurate with industrial production and a total atmospheric halflife of 15–30 years.

Government study groups

Since the model predictions were announced, many groups have met, trying to evaluate the ramifications of the questions raised. One was formed by the Council on Environmental Quality (CEQ) and the Federal Council for Science and Technology (FCST), who created the Federal Interagency Task Force on Inadvertent Modification of the Stratosphere (IMOS). After five months of study, this task force produced a report[2] in June, "Fluorocarbons and the Environment," which recommended that "unless new scientific evidence is found to remove the cause for concern, it would seem necessary to restrict uses of fluorocarbons 11 and 12 to replacement of fluids in existing refrigeration and air-conditioning equipment and to closed recycled systems or other uses not involving release into the atmosphere."

Meanwhile the National Academy of Sciences and National Academy of Engineering are conducting a further study of man-made impacts on the stratosphere. Within the Academies' Climatic Impact Committee a Panel on Atmospheric Chemistry was convened, headed by H. S. Gutowsky (University of Illinois). The IMOS task force recommends, if the NAS–NAE study, due next year, confirms the IMOS assessment, that "Federal regulatory agencies initiate rulemaking procedures for implementing regulations to restrict fluorocarbons uses. Such restrictions could reasonably be effective by January 1978 . . ."

NAS–NAE panel recommendations

The Panel of Atmospheric Chemistry issued a preliminary report in July, recommending atmospheric and laboratory studies that will aid in assessing the extent to which chlorofluoromethanes will affect the stratospheric ozone layer. If we wait until a reduction in ozone is directly measured, the report notes, it would be too late to avoid further, more drastic long-term effects. The report does not discuss whether or not restrictions should be placed on the use of chlorofluoromethanes at this time.

Without identifying relative priorities, the Panel lists the following measurements as of high priority:

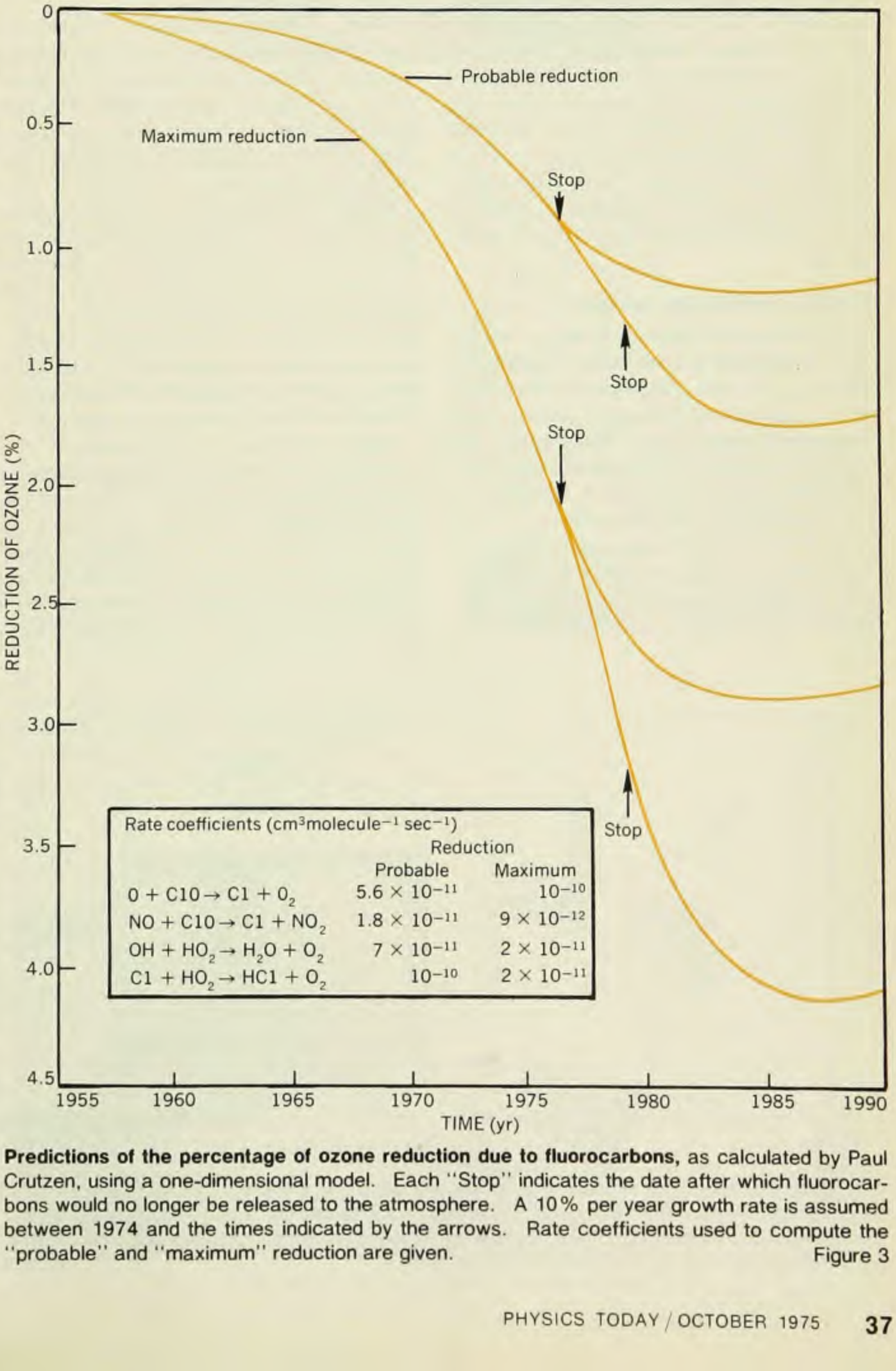
- Atmospheric measurements and modelling: measurements of Cl and ClO as a function of height; measurements of OH, HCl, HF and NO as a function of height; measurements of global distributions of trace gases that have known chemical sinks in the 20- to 50-km region; measurements of abundances at various heights, 0–40 km, of the halocarbons themselves, $CFCl_3$, CF_2Cl_2, CCl_4 and CH_3Cl (and their variation with latitude and season); development of better atmospheric models.
- Reaction rate constants: measurement of rate constants for the reactions of ClO with NO and of ClO with O and for the $Cl + HO_2$ reaction, including temperature dependences and for the $Cl + CH_4$ rate; determination of the major source and sink terms of HO_x; measurement of rate constants for the reaction of OH radicals with $CHFCl_2$, CHF_2Cl and CH_3Cl at stratospheric temperatures.
- Photolysis: measurement of solar flux and scattering parameters for the stratosphere; measurement of photolysis parameters for other chlorohydrocarbons and chlorofluorohydrocarbons; laboratory studies on the photolysis of ClO.
- Sources and sinks: sampling at low altitude to identify and measure additional possible natural and manmade sources of halogen-containing compounds; obtain data on a continuing basis about foreign and domestic production and use of each halocarbon in major use; measure total chlorine in the atmosphere and compare it with the sum of all identified chlorine-containing compounds of natural and manmade origin to determine whether major unidentified sources exist; measure abundance of decomposition products such as COF_2, $COCl_2$ and COFCl; look for other possible sinks for removal of chlorofluoromethanes; examine the source of chlorine-containing stratospheric particulates.
- Other concerns: provide continuous baseline monitoring of the absorption spectrum and composition of "clean air," far removed from local manmade sources; obtain kinetic data for all the important reactions of bromine, which may also be a source of catalytic destruction of ozone.

Industry-supported research

Confronted with a growing controversy about the ozone-depletion question, DuPont, for example, took an almost full-page ad in *The New York Times,* 30 June 1975, which said, "should reputable evidence show that some fluorocarbons cause a health hazard through depletion of the ozone layer, we are prepared to stop production of the offending compounds. To date there is no experimental evidence to support the contention that Freon and other similar compounds have caused a depletion of the ozone layer . . . even if the hypothesis is valid, no significant effect will occur during the three years needed to develop definitive information."

In fact industry has mounted a research program, which is supported by the 19 companies that manufacture fluorocarbons (six domestic, thirteen foreign). The Manufacturing Chemists Association has established a Fluorocarbon Technical Panel, headed by Frank Bower of DuPont, which oversees the research effort. By the end of 1975, the group will have committed \$1–1.2 million. In 1976 and 1977 slightly more is expected to be spent each year, possibly rising to \$1.5 million in 1977.

The industry group is sponsoring a variety of ground-based and airborne



Rate coefficients (cm^{3}molecule^{-1} sec^{-1})

	Reduction: Probable	Reduction: Maximum
$O + ClO \rightarrow Cl + O_2$	5.6×10^{-11}	10^{-10}
$NO + ClO \rightarrow Cl + NO_2$	1.8×10^{-11}	9×10^{-12}
$OH + HO_2 \rightarrow H_2O + O_2$	7×10^{-11}	2×10^{-11}
$Cl + HO_2 \rightarrow HCl + O_2$	10^{-10}	2×10^{-11}

Predictions of the percentage of ozone reduction due to fluorocarbons, as calculated by Paul Crutzen, using a one-dimensional model. Each "Stop" indicates the date after which fluorocarbons would no longer be released to the atmosphere. A 10% per year growth rate is assumed between 1974 and the times indicated by the arrows. Rate coefficients used to compute the "probable" and "maximum" reduction are given. Figure 3

Federal Research Support

Agency	Amount (thousands of dollars)
DOC	$1 125
DOD	1 277
DOT	2 781
EPA	290
ERDA	282
NASA	6 876
NSF	1 608
Total	14 239

Federal support related to the fluorocarbon-ozone issue in FY 1975. Source: reference 2.

observations, as well as modelling efforts. These include: monitoring halogen compounds in the troposphere and the stratosphere; balloon-borne infrared spectroscopy of fluorocarbons, other halogen compounds and expected end products; microwave absorption spectroscopy of the ClO radical; exploration of the chemical behavior of Cl and O compounds by stratospheric simulation; development of spectral data for ClO; development of an instrument that will be flown to measure total Cl and ClO in the stratosphere; reaction rate measurements; sensitivity analysis of models, one-, two- and three-dimensional modelling.

Federal government research

The Department of Transportation has completed a three-year study (the Climatic Impact Assessment Program) of the impact of nitrogen oxides from supersonic transports. They spent $21 million directly, and an estimated $60 million was spent by other agencies in connection with the program.

In FY 1975 the Federal government is spending a total of $14.2 million for stratospheric research related to the fluorocarbon-ozone issue (see table).[2]

NOAA (National Oceanic and Atmospheric Administration) is monitoring total ozone and collecting air samples to look for fluorocarbons 11 and 12, N_2O and CCl_4. It is supporting numerical modelling of climate at the Geophysical Fluid Dynamics Laboratory in Princeton.

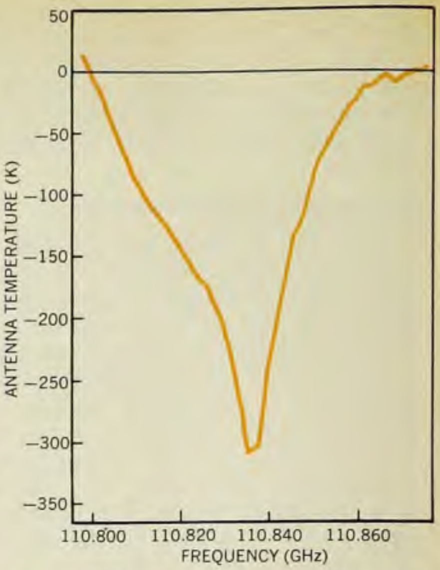
NBS (National Bureau of Standards) is collecting and evaluating reaction-rate data and studying some chemical reactions.

DOD (Department of Defense). The Army is supporting stratospheric modelling, rocket and balloon-borne stratospheric observation and solar measurements. The Navy is doing aircraft and balloon-borne sampling, analyzing both rain and ocean water to see if they have fluorocarbons. The Air Force is supporting instrumentation development, studying chemical processes, doing one-dimensional models and building a global circulation model.

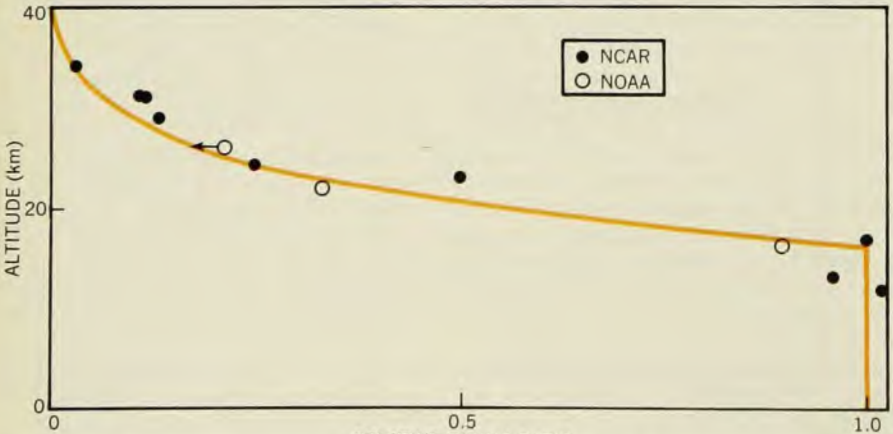
EPA (Environmental Protection Agency) is supporting photo-oxidation studies, doing stratospheric simulations, looking at intermediate reaction products, and trying to learn the transport properties of the fluorocarbons and related compounds.

ERDA (Energy Research and Development Agency) plans to measure fluorocarbons, CCl_4 and SF_6 with balloons and aircraft, and to fly filters to collect HCl, Cl and Br. ERDA is also continuing to support Rowland and Molina, who are now working on stratospheric problems associated with fluorocarbon 22 and other halocarbon compounds.

NASA (National Aeronautics and Space Administration) is supporting by far the biggest program in dollar value. James Anderson at the University of Michigan has flown a balloon to measure O and OH in the stratosphere; the resonance fluorescence instrument is parachuted down from 45–50 km. Similar *in situ* measurements of Cl and NO, followed by the simultaneous measurement of all five of the above species are in progress. Douglas Davis (University of Maryland) is using laser-induced fluorescence to measure OH, NO_2 and SO_2 in the stratosphere and upper troposphere. The system is now being flown in an aircraft and will soon be mounted in a balloon.



The 110-GHz line of ozone measured in absorption against the Sun by a 16-foot millimeter-wave radio telescope. Figure 5



Comparison of observed fluorocarbon-11 mixing ratios vs. altitude with values predicted by Molina and Rowland. The mixing ratio is the percentage of the atmospheric molecules that are fluorocarbon 11, normalized to fluorocarbon-11 concentration in the troposphere. NCAR data are from reference 10; NOAA data are from reference 11. Figure 4

To determine the ClO concentration and the ratio of ClO to Cl, NASA is supporting Anderson and Donald Stedman to use the technique mentioned above. Robert Stokes (Battelle Memorial Institute, Richland, Wash.) has proposed using a 9.1-meter radio telescope to look for ClO. Alan Lazrus, whose work on HCl was mentioned above, is proposing to use the same technique for ClO. Ralph Nicholls (York University, Toronto), who is also supported by the Manufacturing Chemists Association, is doing laboratory spectroscopy on ClO and is also proposing to use a ground-based uv spectrometer to assess stratospheric ClO.

NASA has a continuing program, the Global Atmospheric Sampling Program, which collects stratospheric air samples to look for fluorocarbons. A variety of modelling efforts is supported. One is a three-dimensional model, originally developed by Ronald Prinn (MIT), which is to be adapted for use on the Illiac-IV computer at the Ames Research Center.

Chemical kinetics studies are being supported, primarily at universities, for example by Fred Kaufman (University of Pittsburgh) and by Douglas Davis (whose work is being primarily supported by NASA, Department of Transportation and NSF).

NSF (National Science Foundation) is continuing its normal research effort in atmospheric sciences, for example: support of the National Center for Atmospheric Research, wind measurements in the upper stratosphere (University of Alaska and Georgia Tech), atmospheric reactions of NO_3 (Colorado State University), atmospheric physics and dynamics (Harvard University), high-altitude chemistry (MIT), spectroscopy of OH, H_2O and HO_2 (University of Michigan), chemical reactions in the atmosphere (Pennsylvania State University).

One new program being funded by NSF is led by Edward Lilley (Harvard University), who plans to use a portable 24-inch radio telescope with a filter bank designed to measure atmospheric pressure-broadened lines. The antenna will operate at wavelengths near 3 mm. It will be used to observe the spectra of ClO, NO, NO_2, HNO_3, HO_2 and O_3 in both self-emission and absorption against the solar continuum. Eventually the Harvard astronomers plan to fly the apparatus in a balloon. Already the group has reported observing (figure 5) the 110-GHz line of ozone both in absorption against the Sun and self-emission away from the Sun (using a 16-foot millimeter-wave telescope).

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